HOMOLYTIC AND HETEROLYTIC MECHANISMS OF THE REARRANGEMENT OF SOME N-CHLOROANILIDES.

A thesis presented for the degree of
Doctor of Philosophy in the Faculty
of Science of the University of London

by

Christopher Lee Mason

September, 1971 Bedford College, London.

Abstract

A quantitative estimation of the products of the rearrangement of *N*-chlorobenzanilide, catalysed by hydrogen chloride, has been carried out. The composition of the products, and the kinetics of the rearrangement of *N*-chlorobenzanilide and of *N*-chlorophenylacetanilide in acetic acid alone, have been studied, and possible mechanisms consistent with the rate equation have been suggested. The prescence of silver acetate greatly affected both the kinetics and composition of the product of the reactions in this solvent, and various reasons for this have been considered.

The kinetics and products of the thermal and photolytic rearrangements of several *N*-chloroanilides, in non-polar solvents, both alone and in the presence of added anilides have been investigated. From these results, the various factors which are involved in the autocatalysis, exhibited by many of these reactions, have been determined and a mechanism which correlates all these data has been proposed.

A similar study has been made of the reaction of several *N*-chloroanilide, in carbon tetrachloride, catalysed by benzoyl peroxide. Autocatalysis was again observed and its cause investigated. An attempt has been made to explain, in terms of the mechanism of the reaction, why the *o*:*p* ratio was considerably lower than for the corresponding photolytic reaction.

ACKNOWLEDGEMENTS

The author wishes to thank Professor G.H. Williams, of Bedford College, London, not only for suggesting the problem, but also for continued help and advice throughout the period of the research. Dr. J. Clare is gratefully thanked for invaluable guidance and encouragement throughout the work. Thanks are also due to Dr. K.M. Johnston, Mr. R.M. Luker and to Mr. T.C. Atkins for many helpful discussions, and to Dr. N. Singer and to Mr. J. Waite for assistance with the computer programme.

The author's gratitude must also be offered to Mr. C.W. Hyde and to Dr. N. Singer for making research facilities available.

The author is indebted to his wife for help and infinite patience during the last four years.

The work was carried out during the tenure of a Research Assistantship in the Department of Life Sciences at the Polytechnic of Central London.

INDEX

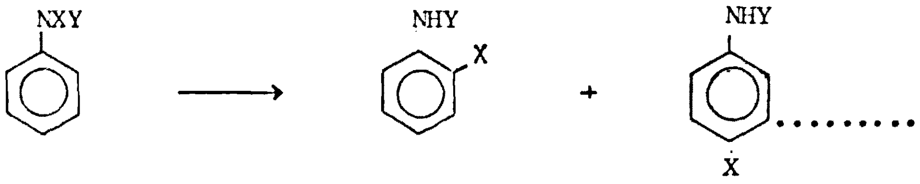
APPENDIX A

APPENDIX B

1. INTRODUCTION

1.1 General Introduction and Origin of the Problem

The aromatic rearrangements of a group of N-substituted anilides may be represented by the following equation:-



(1)

Y = Acyl

X = Halogen (Cl,Br,I), NO, NO_2

Each of these compounds undergoes rearrangement in the presence of acids and, in some cases, the reaction is brought about by heat, light or other catalysts. However, although all these reactions may be represented by the same formal equation, it has been found that the mechanisms may vary with the nature of the anilide and the experimental conditions. The various mechanisms may be classified according to the mode of cleavage of the N-X bond. However, it must first be established that, during the rearrangement, the migrating group, X, is sufficiently free from the parent molecule to be able to be regarded as an independent species. If so, the isomerisation is termed an intermolecular rearrangement, but if the group X remains associated with the parent molecule, then it is said to be an intramolecular rearrangement. In such a rearrangement, it is not possible to determine the movement of electrons during the reaction, and, consequently the mechanism cannot be classified in the same way as for the intermolecular rearrangement, though one mechanism may appear to predominate. In many cases, X may become separated from the nitrogen atom without the electrons of the N-X bond. The migrating group, X^+, then acts as an electrophilic species, and consequently Ingold has termed such processes 'aromatic electrophilic rearrangements'.

Conversely, the group X may separate together with the electrons of the N-X bond. The migrating group, X^-, then acts as a nucleophilic species and such processes are termed aromatic nucleophilic rearrangements.

Both of the above classes of rearrangement are acid-catalysed and involve heterolysis of the N-X bond. However, there is a third mode of cleavage of the bond N-X, namely homolytic fission, in which two uncharged fragments, called free radicals, are formed, each bearing one electron from the N-X bond. This type of reaction is usually promoted by heat, light or free-radical initiators.

The rearrangements of aromatic N-haloamides, where X represents chlorine, bromine, or iodine, are of special interest as they have been considered to proceed, under different conditions, by each of the foregoing mechanisms, with the exception of the intermolecular nucleophilic mechanism. The hydrochloric acid-catalysed rearrangement in polar media has been most extensively studied, and has been found to proceed by an intermolecular electrophilic mechanism.

The mechanism of the rearrangement of N-haloanilides under conditions favouring homolytic fission of the N-X bond is less well understood. Early workers showed that the rearrangement of N-haloanilides could be induced by heat, sunlight or ultraviolet light. Ayad, Beard, Garwood and Hickinbottom[2], and Beard, Boocock and Hickinbottom[3] provided evidence for the initial homolytic fission of the N-X bond during the rearrangement of N-haloanilides under the action of heat, light, and free radical initiators.

The kinetics of the rearrangement of N-haloanilides were studied by both Hickinbottom and co-workers[2,3] and by Cadogan and Foster[4]. The rate curves exhibited the features of autocatalysis, but this increase in rate was not explained in terms of the mechanisms proposed. A further investigation by Coulson, Williams and Johnston[5,6], has provided evidence to show that hydrogen chloride generated in a side reaction is reponsible for the increase in rate. The present work was carried out in order to investigate the origin of the hydrogen chloride, and to correlate the extent of autocatalysis with the nature of the N-chloroanilide.

The ratio of o- to p-chloroanilide in the products of the rearrangement of several N-chloroanilides has been investigated[2,4,5,6] and the results show several anomalies. Therefore a more comprehensive study of the variation of the o :p- ratio with the nature of the N-chloroamide, and with the experimental conditions has been undertaken.

Finally, an investigation into the thermal rearrangement has been carried out.

1.2. Historical Introduction

1.2.1. The Acid Catalysed Rearrangement of N-Haloamides in Polar Solvents

The first N-haloamide, N-chloroacetanilide, was prepared in 1880, by Bender[7], who found that if it was heated with water, or treated with hydrochloric acid, it rearranged to p-chloroacetanilide. Slosson[8] prepared and investigated a series of N-haloamides, and suggested that the hydrolysis of the N-haloamides gave hypohalous acid which then brought about the formation of the p-substituted amide.

Chattaway and Orton[9] carried out an extensive study of these compounds. The slow rearrangement of N-chloroacetanilide in aqueous acetic acid gave not only p- but also o-chloroacetanilide. The rate of rearrangement in water was found to be low also, but it increased on the addition of hydrochloric or hydrobromic acid. They considered that the o- and p-substituted anilides were formed by an intramolecular rearrangement of the N-haloamide, and that the N-haloamide was an intermediate in the halogenation of anilides.

Armstrong[10] also suggested that N-haloanilides were intermediates in the halogenation of anilides but that the rearrangement was an intermolecular process. Hydrochloric acid was shown to be a specific catalyst for the reaction.

Orton and Jones,[11] however showed that the chlorination of an anilide was a direct process, and not an intermolecular rearrangement of an intermediate N-chloroamide. N-Chloroacetanilide and hydrochloric acid were allowed by Orton and Jones to react in aqueous acetic acid, and the free chlorine produced was removed from the system by aspirating it with a small volume of air. A comparison of the amount of free chlorine obtained with the amount of chlorine removed from a standard solution of chlorine under essentially similar conditions, gave an estimate of the concentration of chlorine in the solution, and hence the position of equilibrium for the reaction was determined:

$$\begin{tikzcd}
\text{Ar.NH.Ac} + Cl_2 \arrow[rr, shift left, "(i)"] \arrow[dr, "(ii)"'] & & \text{Ar.NCl.Ac} + HCl \arrow[ll, shift left, "(iii)"] \arrow[dl, dashed, "(iv)"] \\
& \text{o- and p- chloroacetanilide} + HCl \ \text{........(2)} &
\end{tikzcd}$$

The concentration of chlorine in the solution was found to be the same, within the limits of experimental error, when the initial system consisted of either the N-chloroamide and hydrochloric acid or the amide and chlorine. These results indicated that an equilibrium was set up rapidly between the N-chloroamide, hydrochloric acid, chlorine, and the amide, and this was then disturbed by ring chlorination. Orton and Jones[11] employed anilides with a deactivated nucleus, such as 2,4-dichloroacetanilide, so that the equilibrium (i)-(iii) was established much more rapidly than the isomerisation occurred, and hence the routes (ii) and (iv) for the formation of the ring-substituted anilide were indistinguishable.

However Soper[12] showed that in water, reaction (i) was rate determining for the rearrangement of N-chloroacetanilide, and the rate of isomerisation of the N-chloroamide in the presence of hydrochloric acid was equal to the rate of production of chlorine. Consequently, for this system, there was no evidence for the intramolecular mechanism.

Orton and King[13] demonstrated that free chlorine was formed in the reaction between hydrochloric acid in low concentration, and N,2,4 -trichloroacetanilide. In the presence of a more reactive aromatic compound, 2,4-dimethylphenol, a good yield of 2,4-dimethyl-5-chlorophenol was obtained.

The formation of acetanilide and 2,4-dichloroacetanilide as well as o- and p-chloroacetanilide during the rearrangement of N-chloroacetanilide, catalysed by hydrochloric acid in acetic acid, was further evidence for the 'Orton' mechanism.[14] Orton and Bradfield[15] showed that the products of the rearrangement of N-chloroacetanilide in acetic acid in the presence of hydrochloric acid were the same, within the limits of their experimental error, as those from the chlorination of acetanilide under the same conditions of temperature and solvent.

Olson and his co-workers[16,17] carried out a rearrangement of N-chloroacetanilide in the presence of hydrochloric acid, labelled with ^{36}Cl, and found that the proportion of labelled chlorine in the products was such that molecular chlorine, formed from the hydrochloric acid and N-chloroacetanilide, must have been an intermediate.

1.2.1.1. The Kinetics of the Reaction

The first kinetic study of the rearrangement of an N-haloamide was carried out by Blanksma[18] in 1902. The rearrangement of N-chloroacetanilide, catalysed by hydrochloric acid in 20% acetic acid at 10°, was followed iodometrically. The reaction was found to be of the first order with respect to N-chloroacetanilide, and of the second order with respect to hydrochloric acid (3).

$$\frac{-d\,[NCA]}{dt} \propto [NCA]\,[HCl]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Acree and Johnson[19] found that hydrochloric acid was a far more effective catalyst for this rearrangement than hydrobromic acid, and they therefore concluded that the rate of reaction did not depend on the hydrogen ion concentration alone, but also on that of the chloride ion. The rate equation was therefore modified to satisfy the available kinetic data as follows

$$\frac{-d\,[NCA]}{dt} \propto [NCA]\,[H^+][Cl^-] \quad \ldots\ldots\ldots(4)$$

Richardson and Soper[20] provided further evidence to support equation (2), from their investigation of the rearrangement of N-chloroacetanilide, in the presence of hydrobromic acid, in various solvents. Nuclear bromination of the anilide occurred, bromine chloride being considered the most likely intermediate, by a mechanism similar to that suggested by Orton and Jones.

$$C_6H_5NCl.Ac + HBr \longrightarrow C_6H_5NH.Ac + BrCl \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$C_6H_5NH.Ac + BrCl \longrightarrow \text{o- and p- bromoacetanilide} + HCl\ldots\ldots(6)$$

In the aqueous solvent, reaction (5) would be expected to be slow, and therefore rate determining, whereas reaction (6) would be fast. Consequently the hydrogen ion concentration would be virtually constant throughout the reaction and equal to the initial concentration of hydrobromic acid. If hydrobromic acid were acting in the form of its ions, the rate equation could be written

$$\frac{-d\,[NCA]}{dt} \propto [NCA]\,[Br^-] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

The reaction was found to obey this rate expression and the velocity constant was proportional to the initial hydrogen ion concentration. Further evidence for the ionic form of the rate equation was provided by Belton[21].

A contrary view, expressed by Dawson and Millet[22], was that the catalysis was not due to joint action of the ions but to the undissociated acid. The relationship between the concentration of unionized acid, and the concentration of the individual ions can be derived using the law of mass action.

$$[HCl] = \frac{[H^+]\,[Cl^-]}{K} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Where K = Dissociation constant of hydrochloric acid.

Assuming that the acid is almost completely dissociated at the concentration for which equation (7) holds, then

$$[H^{+}] = [Cl^{-}] = c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$\text{therefore } [HCl] = \text{constant} \times c^{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The extent of dissociation of the acid would depend on the polarity of the medium. Thus in a less polar solvent, the concentration of undissociated acid would be greater, and if the catalysis were due to the undissociated acid, a faster reaction would occur. In agreement with their theory, the rate of rearrangement was observed[20] to be greater in ethanol than in a more polar salt solution.

It is not possible, from the available kinetic data, to decide finally whether the rearrangement is catalysed by the undissociated acid, or by the individual ions. However, in view of the highly aqueous nature of the solvent in which these rearrangements have been carried out, Hughes and Ingold[1] considered it more likely that the acid reacts as its ions. The most likely mechanism was thought to involve a bimolecular nucleophilic substitution by the halide ion at the chlorine atom of the protonated N-chloroanilide

$$X^{-} + Cl\text{-}\overset{+}{N}H.Ac.Ar \longrightarrow XCl + NH.Ac.Ar \ldots\ldots\ldots\ldots\ldots (11)$$

An analogous mechanism was suggested to explain the results of Soper and Pryde[23] for the weaker catalytic effect of other acids. Water, being a weaker nucleophile than the chloride ion, a slower rate would be expected.

$$H_2O + Cl\text{-}\overset{+}{N}H.Ac.Ar \longrightarrow H_2O^{+}-Cl + NH.Ac.Ar \ldots\ldots\ldots\ldots (12)$$

An alternative mechanism was suggested which involved an initial unimolecular process

$$Cl-\overset{+}{N}H.Ac.Ar \rightleftharpoons Cl^{+} + NH.Ac.Ar. \ldots\ldots\ldots\ldots\ldots (13)$$

$$H_2O + Cl^{+} \longrightarrow H_2O^{+}-Cl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

1.2.1.2. The Products of the Reaction

Although Bender[7] found that p-chloroacetanilide was the sole product of the rearrangement of N-chloroacetanilide, Chattaway and Orton[9] observed that both the o- and p-isomers were present in the products of the rearrangement in aqueous acetic acid (Table 1).

Jones and Orton[24] showed that in acetic acid the proportions of products from the chlorination of acetanilide, and from the hydrochloric acid catalysed rearrangement of N-chloroacetanilide (Table 1) were similar. The ratio of products was found to be dependent on the temperature, but was unaffected by the water content of the acetic acid.

Orton and King[13,14] studied the products of the chlorination of a series of anilides, by bleaching powder, in acetic acid. On the basis of the 'Orton' mechanism (Equation 2), it would be expected that the products of this reaction should be identical with those of the rearrangement of the N-chloroanilide in the presence of hydrochloric acid under similar conditions. The parent anilide and the 2,4-dichloroderivative, as well as the o- and p-chloroanilides, were obtained as products of the reaction (Table 1).

Orton and Bradfield[15] reinvestigated the products of chlorination of a series of anilides using dichloroamine-T and hydrochloric acid as the source of chlorine. The products from the rearrangement of N-chloroacetanilide in the presence of hydrochloric acid, and from chlorination of acetanilide were shown to contain the same proportions of o- to p-chloroacetanilide (Table 1). In contrast to previous work, the ratio of the products was found to be dependent on the water content of

Table 1

The Products of the Rearrangement of *N*-Chloroanilides and of the Chlorination of Anilides in Acetic Acid

Reactants	Nature of Solvent	Temperature (°)	Molar % of Products				o:p
			o	p	a	d	
N-Chloroacetanilide, HCl[9]	aqueous	0.0	5	95	-	-	1:19
N-Chloroacetanilide, HCl[24]	glacial	8.5	40-46	54-60	-	-	1:1.17-1:1.50
Acetanilide, Cl_2[24]	glacial	8.5	44	50.8	-	1.2	1:1.13
Acetanilide, Cl_2[14]	glacial	-	44	51	1.2	1.2	1:1.12
N-Chloroacetanilide, HCl[15]	glacial	20	33.2	66.8	-	-	1:2.01
Acetanilide, Cl_2[15]	glacial	20	32.5	67.5	-	-	1:2.07
N-Chloroacetanilide, HCl[15]	50% aqueous	20	42.7	57.3	-	-	1:1.35
Acetanilide, Cl_2[15]	50% aqueous	20	39.5	60.7	-	-	1:1.55
N-Chloroacetanilide, HCl[5]	glacial	19	23.2	65.5	11.2	-	1:2.8
Benzanilide, Cl_2[14]	glacial	-	11.2	65.5	9.2	11.1	1:5.9
Benzanilide, Cl_2[15]	glacial	20	30.4	69.6	-	-	1:2.32

the acetic acid, and no evidence was found for the presence of acetanilide or 2,4-dichloroacetanilide in the products.

Cadogan and Foster[4] carried out a detailed study of the products of the rearrangement of some N-chlorophosphoramidates and showed that the relative amounts of o- and p-chloroanilide formed depended on the conditions of the rearrangement, and concluded that, in boiling acetic acid alone, a homolytic mechanism operated instead of the hydrogen chloride catalysed reaction. (Table 2)

Coulson, Williams and Johnston[6] reinvestigated the products of the acid-catalysed rearrangement of N-chloroacetanilide in glacial acetic acid, and showed not only that acetanilide was present to an appreciable extent, but also that the ratio of o- to p-chloroacetanilide differed somewhat from that determined by Orton and Bradfield. (Table 1)

Longmaid[25] has studied the products of the rearrangement of N-chlorodiphenylphosphoramidate under a variety of conditions. The 'Orton' mechanism for the rearrangement of the anilide, catalysed by hydrochloric acid in glacial acetic acid, has been confirmed, but the results show several anomalies when compared with the previous work of Cadogan and Foster[4]. (Table 2)

Table 2

The Products of the Rearrangement of N-Chlorophosphoramidates and of the Chlorination of Phosphoramidates in Acetic Acid

Reactants	Temperature (°)	Molar % of Products				o:p
		o	p	a	d	
Diethyl N-chloro-N-phenylphosphoramidate, HCl[4]	-	18	82	-	-	1:6.4
Diethyl N-chloro-N-phenylphosphoramidate[4]	118	50	50	-	-	1:1.0
Ethyl N-chloro-P-ethyl-N-phenylphosphoramidate, HCl[4]	-	17	83	-	-	1:4.9
Diphenyl N-chloro-N-phenylphosphoramidate, HCl[4]	-	13.5	86.5	-	-	1:6.4
Diphenyl N-phenylphosphoramidate, Cl_2[25]	20	18	66	11	0.2	1:3.7
Diphenyl N-chloro-N-phenylphosphoramidate, HCl[25]	20	18	65	11	1.3	1:3.6
Diphenyl N-phenylphosphoramidate, Cl_2[25]	77.5	23	66	7.4	2.2	1:2.9
Diphenyl N-chloro-N-phenylphosphoramidate, HCl[25]	77.5	23	64	7.2	3.1	1:2.8

1.2.2. The Acid-catalysed Rearrangement in Non-polar Solvents.

Chattaway and Orton[26] showed that the addition of hydrochloric acid to N-chloroacetanilide in light petroleum caused a reaction which gave p-chloroacetanilide as the product. Further work, by Chattaway[27] on the rearrangement of N-chloroacetanilide in carbon tetrachloride showed that an equilibrium similar to that in polar solvents (equation2), was set up rapidly, and was then disturbed by nuclear chlorination.

Bell and his co-workers[28] carried out a study of the rearrangement, in aprotic solvents, of a number of N-haloanilides under the catalytic influence of various acids and phenols. The rearrangements were found to be subject to general acid-catalysis, and initially the reactions were of the first order with respect to the N-haloanilides, but there were deviations from this order as the rearrangement proceeded. In most cases, as the rearrangement proceeded, the rates became greater than the theoretical first-order values and Bell suggested that this autocatalysis involved hydrogen chloride formed by the following slow reaction, which would itself be catalysed by acids:-

$$C_6H_5.NCl\ Ac + C_6H_4Cl.NH.Ac \rightarrow C_6H_5.NAc.NAc.C_6H_4Cl + HCl \quad ....(15)$$

This suggestions was also supported by other evidence.

Bell entrapolated all the results to zero acid-concentration to compensate for errors due to the association of the acids, and found that the catalytic power of the carboxylic acid was proportional to its dissociation constant in aqueous solution. The low concentration of free halogen detected in the reaction was considered insufficient to account for the rate of reaction solely on the basis of the 'Orton' mechanism. Bell suggested that rearrangement also took place by an intramolecular mechanism involving direct transfer of chlorine from the nitrogen atom to the p-position of the aromatic ring. However, the intermediate species involved in such a transformation would be under considerable strain. To overcome this difficulty, Israel, Tuck and Soper[29] suggested that an intermediate halogenating agent was formed by interaction of the N-haloamide and the added acid. They investigated the reactions of certain N-bromoanilides in chloroform in the presence of acetic acid and suggested that in this system the halogenating agent was acetyl hypobromite.

When anisole was added, bromination of the ether took place to a considerable extent although the ether does not not react directly with N-bromoanilides. This was thought to provide evidence for the formation of such an intermediate brominating agent. The rearrangement of N-bromoacetanilide would therefore proceed as follows:-

$$\mathrm{Ph.NBr.Ac} + \mathrm{CH_3CO_2H} \rightarrow \mathrm{Ph.NH.Ac} + \mathrm{CH_3CO_2Br} \ldots.(16)$$

$$\mathrm{CH_3CO_2Br.} + \mathrm{Ph.NH.Ac} \rightarrow \mathrm{C_6H_4Br.NH.Ac} + \mathrm{CH_3CO_2H} \ldots.(17)$$

This mechanism was consistent with Bell's observation that the rate of reaction was greatest for N-iodoanilides and least for N-chloroanilides, as the hypohalite would be formed more readily from iodine, the most electropositive of the halogens.

Hickinbottom[30] however considered that there was no need of postulate acyl hypohalites as intermediates in the rearrangement of N-haloamides in the presence of carboxylic acids. Protonated N-halomides themselves would act as halogenating agents for added substances.

Dewar[31] pointed out that Israel, Tuck and Soper's theory failed to explain two of Bell's observations, namely that there was a direct relationship between the rate of reaction of the N-haloanilides and the dissociation constant of the acid catalyst, and that if

N-bromoacetanilide was allowed to rearrange in the presence of acetic acid and anisole, p-bromoacetanilide was obtained in considerable yield, although when a mixture of acetanilide and anisole in acetic acid was heated with bromine, almost complete bromination of the anisole occurred.

To explain these results, Dewar proposed a mechanism which involved 'π-complex' intermediates. He suggested that heterolysis of the N-X bond of the protonated anilide gave two fragments X^+ and $C_6H_5.NH.R$, and then the X^+ ion, instead of separating from the molecule formed a bond with the π-electron system of the aromatic ring. This intermediate could then rearrange, the group X migrating to the o- or p- position by an intramolecular process, or, alternatively, in the presence of an activated aromatic nucleus, some transfer of X^+ could take place.

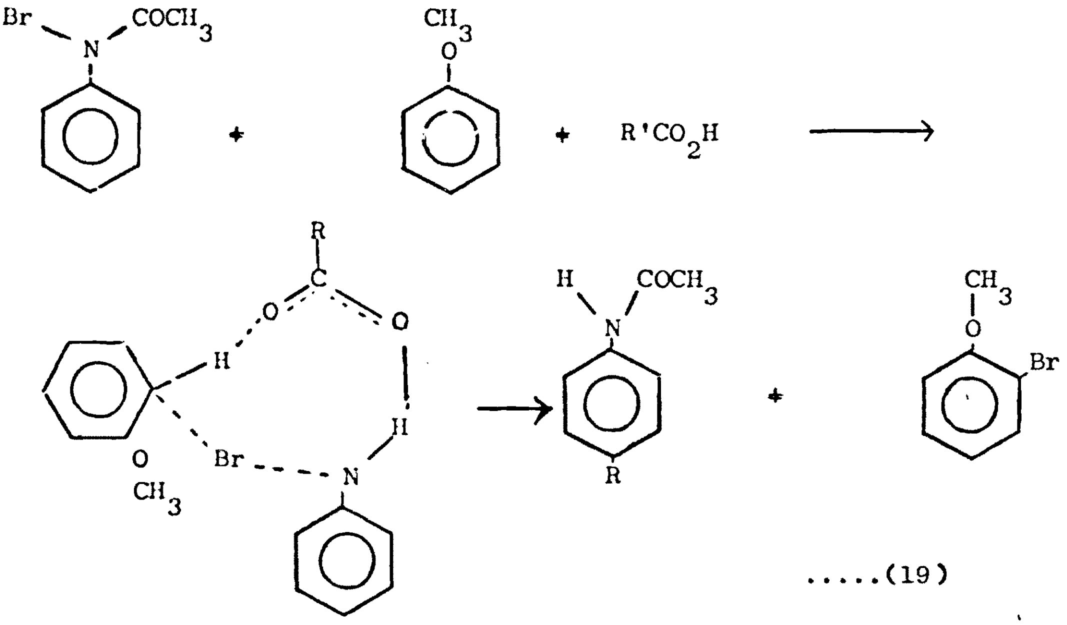
In order to provide evidence to support this view of the mechanism of the rearrangement in aprotic solvents, the transformation was carried out in the presence of isotopically labelled acetanilide[32,33]. However the results were inconclusive, as an equilibrium (equation 18) appeared to be set up rapidly before rearrangement took place.

$$\text{Ph.NBr.Ac} + \overset{*}{\text{Ph}}\text{. NH.Ac} \quad \text{Ph.NH.Ac} + \overset{*}{\text{Ph}}\text{ .NBr.Ac.....(18)}$$

The results obtained from further experiments led Dewar[32] to suggest that the mechanism was a complex one, and that the reaction took place inside aggregates of polar molecules, which would be expected to be present in the non-polar medium employed.

Israel, Tuck and Soper[29] also investigated the reaction between N-bromoacetanilide and acetic acid in chloroform in the presence of aromatic ethers, and found that the rate of reaction depended on the concentration of the aromatic ether. They inferred that the reaction must involve direct bromination by the N-bromoanilide itself and not by any intermediate formed from it.

Scott and Martin[34] suggested a termolecular mechanism to explain the fact that the ratio of *o*- to *p*-bromoanisole, formed when anisole was brominated by *N*-bromoanilides and acetic acid, in chlorobenzene, was dependent on the nature of both the acid and the *N*-bromoanilide (Equation 19).



.....(19)

A similar mechanism was suggested for the analogous reaction of *N*-chloroanilides[35].

1.2.3. The Thermal Rearrangement

In 1886, Bender[7] found that N-chloroacetanilide on melting rearranged to p-chloroacetanilide. Slosson[8] however showed that, if N-chlorobenzanilide was heated to 160°, there was no change in the percentage of active chlorine, although the liquid became yellow. Heating the melt above this temperature caused a vigorous reaction, which gave p-chlorobenzanilide as the sole product. Several N-haloanilides were shown to undergo this thermal rearrangement.

Porter and Wilbur[36] heated N-chloroacetanilide in a sealed tube at 100° and found that it first melted and then resolidified to give slightly discoloured p-chloroacetanilide. An intramolecular migration of the chlorine atom was considered to be the most likely mechanism for this transformation.

Bradfield[37] showed that, when N-chloroacetanilide was heated in a sealed tube, and the external temperature was maintained at 100°, complete rearrangement occurred within 30 minutes. During one reaction the temperature of the melt rose to 200°, and on cooling purple crystals formed inside the tube. Acid fumes were released from the tube when it was opened. The results of the analyses of the solid product are given in Table 3.

Table 3

Product	Experiment I (Air-bath at 100°)		Experiment II (Water-bath at 100°)	
	(g.)	%	(g.)	%
o-chloroacetanilide	3.65	18.2	--	16.5
p-chloroacetanilide	8.19	41.0	--	45.7
2,4-dichloroacetanilide	1.40	7.0	--	4.0
acetanilide	1.20	6.3	--	--
Total weight	14.5	72.5	2.85	71.2
o:p ratio	1:2.3		1:3.0	

The presence of acetanilide and 2,4-dichloroacetanilide in the product was considered to indicate that molecular chlorine had been produced and that the rearrangement proceeded by an intermolecular mechanism, similar to that of the 'Orton' rearrangement in hydroxylic solvents.

Robertson and Waters[38] showed that N-chloroanilides caused an increase in the rate of autoxidation of tetralin at 76° and suggested that homolytic fission of the N-chloroanilides gave rise to radicals (X·) which abstracted hydrogen from the tetralin and thus initiated the oxidation as follows:-

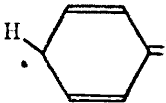
$$X\cdot + C_{10}H_{12} \longrightarrow X - H + \cdot C_{10}H_{11} \ldots\ldots\ldots\ldots\ldots (20)$$

$$\cdot C_{10}H_{11} + O_2 \longrightarrow C_{10}H_{11}{-}O{-}O\cdot \ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

$$C_{10}H_{11}{-}O{-}O\cdot + C_{10}H_{12} \longrightarrow C_{10}H_{11}OOH + \cdot C_{10}H_{11} \ldots\ldots (22)$$

In 1960 Beard, Boocock and Hickinbottom[3] published results which, in their view, indicated that the rearrangement of N-chloroacetanilide in the fused state was an intermolecular reaction. When N,2,4,6-tetrachloroacetanilide was heated in the dark under an atmosphere of nitrogen in toluene and in p-xylene, from which all traces of peroxide had been removed, benzyl chloride and p-methybenzyl chloride respectively were obtained. The products obtained when N-chloroacetanilide reacted under similar conditions, showed that chlorination had occurred both in the sidechain of the alkylbenzene and at the para-position of the anilide. In more reactive solvents, such as acetylacetone, acetophenone, or nitroaniline, the transfer of chlorine to the substrate was complete. The fact that chlorination occurred in the sidechains and not in the nuclei of the aromatic solvents suggested that the thermal reaction of N-chloroanilides proceeds by a free radical mechanism involving chlorine atoms.

The following mechanism was suggested for the chlorination of the solvent by N-chloroacetanilide:-

$\mathrm{Ph.NCl.Ac} \longrightarrow \mathrm{Cl}\cdot + \mathrm{Ph.\dot{N}.Ac} \longleftrightarrow$  =NAc etc..............(23)

$\mathrm{Ph.\dot{N}.Ac} + \mathrm{CH_2RR'} \rightarrow \mathrm{Ph.NH.Ac} + \cdot\mathrm{CHRR'}$ ....(24)

$\mathrm{Cl}\cdot + \mathrm{CH_2RR'} \longrightarrow \mathrm{HCl} + \cdot\mathrm{CHRR'}$ ....(25)

$\cdot\mathrm{CHRR'} + \mathrm{Ph.NClAc} \rightarrow \mathrm{ClCHRR'} + \mathrm{Ph.\dot{N}.Ac}$..........................(26)

It was considered that the amount of hydrogen chloride formed by reaction (25) was insufficient to alter the mechanism from a homolytic to an acid-catalysed one. A bimolecular homolytic reaction between N-chloroacetanilide and the solvent without preliminary dissociation into free radicals was also considered, but the former mechanism was preferred as it accounted for the formation of molecular chlorine, acetyl chloride and other by-products from the N-chloro-di- and N-chloro-tri-chloroacylanilides when they were heated alone. However no attempt was made to obtain further evidence for this mechanism by a study of the kinetics of the reaction.

1.2.4. The Photolytic Rearrangement

Blanksma[39,40] noted that the rearrangement of N-chloroacetanilide was accelerated by light. In both alcohol and acetic acid, the product was p-chloroacetanilide, whereas in decalin, the products were acetanilide and the chlorinated solvent. The rate of rearrangement was shown to increase with time; the first recorded example of autocatalytic decomposition of N-chloroacetanilide. Sodium carbonate and sodium acetate were found to inhibit the reaction.

Chattaway and Orton[41] found that N-chloroacetanilide, in chloroform or acetic acid, rearranged in sunlight, the solution turned yellow and acquired a so-called "chlorous" smell. The solution gave a precipitate with silver nitrate solution and it was concluded that light-induced decomposition of N-chloroacetanilide had occurred, and during the course of the reaction a catalytic agent, presumably hydrogen chloride,was formed.

An extensive study of the photolytic rearrangement of N-chloroacetanilide was undertaken by Matthews and Williamson[42]. The kinetics were found to be of the first order in 90% acetic acid, but in glacial acetic acid, ethanol, and benzene the characteristics of autocatalysis were observed. In this latter case, if the light was extinguished, the rearrangement continued for several minutes whereas in the presence of water, this rearrangement stopped as soon as the light was extinguished. No explanation, in terms of mechanism, was given for these observations.

The effect of change of solvent on the photolytic rearrangement of N-chloroacetanilide was studied also by Hodges[43]. Coloured crystals were isolated at the end of the reaction in carbon tetrachloride and in bromobenzene, and were characterised as N,N'-diacetylhydrazobenzene. The high quantum yield was considered to indicate a supplementary reaction which succeeded the primary dissociation. In carbon tetrachloride, catalysis by hydrogen chloride, formed in a side reaction was considered to be the cause of the high quantum yield. A radical chain mechanism was postulated to account for the experimental evidence.

Ayad, Beard, Garnwood and Hickinbottom[2] photolysed N-chloroacetanilide in carbon tetrachloride and found that the ratio of o- to p-chloroacetanilide in the product was similar to that for the rearrangement induced by a free-radical initiation (Table 4). They suggested that the photolysis proceeded by a free-radical mechanism.

Cadogan and Foster[4] showed that a homolytic rearrangement occurred readily when diethyl or diphenyl N-chloro-N-phenylphosphoramidate, in benzene, was irradiated by white light, and also observed that the rate curves exhibited the characteristics of autocatalysis. A comparison was made between the high proportion of o- substituted anilide obtained in this reaction, and that usually associated with homolylic aromatic arylation.

Tanner and Protz[44], in a study of the photoinitiated dissociation of N-bromoacetanilide and of N-bromo-2',4,6-trichloroacetanilide, in carbon tetrachloride, considered that three distinct free-radical mechanisms were possible in principle. The products were analysed by gas chromatography, and coupling products, N,N'-diacetyl-4,4'-diaminabiphenyl (3%), and diacetylhydrazabenzene (trace), were shown to be present, indicating a radical mechanism. Addition of toluene was found to increase the quantum yield of the reaction, and to alter the ratio of products, effects which were also observed when toluene was present during the rearrangement of N-bromoacetanilide induced by benzoyl peroxide. The possibility of a side-reaction involving an ionic mechanism was discounted because the reaction stopped as soon as the light source was removed. The change in the ratio of o- to p-bromoacetanilide which

which arose from the addition of toluene, was explained by assuming the formation of solvated radicals, whose positional selectivity differs from the uncomplexed species. An investigation involving the addition of several aromatic compounds to the system and determination of the effect on the o- to p- ratio was considered to substantiate this view. A study of the photolysis of N-bromo-2,4,6-trichloroacetanilide, in the presence of various derivatives of toluene, provided evidence for a chain mechanism involving bromine atoms, similar to that established for N-bromosuccinimide under similar conditions[45].

Coulson, Williams and Johnston[6] investigated the kinetics and the products of the photolysis of N-chloroacetanilide. The rate curves showed characteristics of autocatalysis, and when a solution containing N-chloroacetanilide, undergoing rearrangement, was aspirated with dry nitrogen, the kinetics altered tending towards first order. Hydrogen chloride and chlorine were detected in the effluent gas and were found to account for about 10% of the available chlorine in the N-chloroacetanilide. It was suggested that the autocatalysis was due to the formation of hydrogen chloride by a side reaction, probably involving the abstraction from the products of hydrogen by chlorine atoms. The hydrogen chloride thus formed would catalyse the 'Orton' mechanism for rearrangement. The products of the rearrangement were analysed (Table 4) and the ratio of o- to p-chloroacetanilide differed from the value obtained by Ayad, Beard, Boocock and Hickenbottom[2]. The results indicated the participation of hydrogen chloride, since the o:p ratio was appreciably increased when hydrogen chloride was removed by the passage of nitrogen.

Further studies of the products (Table 4) and kinetics of the rearrangement of diphenyl N-chloro-N-phenylphosphoramidate, and N-bromoacetanilide were carried out by Longmaid[25] and Atkins[46] respectively. The view that hydrogen halide was responsible for the autocatalysis observed in the photolytic rearrangement of these compounds was confirmed. However, Coulson[5] found that the photolytic decomposition of N-chlorobenzenesulphonanilide was a first-order reaction.

Table 4

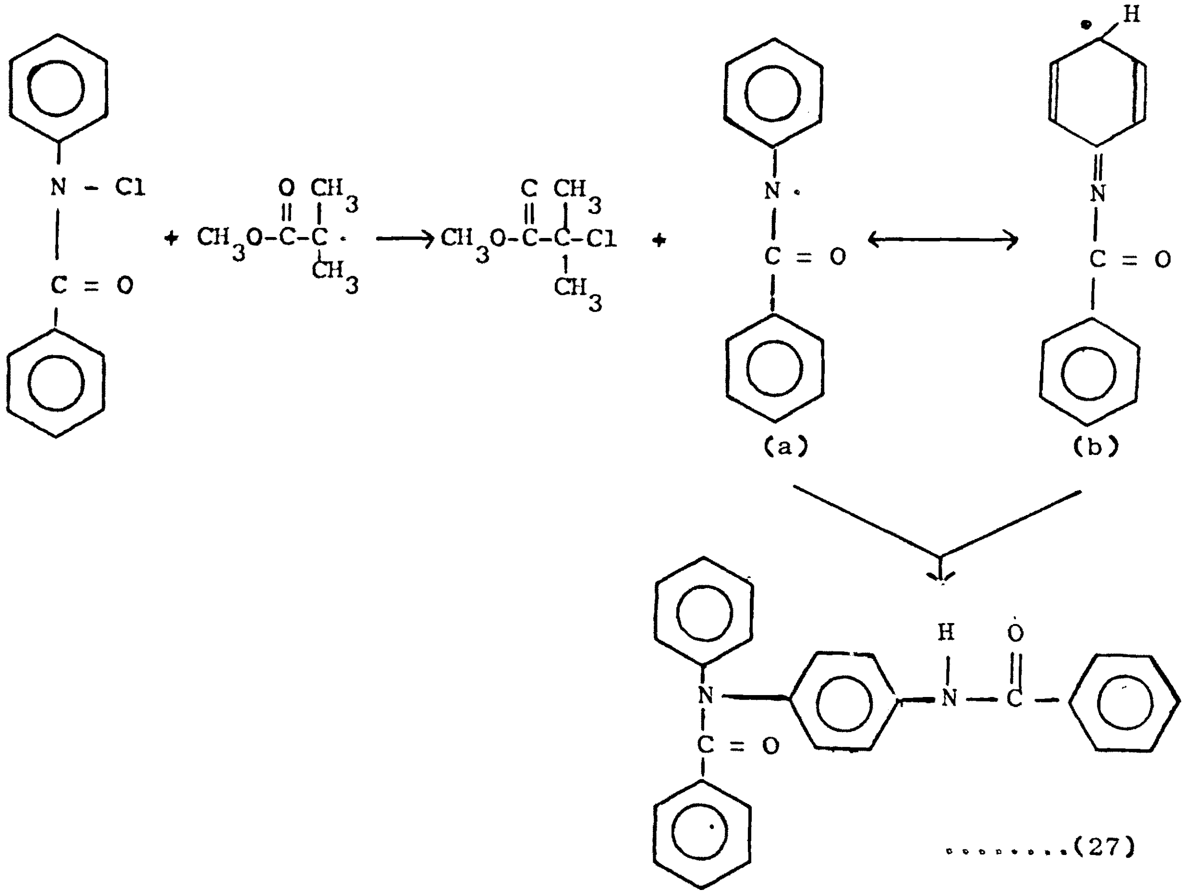
The Products of the Photolytic Rearrangement of N-Chloroanilides

N-Chloroanilide	Solvent	Temperature (°)	Molar % of Products a	o	p	d	*o*:*p*
N-Chloroacetanilide[2]	Carbon tetrachloride	-	-	14.7	77	-	1:5.24
N-Chloroacetanilide[6]	Carbon tetrachloride	77	26	23	50	-	1:2.15
N-Chloroacetanilide[6]	Carbon tetrachloride*	77	32	27	40	-	1:1.45
N-Chlorobenzenesulphonanilide[5]	Carbon tetrachloride	77	30	29.5	38.5	2.0	1:1.25
Diphenyl *N*-Chloro-*N*-phenylphosphoramidate[4]	Benzene	20	2	53	46	-	1:0.87
Diphenyl *N*-Chloro-*N*-phenylphosphoramidate[25]	Carbon tetrachloride	77	38	34	23	3.3	1:1.48

* The solution was aspirated with nitrogen continuously throughout the reaction.

1.2.5. The Rearrangement in the Presence of Free-radical Initiators

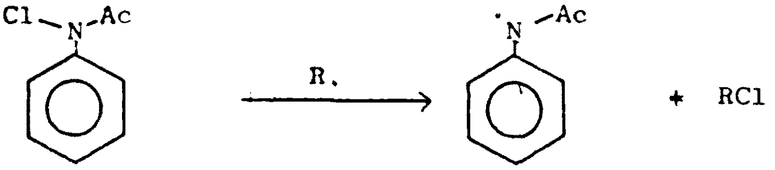
Ford, Hunt and Waters[47] have shown that the rearrangement of N-haloanilides can be brought about by free radical initiators. In benzene 2-methoxycarbonyl-2-propyl radicals, generated by the pyrolysis of dimethyl α, α'-azobutyrate, were found to abstract the N-halogen to give the corresponding α-halogenoisobutyrate in good yield. The other products could be explained in terms of the newly formed acylamino-radicals (Ph.Ṅ.COR) which resulted from the abstraction of the N-halogen from the N-haloamide. For example, N-chlorobenzanilide gave 4-benzamido-N-benzoyldiphenylamine (26%) formed by combination of the two forms of the benzoylamino-radicals (a and b)



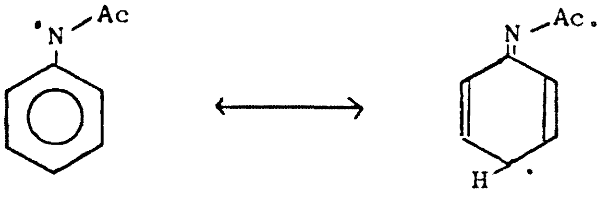
........(27)

Ayad, Beard, Garwood and Hickinbottom[2] found that N-chloroacetanilide, in hot carbon tetrachloride, rearranged to o- and p-chloroacetanilide in the absence of light, if a small quantity of benzoyl peroxide or azoisobutyronitrile was present. It was suggested that these additives initiated rearrangement by a free-radical mechanism involving homolytic fission of the N-Cl bond. N,2,4,6-tetrachloroacetanilide was found to chlorinate the side chain of alkylbenzenes in the presence of benzoyl peroxide, and, as bromination of the side chain of alkylbenzenes by N-bromosuccinimide in the presence of benzoyl peroxide was known to involve bromine atoms, it was considered probable that this chlorination also proceeded by a homolytic mechanism. For comparison, the chlorination was carried out in acetic acid, when substitution occurred entirely in the nucleus of the alkylbenzene, as is characteristic of electrophilic substitution.

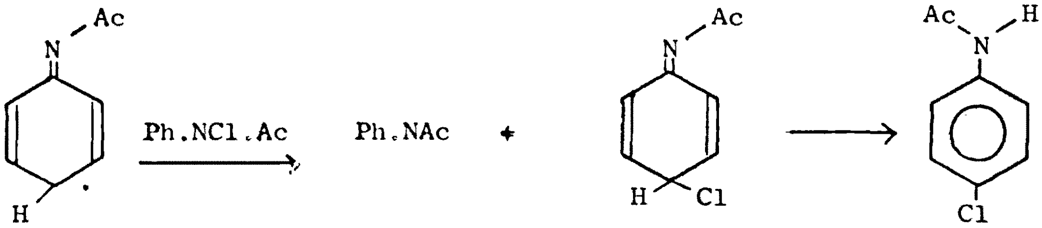
A possible mechanism for the rearrangement of N-chloroacetanilide in the presence of benzoyl peroxide was suggested:-



.......................(28)



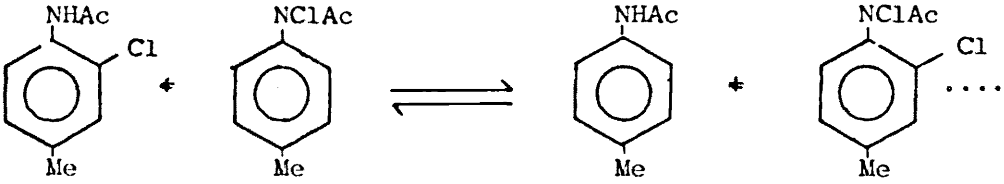
.......................(29)



.....(30)

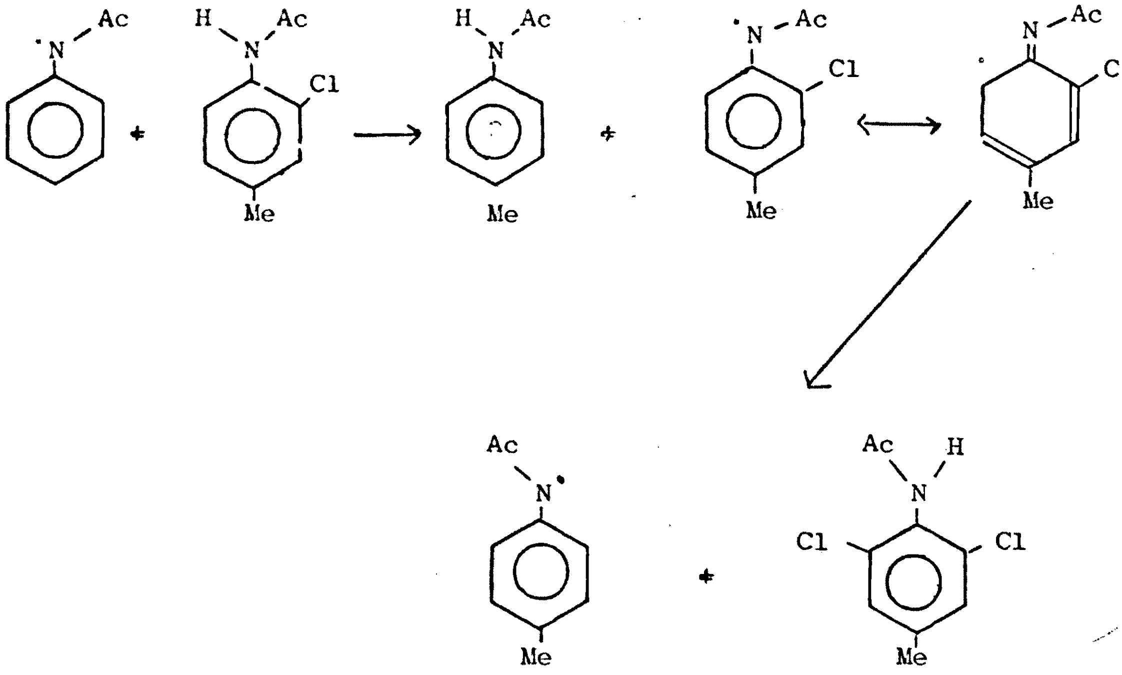
where R· represents the radical formed from benzoyl peroxide *o*-Chloroacetanilide can be formed by an analogous mechanism.

p-*N*-Chloroacetamidotoluene reacted under similar conditions to yield not only the expected product, 4-acetamido-3-chlorotoluene, but also 4-acetamido-3,5-dichlorotoluene, and *p*-acetamidotoluene. Two explanations were offered to account for the formation of these products. Exchange might occur between the *N*-hydrogen of the monochlorinated acetamidotoluene and the chlorine of the *N*-chloroamide (equation 31).



............(31)

Alternatively *p*-tolylacetylamino-radicals or phenyl radicals might abstract the *N*-hydrogen of the *o*-chloroamide, giving rise to 2-chloro-*p*-tolylacetylamino-radicals, which could then give the dichloro-compound (equation 32) :-



.............(32)

The isomerisations of several N-haloanilides, in the presence of catalytic quantities of either benzoyl peroxide or azoisobutyronitrile, was found to be autocatalysed. These authors did not, however, comment upon this increase in rate or attempt to explain it in terms of the proposed mechanism of the rearrangement.

Cadogan and Foster[4] carried out an investigation of the rearrangement of some N-chlorophosphoramidates, and showed that the rearrangement of these compounds in bromobenzene, at 105°, in the presence of benzoyl peroxide was also autocatalysed.

A more recent investigation[6] of the benzoyl peroxide initiated rearrangement of N-chloroacetanilide showed that initially the reaction was of the first order with respect to both the N-chloroanilides and the peroxide. However as the reaction progressed, there was an increase in the rate of reaction, which was shown to be due to catalysis by hydrogen chloride, generated in a side-reaction, which brought about rearrangement by the 'Orton' mechanism. Aspiration of the reaction mixture with nitrogen caused a decrease in the deviation from first-order kinetics, and hydrogen chloride and chlorine were detected in the effluent gas. The rate-curves for the rearrangement of diphenyl N-chloro-N-phenylphosphoramidate[25] and N-bromoacetanilide[46], catalysed by benzoyl peroxide, have been found to exhibit deviations from first-order kinetics. However, the rearrangement of N-chlorobenzenesulphonanilide was observed[5] to be almost exactly a first-order process with respect to the N-chloroanilide throughout the reaction, and no evidence was obtained to suggest that any rearrangement of this N-chloroamide occurred by the 'Orton' mechanism. Analysis of the products of the rearrangement of N-chloroacetanilide[6] showed that the ratio of o- to p-chloroacetanilide when radical initiators were used was considerably lower than that for the photolytic rearrangement. Previous workers[2,4] had found these two ratios to be approximately the same and had concluded that an essentially similar mechanism was involved in the two cases. Coulson, Williams and Johnston[6] proposed that during the reaction of N-chloroacetanilide in the presence of benzoyl peroxide, some benzoyl hypochlorite was formed by abstraction of chlorine from N-chloroacetanilide by benzoyloxy-radicals. Chlorination of acetanilide by this hypochlorite would be expected to yield a higher proportion of para-substituted product than the 'Orton' rearrangement under comparable conditions, since benzoyl hypochlorite is more powerfully electrophilic than molecular chlorine.

Table 5

The Products of the Rearrangements of *N*-Chloroanilides, in the Presence of Benzoyl Peroxide

N-Chloroanilide	Solvent	Temperature (°)	Molar% of Products				
			o	p	a	d	*o*:*p*
N-Chloroacetanilide[2]	Carbon tetrachloride	80	-	-	-	-	1:5.3
N-Chloroacetanilide[6]	Carbon tetrachloride	77.5	15.4	57.5	27.1	-	1:3.7
Diphenyl-*N*-chloro-*N*-phenyl-phosphoramidate[4]	Bromobenzene	105.	49.	51	-	-	1:1.0
Diphenyl-*N*-chloro-*N*-phenyl-phosphoramidate[25]	Carbon tetrachloride	77.5	24.	19	49	-	1:0.78

2. EXPERIMENTAL SECTION

2.1. Preparation and Purification of Reagents.

2.4. The Rearrangement of N-Chloroanilide in Carbon Tetrachloride in the Presence of Hydrogen Chloride.

2.5. The Thermal Rearrangement of N-Chloroanilides in Nitrobenzene.

2.6. The Thermal Rearrangement of N-Chloroanilides in the presence of added Anilides.

2.7. The Photolytic Rearrangement of N-Chloroanilides.

2.8. The Rearrangement of N-Chloroanilides in Carbon Tetrachloride, in the presence of Benzoyl Peroxide.

2.1. Preparation and Purification of Reagents.

All solids were recrystallised to constant melting point. All melting points quoted are uncorrected. The melting points of the *N*-chloroanilides and benzoyl peroxide were taken using a Kofler 'Hotbench'. Recorded values for melting points are given in parentheses. Yields quoted are not necessarily the optimum values, but were actually obtained in the experiments described.

2.1.1. Amines.

2.1.1.1. Aniline, 2-chloroaniline and 3-chloroaniline.

The commercial products (Hopkin and Williams) were purified by distillation under reduced pressure, using a Vigreux column. (Table 6)

2.1.1.2. 4-Chloroaniline, 2,4-dichloroaniline and 2,4,6-trichloroaniline.

The commercial products (Hopkin and Williams) were distilled under reduced pressure using a short Vigreux column and then recrystallised from aqueous ethanol. (Table 6)

2.1.1.3. 2,6-Dichloroaniline.

The commercial product (Koch-Light) was purified by the method described above (Section 2.1.1.2.).

2.1.2. Formanilide.

The commercial specimen (B.D.H.) was purified by distillation under reduced pressure using a short Vigreux column (b.p. 170°/5 mm.), and subsequent recrystallisation from *p*-xylene/light petroleum (b.p. 100-120°) gave needle of pure formanilide. m.p. 47° (lit.,[48] 47°).

Table 6

Physical Constants of Aniline and Chloroanilines.

	b.p. (°)	Pressure (mm.)	m.p. (°)	Lit. m.p. (°)
Aniline	63	1.8	-	-
2-Chloroaniline	90	6.0	-	-
3-Chloroaniline	93	2.0	-	-
4-Chloroaniline	67	0.6	72	72.5[49]
2,4-Dichloroaniline	96	1.4	63.5	63[50]
2,6-Dichloroaniline	96	0.6	38.5	39[51]
2,4,6-Trichloroaniline	82	1.2	79	78.5[52]

All these compounds were shown to be pure by gas chromatography.

2.1.3. Acetanilide and Derivatives of Acetanilide.

2.1.3.1. Acetanilide, N-methylacetanilide and N-phenylacetanilide.

Commercial specimens (Hopkin and Williams) were recrystallised from absolute alcohol.

Table 7

Acetanilide and its N-substituted Derivatives.

	m.p. (°)	Lit. m.p. (°)
Acetanilide	115	115[53]
N-Methylacetanilide	100-100.5	101[54]
N-Phenylacetanilide	102	101-102[55]

2.1.3.2. 2'-Chloro-2-phenylacetanilide.

Phenylacetyl chloride (8.7 g., 0.055 mole) was added slowly to an emulsion of 2-chloroaniline (7.0 g., 0.055 mole) and sodium hydroxide solution (2 M., 150 ml.) with rapid stirring. After the mixture had been stirred for 10 min., the aggregates of crude solid anilide were crushed and the stirring continued for a further 10 min. The product was filtered off and washed with sodium hydroxide solution (2 M , 2 x 10 ml.), water (2 x 10 ml.), sulphuric acid (1 M , 2 x 10 ml.), water (2 x 10 ml.) and dried in a vacuum desiccator. The crude product was decolourised with activated charcoal, and recrystallised from aqueous ethanol to give white needles of pure 2'-chloro-2-phenylacetanilide. (9.7 g., 0.040 mole, 74%), m.p. 119.5° (Found: C, 68.6; H, 5.1; Cl, 14.3; N, 5.9. $C_{14}H_{12}ClNO$ requires C, 68.4; H, 4.9; Cl, 14.5; N, 5.7%)

2.1.3.3. 2-Phenylacetanilide.

2-Phenylacetanilide was prepared in the same way as 2'-chloro-2-phenylacetanilide. Aniline (40 g., 0.43 mole), sodium hydroxide solution(450 ml., 10%) and phenylacetyl chloride (66.7 g., 0.43 mole) gave a crude product, which after recrystallisation from aqueous ethanol gave needles of pure 2-phenylacetanilide (77 g.,0.365 mole, 84%) m.p. 116.5-117° (lit.,[56] 116-117°)

2.1.3.4. 3'-Chloro-2-phenylacetanilide. (Bunnett, Kato and Flynn's method[57])

Phenylacetyl chloride (4.25 g., 0.0275 mole) was slowly added to a refluxing mixture of 3-chloroaniline (3.5 g., 0.0275 mole) and pyridine (2.15 g., 0.0275 mole) in carbon tetrachloride (50 ml.), and the resultant solution was refluxed for 2 hr. to complete the reaction. After the addition of light petroleum (b.p. 40-60°), the mixture was cooled, when a red oil formed, which soon solidified. The solid was filtered and purified as described for 2'-chloro-2-phenylacetanilide to give needles of 3'-chloro-2-phenylacetanilide. (5.4 g., 0.022 mole, 80%)

m.p. 95° (Found: C, 68.6; H, 5.0; Cl, 14.3; N, 5.8. $C_{14}H_{12}ClNO$ requires C, 68.4; H, 4.9; Cl, 14.5; N, 5.7%).

2.1.3.5. 4'-Chloro-2-phenylacetanilide, 2',4'-dichloro-2-phenylacetanilide and 2',4',6'-trichloro-2-phenylacetanilide.

These anilides were prepared in the same way as 3'-chloro-2-phenylacetanilide (section 2.1.3.4.)

Table 8

Derivatives of 2-Phenylacetanilide.

	Yield (%)	m.p. (°)	Lit. m.p. (°)
4'-chloro-2-phenylacetanilide	85	74	72[83]
2',4'-Dichloro-2-phenylacetanilide	88	137	*
2',4',6'-Trichloro-2-phenylacetanilide	77	176	‡

* Found: C, 60.2; H, 3.8; Cl, 25.4; N, 4.6. $C_{14}H_{11}Cl_2NO$ requires C, 60.0; H, 3.9; Cl, 25.4; N, 4.7%

‡ Found: C, 53.7; H, 3.4; Cl, 34.1; N, 4.6. $C_{14}H_{10}Cl_3NO$ requires C, 53.5 ; H, 3.3; Cl, 33.9; N, 4.5%

2.1.3.6. 2,2-Diphenylacetanilide (Bunnett, Kato and Flynn's method[57])

Diphenylacetyl chloride was prepared by allowing thionyl chloride (300 ml., 4.1 mole) to react with diphenylacetic acid (77.7 g., 0.37 mole) overnight, under anhydrous conditions. The thionyl chloride was distilled off under reduced pressure, and the residue was recrystallised from light petroleum (b.p. 80-100°) using a solid carbon dioxide/alcohol cooling mixture, to give white crystals of diphenylacetyl chloride (77.8 g., 0.337 mole, 92%) m.p. 56° (lit.,[84] 55°).

A solution of diphenylacetyl chloride (77.8 g., 0.037 mole) in carbon tetrachloride(150 ml.) was added to a refluxing mixture of aniline (34 g., 0.337 mole) and pyridine (27.2 g., 0.0337 mole) in carbon tetrachloride (600 ml.). After refluxing for two hours, the mixture was cooled and diluted with light petroleum (b.p. 60-80°, 1000 ml.). The solid which precipitated was filtered off, washed with light petroleum, dried overnight in a vacuum desiccator, and recrystallised from aqueous ethanol giving needles of pure 2,2-diphenylacetanilide. (90.7 g.,0.314 mole, 92%) m.p. 180° (lit.,[58] 180°)

2.1.3.7. 2,2,2-Trichloroacetanilide.

Bunnett, Kato and Flynn's method (section 2.1.3.6.),using trichloroacetyl chloride as the acid chloride, gave needles of 2,2,2-trichloroacetanilide (40%) m.p. 94.5° (lit.,[59] 94-95°)

2.1.4. Benzanilide and Derivatives of Benzanilide.

2.1.4.1. Benzanilide.

A commercial specimen (Hopkin and Williams) was recrystallised from alcohol (m.p. 164.5-165°)(lit.,[60] 163°)

2.1.4.2. N-Phenylbenzanilide, 4'-Bromobenzanilide, 4'-Iodobenzanilide, 4'-Phenylbenzanilide, 4'-Phenoxybenzanilide, 4'-Nitrobenzanilide and 4'-Benzoylbenzailide.

The anilides were prepared by Bunnett, Kato and Flynn's method (section 2.1.3.6.). The yields and melting points are given in Table. 9.

2.1.4.3. 2'-Chlorobenzanilide, 3'-Chlorobenzanilide,4'-Chlorobenzanilide 2',4'-Dichlorobenzanilide, 2',4',6'-Trichlorobenzanilide and 4'-Fluorobenzanilide.

These anilides were prepared by the Schotten-Baumann method using benzoyl chloride and the appropriate amine. The products were all recrystallised from aqueous ethanol. The yields and melting points are given in Table 9.

Table 9

Derivatives of Benzanilide.

Anilide	Yield (%)	m.p. (°)	Lit m.p. (°)
N-Phenylbenzanilide	77	180	180[61]
4'-Bromobenzanilide	84	202	202[62]
4'-Iodobenzanilide	51	219	222[63]
4'-Phenylbenzanilide	78	233	230[64]
4'-Phenoxybenzanilide	89	160-160.5	*
4'-Nitrobenzanilide	84	200.5-201	201.5[65]
4'-Benzoylbenzanilide	73	154	152[66]
2'-Chlorobenzanilide	92	103	99[67]
3'-Chlorobenzanilide	86	121.5	118-120[68]
4'-Chlorobenzanilide	73	195	192-192[69]
2',4'-Dichlorobenzanilide	78	118	117[70]
2',4',6'-Trichlorobenzanilide	92	174	174[71]
4'-Fluorobenzanilide	71	185	185[72]

* Found: C, 78.7; H, 5.3: N, 4.9. $C_{19}H_{15}NO_2$ requires C, 78.9; H, 5.2; N 4.8%.

2.1.4.4. 4-Chlorobenzanilide.

4-Chlorobenzoic acid (7.3 g., 0.046 mole) was refluxed with thionyl chloride (25 ml., 40.9 g., 0.35 mole) until the mixture became homogenous (2 hr.). The excess thionyl chloride was removed, and the crude acid chloride was added slowly with stirring, to an emulsion of aniline (4.4 g.,0.046 mole) in sodium hydroxide solution (10%, 50 ml.). Stirring was continued for 10 min., and the crude product was filtered, washed as in the preparation of 2'-chloro-2-phenylacetanilide (section 2.1.3.2.) and recrystallised from aqueous ethanol (9.6 g., 0.041 mole, 89%) m.p. 194° (lit.,[73] 193°).

2.1.4.5. 4-Nitrobenzanilide.

Using a method analogous to that used for the preparation of 4-chlorobenzanilide (section 2.1.4.4.), 4-nitorbenzoic acid gave a crude product, which on recrystallisation yielded pale yellow needles of 4-nitrobenzanilide (78%) m.p. 215° (lit.,[74] 214°).

2.1.5. Sulphonanilides.

2.1.5.1. Benzenesulphonanilide (Shepherd's method[75]).

A mixture of aniline (37.2 g., 0.40 mole) and glacial acetic acid (150 ml.) was heated to 100°, and benzenesulphonyl chloride (88 g., 0.50 mole) and fused anhydrous sodium acetate (16.4 g., 0.20 mole) were added. The mixture was heated to its boiling point, allowed to cool to 100°, and a further portion of sodium acetate (8.2 g., 0.10 mole) was added. This procedure was repeated for further additions of 4.1 g., 4.1 g. and 8.3 g.

Hot water was then added to dissolve the precipitated sodium chloride and the mixture was left to cool. The product which crystallised out was filtered off and washed successively with acetic acid (60%, 2 x 30 ml.), hydrochloric acid (5 M, 2 x 30 ml.) and water (2 x 30 ml.). The product was recrystallised from aqueous ethanol giving pure benzenesulphonanilide (68 g., 73%) m.p. 111° (lit.,[75] 111°).

2.1.5.2. Methanesulphonanilide, N-Methylmethanesulphonanilide, 2'-Chloromethanesulphonanilide, 3'-Chloromethanesulphonanilide, 4'-Chloromethanesulphonanilide, 2',4'-Dichloromethanesulphonanilide and 2',4',6'-Trichloromethanesulphonanilide.

Using a method similar to that for benzenesulphonanilide (section 2.1.5.1.), methanesulphonyl chloride and the appropriate amine gave white crystals after recrystallisation from aqueous ethanol. The yields and melting points are given in Table 10.

Table 10

Sulphonanilides

Anilide	Yield (%)	m.p. (°)	Lit. m.p. (°)
Methanesulphonanilide	91	99.5-100	99[76]
N-Methylmethanesulphonanilide	61	77-77.5	•
2'-Chloromethanesulphonanilide	57	90.5	90.5[77]
3'-Chloromethanesulphonanilide	71	84.5	98-98.5[78]
4'-Chloromethanesulphonanilide	80	148	148[79]
2',4'-Dichloromethanesulphonanilide	62	174	174[77]
2',4',6'-Trichloromethanesulphonanilide	69	76.5-77	‡

• Found C, 35.4; H, 3.3; Cl, 29.6; N, 5.9. $C_7H_8Cl_2NO_2S$ requires C, 35.3; H, 3.3, Cl, 29.5; N, 5.8%.

‡ Found C, 30.6; H, 2.5; Cl, 38.6; N, 5.0. $C_7H_7Cl_3NO_2S$ required C, 30.5; H, 2.5, Cl, 38.7; N, 5.1%.

2.1.6. N-Chloroanilides.

2.1.6.1. N-Chloroacetanilide.

This was prepared by Chalsty and Israelstam's method[80] from t-butyl hypochlorite, which was made by two methods.

2.1.6.1.1. Teeter and Bell's method[81].

t-Butyl alcohol (38 ml., 30.0 g., 0.40 mole) was added to aqueous sodium hydroxide solution (250 ml., 4 M), together with enough water to make a homogenous solution. With constant stirring, chlorine was passed in until the formation of a second layer was complete. The mixture was kept below 15^0 throughout the reaction. The upper layer was seperated, washed with sodium carbonate solution (25 ml., 10%) until the washings were no longer acid to congo red, with water (2 x 25 ml.), dried ($CaCl_2$) and stored in a dark bottle in a refrigerator. A 68% yield of t-butyl hypochlorite, with purity greater than 99%, was obtained.

2.1.6.1.2. A modification of Geneste and Kergomad's method[105].

A cold mixture of glacial acetic acid (17.1 ml., 15 g., 0.30 mole) was slowly added to a well stirred solution of sodium hypochlorite (60% w/v, 80 ml.) so that the temperature of the mixture did not rise above 4°. After the solution had been stirred for 5 min., to complete the reaction, the crude t-butyl hypochlorite was seperated, washed and stored as described previously (section 2.1.6.1.1.)(11.2 g., 52%, purity 99%).

2.1.6.1.3. Chalsty and Israelstam's method[80].

Acetanilide (10.0 g., 0.074 mole) was dissolved in a 4% solution of borax in methanol (200 ml.), and t-butyl hypochlorite (8.0 g., 0.074 mole) was added slowly with constant stirring. After 10 min., the solution was poured into an ice/water mixture (500 ml.) and stirred in the dark for 20 min. The white granular solid was filtered off, washed well with water, dried overnight in a vacuum desiccator and recrystallised from acetone-light petroleum (b.p. 60-80°)(1:9) to give needles of *N*-chloroacetanilide (Table 11).

2.1.6.2. N-Chlorophenylacetanilide, N-Chlorodiphenylacetanilide, N-Chlorobenzanilide, N-Chloro-4-nitrobenzanilide and N-Chloro-4'-nitrobenzanilide.

The preparation was carried out using Chalsty and Israelstam's method (section 2.1.6.1.) and the appropriate anilide. In those cases in which the *N*-chloroanilide was an oil after the solution had been poured into water, crystallisation was initiated by the addition of crushed solid carbon dioxide. (Table 11)

2.1.6.3. N-Chloromethanesulphonanilide and N-Chlorobenzenesulphonanilide.

A modification of Chalsty and Israelstam's method[80] was employed, which prevented the N-chloroanilide from reacting to give a red oil. The solution of the anilide in methanol, saturated with borax, was kept in a freezing mixture (sodium chloride/ice), in the dark, and an equimolar quantity of t-butyl hypochlorite, cooled in a similar manner, was added slowly. After allowing 10 min. for the reaction to go to completion, the mixture was poured into a well-stirred ice/water mixture and crystallisation was initiated by the addition of crushed solid carbon dioxide. As soon as the solid N-chloroanilide precipitated, it was filtered, washed with a little water and dried in a vacuum desiccator. The crude product was recrystallised from methanol (Table 11).

Table 11

N-Chloroanilides

N-Chloroanilide	Yield (%)	m.p. (°)	Lit. m.p. (°)	% Chlorine	
				Calc.	Actual
N-Chloroacetanilide	92	90.5	91[2]	20.7	20.5
N-Chlorophenylacetanilide	94	52.5	-	14.5	14.4
N-Chlorodiphenylacetanilide	98	118	-	11.0	11.0
N-Chlorobenzanilide	95	81.5	81[8]	15.3	15.3
N-Chloro-4'-nitrobenzanilide	94	95	-	12.8	12.7
N-Chloro-4-nitrobenzanilide	96	160.5	-	12.8	12.8
N-Chlorobenzenesulphonanilide	97	59	59[2]	13.3	13.3
N-Chloromethanesulphonanilide	85	75	-	17.7	17.7

* The percentage of chlorine was determined iodometrically.

To prevent decomposition, the N-chloroanilides were stored in a vacuum dessicator in the dark.

2.1.7. Benzoyl Peroxide.

The commercial product (Hopkin and Williams) was dissolved in hot chloroform. After rapid filtration of the solution, two volumes of cold methanol were added and the precipitate of benzoyl peroxide was filtered off. The peroxide was further purified by repeating this process and it was dried and stored in a vacuum desiccator, in the dark. m.p. 107.5-108° (lit.,[82] 106°)

2.1.8. General Reagents.

2.1.8.1. Carbon Tetrachloride, Chlorobenzene and Nitrobenzene.

To remove any traces of hydrochloric acid, these were washed well with sodium hydroxide solution and water. They were dried ($MgSO_4$), redistilled using a 70 cm. Vigreux column and stored in well-stoppered bottles in the dark over molecular sieves (Hopkin and Williams, Type 4A). Each solvent was found to be pure, by gas chromatography.

2.1.8.2. Glacial Acetic Acid.

The commercial sample (Hopkin and Williams, Analar Grade) was shown to have no oxidisable impurity and had constant melting point (16°), and was used without further purification.

2.1.8.3. Silver Acetate.

The commercial specimen (Hopkin and Williams) was recrystallised from glacial acetic acid, dried in a vacuum desiccator and stored in the dark.

2.1.8.4. Nitrogen.

The commercial sample (British Oxygen Co. Ltd., White Spot Grade) was dried by passage through anhydrous silica gel before use.

2.1.8.5. Chlorine.

The commerical sample (I.C.I.) was dried by passage through concentrated sulphuric acid before use.

2.1.8.6. Hydrogen Chloride.

Concentrated sulphuric acid was dropped onto sodium chloride. The gas was dried by passage through concentrated sulphuric acid before use.

2.2. Analysis of the Products of the Rearrangement.

2.2.1. The Products of the Rearrangement of N-Chlorobenzanilide and N-Chlorophenylacetanilide.

As the anilides obtained directly from the rearrangement were not sufficiently volatile to be purified by distillation under reduced pressure, or to be used in a gas chromatography method, it was necessary to convert them to more volatile derivatives. The anilides were therefore hydrolysed to the corresponding amines, and it was necessary to show that the hydrolysis could be carried out in good yield and without significantly altering the proportions of the isomers.

2.2.1.1. Hydrolysis of benzanilide and its chloro-derivatives.

The method is typified by the following conversion of 4'-chlorobenzanilide to 4-chloroaniline. Recrystallised 4'-chlorobenzanilide (1.02 g., 0.0043 mole) was refluxed with glacial acetic acid (6 ml .) and hydrobromic acid (50/50 w.v., 8 ml .) for 10 hours. After neutralisation with saturated sodium carbonate solution, the mixture was extracted with dichloromethane (5 x 50 ml .), dried ($MgSO_4$), and filtered, the magnesium sulphate being well washed with further portions of dichloromethane. The solvent was largely removed by distillation using a rotary evaporator below 30°, and the resulting solution (about 5 ml .) was transferred, with the aid of further small portions of dichloromethane, to a pear-shaped distilling flask packed with glass-wool. After removal of the remaining solvent on a water-bath (60°), the flask was connected to an ice-cooled receiver and a small trap immersed in an acetone-solid carbon dioxide mixture. The product was distilled under reduced pressure to give pure 4-chloroaniline (see Table 6). The other anilides were hydrolysed by the same method, the yields obtained are given in Table 12.

2.2.1.2. Hydrolysis of phenylacetanilide and its chloro-derivatives

Milder conditions were used for this hydrolysis. A mixture of glacial acetic acid (10 ml.) and sulphuric acid (60%, 10 ml.) was refluxed with the anilide for 10 hours. Using the method described for the hydrolysis of 4'-chlorobenzanilide, the corresponding aniline was obtained in a pure state. The yields are given in Table 12.

Table 12

Hydrolysis of the Anilides

	Yield of the pure amine obtained after hydrolysis of:-	
	benzoyl derivative (%)	phenylacetyl derivative (%)
Aniline	93	93
2-Chloroaniline	95	97
3-Chloroaniline	94	97
4-Chloroaniline	94	95
2,4-Dichloroaniline	91	99
2,4,6-Trichloroaniline	92	94

2.2.1.3. Analysis of the hydrolysed product.

A Perkin-Elmer Gas Chromatography Apparatus (F 11) with a flame-ionisation detector was employed. The one metre stainless steel column was packed with a stationary phase consisting of Silicone oil (MS 555) and Bentone (34) on Chromosorb W (80-100 mesh) (11½ : 11½ : 77 w/w). The oven temperature was maintained at 190° and the carried-gas flow-rate at 1.8 l.of nitrogen per hour. As some of the chloroanilines are solids at room temperature, mixtures of isomeric chloroanilines were dissolved in a small quantity of benzene, to give an approximately 40% solution, before injecting samples (0.1 - 1.0 µl) onto the column.

As can be seen from Fig.1 each of the possible hydrolysed products could be identified and estimated. The peak heights were not to be found in simple proportion to the molecular concentrations of the components. Mixtures of known composition were analysed on the chomatograph, and the ratio of the height of each peak to that of 2-chloroaniline, was plotted against the ratio of the weight of the corresponding component to that of 2-chloroaniline. Using these calibration curves it was possible to calculate, from the peak height of each component, the molar percentage of the corresponding anilide in the original mixture. A standard mixture was analysed each time the chromatograph was used, but no significant variation in its response was detected, as long as the sample size was less than 1μl.

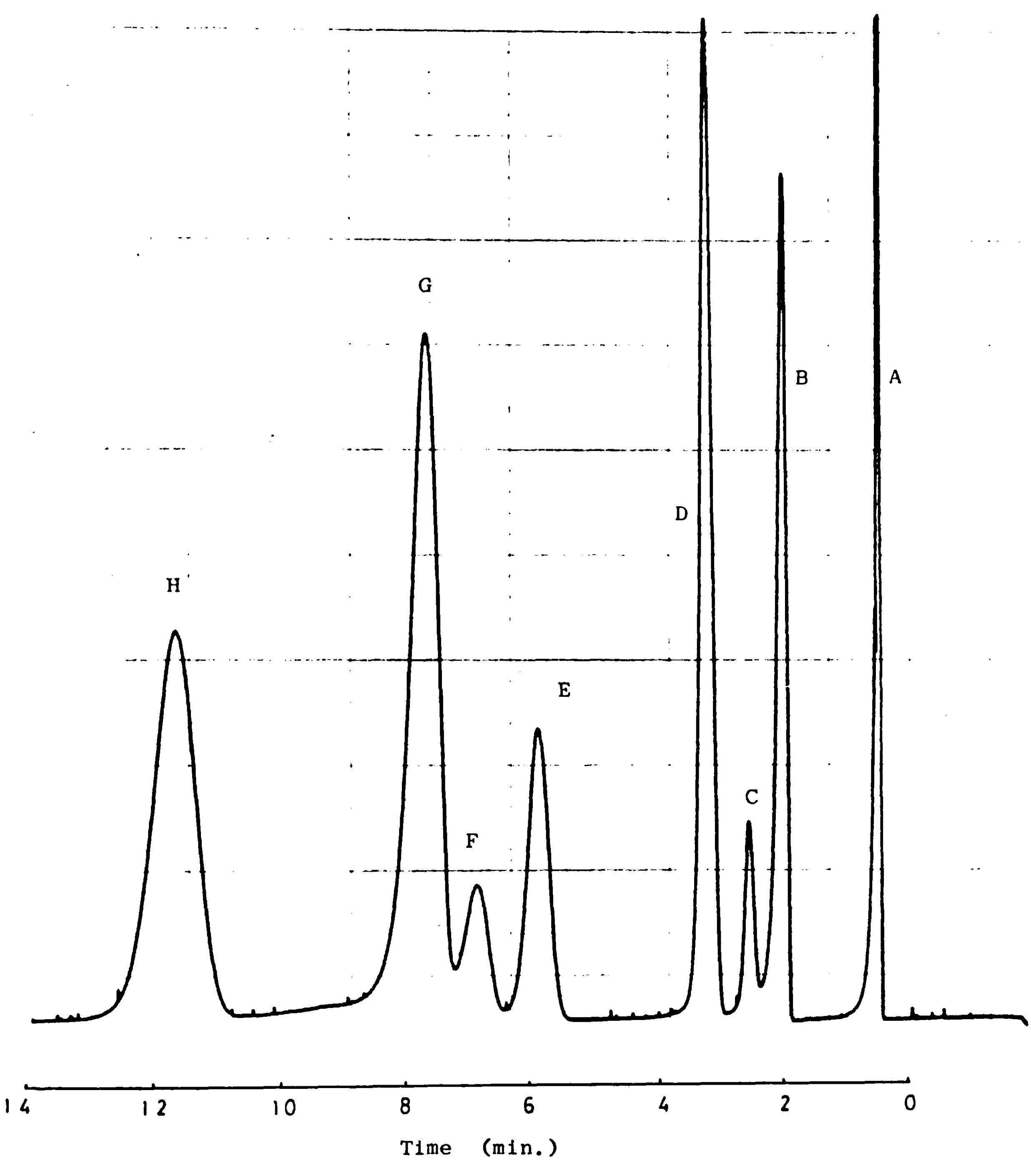
As a test of the validity of the method of hydrolysis and analysis of the mixture of products of the rearrangement, several mixtures of anilides were made up and hydrolysed. Then the hydrolysates were subjected to analysis by gas chromatography. The results obtained show good agreement between the experimentally determined composition and the actual, original composition (Table 13).

2.2.2. Products of the Rearrangement of N-Chloromethanesulphonanilide.

No method of hydrolysis of these compounds which gave satisfactorally high yields of the corresponding amines, could be found. However, the anilides obtained directly from the rearrangement were sufficiently volatile to be used in a gas chromatographic method.

A Perkin-Elmer Gas Chromatography Apparatus (F 11) was employed. A two metre stainless steel column was packed with a stationary phase of Versamid 930 on AW-DMCS Chromosorb W (80-100 mesh) (2 : 98). The oven temperature was maintained at 245°C and the carrier-gas flow-rate at 1.8.1. of nitrogen per hour.

Gas Chromatogram of a Mixture of Aniline and Chloroanilines. Fig. 1



A - Solvent (benzene)

B - Aniline

C - 2,6-Dichloroaniline

D - 2-Chloroaniline

E - 2,4,6-Trichloroaniline

F - 3-Chloroaniline

G - 4-Chloroaniline

H - 2,4-Dichloroaniline

Table 13

Analysis of Mixtures of Anilides of Known Composition

Anilides	Yield	Components in the original mixture						Composition determined by g.c.					
	%	Molar percentages						Molar percentages					
		o	p	a	d	t	o:p	o	p	a	d	t	o:p
Benzoyl Derivative	96	43.6	56.4	--	--	--	1:1.29	43.9	56.1	--	--	--	1:1.25
	90	23.0	13.1	59.4	4.5	--	1:0.57	23.9	13.9	57.9	4.6	--	1:0.59
	95	25.1	57.9	7.8	--	9.2	1:2.31	26.4	58.3	6.4	--	9.0	1:2.20
Phenylacetyl Derivative	97	37.9	62.1	--	--	--	1:1.64	38.2	61.8	--	--	--	1:1.62
	96	16.1	43.4	31.8	5.2	3.5	1:2.71	16.2	44.7	30.7	5.2	3.4	1:2.76

As the anilides are solids at room temperature, they were dissolved in a small quantity of ethanol, giving an approximately 20% solution. It was not found possible to resolve 3- and 4- chloromethanesulphonanilide. Mixtures were analysed using a method analogous to that described previously (section 2.2.1.3.). The peaks obtained for 2',4'-dichloro- and 2',4',6'-trichloro-methanesulphonanilide were too diffuse to allow anything more than an approximate estimation. Each time a set of mixtures were analysed by this method, the instrument was recalibrated in case there was any variation in response.

2.3. The Rearrangement in Glacial Acetic Acid

The kinetics and the products of the rearrangement of N-chloroacetanilide in glacial acetic acid, in the presence and absence of hydrogen chloride, have, as indicated in the historical section, been the subject of much research, and from these studies a clear picture of this reaction has emerged. However little work has been carried out on the corresponding rearrangement of N-chlorobenzanilide and it was thought advisable to study this reaction before proceeding to examine the rearrangement which occurs under conditions favourable to homolytic fission. An accurate comparison of the kinetics and proportions of products obtained under the two different sets of conditions would then be possible.

Recent work[6] has shown that the presence of silver acetate has a significant effect on the kinetics and the products of the rearrangement of N-chloroacetanilide in glacial acetic acid, and it was thought of interest to investigate the effect of the presence of silver acetates on the rearrangements of other N-chloroanilides in glacial acetic acid.

2.3.1. Rearrangement of N-Chlorobenzanilide at 17° .

Immediately after N-chlorobenzanilide (1.5 g., 0.0648 mole) had dissolved in glacial acetic acid (100 ml.), hydrochloric acid (one drop) was added, and the solution was well stirred. The mixture became warm and a little chlorine was shown to be evolved. When the rearrangement was complete, the acetic acid was distilled off under reduced pressure, the white residue was hydrolysed and the hydrolysate was analysed as described previously. The results obtained are given in Table 14. In two further experiments, the reactions were carried out in stoppered

Table 14

Products of the Rearrangement of N-Chlorobenzanilide, catalysed by Hydrochloric Acid, at 17°, in Glacial acetic Acid

Experiment No.	% Yield		Molar % of Products					
	Distillate	Residue	a	o	p	d	t	o:p
1	82	0.3	47.1	12.9	39.5	0.5	0.01	1:3.05
2	83	0.8	46.6	13.6	39.4	0.4	0.01	1:2.88
3	90	0.3	25.9	20.6	52.5	0.7	0.02	1:2.55
4	94	0.9	22.7	19.4	57.2	0.7	0.02	1:2.96

Experiments 3 and 4 were carried out in sealed flasks.

Mean o:p ratio - 1:2.86

flasks which were completely filled with acetic acid, in order to limit the loss of chlorine. Analysis of the products was carried out as described above and the results are given in Table 14.

2.3.2. Kinetics of the Rearrangement at 77.7°.

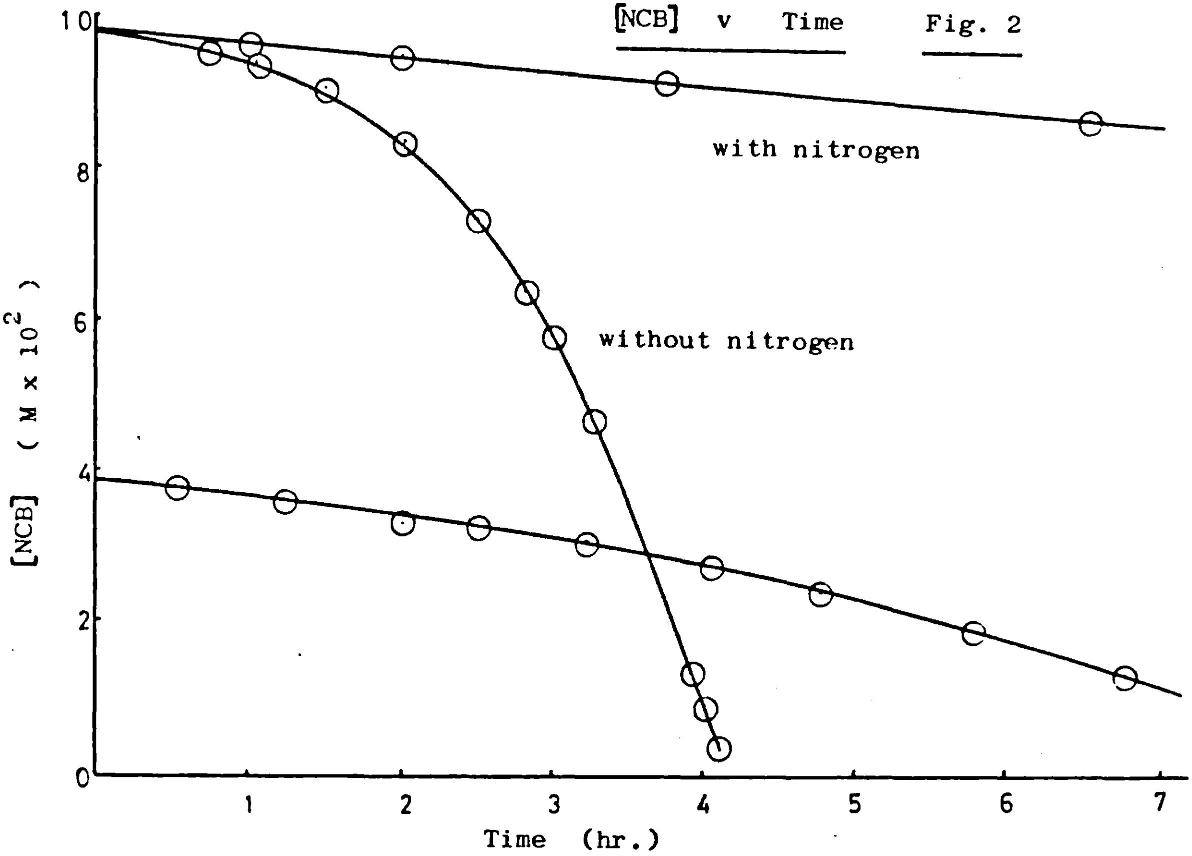
The rate of decomposition of the N-chloroanilide, dissolved in glacial acetic acid, was studied by iodimetric estimation, at intervals, of the quantity of the N-chloroanilide remaining in solution.

2.3.2.1. The rearrangement of N-chloroanilides alone.

Each reaction was carried out in the dark, at 77.7 ± 0.2°. A flask containing glacial acetic acid (85 ml.) and fitted with a double-surface reflux-condenser which was fitted with a guard-tube packed with silica gel and soda-lime, was left in the thermostat for 30 min. to allow the solvent to reach the temperature of the bath. N-chlorobenzanilide (2.036 g., 0.0085 mole) was added and the flask was well shaken. Samples (2 ml.) withdrawn from the solution, at intervals, and run into excess potassium iodide solution (20 ml., 10%) acidified with sulphuric acid (20 ml., 1 M.). Immediately, the liberated iodine was titrated against standard sodium thiosulphate solution (0.01 M.) using starch as indicator. Under these conditions, N-chloroanilides react quantitatively with acidified potassium solution[6]. Further experiments were carried out using solutions of N-chlorobenzanilide (0.040 M.) and N-chlorophenylacetanilide (0.100 M.) initially. The results obtained are given in Tables A1 and A2, Fig.2 and Fig.4 respectively.

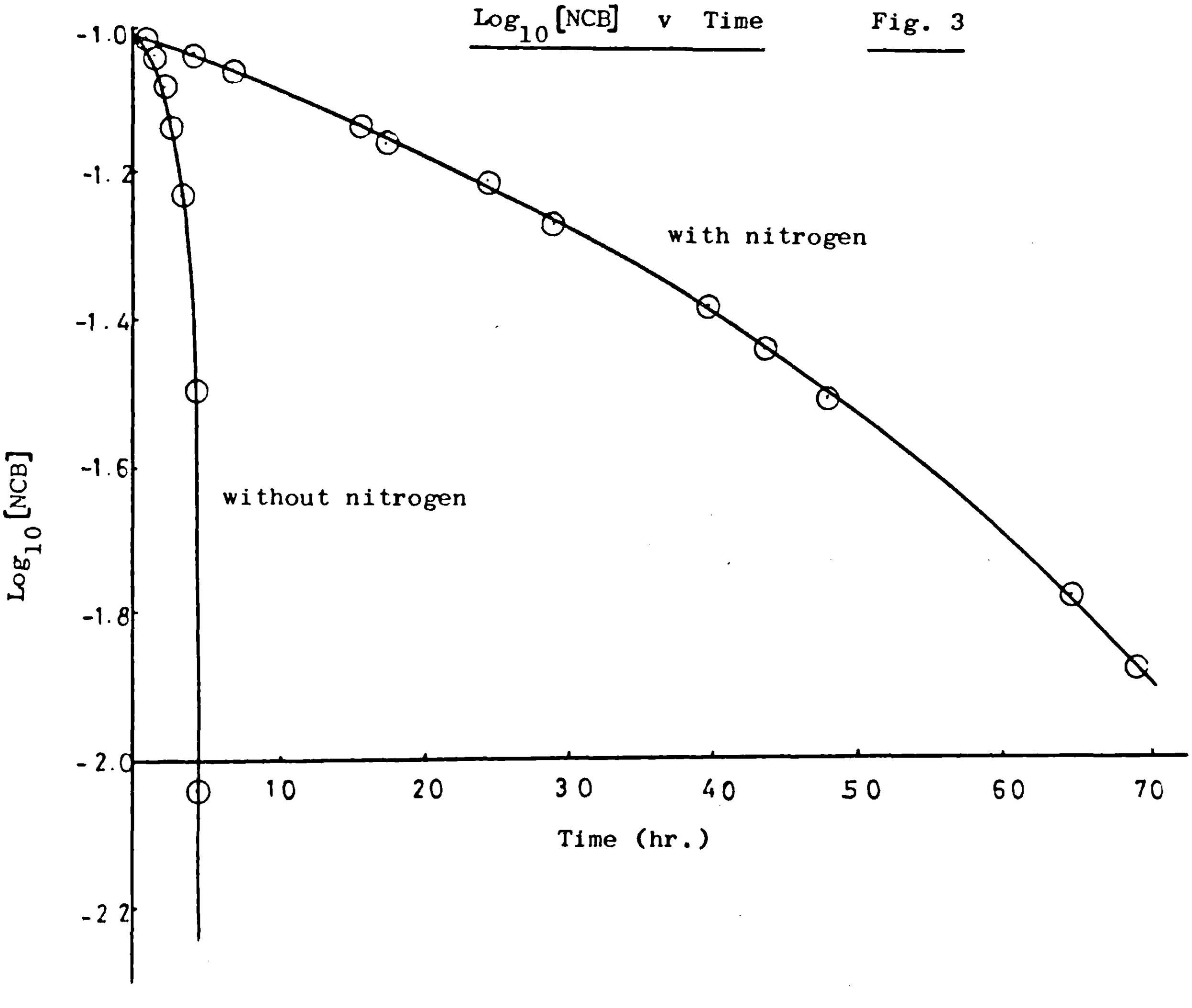
In this and all other kinetic studies, the experiments were performed at least twice in order to be certain that the results obtained were reproducible.

The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid at 77.7°.



[NCB] v Time

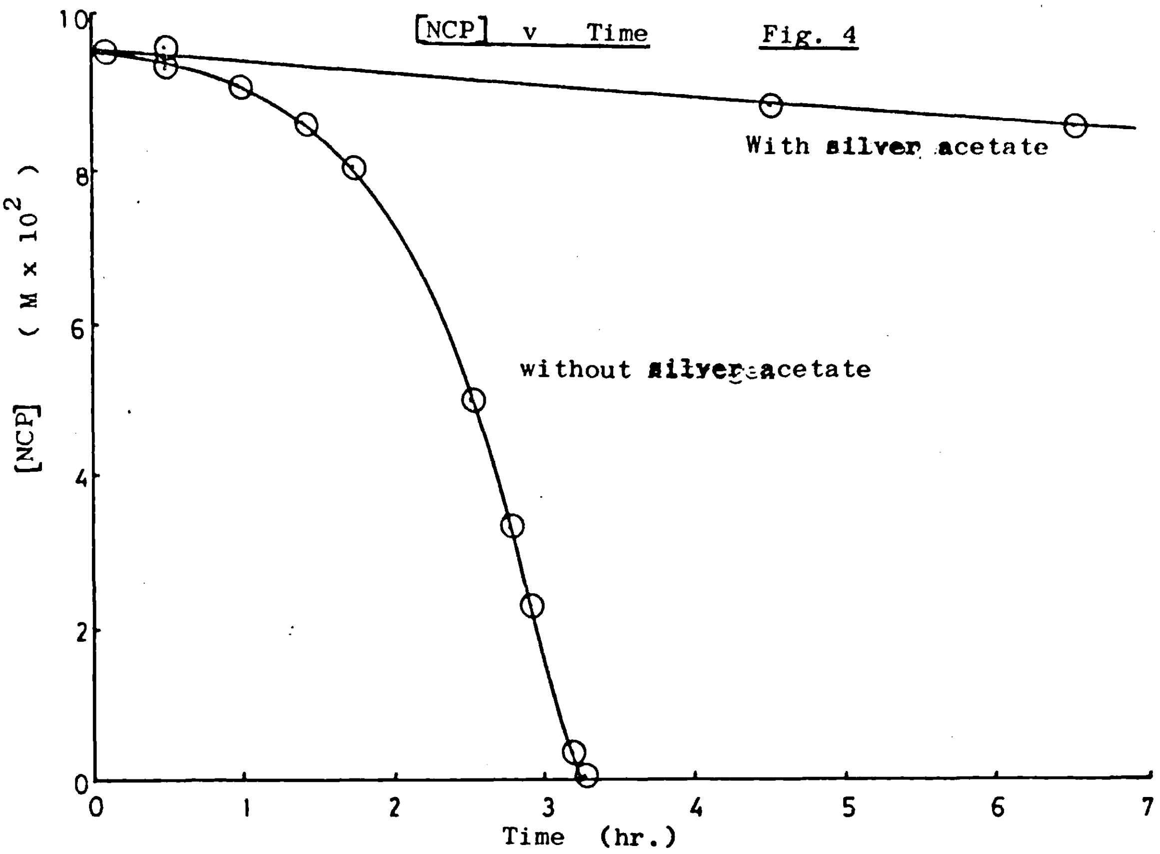
Fig. 2



Log_{10}[NCB] v Time

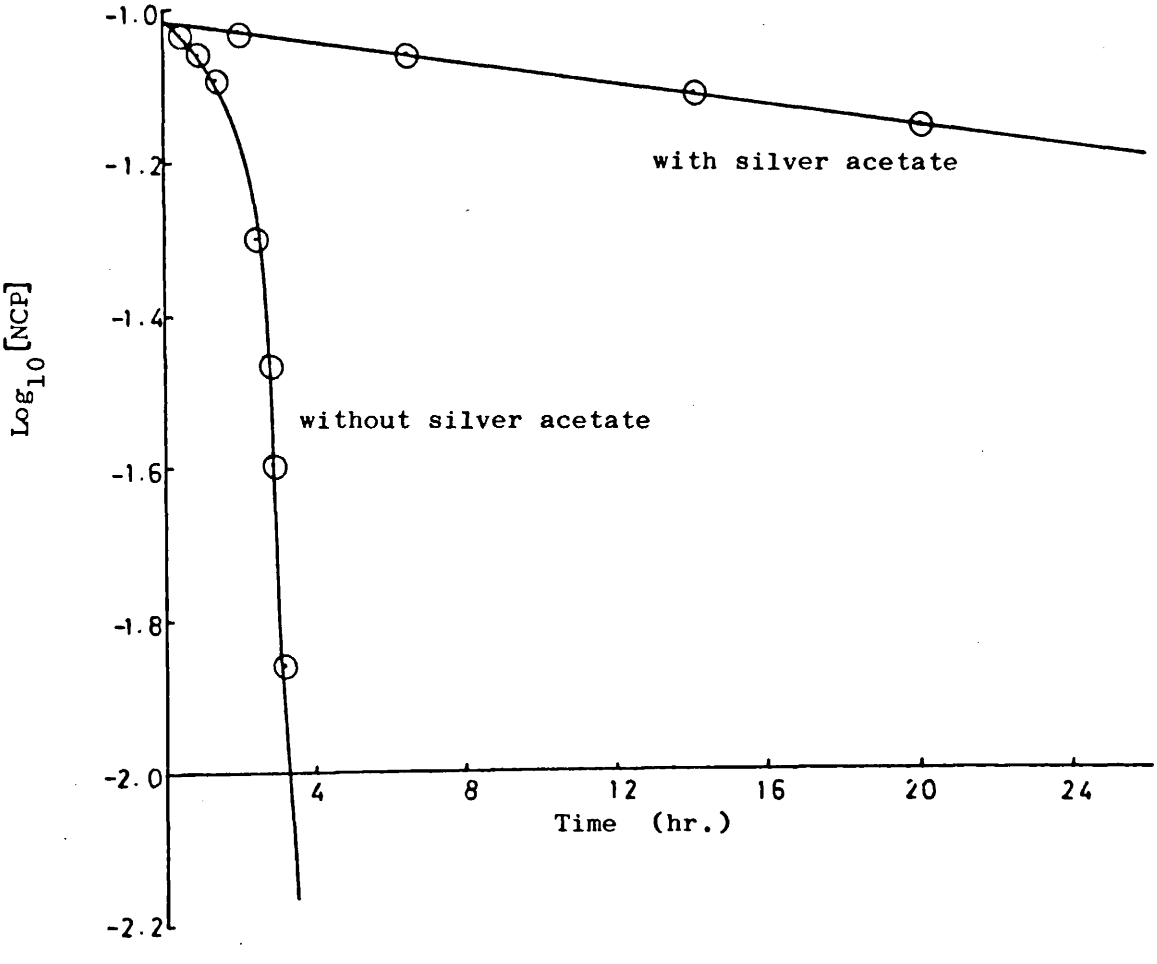
Fig. 3

The Rearrangement of N-Chlorophenylacetanilide in Glacial Acetic Acid at 77.7°.



[NCP] v Time Fig. 4

Log$_{10}$[NCP] v Time Fig. 5



2.3.2.2. The effect of aspirating with nitrogen

The rearrangement was carried out using the procedure described previously (section 2.3.2.1.) however, dry nitrogen, saturated with acetic acid vapour, was passed continuously at a flow-rate of 1.5 l. $hr.^{-1}$, through the solution during the reaction. Chlorine was shown to be present in the effluent gas by the bleaching of damp litmus paper. The results obtained are given in Table A3 and Fig.2. Fig.3 shows the corresponding logarithmic plot.

2.3.2.3. The effect of added silver acetate

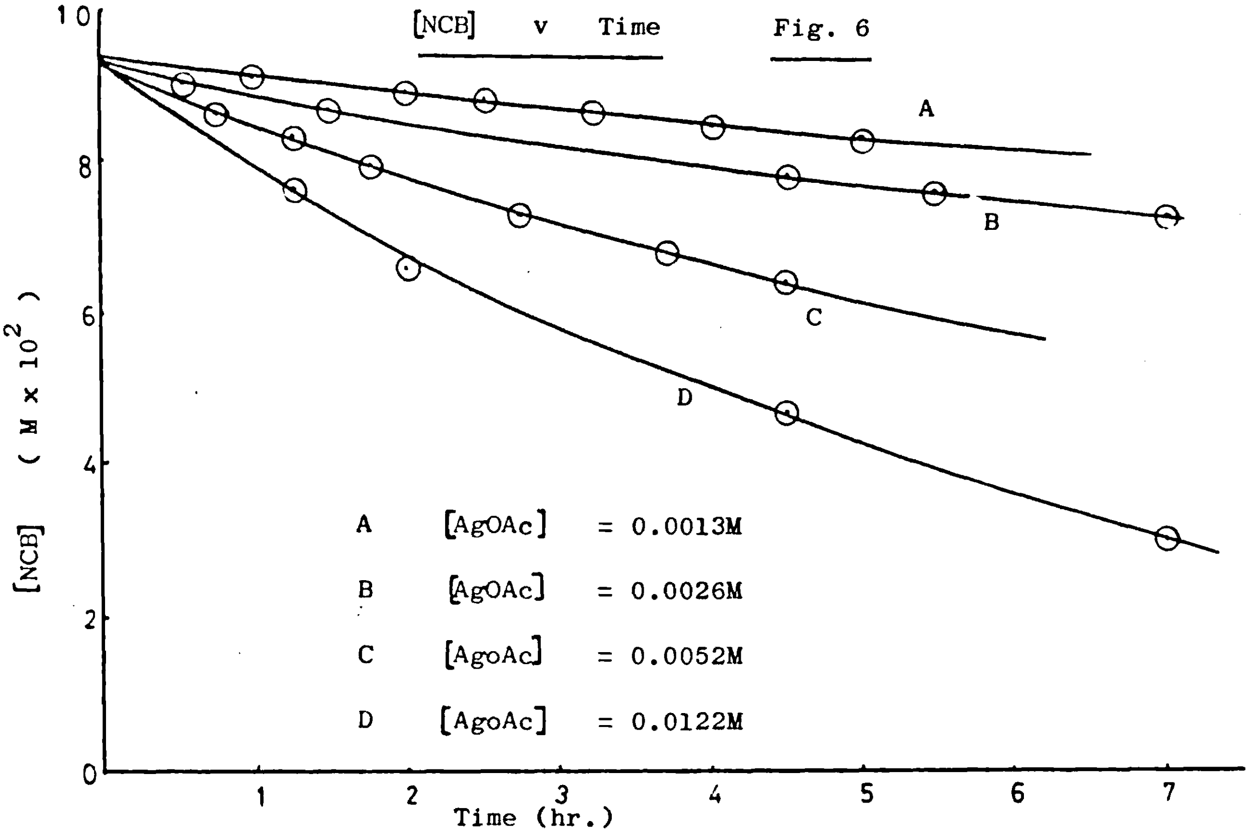
Each experiment was carried out as described previously, except that the *N*-chloroanilide was added in solutions of silver acetate in glacial acetic acid.

In the first series of experiments, the initial concentration of *N*-chlorobenzanilide was the same but the initial concentration of silver acetate was varied. The results obtained are given in Table A4, and Fig.6. Fig.7 shows the corresponding plot of the initial rate of *N*-chlorobenzanilide decomposition against the initial concentration of silver acetate.

In further experiments, the initial concentration of silver acetate was constant (0.0052M.) but the initial concentration of *N*-chlorobenzanilide was varied. The results obtained are given in Table A5 and Fig.8. Fig. 9 shows the corresponding plot of the initial rates of *N*-chlorobenzanilide decomposition against the initial concentration of *N*-chlorobenzanilide.

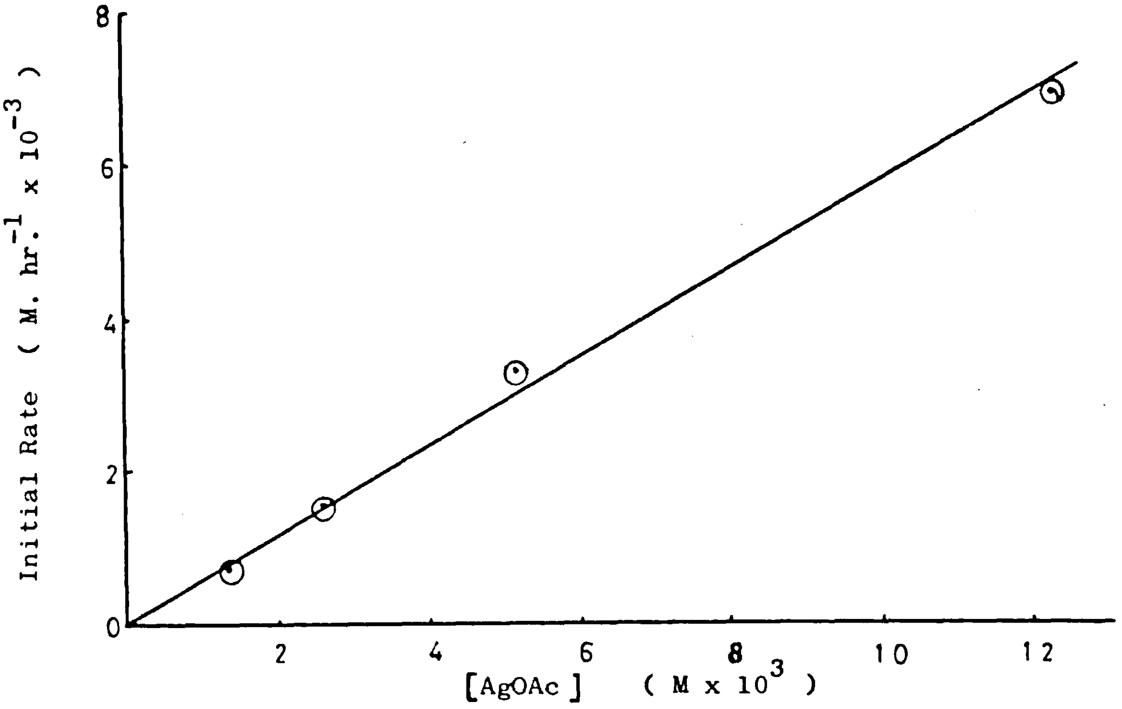
N-chlorophenylacetanilide was also added to a solution of silver acetate in acetic acid and the kinetics were followed in the usual way. The results are given in Table A2 and Fig.3. Fig.4 gives the corresponding logarithmic plot.

The Rearrangement of N-Chlorobenzanilide at 77.7^0, in Glacial Acetic Acid, with added Silver Acetate.



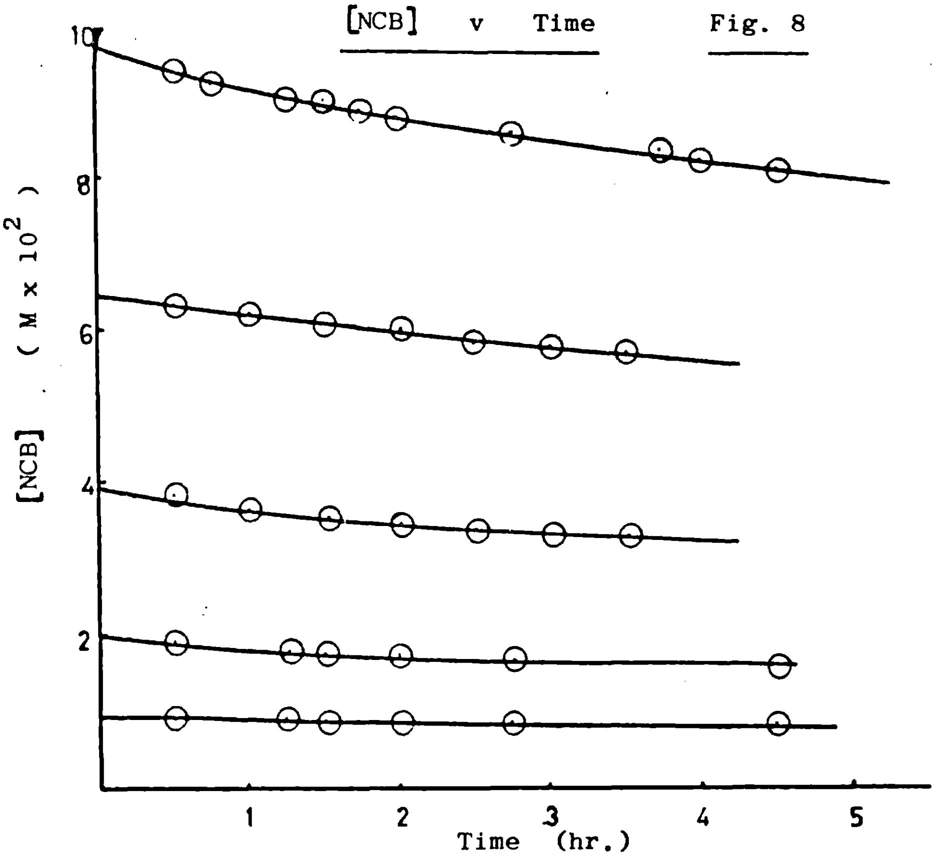
[NCB] v Time Fig. 6

Initial Rate v [AgOAc] Fig. 7

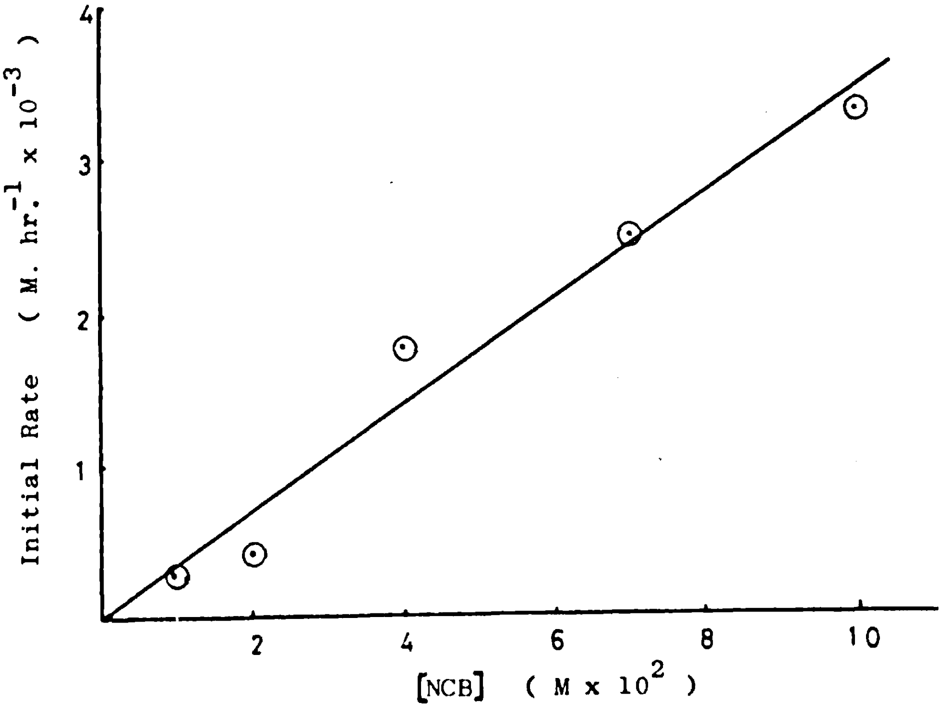


The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid, with added Silver Acetate.

[NCB] v Time Fig. 8



Initial Rate v [NCB] Fig. 9



2.3.3. The Products of the Reactions in Glacial Acetic Acid at 77.7°

2.3.3.1. The rearrangement catalysed by hydrochloric acid

Immediately after the N-chloroanilide (0.0085 mole) had dissolved in hot solvent, in the dark, concentrated hydrochloric acid (one drop) was added. When the rearrangement was complete (1 hr.), the acetic acid was removed, by distillation under reduced pressure. The white residue was analysed as described previously by (section 2.2.) and the results are given in Table 15.

2.3.3.2. The rearrangement in glacial acetic acid alone with nitrogen passing through the solution.

Dry nitrogen, saturated with acetic acid vapour, was passed (flow-rate 2 $l.hr.^{-1}$) continuously through a solution of N-chlorobenzanilide (2.036 g., 0.0085 moles) in acetic acid (85 ml.) at 77.7°, in the dark. When the rearrangement was complete (48 hr.) the acetic acid was distilled off from the pale orange solution. The residue was hydrolysed, and the hydrolysate analysed, giving results shown in Table 16. The bleaching of damp litmus indicated the presence of chlorine in the effluent gas.

2.3.3.3. The rearrangement in glacial acetic acid alone

Each N-chloroanilide (0.0085 mole) in turn was dissolved in acetic acid (85 ml.), at 77.7°, and the solution was maintained at this temperature until the rearrangement was complete. Then the acetic acid was removed, and the white residue analysed in the usual way. The results obtained are given in Table 16.

Table 15

Products of the Rearrangement of N-Chloroanilides in Glacial Acetic Acid, catalysed by Hydrochloric Acid.

N-Chloroanilide	% Yield		Molar % of Products					
	Distillate	Residue	a	o	p	d	t	o:p
N-Chlorobenzanilide	90	2.0	6.9	33.9	57.7	1.3	0.04	1:1.70
N-Chlorobenzanilide	94	0.0	5.4	32.7	60.4	1.2	0.04	1:1.84
N-Chlorobenzanilide	92	0.06	5.6	31.8	61.4	1.2	0.04	1:1.93
N-Chlorophenylacetanilide	99	0.1	2.9	34.0	62.8	0.2	0.1	1:1.85
N-Chlorophenylacetanilide	91	0.8	6.9	31.4	58.6	0.9	0.1	1:1.87
N-Chlorophenylacetanilide	97	0.1	4.6	32.7	61.9	0.9	0.1	1:1.88
N-Chlorophenylacetanilide	-	-	4.2	33.0	61.8	0.6	0.3	1:1.87
N-Chloromethanesulphonanilide	-	-	5.1	37.8	58.1	1	-	1:1.58
N-Chloromethanesulphonanilide	-	-	5.4	35.8	58.8	1	-	1:1.65
N-Chloromethanesulphonanilide	-	-	5.3	37.2	57.5	1	-	1:1.54

Table 16

Products of the Rearrangement of N-Chlorobenzanilide, in Glacial Acetic Acid alone at 77.7°.

N-Chloroanilide	Nitrogen Flow-Rate	% Yield		Molar % of Products					
	(l. hr^{-1}.)	Distillate	Residue	a	o	p	d	t	*o*:*p*
N-Chlorobenzanilide	-	95	0.2	5.5	30.1	61.6	2.5	0.1	1:2.05
N-Chlorobenzanilide	-	94	0.4	5.3	30.9	60.4	3.8	0.1	1:1.95
N-Chlorobenzanilide	-	93	0.3	4.3	30.2	60.8	4.7	0.1	1:2.01
N-Chlorobenzanilide	5.0	92	1.8	10.8	25.4	61.5	2.2	1.1	1:2.42
N-Chlorobenzanilide	8.0	87	1.5	30.4	20.8	48.6	0.2	0.1	1:2.35
N-Chlorophenylacetanilide	-	97	0.3	5.7	32.2	61.0	1.0	0.1	1:1.90
N-Chlorophenylacetanilide	-	97	0.1	4.2	31.9	63.4	0.8	0.1	1:1.97
N-Chlorophenylacetanilide	-	96	0.9	4.7	31.3	63.4	0.7	0.1	1:2.02

2.3.3.4. The Rearrangement in the presence of silver acetate

When the N-chloroanilide (0.0058 mole) had been added to a mixture of glacial acetic acid (50 ml.) and silver acetate (0.244 g.) at 77.7°, the mixture was maintained at this temperature in the dark, with occasional shaking, until the rearrangement was complete (24 hr.). After the product mixture had been filtered to remove silver chloride, the acetic acid was removed from the orange filtrate, by distillation under reduced pressure, and the residue was analysed by the standard method. The results obtained are given in Table 17.

2.3.3.5 The Chlorination of Benzanilide

Chlorine gas (approx. 0.0085 mole) was bubbled slowly through a solution of benzanilide (1.97 g., 0.0085 mole) in acetic acid (85 ml.) at 76.8° in the dark. When the passage of chlorine was complete, the mixture was maintained at the same temperature for a further three hours, and then acetic acid was distilled off. The white residue was hydrolysed and the hydrolysate was analysed in the usual way. The results obtained are given in Table 18.

Table 18

Products of the Chlorination of Benzanilide in Glacial Acetic Acid.

% Yield		Molar % of Products					o:p
Distillate	Residue	a	o	p	d	t	
77	0.7	49.4	17.8	32.8	0.2	0.1	1:1.84
87	0.4	30.2	24.0	45.7	0.2	0.1	1:1.91

Mean o:p ratio 1:1.87

Table 17

Products of the Rearrangements of N-Chloroanilide in Glacial Acetic Acid, at 77.7° in the presence of Silver Acetate

N-Chloroanilide	% Yield		Molar % of Products					
	Distillate	Residue	a	o	p	d	t	o:p
N-Chlorobenzanilide	73.5	26	10.7	74.3	9.4	3.2	2.8	1:0.126
N-Chlorobenzanilide	74	62	8.1	70.2	13.3	6.1	2.3	1:0.192
N-Chlorophenylacetanilide	70	6.4	22.7	50.4	23.6	1.2	0.2	1:0.47
N-Chlorophenylacetanilide	68	6.1	17.5	57.9	23.7	1.3	0.2	1:0.41
N-Chlorophenylacetanilide	72	5.0	16.7	59.2	22.4	2.0	0.3	1:0.38

Mean o:p for N-Chlorobenzanilide - 1:0.158.

Mean o:p for N-Chlorophenylacetanilide - 1:0.42.

2.3.4. The Kinetics of the Rearrangement of N-chlorobenzanilide in Glacial Acetic Acid at 100° (a) alone, (b) in the presence of Silver Acetate.

In order to investigate the effect of an increase in temperature on the kinetics of the rearrangement, further experiments were carried out similar to those described previously (sections 2.3.2.1. and 2.3.2.4.) except that the thermostat was maintained at 100 ± 0.5° throughout the reaction. The results obtained are given in Table A6 and Fig.10. Fig.11 shows the corresponding logarithmic plot.

2.3.5. The Products of Reactions at 100°.

2.3.5.1. The Rearrangement in Glacial Acetic Acid alone.

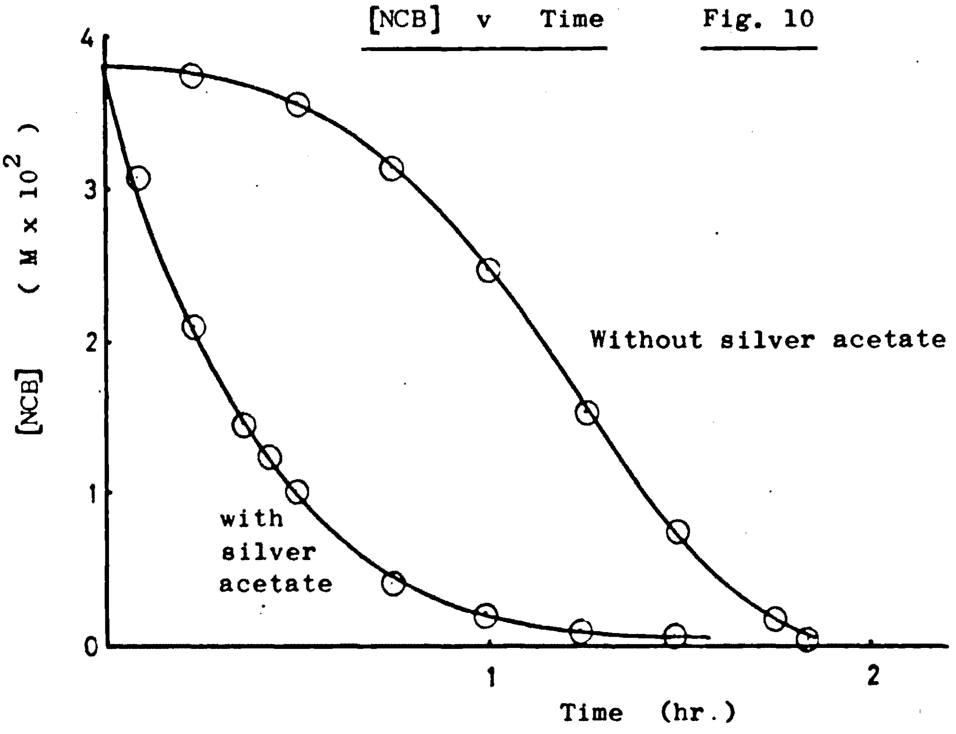
N-Chlorobenzanilide (1.404 g., 0.006 mole) was dissolved in hot glacial acetic acid (100 ml.) and the solution was maintained at 100° in the dark. When the rearrangement was complete, acetic acid was distilled off. The white residue was hydrolysed and the hydrolysate analysed by the standard method. The results obtained are given in Table 19.

2.3.5.2. The Rearrangement in the presence of Silver Acetate.

N-Chlorobenzanilide (0.814 g., 0.0035 mole) was dissolved in a hot solution of silver acetate (0.631 g.) in acetic acid (200 ml.). The solution was heated in the dark for 5 hr. with occasional shaking, until the reaction was complete. After the mixture had been filtered and the acetic acid had been distilled off from the red filtrate, the residue was hydrolysed to give a grey product which was distilled and analysed in the usual way. The results are given in Table 19.

The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid at 100°.

[NCB] v Time Fig. 10



Log_{10} [NCB] v Time Fig. 11

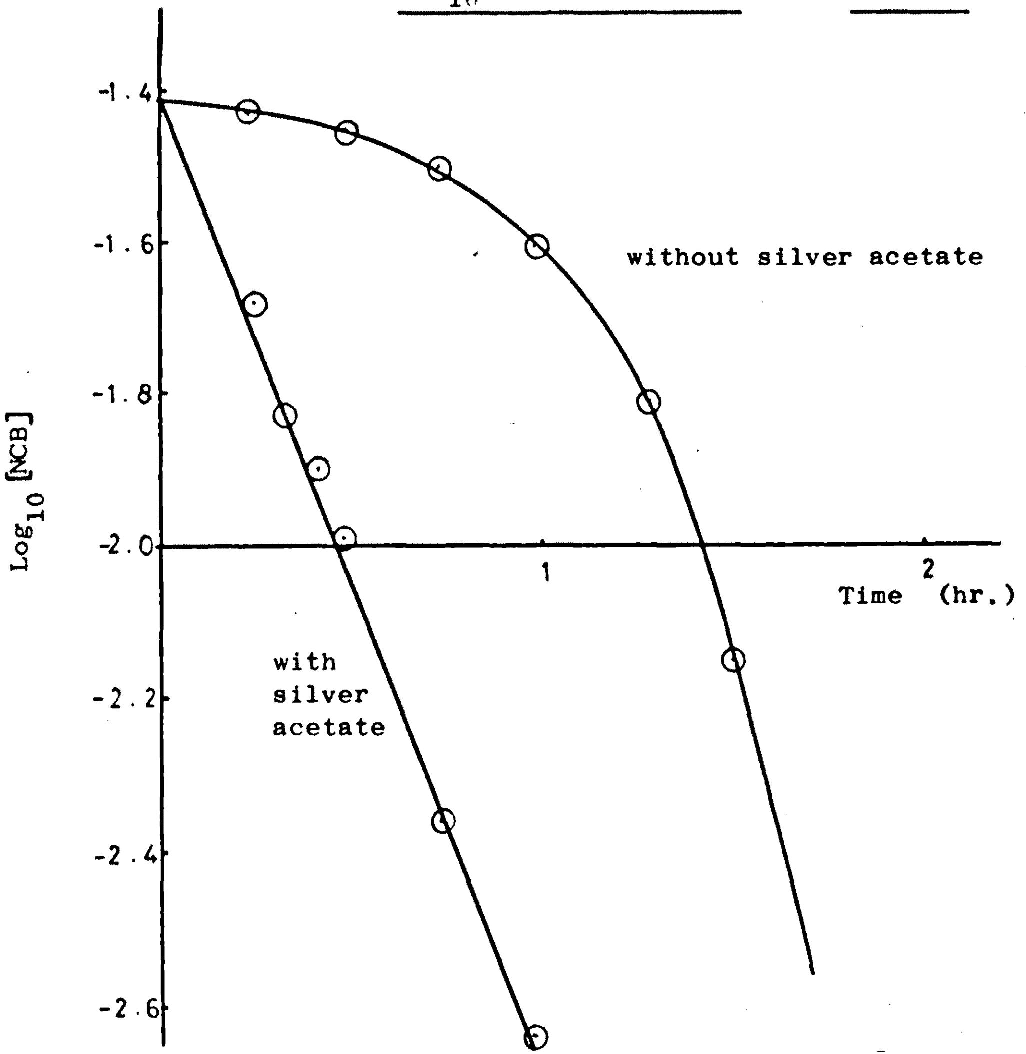


Table 19

Products of the Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid, at 100°.

Experiment No.	% Yield		Molar % of Products					
	Distillate	Residue	a	o	p	d	t	o:p
1	95.5	0.9	5.1	31.4	58.8	4.5	0.1	1:1.87
2	98.5	0.8	5.7	32.4	57.6	4.3	0.1	1:1.77
3	96	0.1	5.8	32.6	56.6	4.6	0.1	1:1.74
4	74	24.1	15.7	74.7	5.9	2.6	0.6	1:0.080
5	76	38.7	17.8	70.7	6.4	2.5	1.8	1:0.090
6	-	-	14.9	68.3	5.6	8.1	3.5	1:0.082

Experiments 4, 5, and 6 were carried out in the presence of added silver acetate carried out.

2.4. The Rearrangement of N-Chloroanilides in Carbon Tetrachloride in the presence of Hydrogen Chloride.

The rearrangement of N-chloroanilides in non-polar solvents has not been investigated nearly so extensively as has the reaction in polar media. It was therefore considered necessary to carry out a study of the kinetics and products of the rearrangement under these conditions, before proceding to investigate the reaction, in the same or similar solvents, but under conditions which would be expected to give rise to a homolytic reaction.

2.4.1. The Products of the Rearrangement of N-Chlorobenzanilide at 17°.

Concentrated hydrochloric acid (2 drops) was added to a solution of N-chlorobenzanilide (2.04 g.) in carbon tetrachloride (100 ml.). To prevent loss of chlorine from the solution, the flask was securely stoppered immediately. The solution was shaken in the dark overnight and the solid residue obtained after washing (Na_2CO_3) and solvent removal was hydrolysed. The product was analysed as previously described (section 2.2.). The results are given in Table 20.

Table 20

Products of the Rearrangement of N-Chlorobenzanilide, catalysed by Hydrogen Chloride, in Carbon Tetrachloride at 17°.

% Yield		Molar % of Products					
Distillate	Residue	a	o	p	d	t	o:p
85	0.9	7.2	9.2	71.4	7.8	4.5	1:7.75
-	-	8.7	8.8	71.8	7.6	2.8	1:8.15
79	0.7	8.2	8.8	73.0	7.7	2.2	1:8.24

Mean o:p ratio - 1:8.05

2.4.2. The Products of the Rearrangement of N-Chloroanilides at 77.7°.

When the N-chloroanilide (0.0085 mole) had dissolved in refluxing carbon tetrachloride (100 ml.) in the dark, concentrated hydrochloric acid (6 drops) was run in. After the rearrangement was complete, the mixture of products was analysed by the standard method and the results are given in Table 21.

Further experiments were carried out, using anhydrous hydrogen chloride to catalysed the rearrangement. Dry hydrogen chloride was passed into the solution of the N-chloroanilide (0.005 mole) in refluxing carbon tetrachloride (50 ml.) in the dark. When the rearrangement was complete the mixture of products was analysed, and the results obtained are given in Table 21.

2.4.3. The Products of the Chlorination of Benzanilide at 77°.

Dry Chlorine (0.0025 mole) was slowly bubbled into a solution of benzanilide (0.0025 mole) in refluxing carbon tetrachloride (50 ml.), in the dark with stirring. When the passage of chlorine was complete, the mixture was left for one hour to allow chlorination to go to completion. The products were analysed as before and the results are given in Table 22.

Table 22

Products of the Chlorination of Benzanilide in Carbon Tetrachloride at 77°.

% Yield		Molar % of Products					
Distillate	Residue	a	o	p	d	t	o:p
80	0.9	46.1	6.1	41.7	4.3	1.6	1:6.8
81	0.8	38.8	6.8	47.5	5.4	1.8	1:7.0

Mean o:p ratio - 1:6.9

Table 21

Products of the Rearrangement of *N*-Chloroanilides in Carbon Tetrachloride, catalysed by Hydrogen Chloride at 77°.

N-Chloroanilide	Experiment No.	% Yield		Molar % of Products					
		Distillate	Residue	a	o	p	d	t	o:p
N-Chlorobenzanilide	1	88	0.9	41.7	8.35	40.4	7.9	1.6	1:4.87
N-Chlorobenzanilide	2	92	0.3	35.1	9.4	45.0	8.6	1.7	1:4.77
N-Chlorobenzanilide	3	83	1.8	33.5	9.04	43.2	8.8	1.5	1:4.95
N-Chlorobenzanilide	4	-	-	36.4	9.48	50.4	3.2	1.8	1:5.32
N-Chlorophenylacetanilide	5	98	1.0	41.9	16.8	37.8	3.2	0.3	1:2.25
N-Chlorophenylacetanilide	6	96	0.8	20.5	22.8	50.1	5.4	1.4	1:2.20
N-Chloromethanesulphonanilide	7	-	-	36.6	25.9	37.4	1.0	-	1:1.44
N-Chloromethanesulphonanilide	8	-	-	54.4	19.6	28.8	1.0	-	1:1.46

Experiments 4, 7, and 8 employed anhydrous hydrogen chloride

Experiments 1, 2, 3, 5, and 6 employed concentrated hydrochloric acid

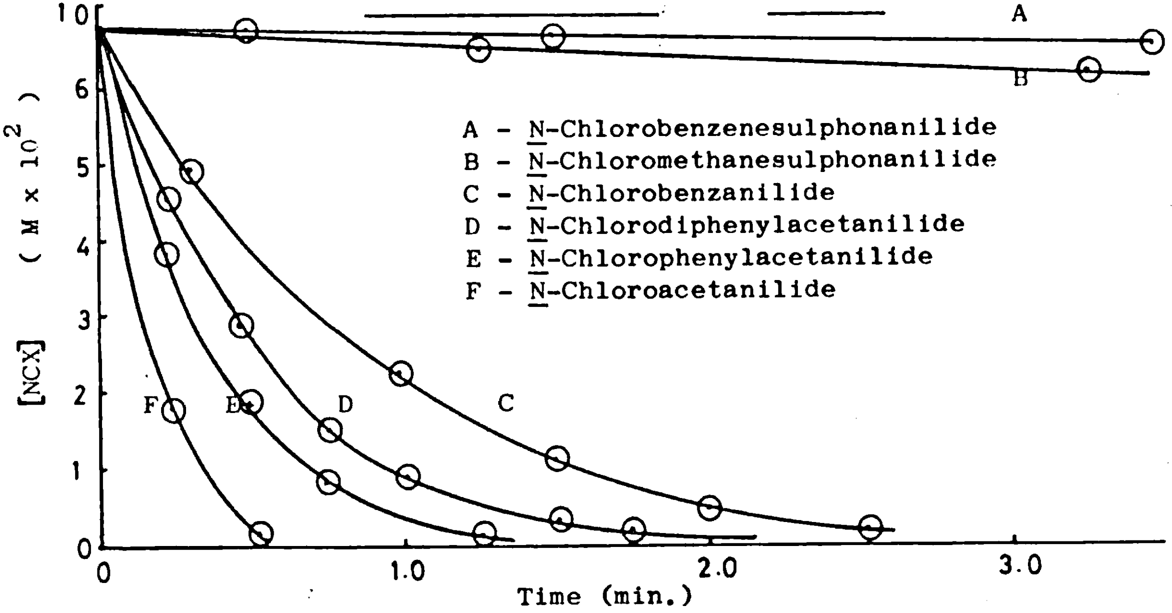
2.4.4. The Kinetics of the Rearrangement of N-Chloroanilides catalysed by Hydrogen Chloride, at 77°.

Dry hydrogen chloride was passed through carbon tetrachloride (49 ml.), maintained at 77°, for 15 min., and then a slurry of the N-chloroanilide (0.0035 mole) and carbon tetrachloride (1 ml.) was poured rapidly into the carbon tetrachloride, and the vessel was shaken thoroughly. The slow passage of hydrogen chloride (l. hr.$^{-1}$) was continued throughout the reaction, and samples (2 ml.) were withdrawn rapidly from the solution at intervals and estimated in the usual way. The effluent gas bleached damp litmus paper indicating that chlorine was evolved during the reaction. The results are given in Tables A7 and A8 and Fig. 12. Fig. 13 shows the corresponding logarithmic plot.

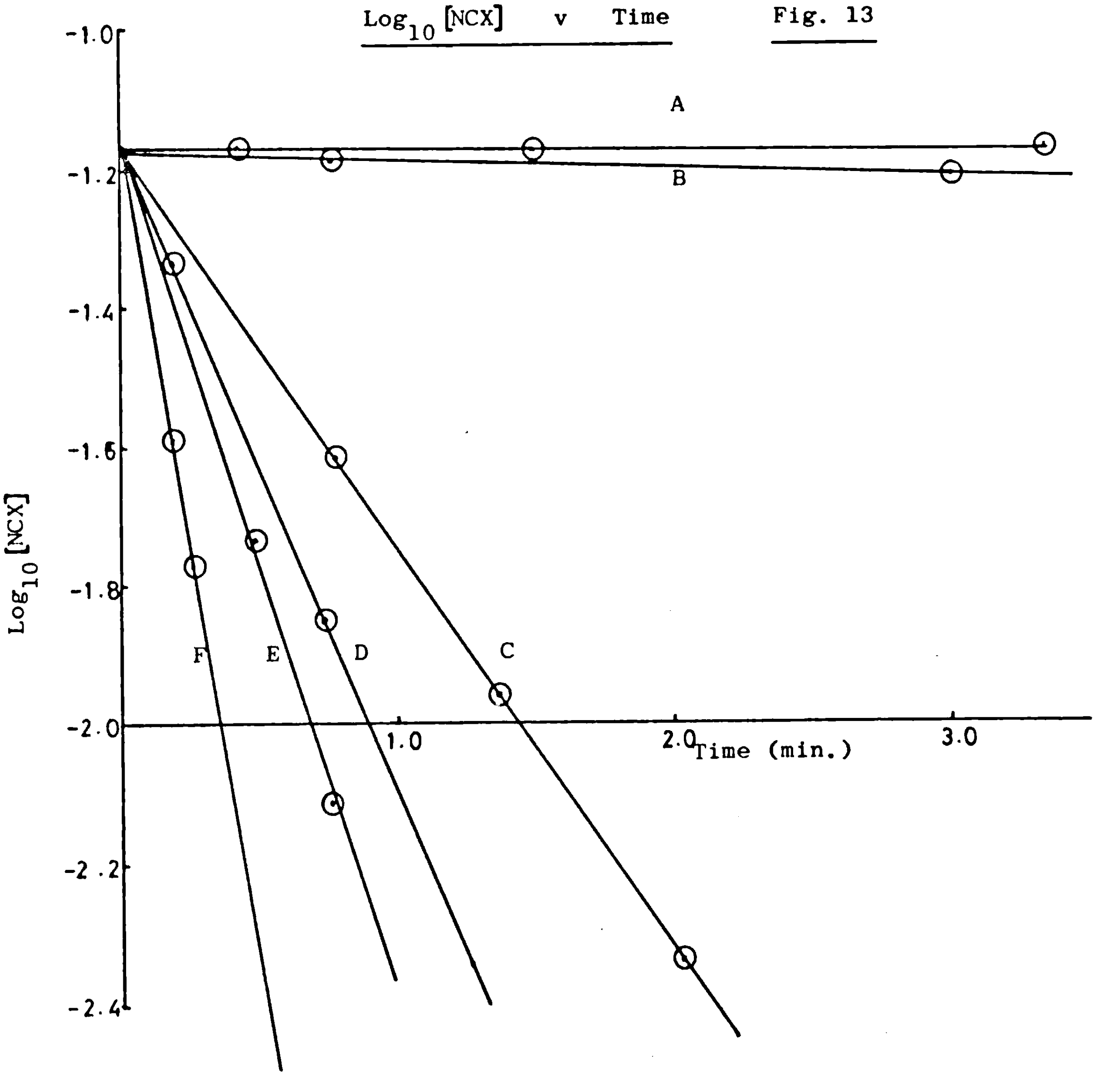
It was considered possible that hydrogen chloride and the N-chloroanilide might react very quickly, under the conditions employed, to give chlorine and the anilide. If so, the kinetics being followed would not be those for the reaction between the N-chloroanilide and hydrogen chloride. In order to test this possibility, the reaction between N-chlorobenzanilide and hydrogen chloride was repeated in the presence of diphenyl-ether, a compound with activated aromatic nuclei which would react very quickly with chlorine. The results are given in Table A7 and Fig. 14. Fig. 15 shows the corresponding logarithmic plot. The kinetics of the rearrangement, without added diphenyl ether, are given for comparison and the similarity of the kinetics clearly indicates that the presence of this ether had little effect on the reaction.

The Rearrangement of N-Chloroanilides in Carbon Tetrachloride, catalysed by Hydrogen Chloride.

[NCX] v Time Fig. 12

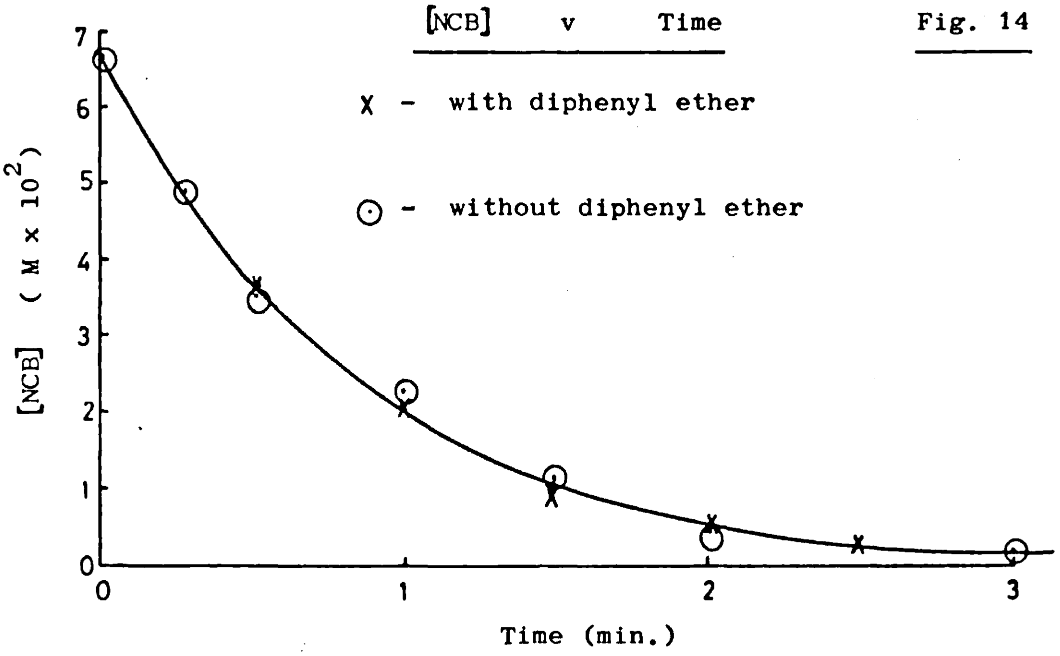


Log$_{10}$ [NCX] v Time Fig. 13

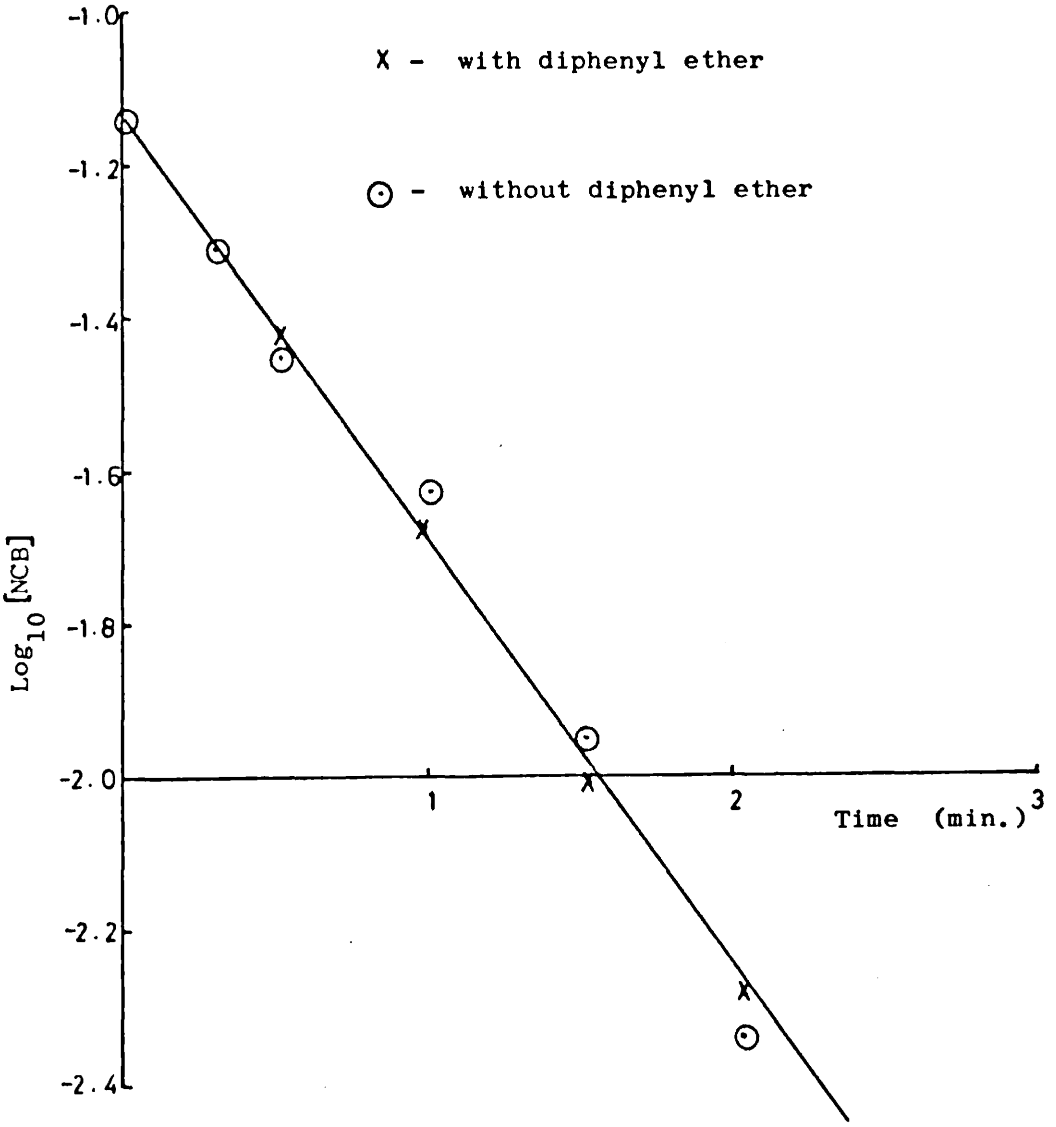


The Rearrangement of N-Chlorobenzanilide in Carbon Tetrachloride Catalysed by Hydrogen Chloride.

[NCB] v Time **Fig. 14**



Log$_{10}$[NCB] v Time **Fig. 15**



2.5. The Thermal Rearrangement of N-Chloroanilides in Nitrobenzene.

2.5.1. The Kinetics of the Rearrangement.

2.5.1.1. The reaction of the N-chloroanilide alone.

The N-chloroanilide (0.05 mole) was dissolved in nitrobenzene (50 ml.) at 156°, in the dark and the solution was shaken. The concentration of N-chloroanilide remaining in solution was determined, at intervals, iodometrically. The results are given in Tables A9, A13, A16, A17, A18, A21, and A25, and Fig. 16, 20, 24, 26, 28, 32, 36, and 38. The corresponding logarithmic plots are also given.

2.5.1.2. The effect of aspirating with nitrogen.

Dry nitrogen, saturated with nitrobenzene, was passed through solutions of each N-chloroanilide (0.0050 mole) in turn, in nitrobenzene (50 ml.) at 156°, in the dark. Samples were removed at intervals and titrated in the usual way. The results are given in Tables A9, A13, A16, A17, A18, A21, A24, and A25, and Fig. 16, 20, 24, 26, 28, 32, 36, and 38. The corresponding logarithmic plots are also given.

Further experiments were carried out at several other temperatures and the results obtained are given in Tables A10, A11, A12, A14, A15, A19, A20, A22, and A23, and Fig. 18, 22, 30 and 34. The corresponding logarithmic plots are also given.

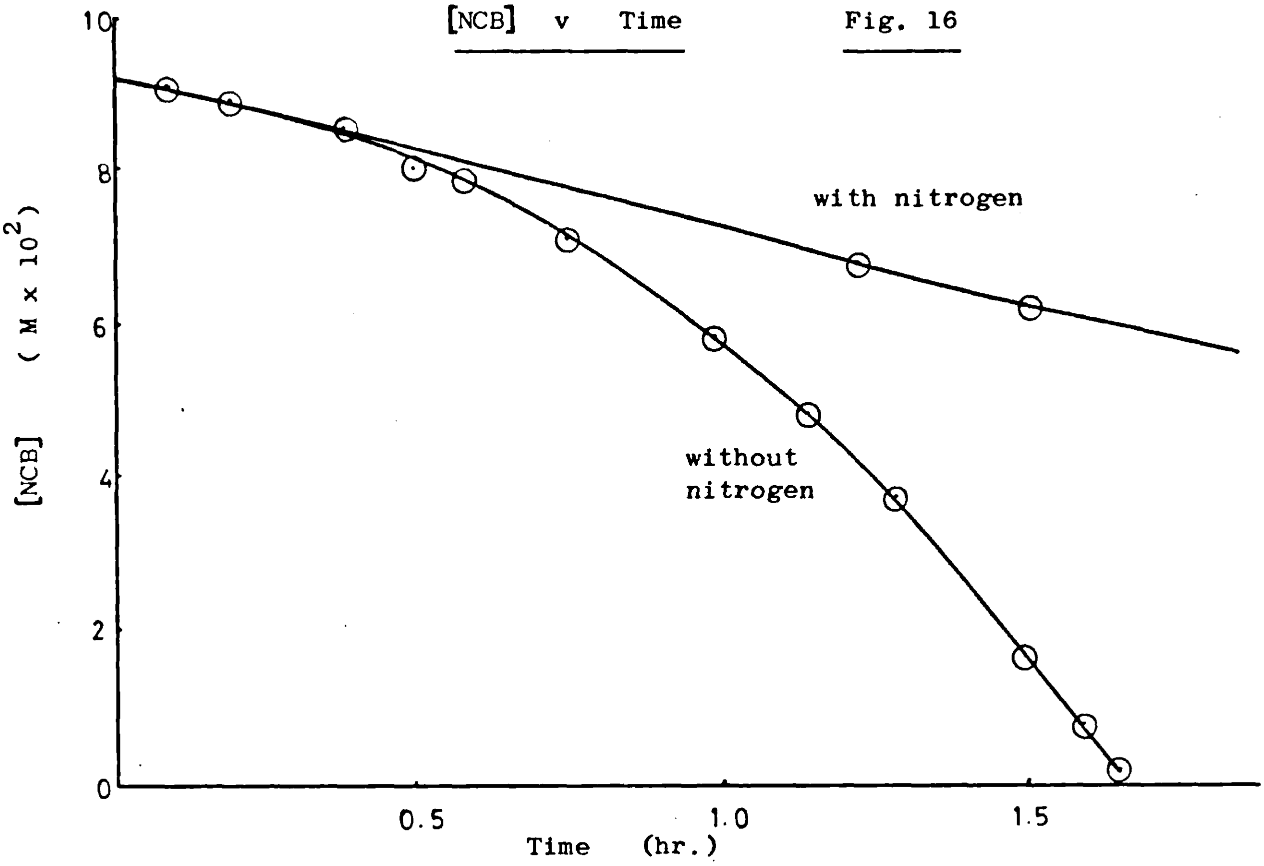
2.5.2. The Products of the Reaction

2.5.2.1. The analysis of the gases removed by the passage of nitrogene.

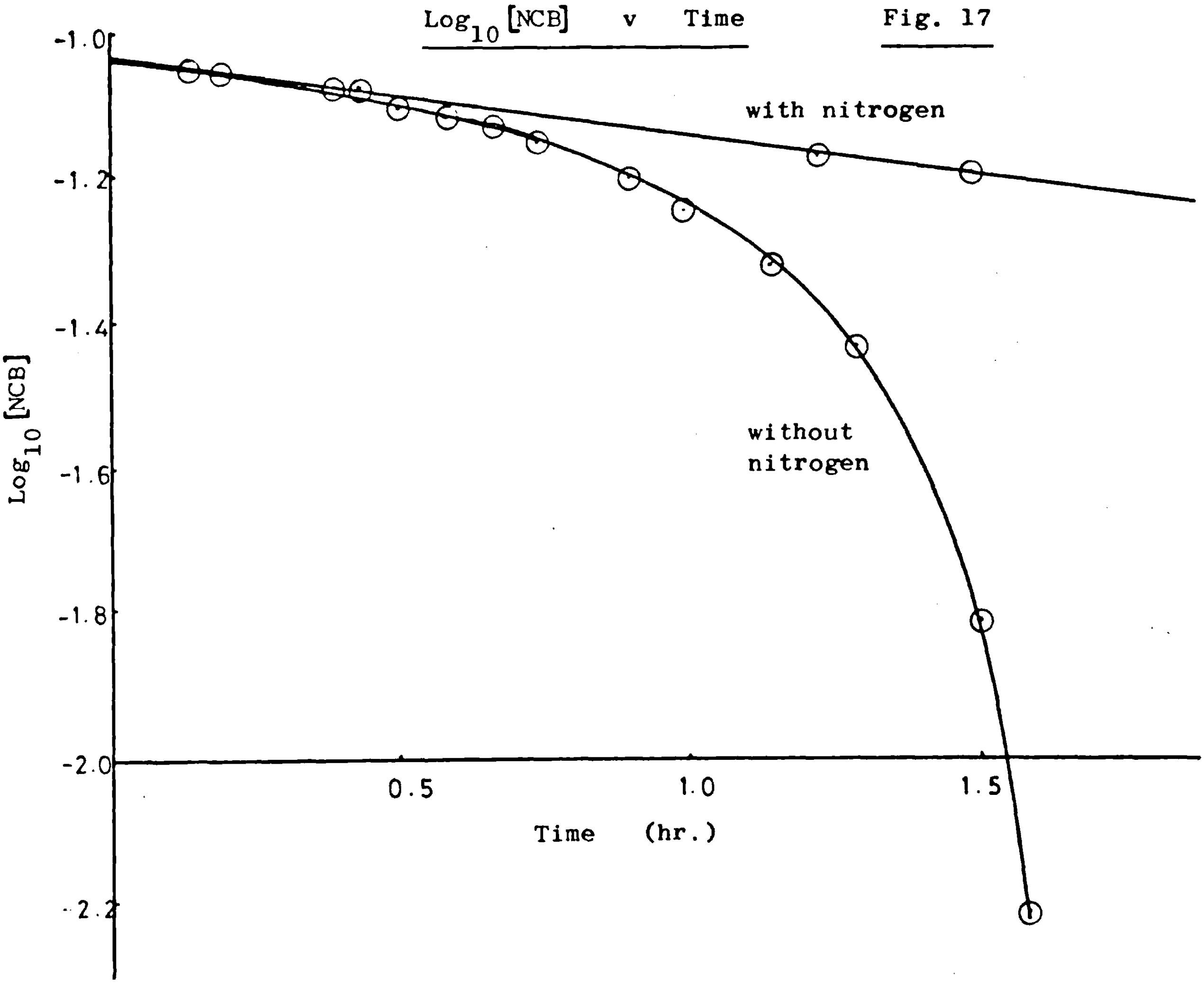
The thermal rearrangement of N-chlorobenzanilide at 156° was carried out as described previously (section 2.5.1.2.), however the effluent gas was then passed through sodium hydroxide solution (50 ml., 0.10 M) in the dark. A guard-tube containing soda-lime prevented the passage of any acidic gases from the atmosphere into the sodium hydroxide

The Thermal Rearrangement of N-Chlorobenzanilide at 156° in Nitrobenzene.

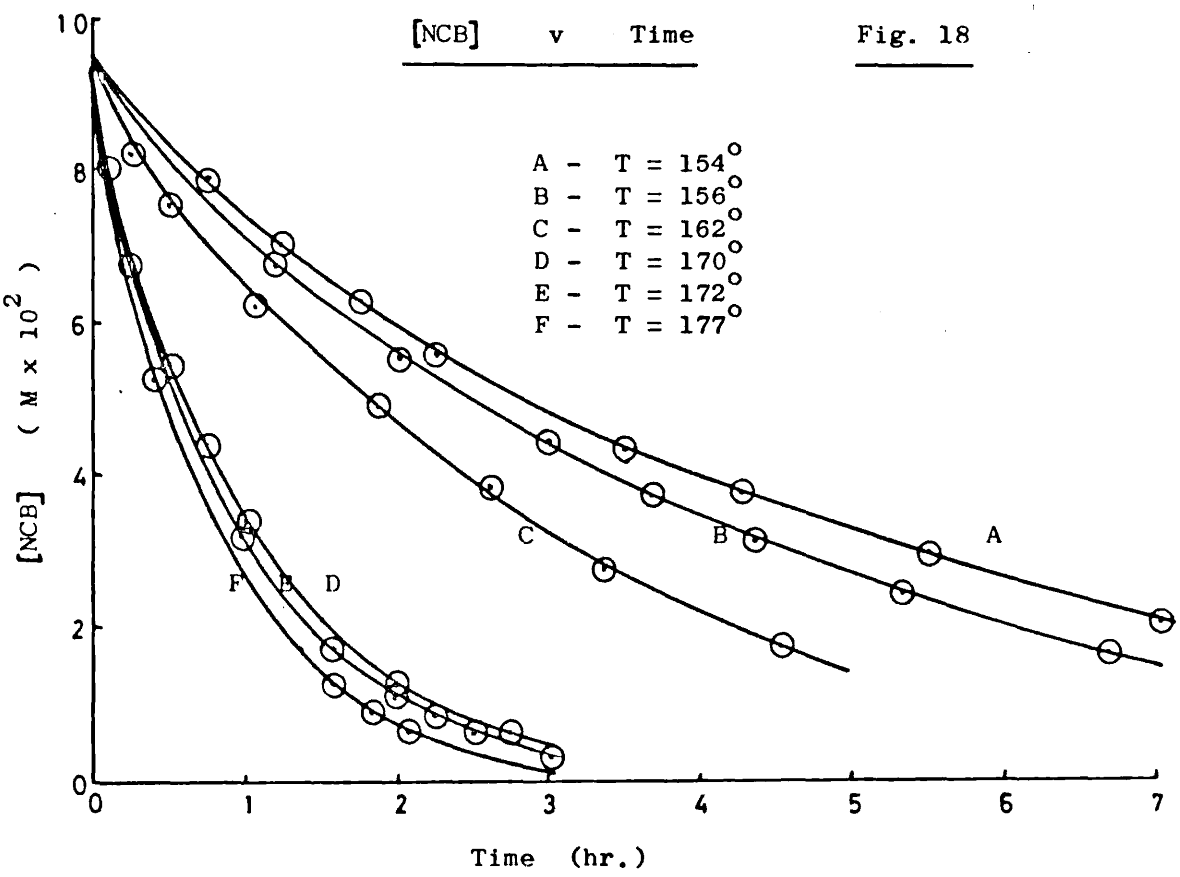
[NCB] v Time Fig. 16



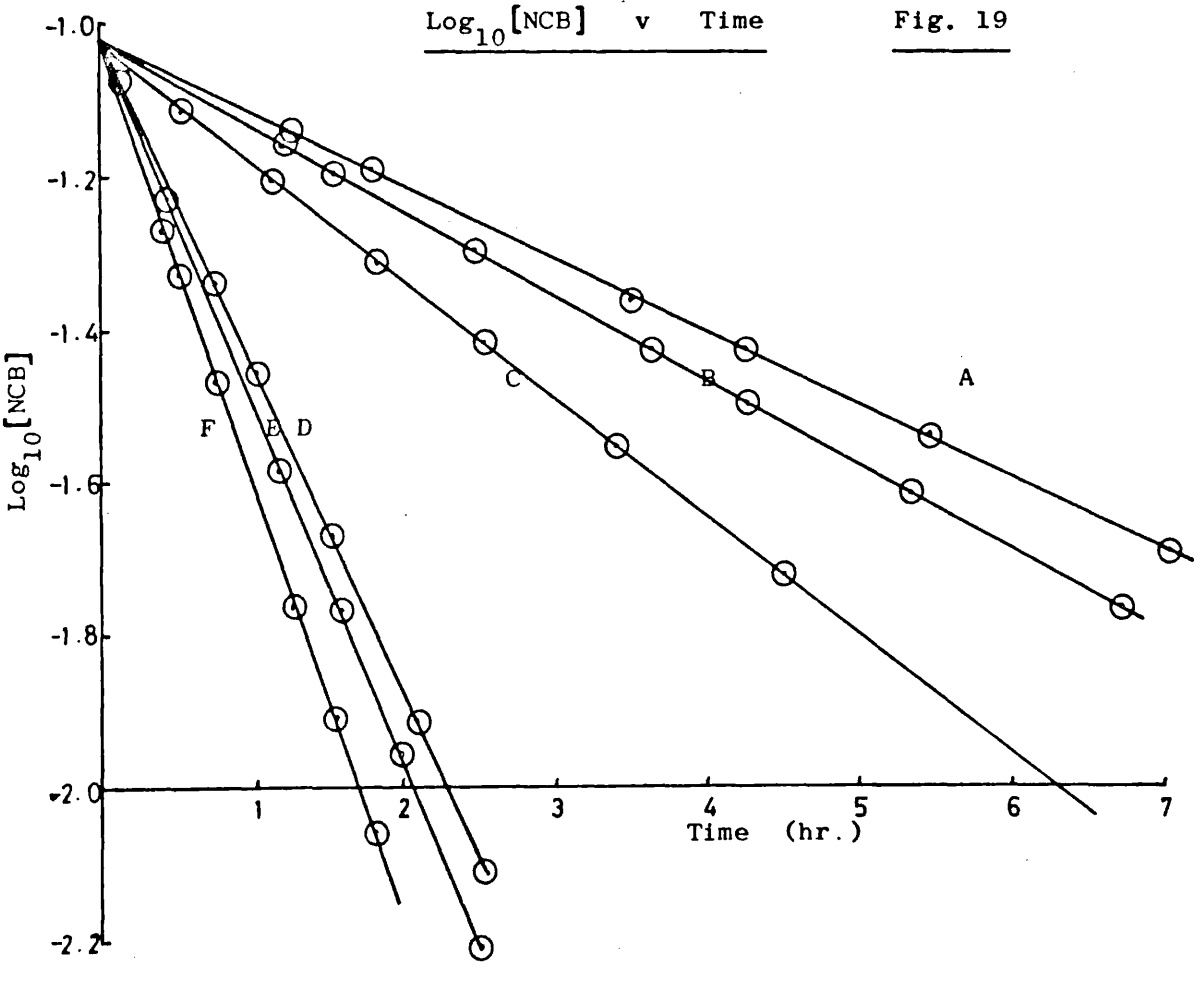
Log_{10} [NCB] v Time Fig. 17



The Thermal Rearrangement of N-Chlorobenzanilide, in Nitrobenzene, aspirated with Nitrogen.



[NCB] v Time Fig. 18

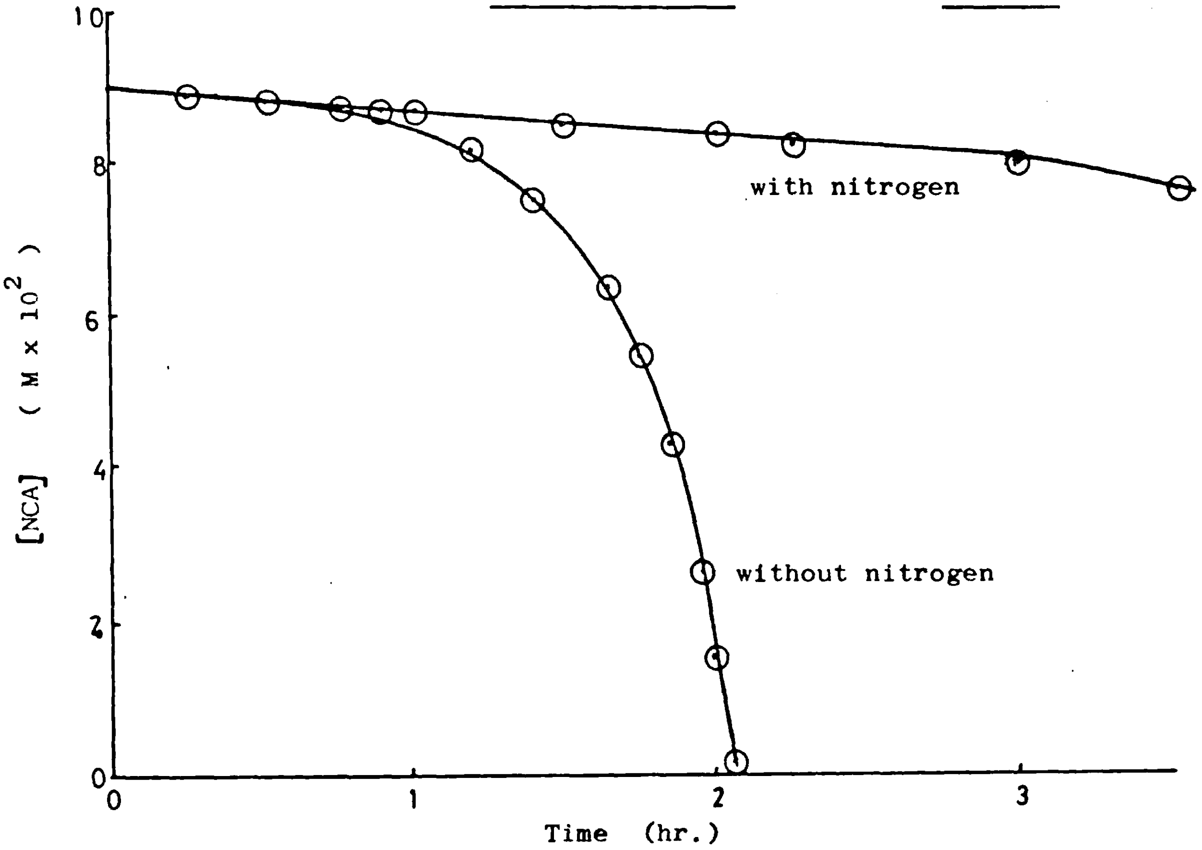


Log$_{10}$[NCB] v Time Fig. 19

The Thermal Rearrangement of N-Chloroacetanilide in Nitrobenzene at 156°.

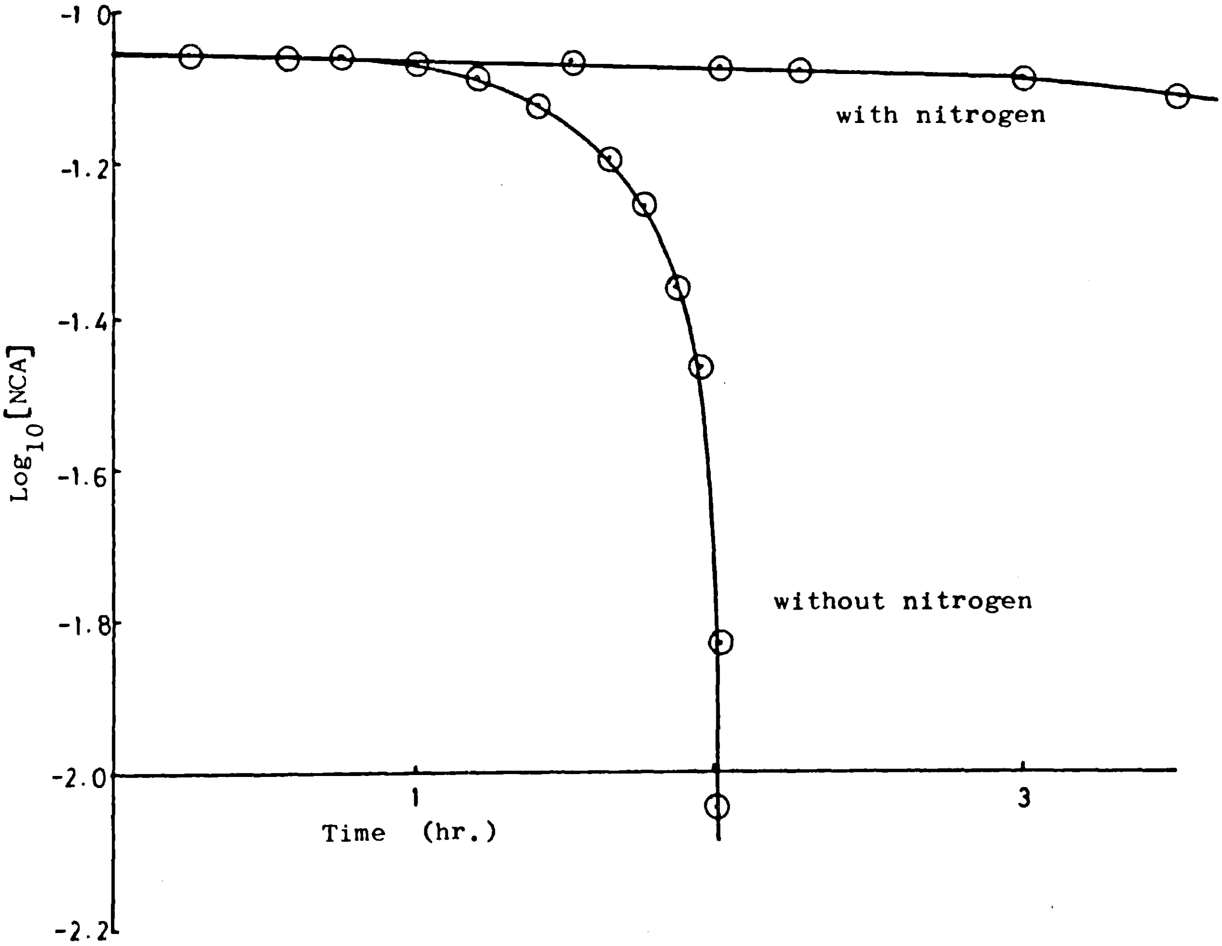
[NCA] v Time

Fig. 20

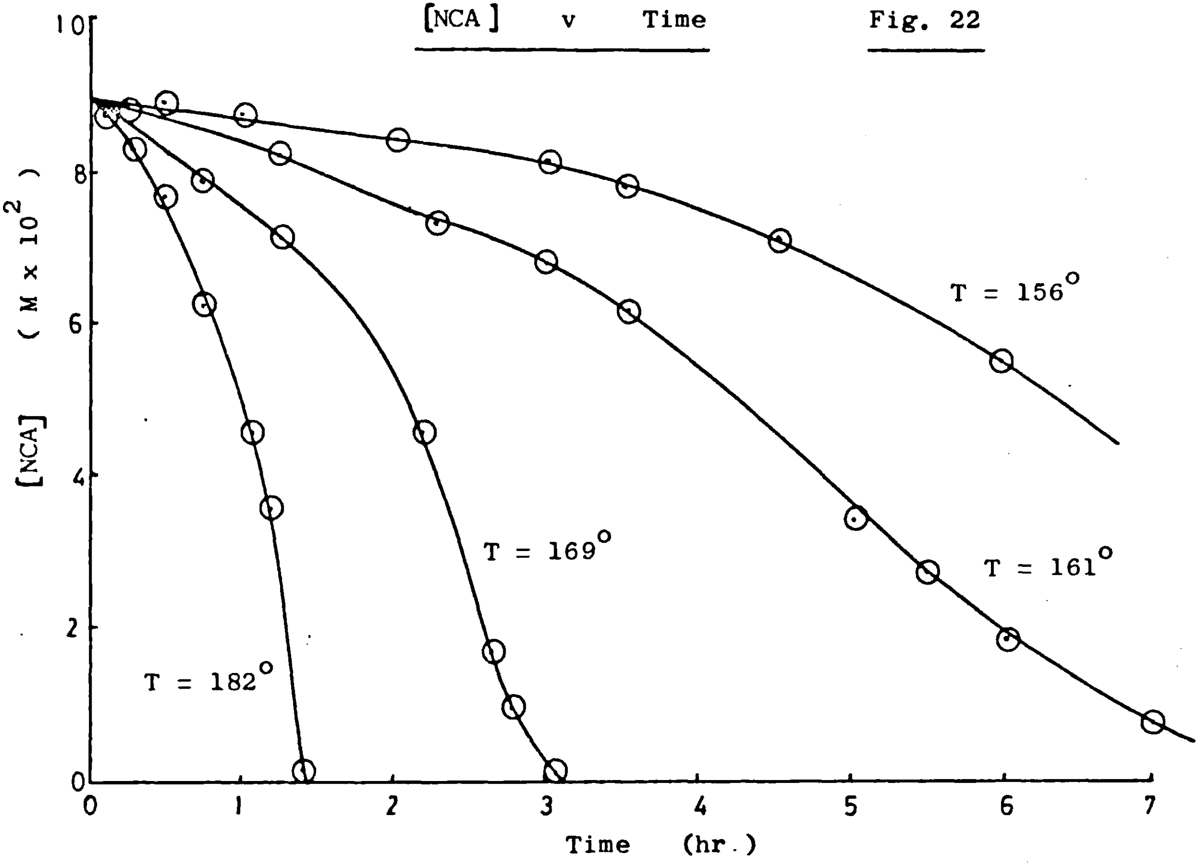


Log_{10}[NCA] v Time

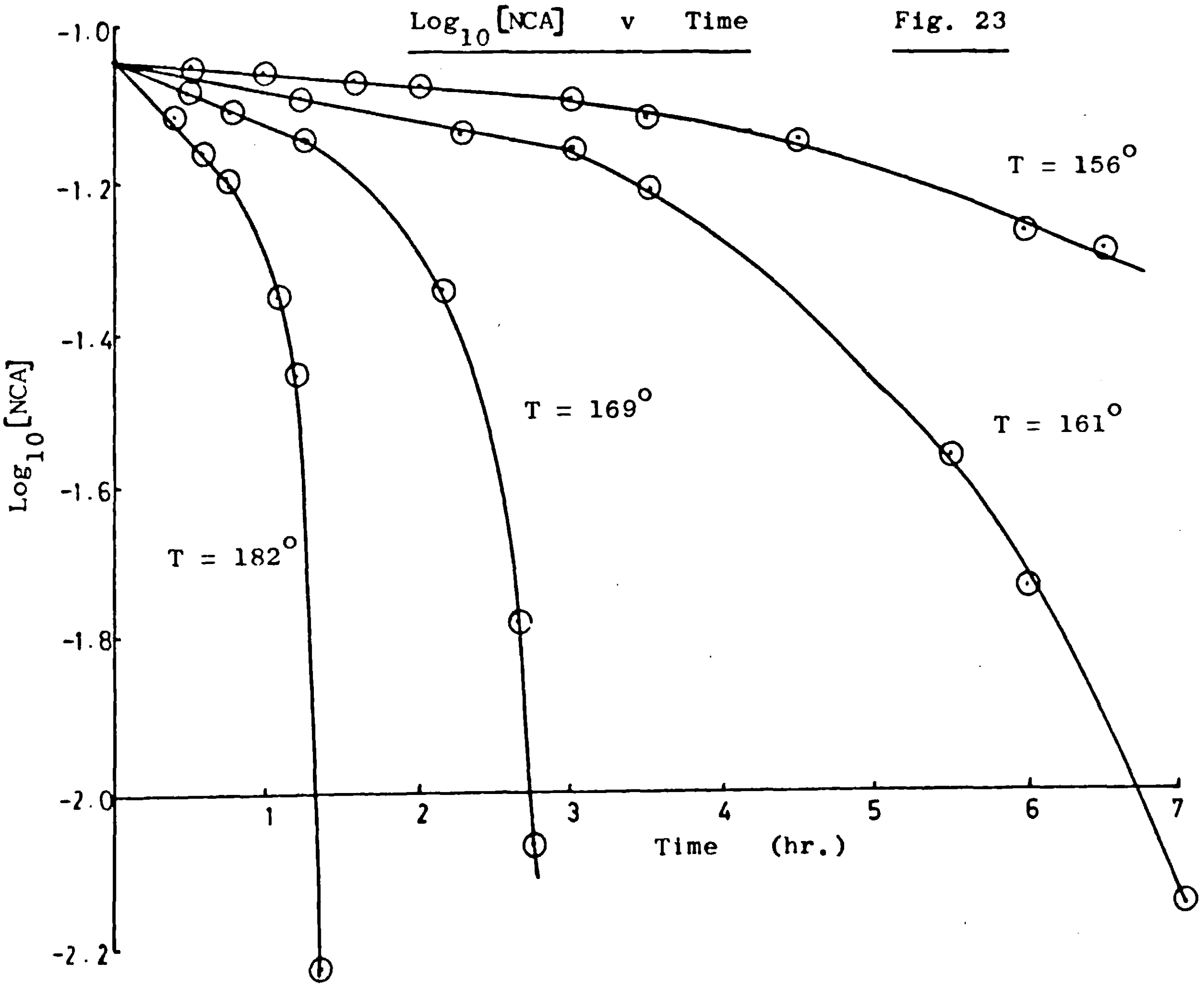
Fig. 21



The Thermal Rearrangement of N-Chloroacetanilide in Nitrobenzene, aspirated with Nitrogen.



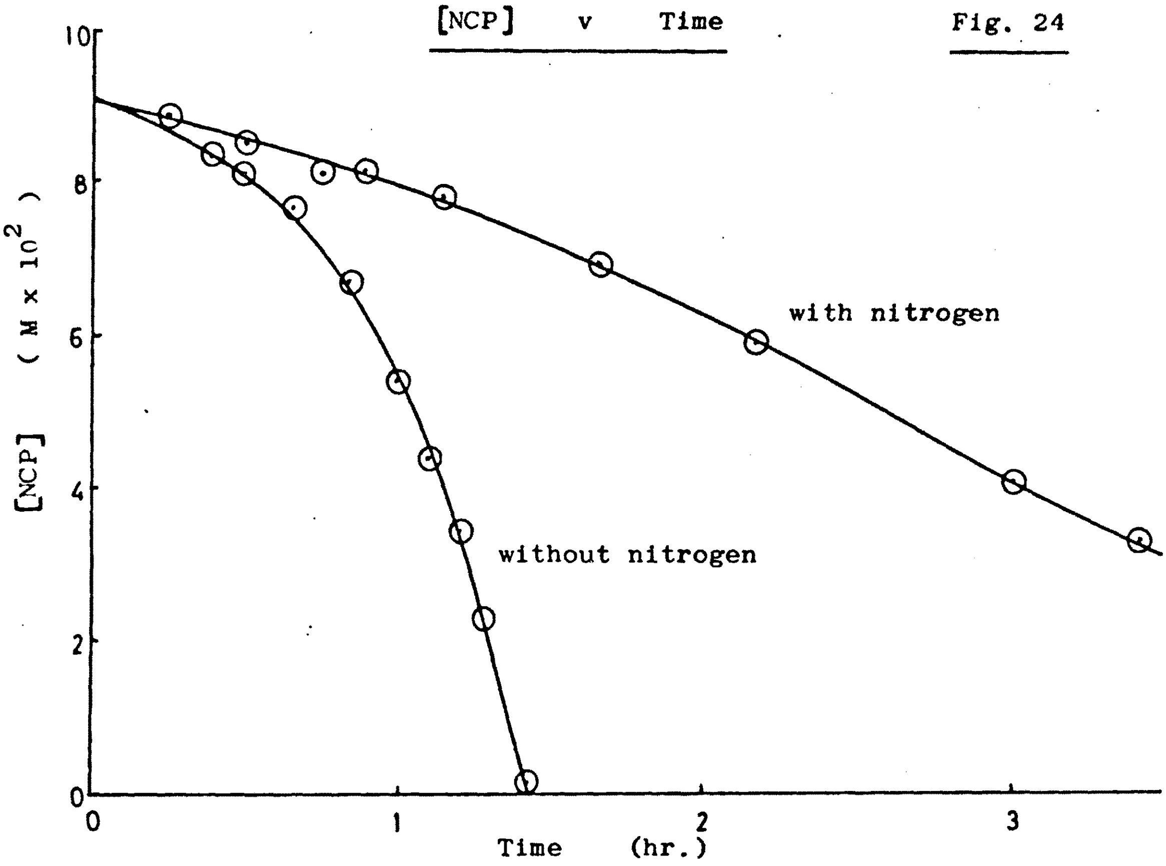
[NCA] v Time Fig. 22



Log_{10}[NCA] v Time Fig. 23

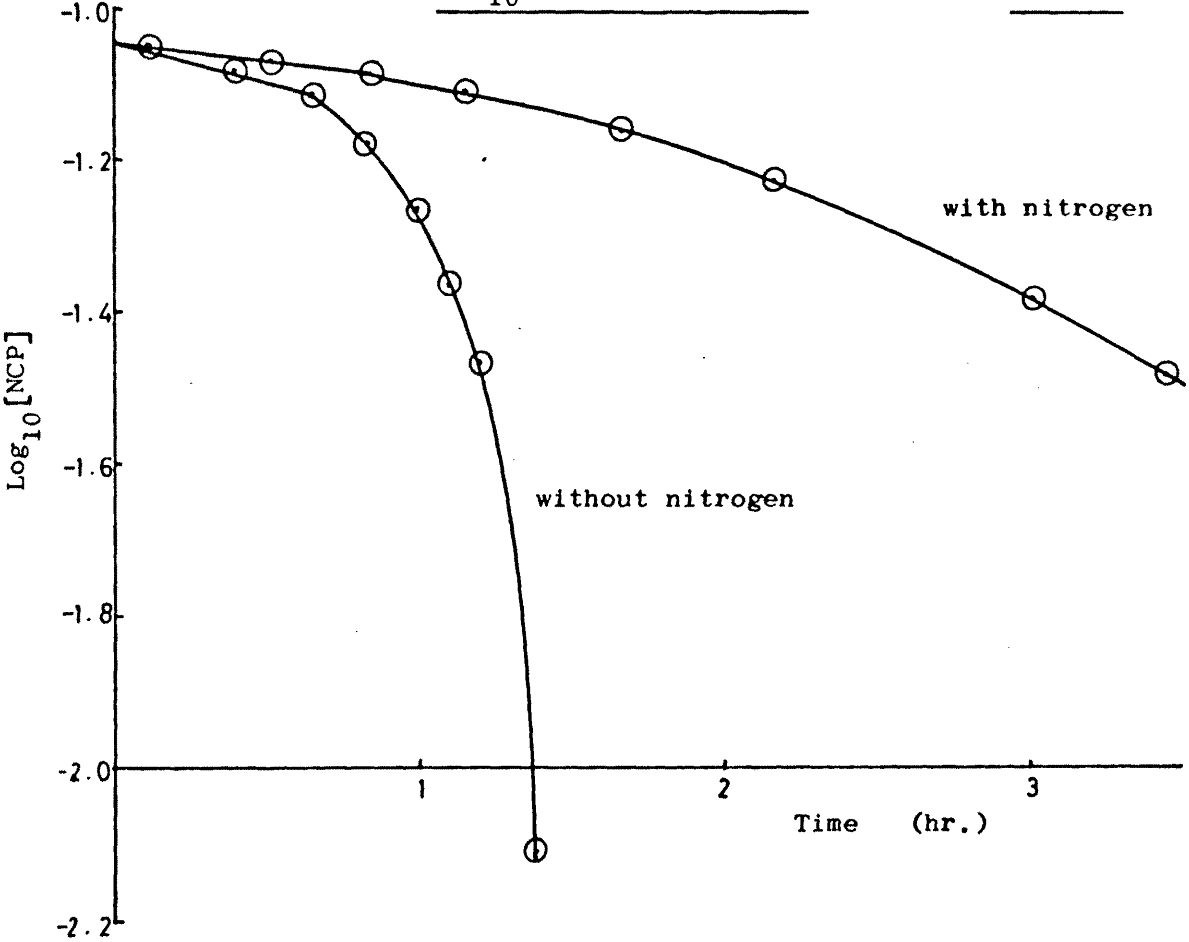
[NCP] v Time

Fig. 24



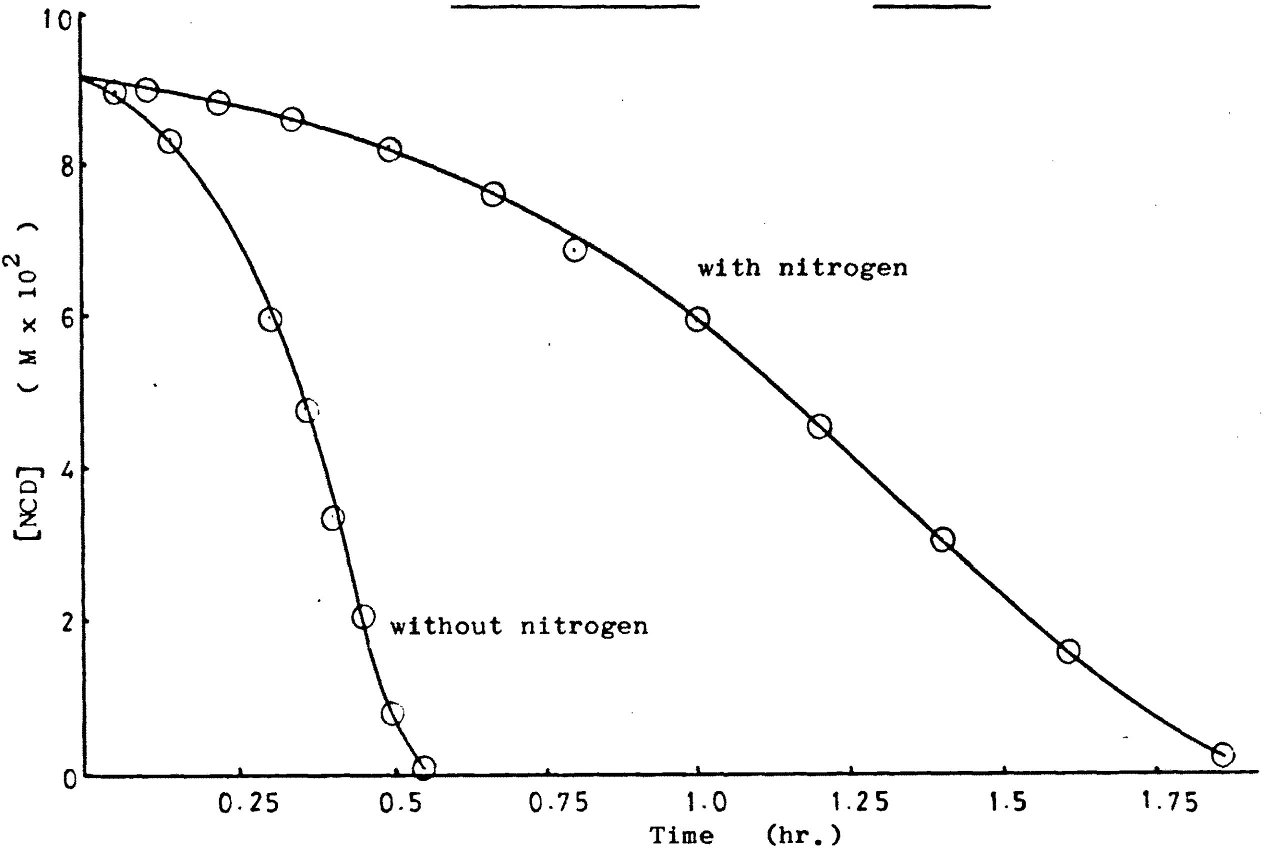
Log$_{10}$[NCP] v Time

Fig. 25

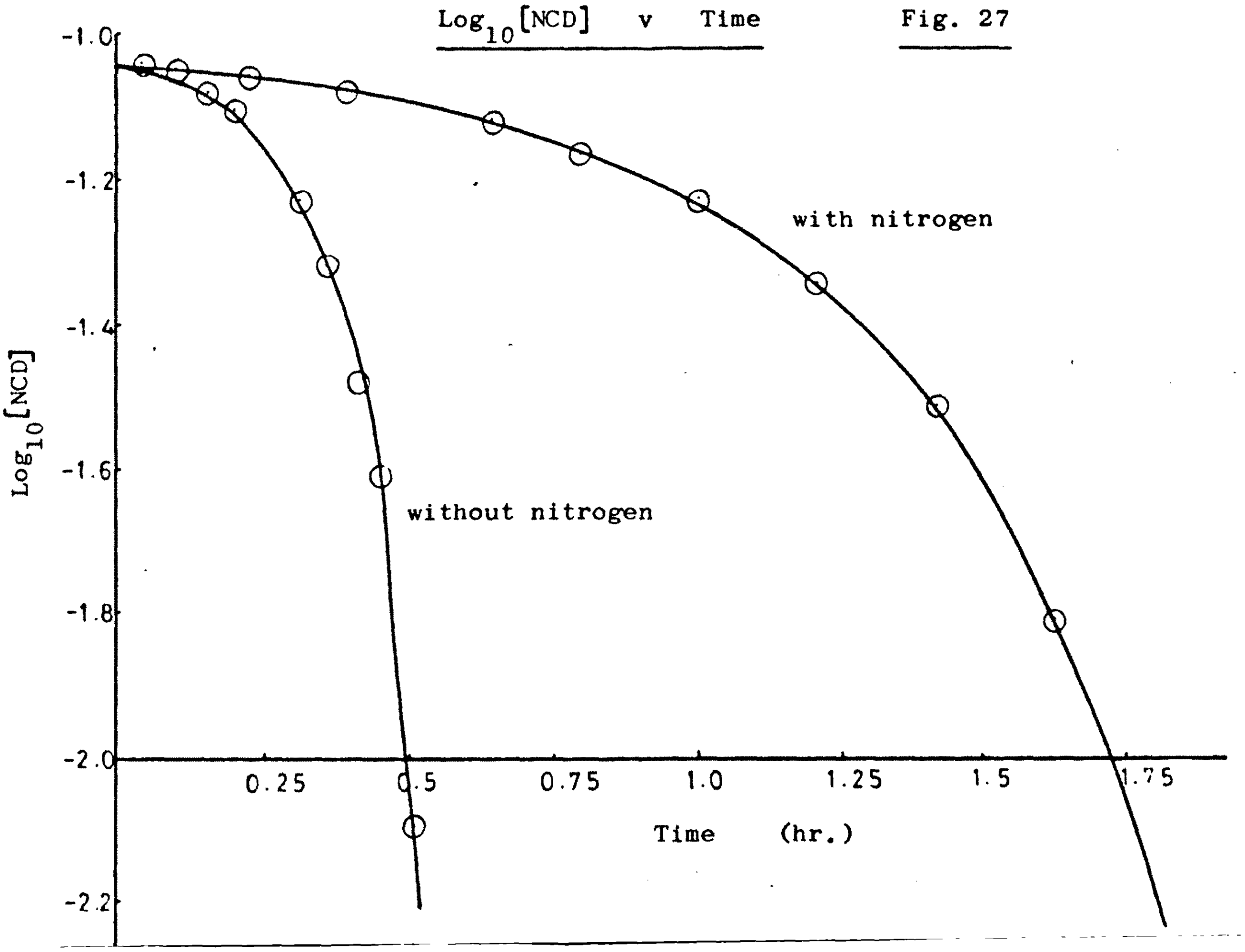


The Thermal Rearrangement of N-Chlorodiphenylacetanilide in Nitrobenzene.

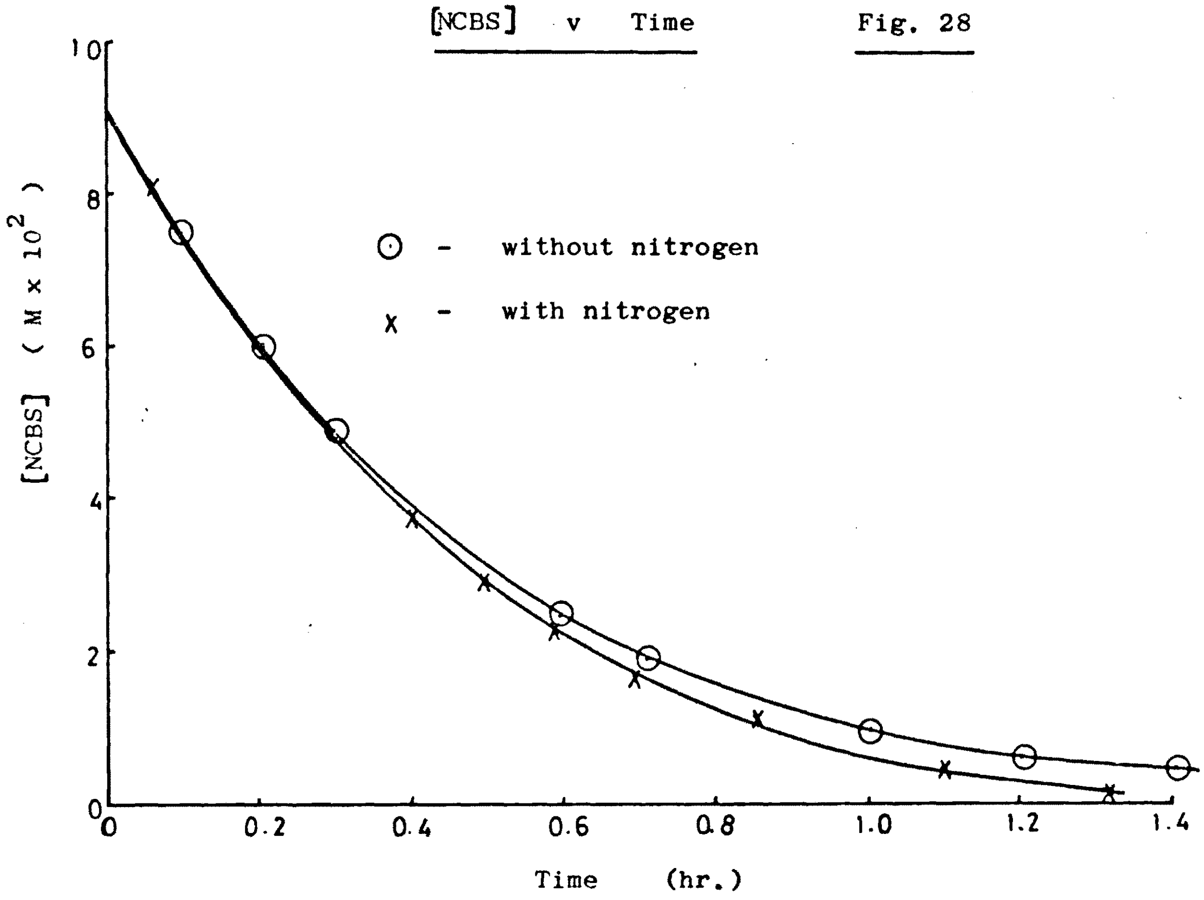
[NCD] v Time Fig. 26



Log_{10}[NCD] v Time Fig. 27

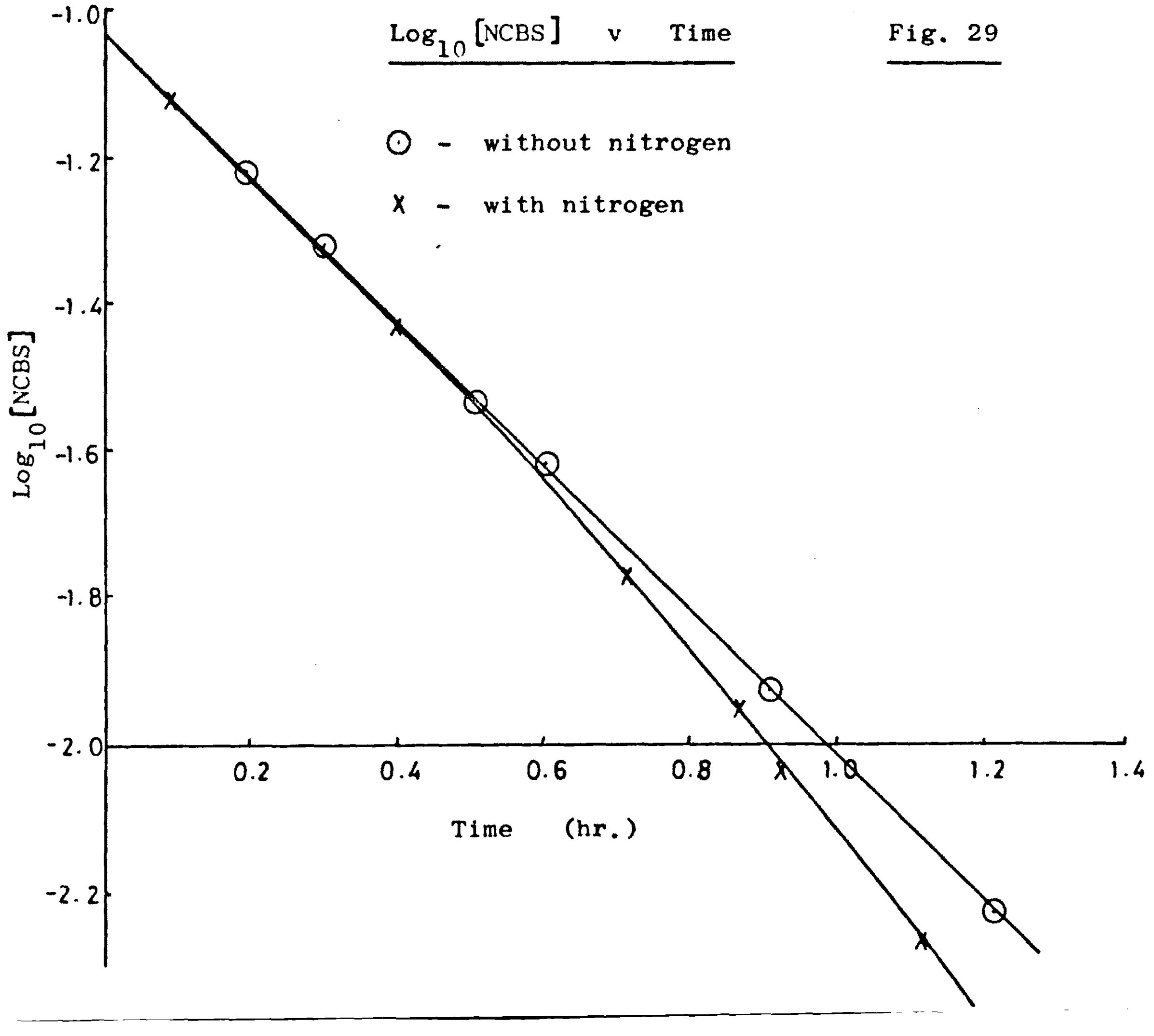


The Thermal Rearrangement of N-Chlorobenzenesulphonanilide in Nitrobenzene.



[NCBS] v Time

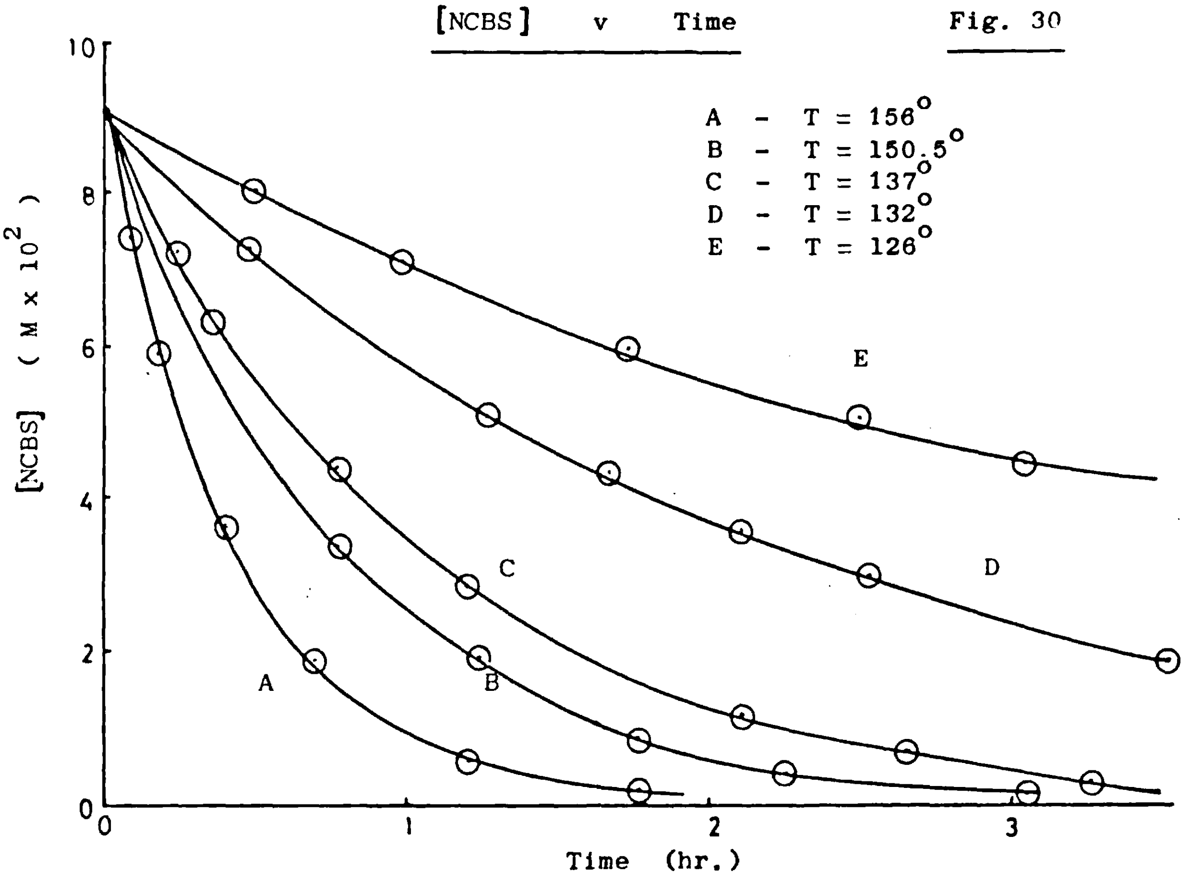
Fig. 28



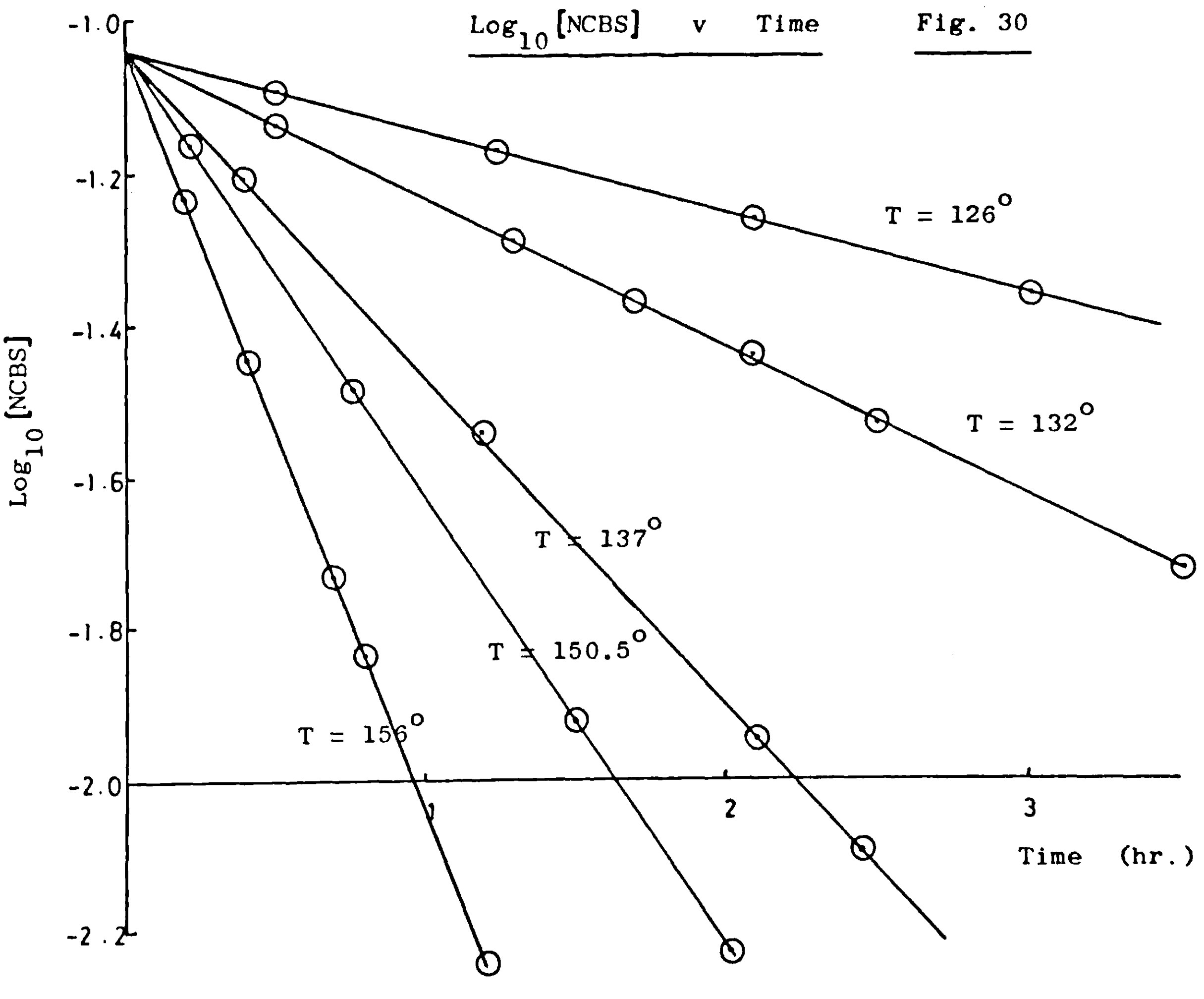
Log_{10}[NCBS] v Time

Fig. 29

The Thermal Rearrangement of N-Chlorobenzenesulphonanilide in Nitrobenzene, aspirated with Nitrogen.

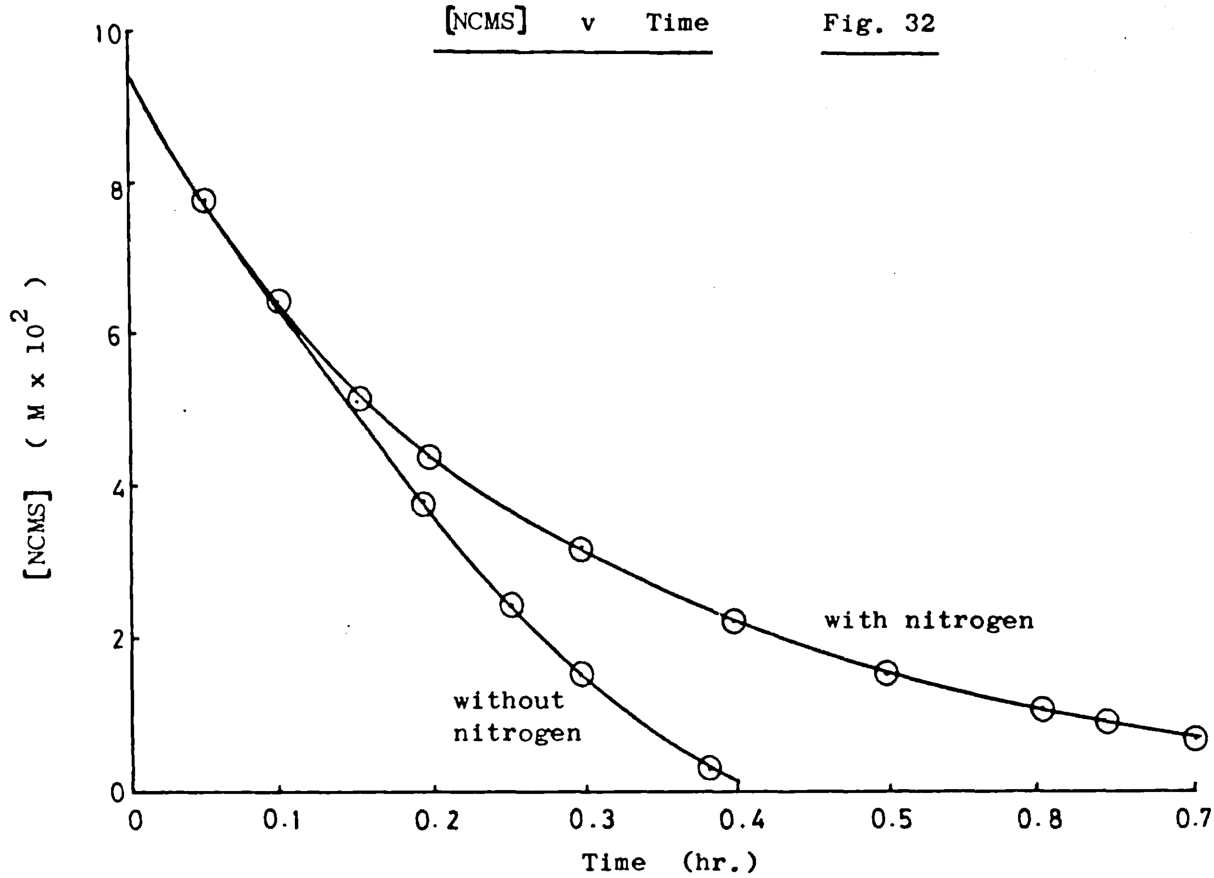


[NCBS] v Time Fig. 30

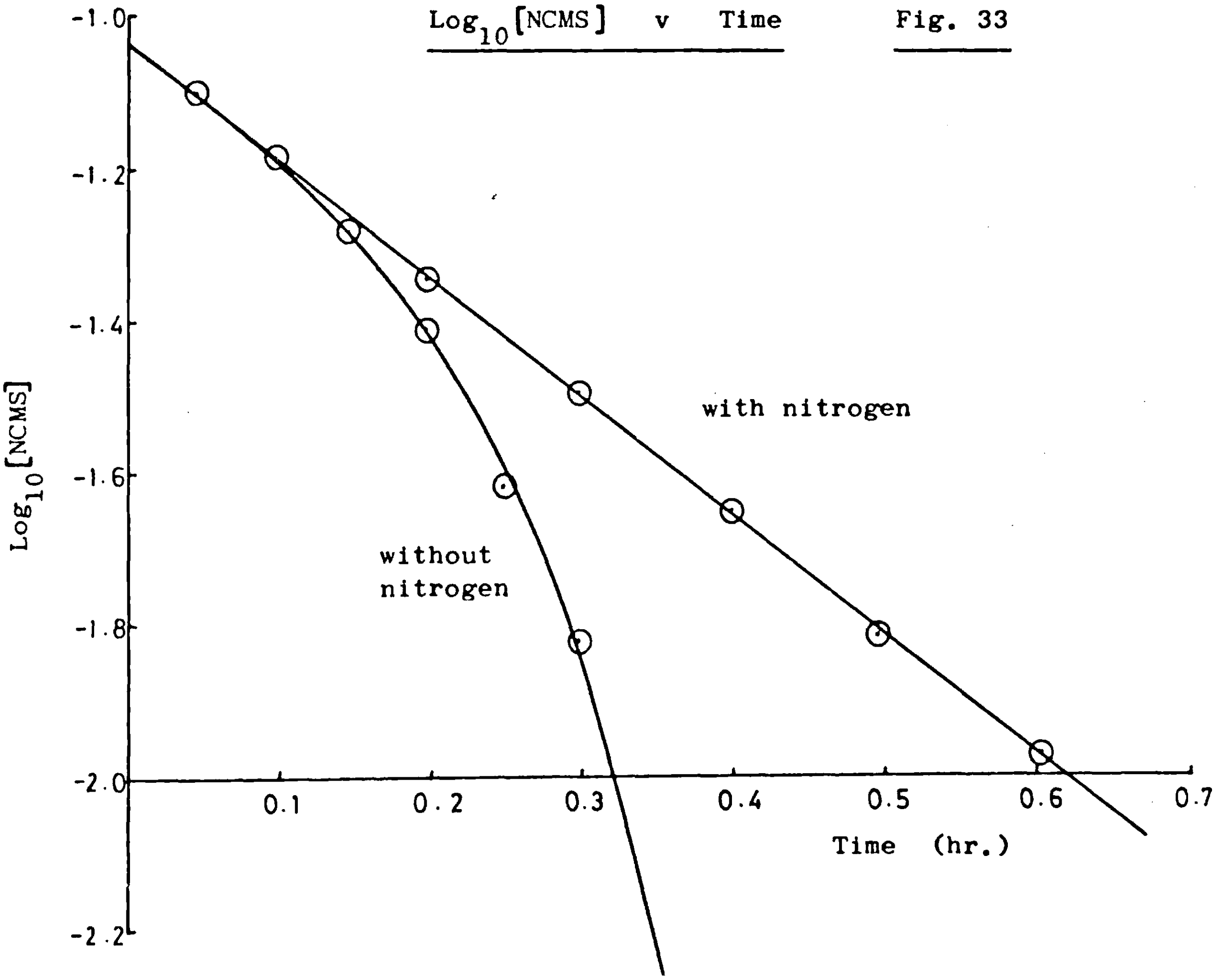


Log$_{10}$[NCBS] v Time Fig. 30

The Thermal Rearrangement of N-Chloromethanesulphonanilide in Nitrobenzene.



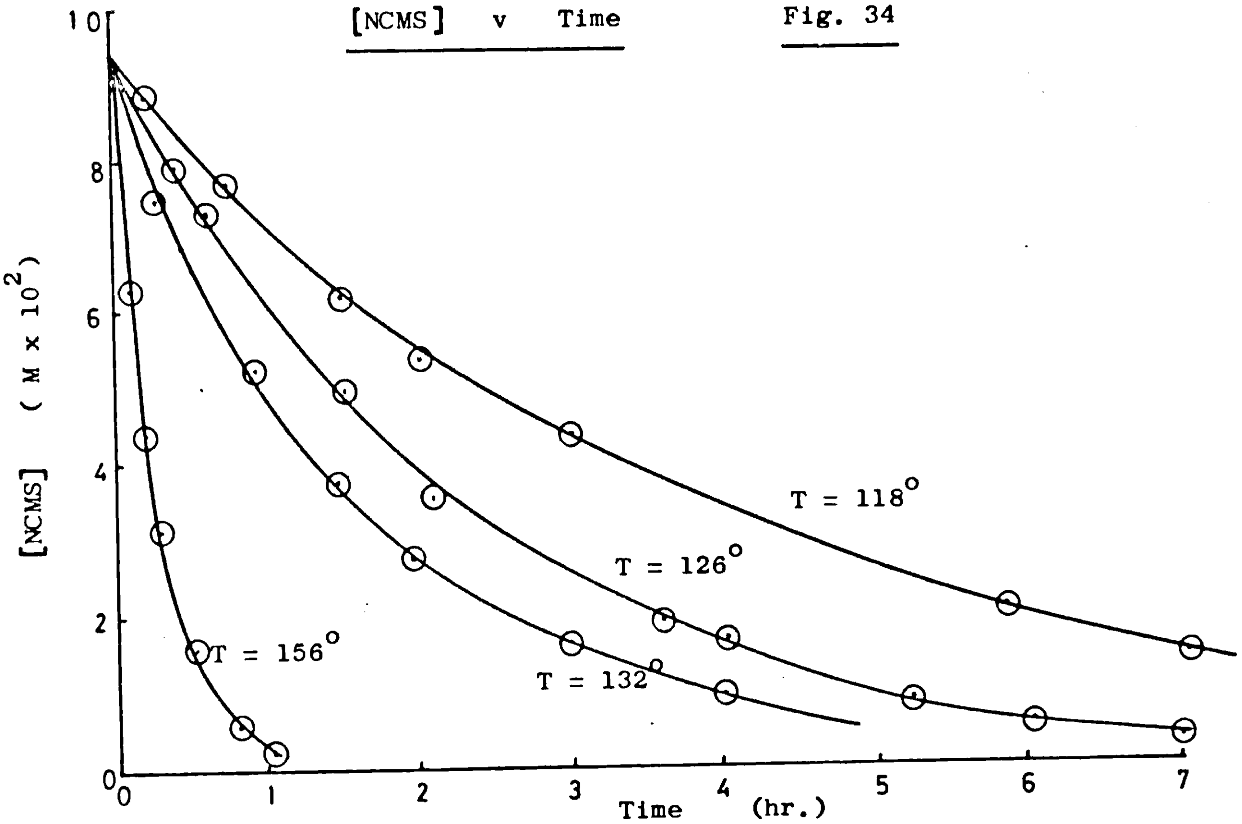
[NCMS] v Time Fig. 32



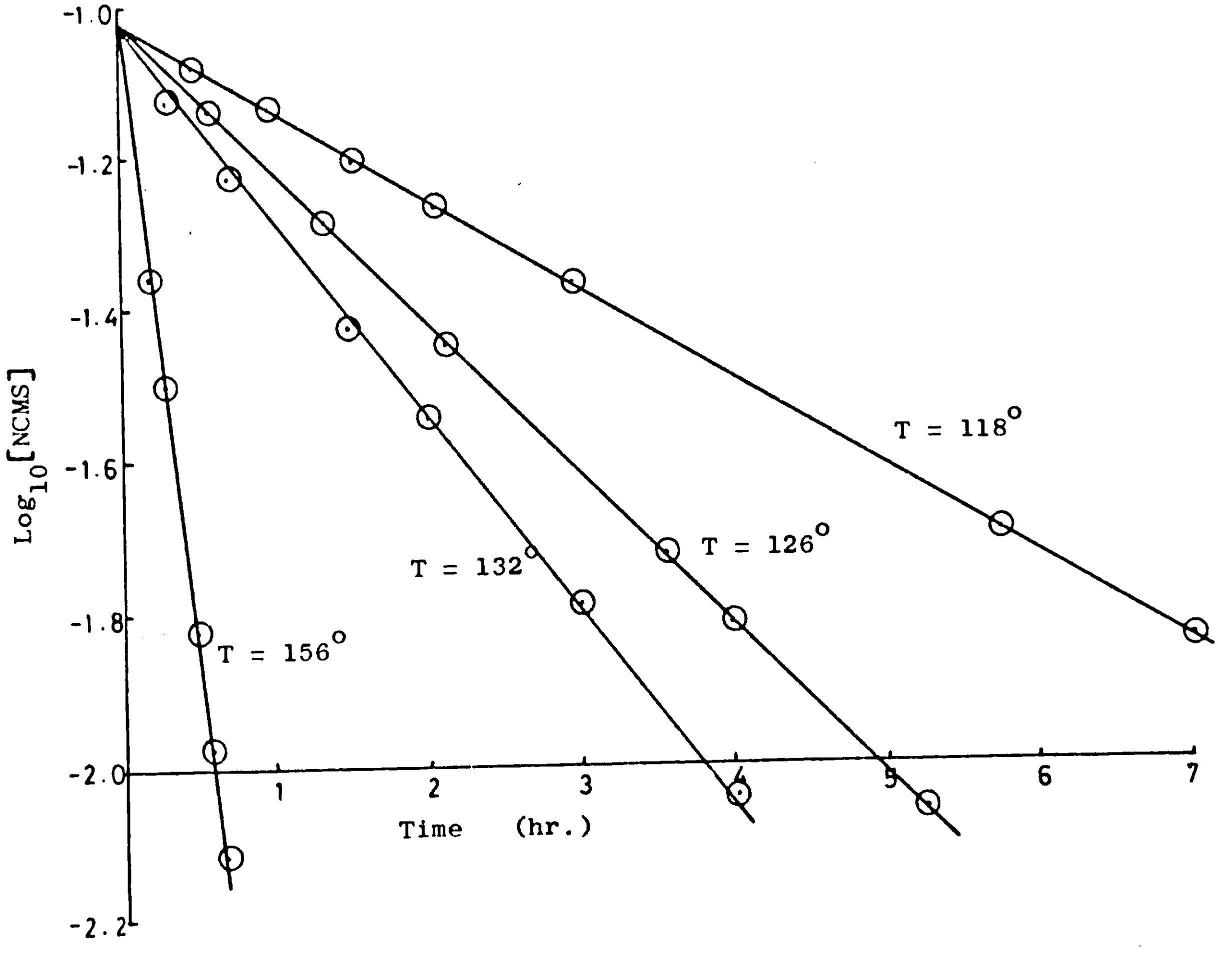
Log_{10}[NCMS] v Time Fig. 33

The Thermal Rearrangement of N-Chloromethanesulphonanilide in aspirated with Nitrogen.

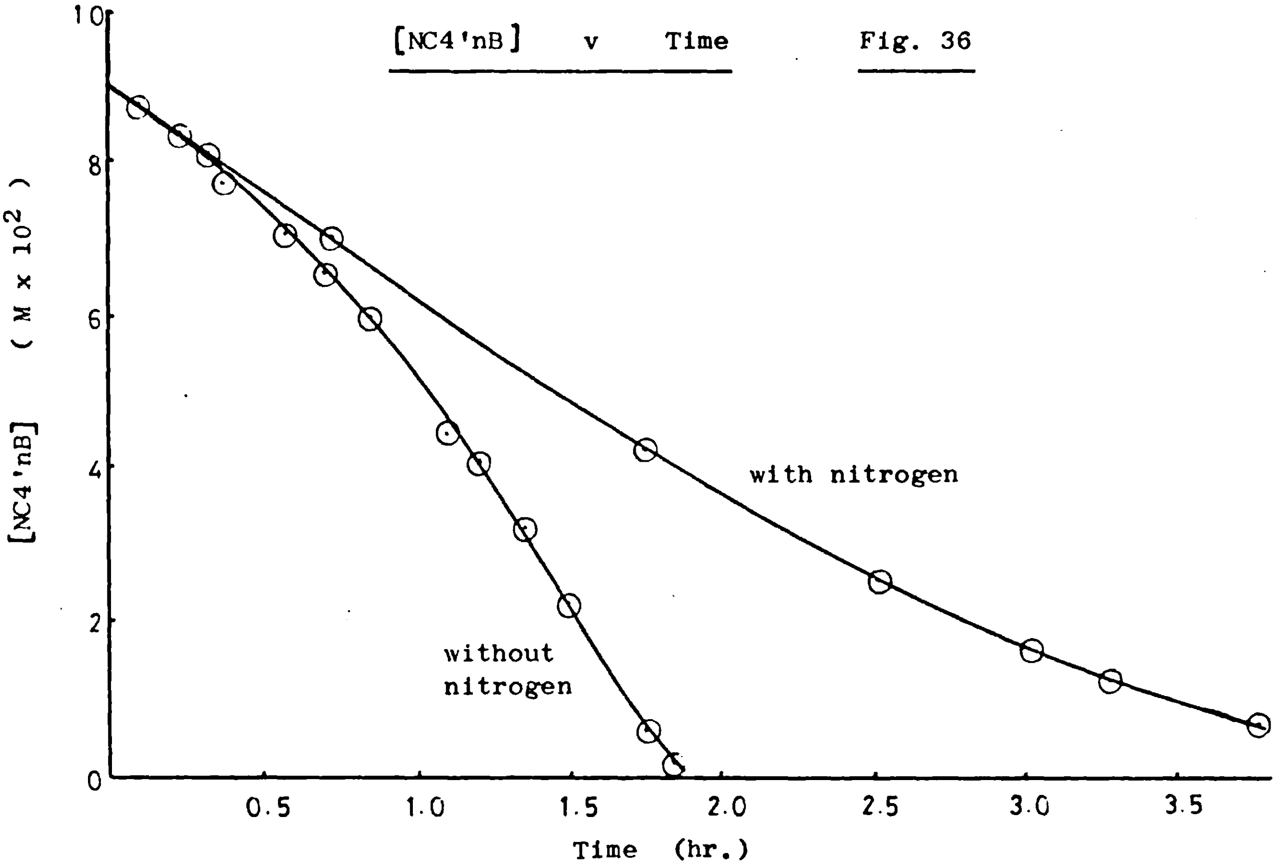
[NCMS] v Time Fig. 34



Log$_{10}$[NCMS] v Time Fig. 35

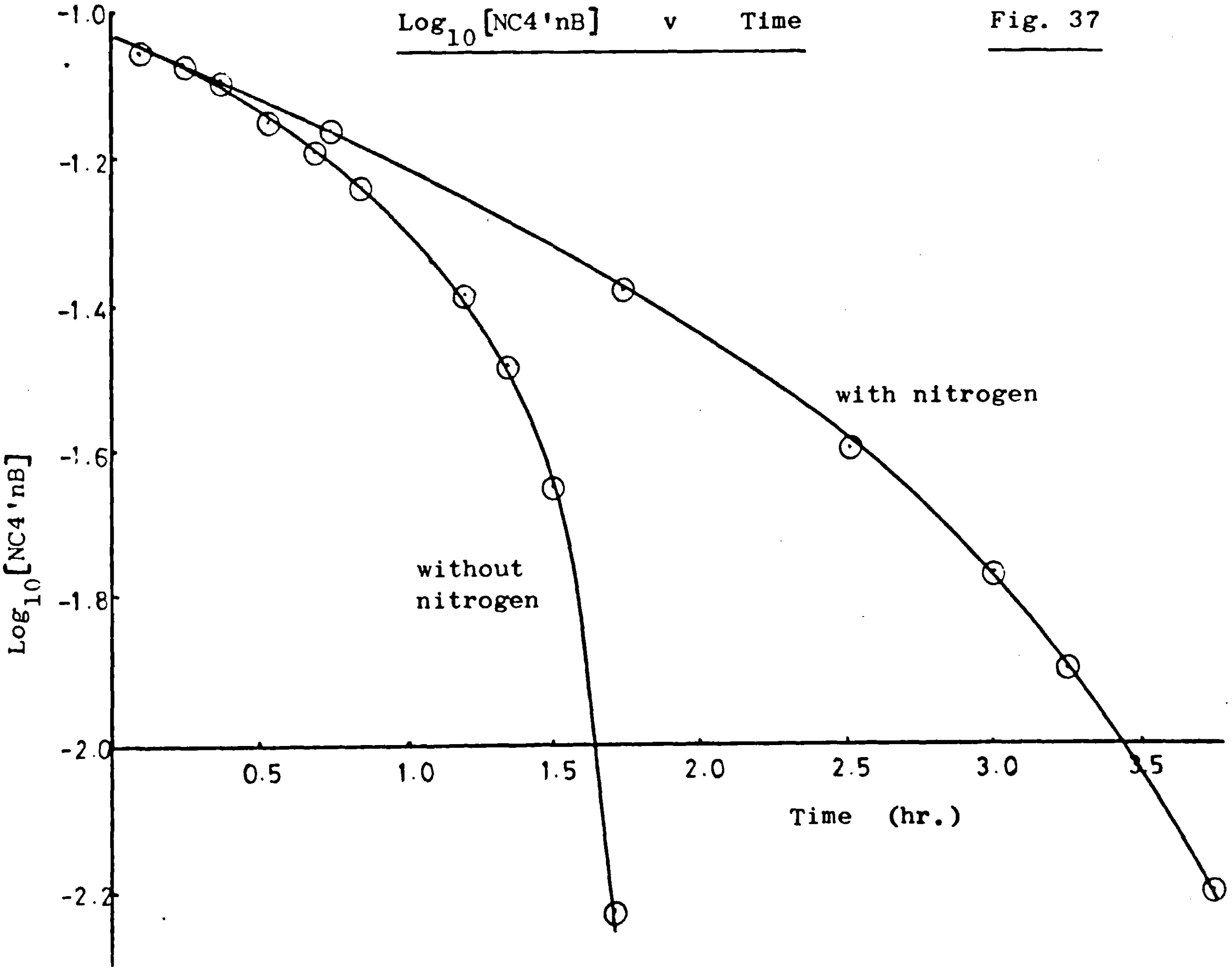


The Thermal Rearrangement of N-Chloro-4'-nitrobenzanilide at 156°
in Nitrobenzene.



[NC4'nB] v Time

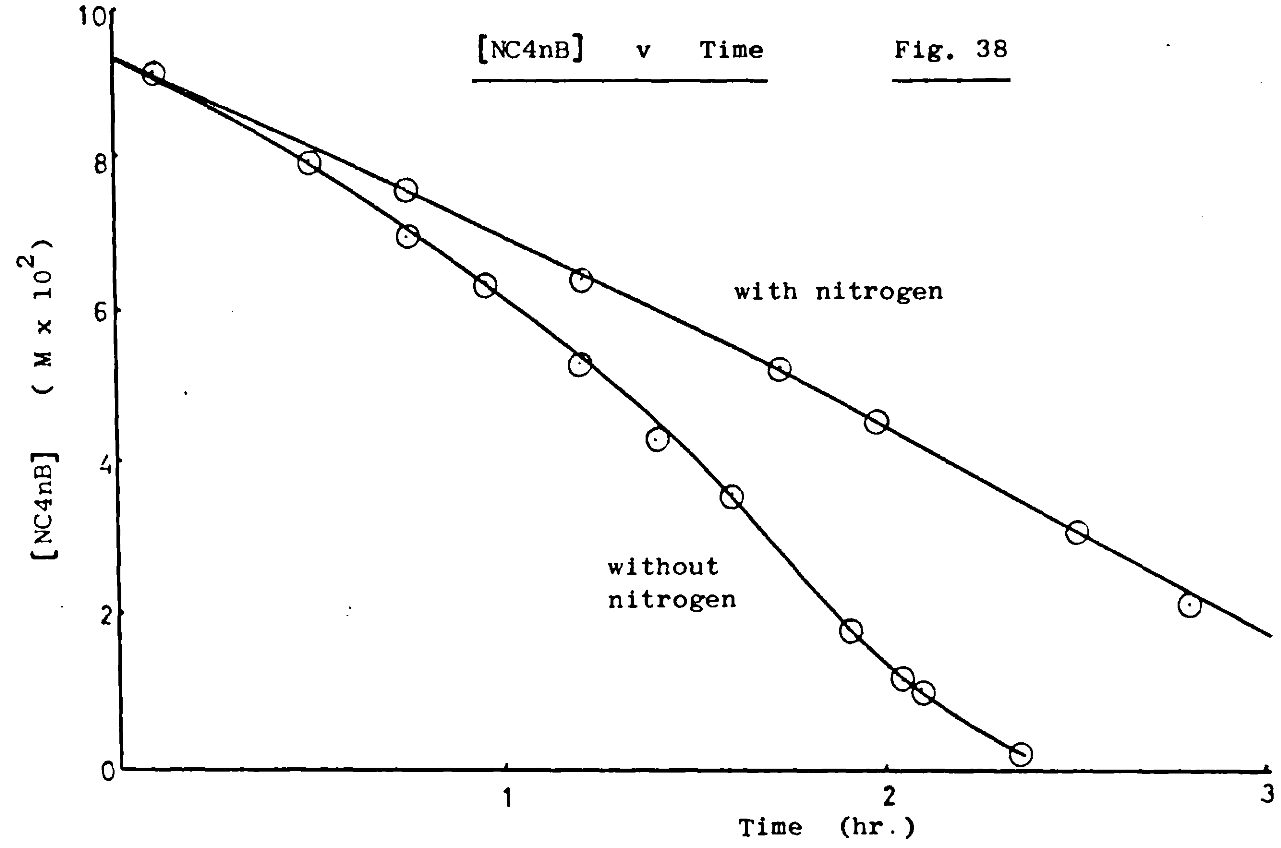
Fig. 36

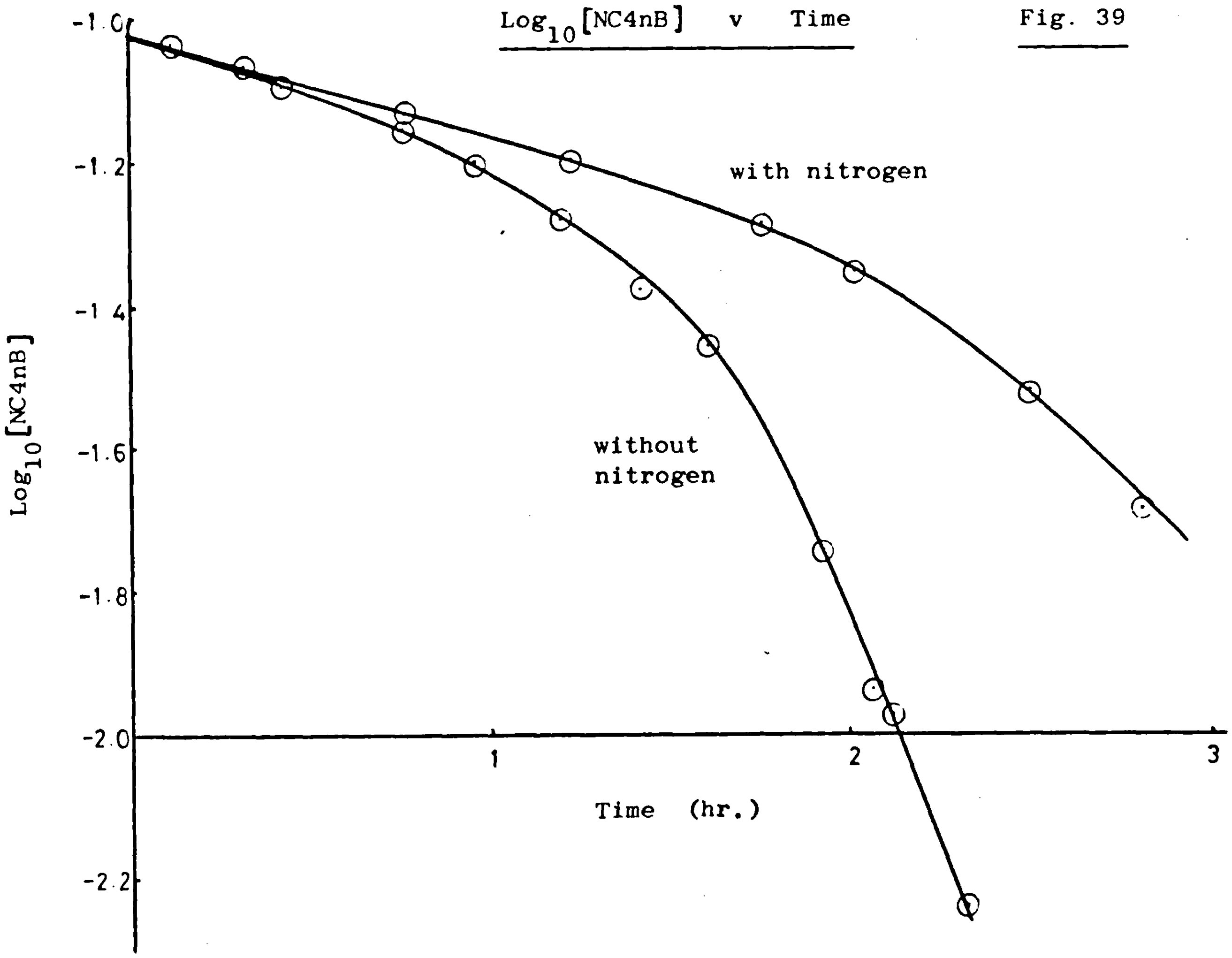


Log$_{10}$[NC4'nB] v Time

Fig. 37

The Thermal Rearrangement of N-Chloro-4-nitrobenzanilide at 156° in Nitrobenzene.





solution. The solution was then analysed for chlorine and hydrogen chlorine using the method described by Clare, Williams and Johnston[6]. Two aliquot portions (10 ml.) were added to an excess of acidified potassium iodide, and the liberated iodine titrated against standard sodium thiosulphate solution (0.010 M) using starch as indicator. From the mean volume of sodium thiosulphate solution used, the concentration of chlorine in the solution was calculated. To each of the three remaining aliquot portions (10 ml.) of sodium hydroxide solution, a volume of sodium thiosulphate equal to the mean volume required in the previous experiment, was added to prevent bleaching of the indicator near the end-point. Then each aliquot was titrated against standard hydrochloric acid (0.10 M) using screened methyl orange as indicator. From the mean value of acid used, the total acid content of the solution was calculated, and hence the number of moles of hydrogen chloride removed from the reaction mixture was determined. The results obtained for these experiments are given in Table 23. Results obtained from a similar series of experiments with N-chloroacetanilide are given in Table 23.

2.5.2.2 The products of the thermal reaction.

A solution of N-chloroanilide (1.158 g., 0.0050 mole) in nitrobenzene (50 ml.) was maintained at 156°, in the dark, until rearrangement was complete (4 hr.). After the solvent had been removed by distillation, the pale orange residue was hydrolysed, and the hydrolysate was analysed in the usual way. The results are given in Table 24.

2.5.2.3. The thermal reaction, aspirated with nitrogen.

Dry nitrogen was passed slowly (1 l. hr^{-1}.) through nitrobenzene (50 ml.) in the dark at 156°, then N-chlorobenzanilide (1.158 g., 0.0050 mole) was added and the mixture was stirred. When the rearrangement was complete (10 hr.) the products were analysed by the standard method and the results are given in Table 24.

Table 23

Analysis of the Volatile of the Thermal Rearrangement of N-Chloroanilides in Nitrobenzene.

	N-Chlorobenzanilide			N-Chlorophenylacetanilide		
	1	2	3	1	2	3
N-Chloroanilide (mole)	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}
Nitrogen Flow ($l.\ hr^{-1}$.)	1.0	1.0	1.5	1.0	1.0	2.0
Hydrogen Chloride evolved (mole)	1.95×10^{-5}	1.70×10^{-5}	2.00×10^{-5}	4.12×10^{-5}	5.08×10^{-5}	9.5×10^{-5}
Chlorine evolved (mole)	0.5×10^{-6}	0.7×10^{-6}	3.0×10^{-6}	2.3×10^{-6}	2.0×10^{-6}	1.5×10^{-6}
Total number of moles of chlorine lost from the solution	2.05×10^{-5}	1.95×10^{-5}	2.6×10^{-5}	4.62×10^{-5}	5.47×10^{-6}	9.8×10^{-5}
Chlorine lost from the solution as a percentage of the available chlorine	0.4	0.4	0.5	0.9	1.1	2.0

2.5.2.4. The rearrangement in the presence of hydrogen chloride.

As the kinetics indicated that hydrogen chloride is formed during the thermal rearrangement, and is responsible for the deviation from first-order kinetics, it was thought of interest to carry out the rearrangement catalysed by hydrogen chloride under conditions comparable to those used for the thermal reaction. N-Chlorobenzanilide (1.158 g., 0.0050 mole) was dissolved in nitrobenzene (50 ml.), at 156°, in the dark, and then dry hydrogen chloride was passed through the solution until the rearrangement was complete (4 min.). The products were analysed as described previously and the results obtained are given in Table 24.

Table 24

Products of the Reactions of N-Chlorobenzanilide, in Nitrobenzene, at 156°.

	Molar % of Products					
	a	o	p	d	t	o:p
Thermal reaction in nitrobenzene, alone.	4.2	11.7	79.6	3.8	0.8	1:6.80
Thermal reaction in nitrobenzene, alone.	5.0	12.2	79.1	3.3	0.5	1:6.48
Thermal reaction, aspirated with nitrogen.	11.7	13.3	69.2	5.2	1.3	1:5.25
Thermal reaction, aspirated with nitrogen.	15.4	14.8	62.0	6.0	1.8	1:4.20
Thermal reaction, aspirated with nitrogen.	11.9	14.9	65.7	4.3	3.1	1:4.41
Reaction catalysed by hydrogen chloride.	67.8	1.5	29.5	1.2	0.2	1:19.5
Reaction catalysed by hydrogen chloride.	67.0	1.8	31.4	0.4	0.2	1:20.7

2.6. The Thermal Rearrangement of N-Chloroanilides in the Presence of Added Anilides.

Bell and Danckwerts[28] showed that the acid-catalysed rearrangements of N-chloroacetanilide in non-polar solvents exhibited the characteristics of autocatalysis. The presence of added o- or p-chloroacetanilide did not affect the initial rate of rearrangement but caused an increase in the deviation from first-order kinetics. An analogous effect of these anilides was observed by Coulson[5], in a study of the photolysis of N-chloroacetanilide in carbon tetrachloride. It was therefore thought to be of interest to study the rearrangement of N-chlorobenzanilide in the presence various anilides and so to investigate the relationship between the nature of the anilide and the extent of the deviation from first-order kinetics. N-Chlorobenzanilide was chosen because the rate of reaction of this N-chloroanilide with hydrogen chloride is relatively high, but little hydrogen chloride is formed during the thermal rearrangement. Therefore if interaction of this N-chloroanilide with the anilide were to produce an appreciable quantity of hydrogen chloride, it should cause a marked increase in the rate of disappearance of the N-chlorobenzanilide.

2.6.1. The Kinetics of the Reaction.

2.6.1.1. The control experiment.

A flask containing chlorobenzene (50 ml.) and fitted with a condenser, to which was attached a guard-tube packed with silica gel and soda lime, was placed in a thermostat (114 ± 0.3°), and N-chlorobenzanilide (0.810 g., 0.0035 mole) was then added and the flask was well shaken. Samples (2 ml.) were removed at suitable intervals and titrated in the usual way. The results obtained are given in Table A26 and Fig. 40.

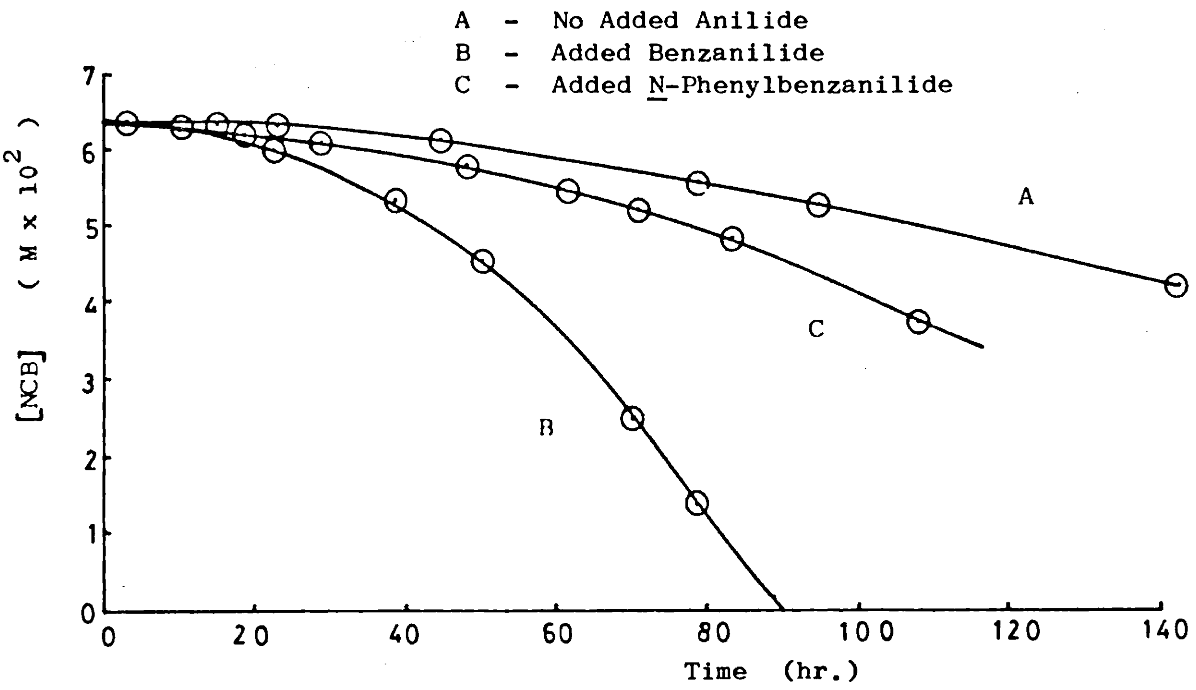
2.6.1.2. The kinetics in the presence of added anilides

In a series of experiments, various anilides (0.0035 mole) in turn, were dissolved in hot chlorobenzene (50 ml.) before the addition of N-chlorobenzanilide (0.0035 mole). The experiments were then carried out as described previously (section 2.6.1.1.)

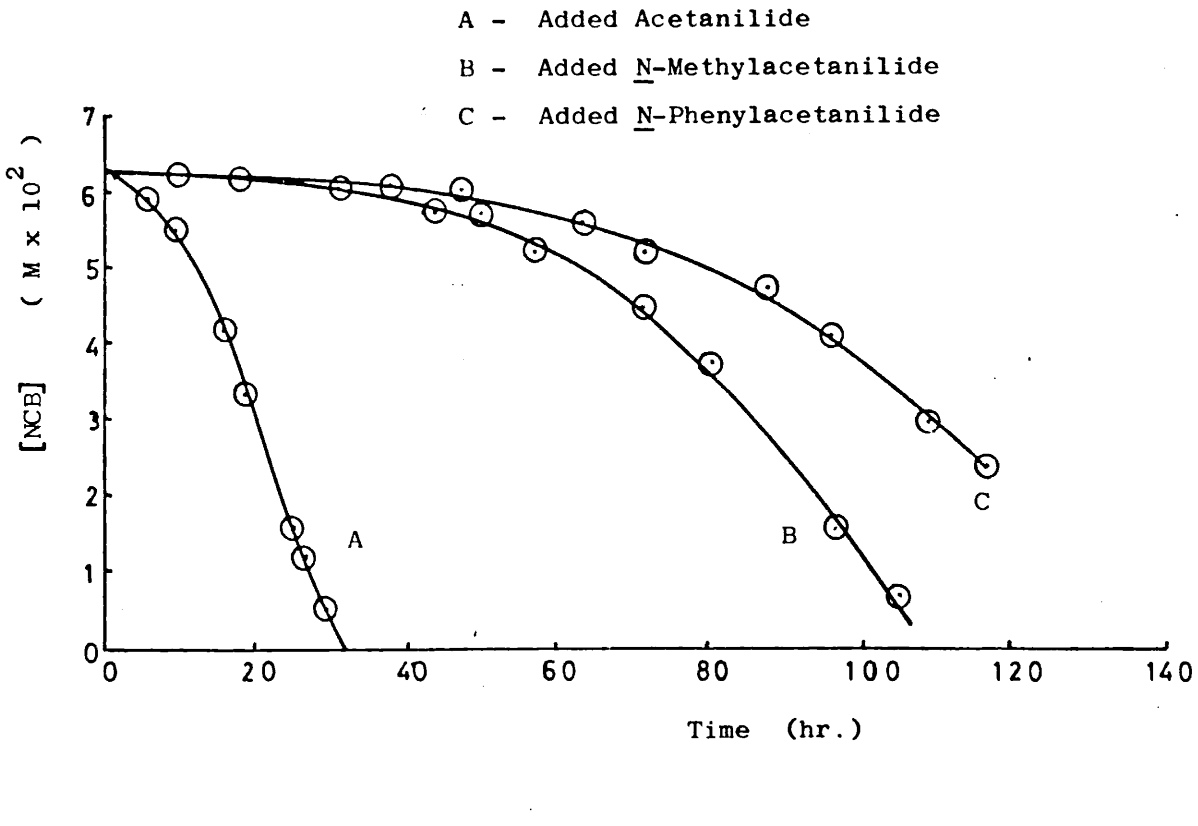
Added Anilide	Fig. No.	Table No.
Acetanilide	41	A27
N-Methylacetanilide	41	A27
N-Phenylacetanilide	41	A27
2-Phenylacetanilide	42	A28
2,2-Diphenylacetanilide	42	A28
2,2,2-Trichloroacetanilide	42	A29
Formanilide	42	A39
Benzanilide	40	A26
N-Phenylbenzanilide	40	A26
2'-Chlorobenzanilide	43	A30
3'-Chlorobenzanilide	43	A30
4'-Chlorobenzanilide	43	A30
4'-Fluorobenzanilide	43	A31
4'-Bromobenzanilide	43	A31
4'-Iodobenzanilide	43	A31
4'-Phenylbenzanilide	44	A32
4'-Nitrobenzanilide	44	A32
4'-Phenoxybenzanilide	44	A32
4'-Benzoylbenzanilide	44	A32
4-Chlorobenzanilide	45	A33
4-Nitrobenzanilide	45	A33
Methanesulphonanilide	46	A34
N-Methylmethanesulphonanilide	46	A34
Benzenesulphonanilide	46	A34
N-Phenyl Diphenylphosphoramidate	46	A34

The Thermal Rearrangement of N-Chlorobenzanilide at 114°, in Chlorobenzene, with Added Anilides.

[NCB] v Time Fig. 40



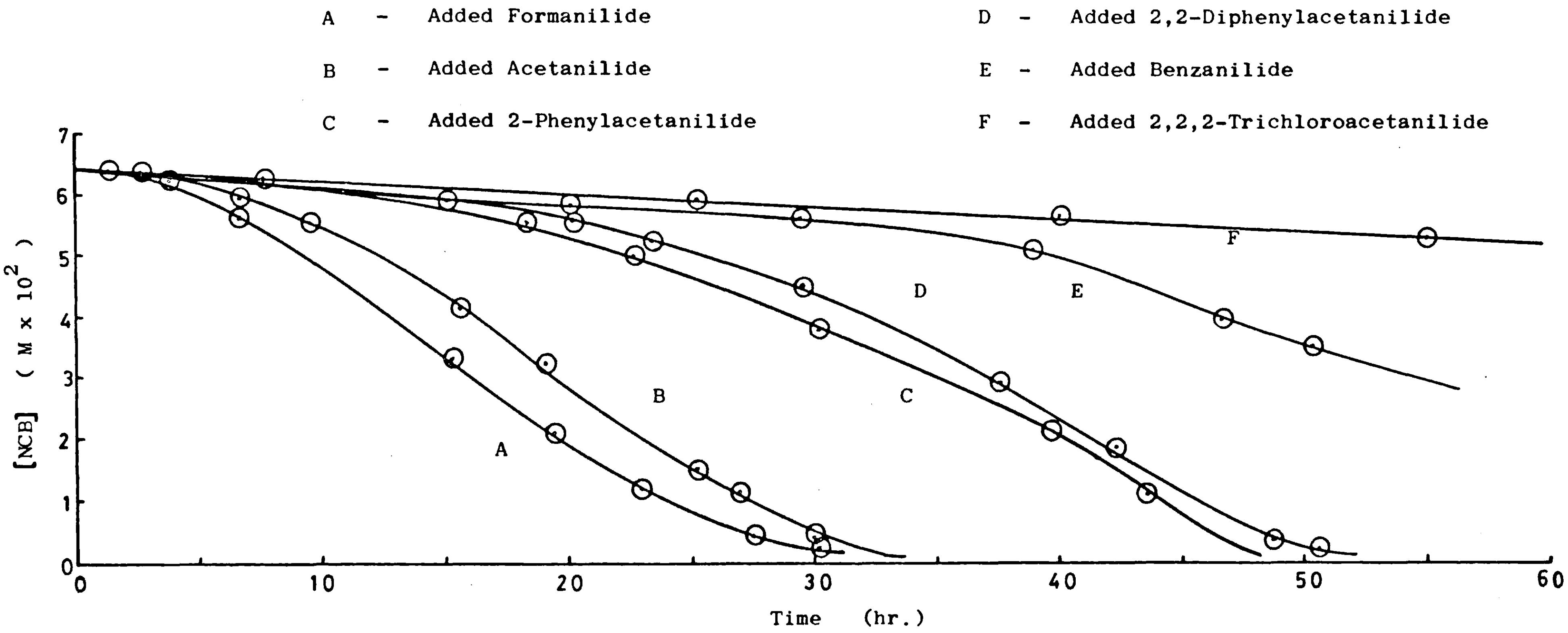
[NCB] v Time Fig. 41



The Thermal Rearrangement of N-Chlorobenzanilide at 114° in Chlorobenzene, in the presence of added Anilides.

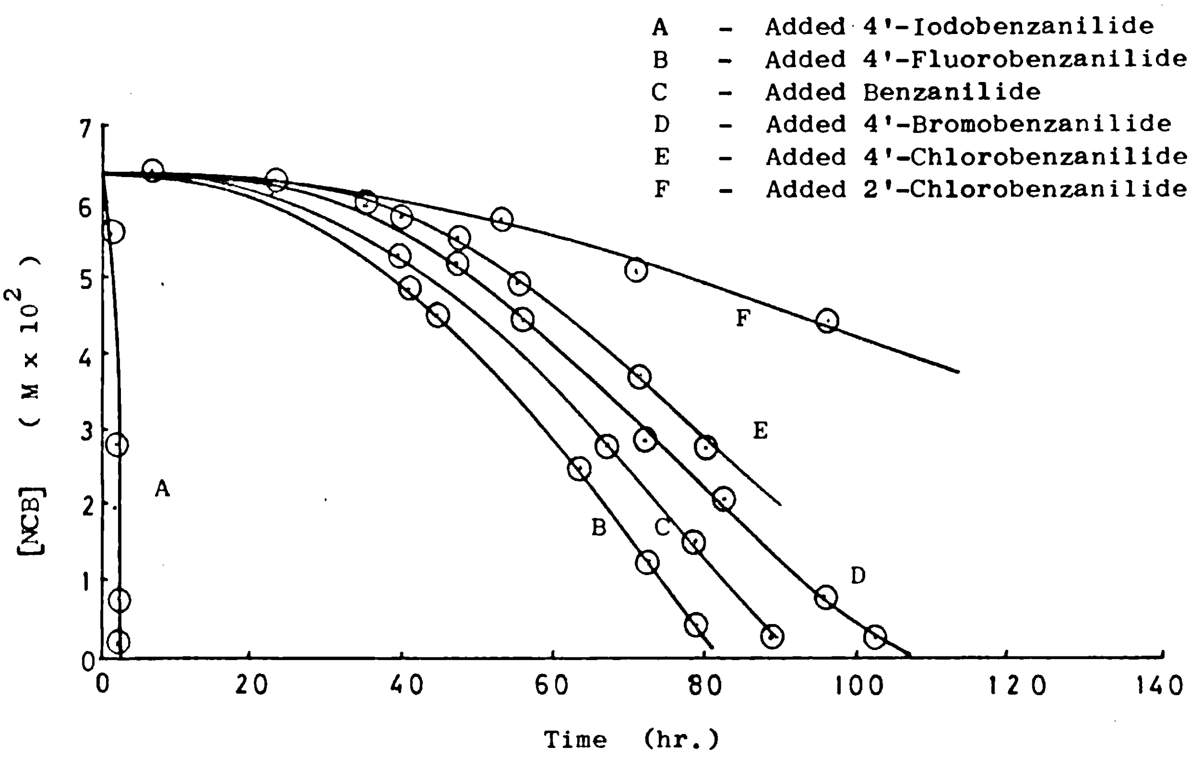
[NCB] v Time

Fig. 42

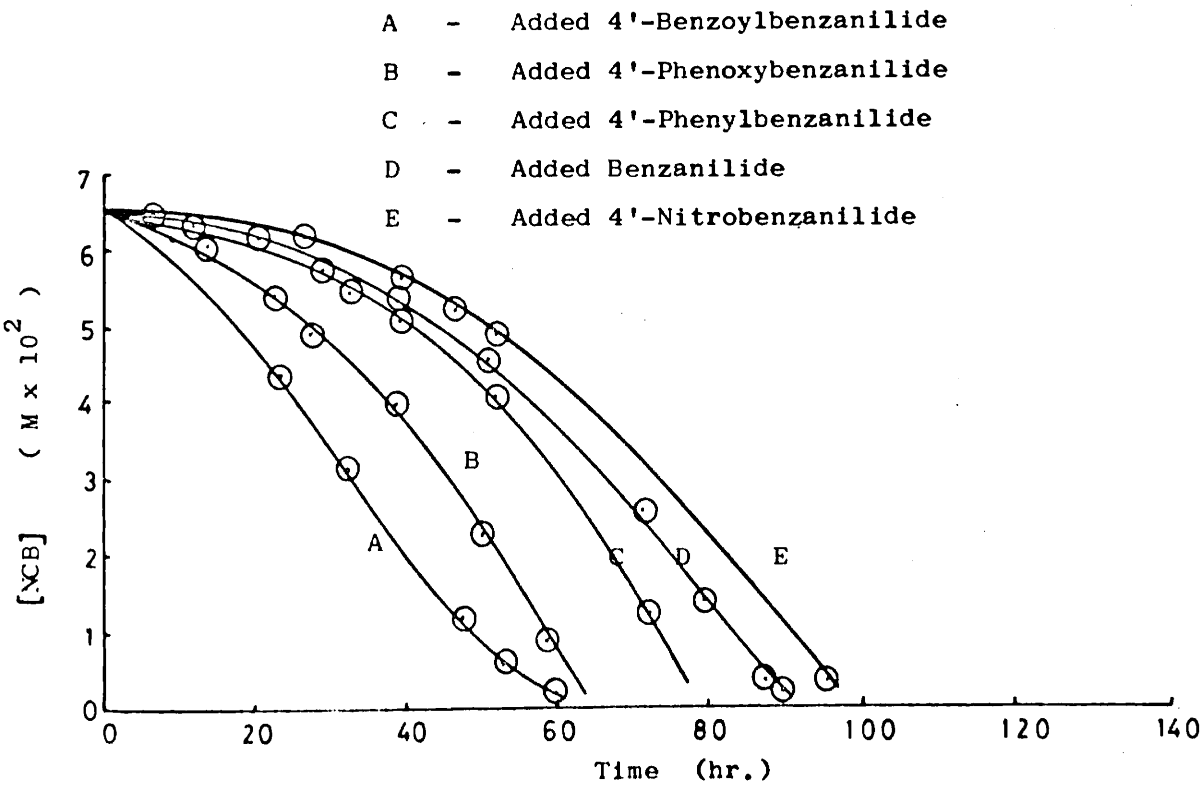


The Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114°, in the presence of added Anilides.

[NCB] v Time Fig. 43

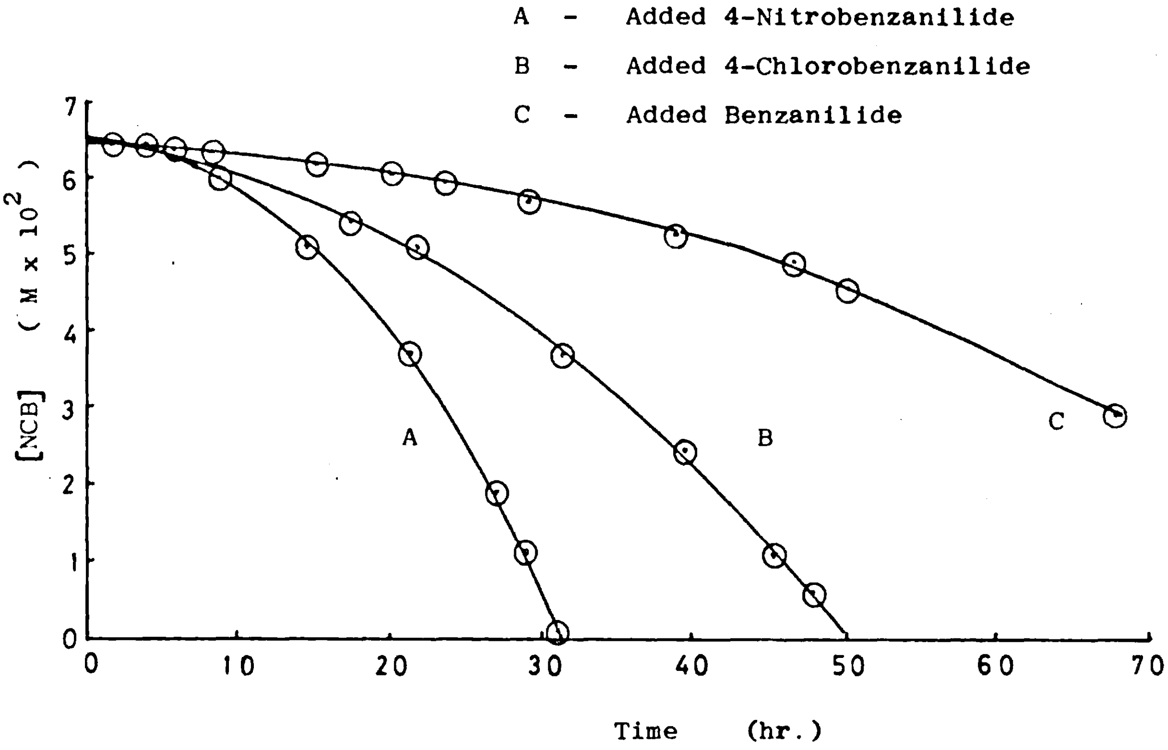


[NCB] v Time Fig. 44

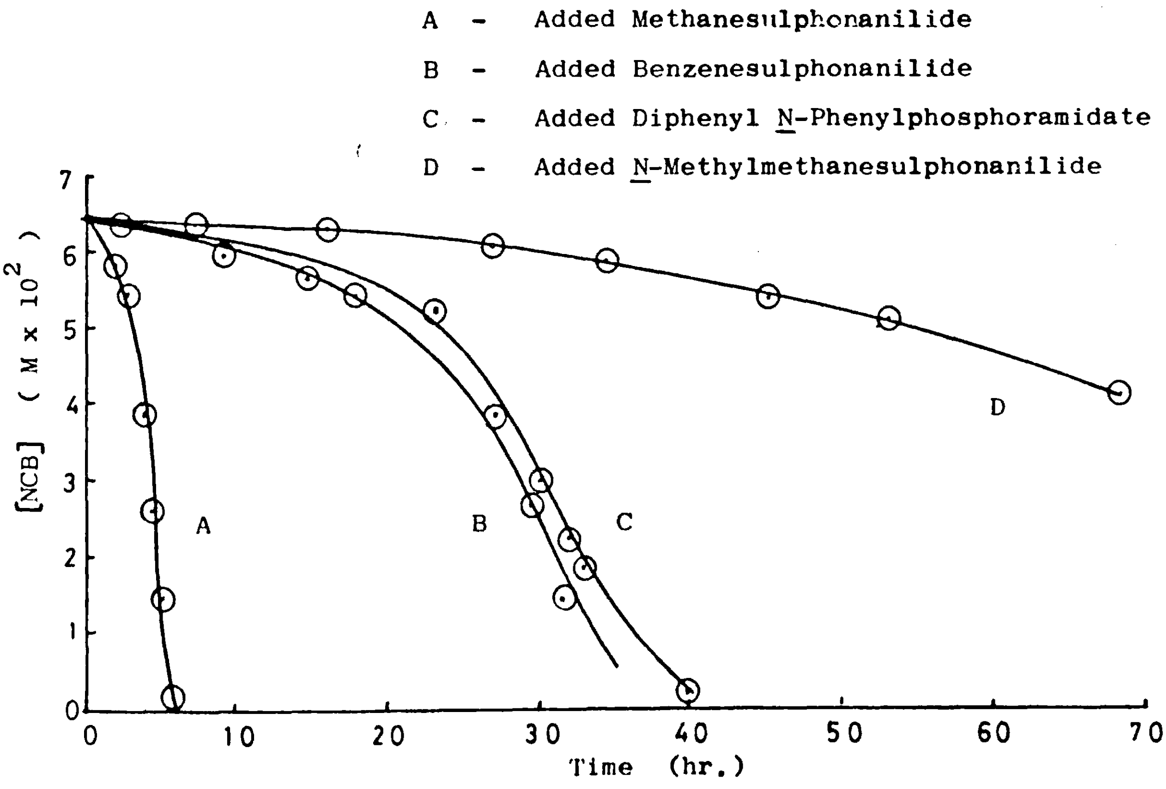


The Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene, at 114°, in the presence of added Anilides.

[NCB] v Time Fig. 45


A - Added 4-Nitrobenzanilide
B - Added 4-Chlorobenzanilide
C - Added Benzanilide

[NCB] v Time Fig. 46


A - Added Methanesulphonanilide
B - Added Benzenesulphonanilide
C - Added Diphenyl N-Phenylphosphoramidate
D - Added N-Methylmethanesulphonanilide

2.6.1.3. The effect of the passage of nitrogen.

The rearrangement was carried out as described previously (section 2.6.1.2.) however dry nitrogen, saturated with chlorobenzene vapour, was passed through the solution, continuously throughout the reaction. The concentration of N-chlorobenzanilide remaining in the solution was estimated in the usual way, and the results obtained are given in Table A35 and Fig. 47 and 48.

2.6.2. The Rearrangement of other N-Chloroanilides in Chlorobenzene at 114°.

A series of experiments were carried out using a similar method to that described previously (section 2.6.1.2.). Each N-chloroanilide (0.0035 mole) in turn, was allowed to rearrange in chlorobenzene (50 ml.) in the dark, either alone or in the presence of an added anilide. The kinetics of each of these reactions were followed by the standard method.

N-Chloroanilide	Added Anilide	Fig. No.	Table No.
N-Chloroacetanilide	-	49	A36
N-Chloroacetanilide	Benzanilide	49	A36
N-Chloromethanesulphonanilide	-	50	A37
N-Chlorobenzenesulphonanilide	-	50	A37

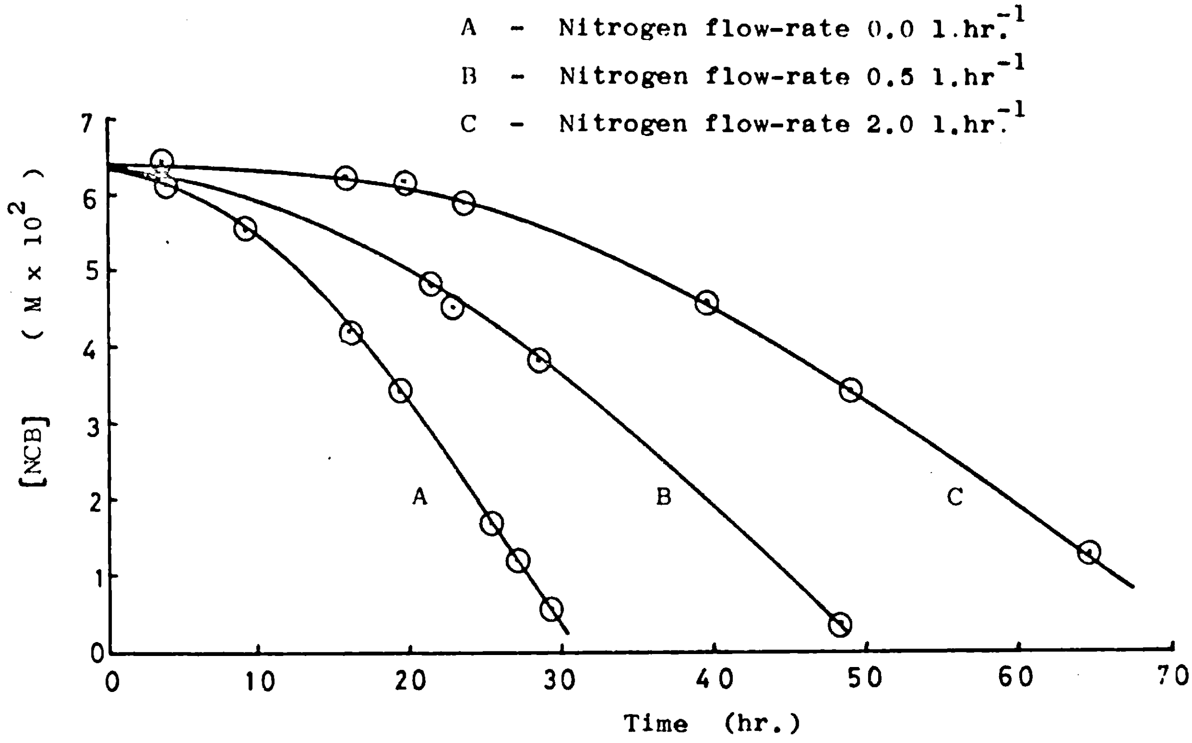
2.6.3. The Analysis of the Products of Reactions in Chlorobenzene.

2.6.3.1. The analysis of the gases removed by the flow of nitrogen.

The experiments were carried out as described previously (section 2.6.1.3.) however nitrogen was passed through the solution and then through sodium hydroxide solution (50 ml., 0.1 M) in the dark. When the rearrangement was complete, the chlorine and hydrogen chloride removed from the chlorobenzene solution, were estimated by the method described previously (section 2.5.2.1.). The results obtained are given in Table 25.

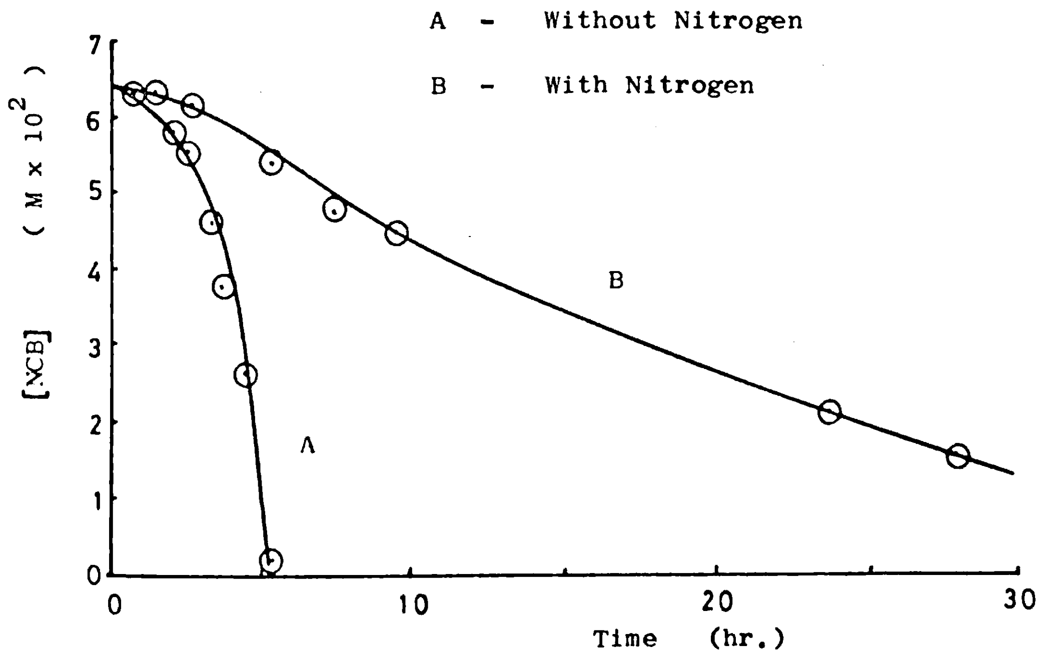
The Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene, aspirated with Nitrogen, at 114°, in the presence of added Acetanilide.

[NCB] v Time Fig. 47



The Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene, with Nitrogen, at 114°, in the presence of added Methanesulphonanilide.

[NCB] v Time Fig. 48

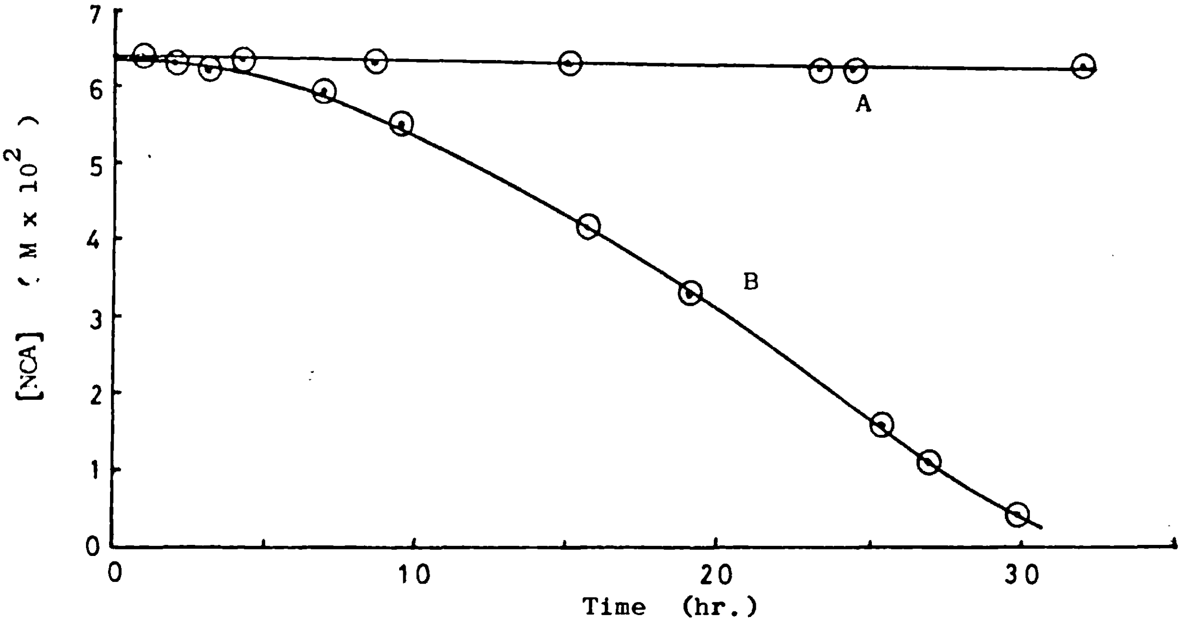


The Thermal Rearrangement of N-Chloroacetanilide in Chlorobenzene at 114°.

[NCA] v Time Fig. 49

A - no added anilide

B - added benzanilide



The Thermal Rearrangement of N-Chloroanilide in Chlorobenzene at 114°.

[NCX] v Time Fig. 50

A - N-Chlorobenzanilide and methanesulphonanilide
B - N-Chloromethanesulphonanilide alone
C - N-Chlorobenzenesulphonanilide alone
D - N-Chlorobenzanilide and benzenesulphonanilide

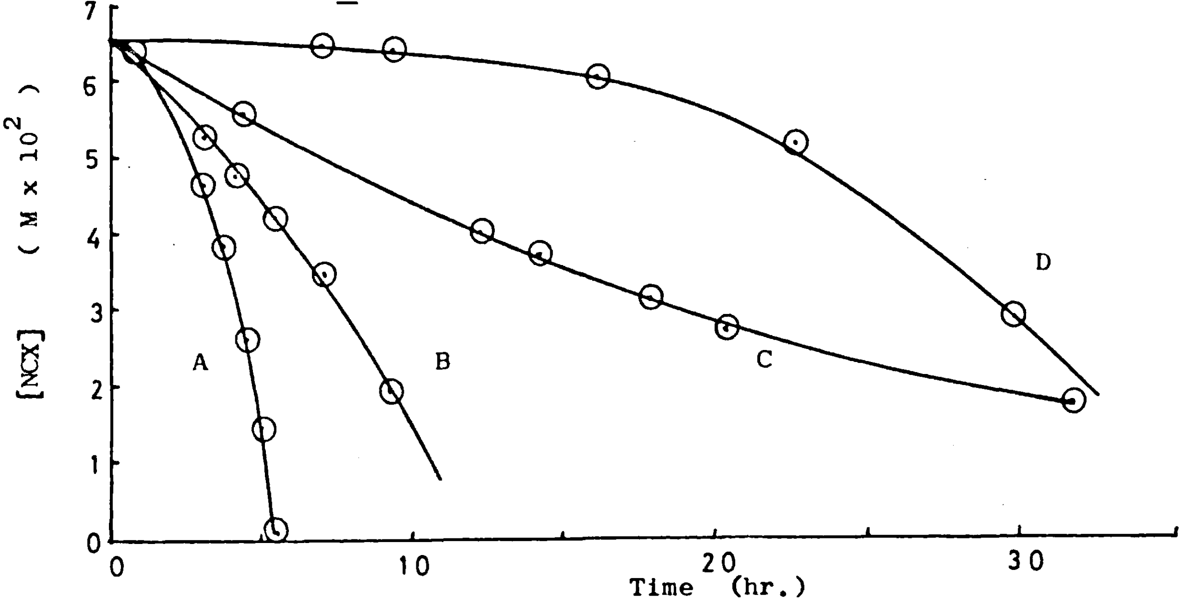


Table 25

Analysis of the Volatile Products of the Thermal Rearrangement of N-Chlorobenzanilide, in the Presence of Added Anilides.

	Benzanilide		Acetanilide	
	1	2	1	2
N-Chlorobenzanilide (mole)	3.5×10^{-3}	3.5×10^{-3}	3.5×10^{-3}	3.5×10^{-3}
Added anilide (mole)	1.85×10^{-3}	1.85×10^{-3}	1.85×10^{-3}	1.85×10^{-3}
Nitrogen Flow-rate (l. hr.$^{-1}$)	1.0	1.0	1.2	1.0
Hydrogen Chloride evolved (mole)	1.74×10^{-6}	1.5×10^{-6}	1.0×10^{-6}	1.3×10^{-6}
Molecular Chlorine evolved (mole)	4.05×10^{-5}	3.5×10^{-5}	6.0×10^{-5}	4.7×10^{-5}
Total Chlorine lost from the solution (mole)	4.4×10^{-5}	3.8×10^{-5}	6.2×10^{-5}	5.0×10^{-5}
Chlorine lost from the solution as a percentage of the available chlorine	1.3	1.1	1.8	1.4

2.6.3.2. The rearrangement of N-chlorobenzanilide in the presence of benzanilide.

A solution of benzanilide (1.579 g., 0.0070 mole) and N-chlorobenzanilide (1.619 g., 0.0070 mole) in chlorobenzene (100 ml.) was maintained at 114° in the dark, until rearrangement was complete (120 hr.). Chlorobenzene was distilled off, under reduced pressure, and the pink residue was hydrolysed. The hydrolysate was analysed in the usual way (section 2.2.) and the results obtained are given in Table 26.

2.6.3.3. The rearrangement of N-Chlorobenzanilide catalysed by hydrogen chloride.

Dry hydrogen chloride was passed slowly through a solution of N-chlorobenzanilide (1.521 g., 0.0066 mole) in chlorobenzene, at 114°, in the dark. When the rearrangement was complete (5 min.) the chlorobenzene was distilled off and the product analysed by the standard method. The results obtained are given in Table 26.

2.6.3.4. The photolysis of N-chlorobenzanilide, aspirated with nitrogen.

Beard, Boocock and Hickenbottom[3] have suggested that the thermal and photolytic rearrangement proceed by essentially the same mechanism. It was thought to be of interest to carry out a photolysis of N-chlorobenzanilide under conditions comparable to those used for the thermal rearrangement. Nitrogen was passed through the solution to suppress the "Orton" rearrangement.

Chlorobenzene (50 ml.) was placed in a "Quickfit" round-bottomed flask above a "Hanovia" mercury-vapour lamp, at a fixed distance above the lamp-casing and shielded from draughts by a black screen. The heat of the lamp was sufficient to raise the temperature of the chlorobenzene to 125°. Dry nitrogen was bubbled through the solution, at such a rate that the temperature of the chlorobenzene was 114 ± 3° (nitrogen flow-rate 2.5 l.hr.^{-1}), and then N-chlorobenzanilide (0.810 g., 0.0075 mole) was dissolved in the chlorobenzene. When the rearrangement was complete (24 hr.), chlorobenzene was removed from the deep red solution. The residue was hydrolysed and the hydrolysate was analysed in the usual way. The results obtained are given in Table 26.

Table 26

Products of the Reactions of N-Chlorobenzanilide in Chlorobenzene at 114°.

	% Yield		Molar % of Products					o:p
	Distillate	Residue	a	o	p	d	t	
Reaction in the presence of benzanilide	93	0.7	31.2	7.4	54.3	4.2	0.4	1:7.10
Reaction in the presence of benzanilide	91	1.1	34.4	7.2	50.2	3.7	0.5	1:6.97
Reaction catalysed by hydrogen chloride	88	0.9	54.7	5.4	38.4	1.5	0.2	1:7.15
Reaction catalysed by hydrogen chloride	89	1.1	59.2	5.2	35.4	1.5	0.3	1:6.81
Photolytic reaction	72	12	16.7	7.8	53.7	17.3	4.7	1:6.80
Photolytic reaction	71	21	18.2	8.4	55.8	16.6	2.3	1:6.58

2.7. The Photolytic Rearrangement of N-Chloroanilides.

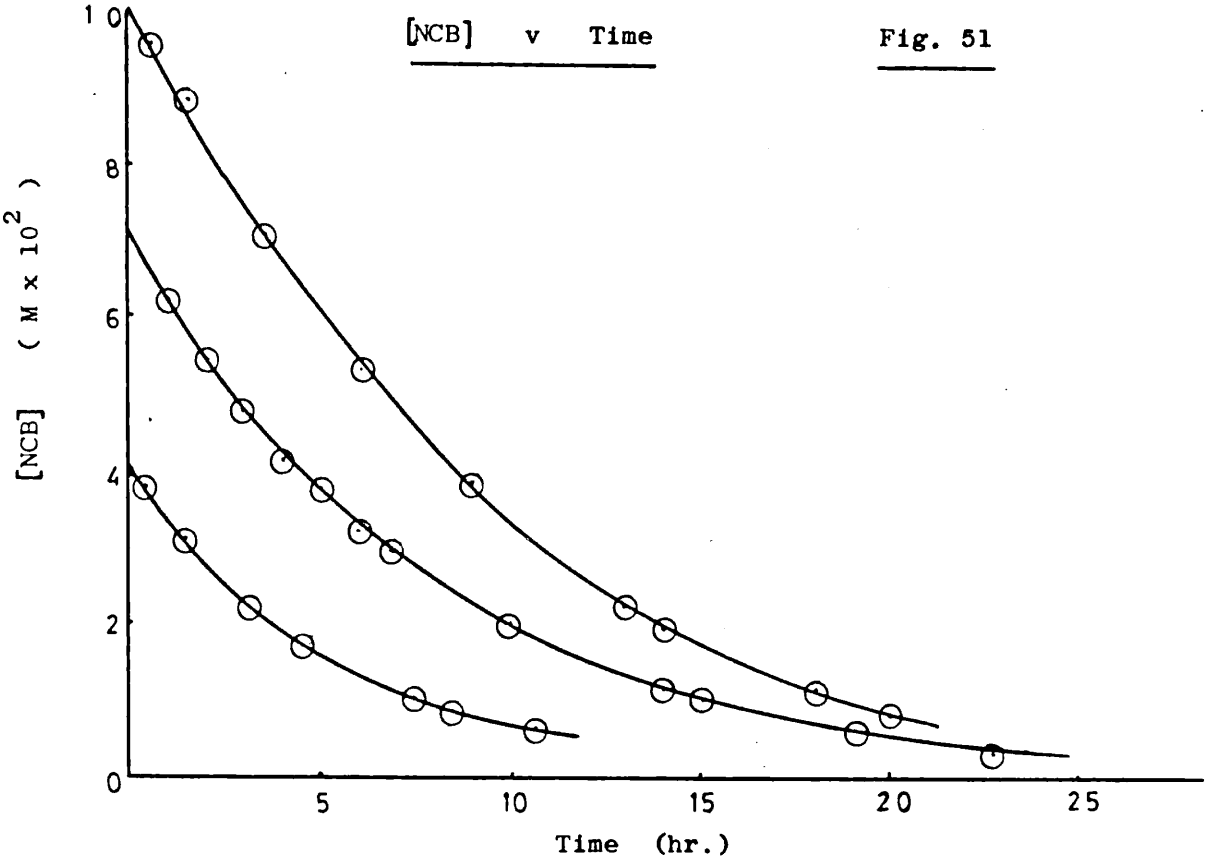
2.7.1. The Kinetics of the Reaction in Carbon Tetrachloride alone.

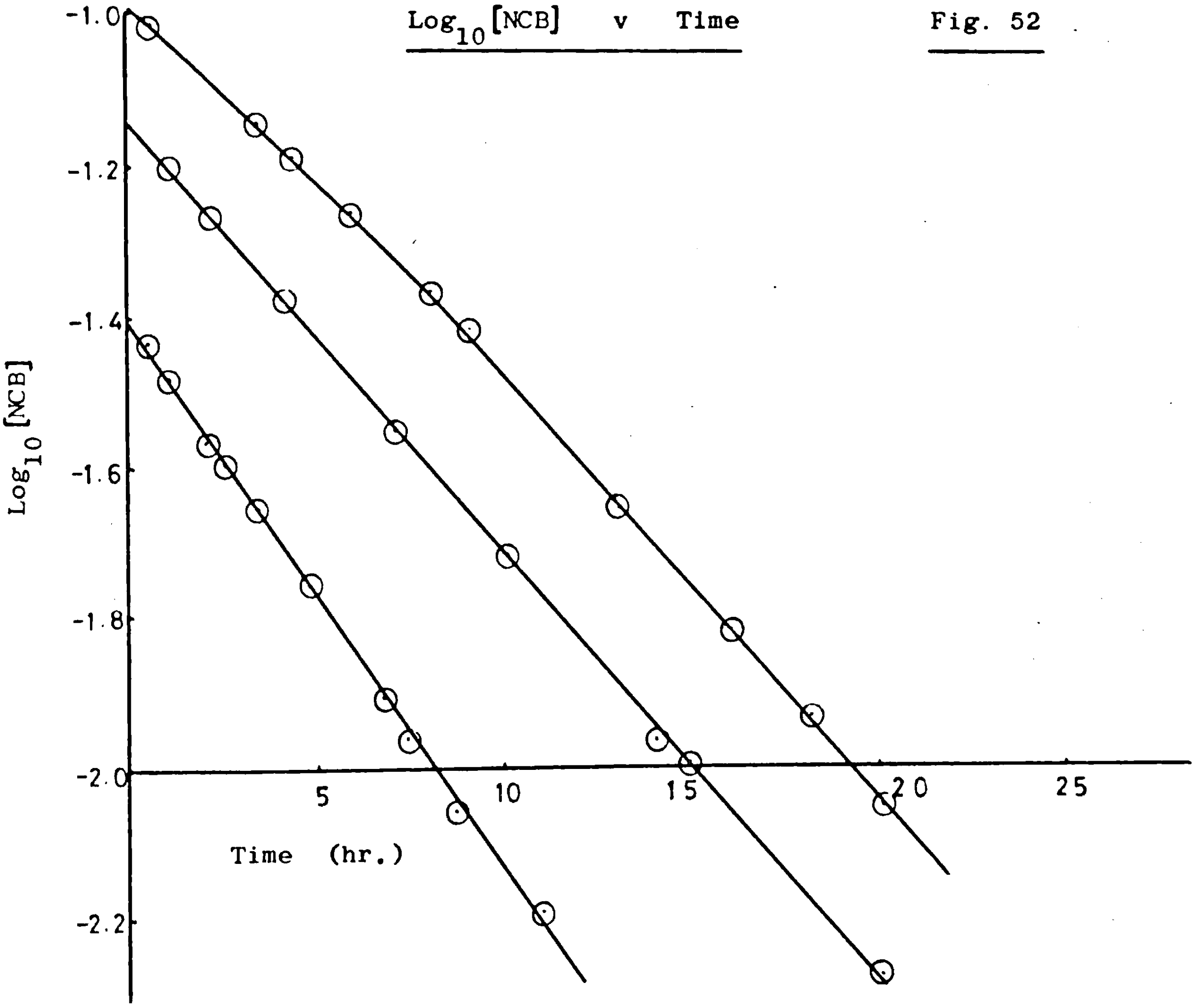
Before studying the kinetics of the photo-induced decomposition of the N-chloroanilides, it was necessary to show that they did not rearrange in the dark at the temperature employed. A solution of each of the N-chloroanilides (0.0085 mole) in carbon tetrachloride (85 ml.) were kept in the dark at 77.7°. In each case samples (2 ml.) were withdrawn at intervals and the concentration of the N-chloroanilides was estimated iodometrically. The results obtained are given in Tables A38, A40, A42 and A44. It can be seen that there was little change in the concentration of any of the N-chloroanilides and it was therefore concluded that there was no appreciable thermal rearrangement of these compounds at 77.7°.

Carbon tetrachloride (85 ml.) was placed in a "Quickfit" round-bottomed flask which was placed directly above a "Hanovia" (Fluorescence Model 16) mercury-vapour lamp, at fixed distance above the lamp-casing, and shielded from draughts by a black screen. When the heat of the lamp had raised the temperature of the solvent to its boiling point, the N-chloroanilide (0.0085 mole) was added and the mixture was shaken. The concentration of N-chloroanilide remaining in the solution, was estimated, at intervals by the standard method. The results of these experiments and of similar reactions in which the initial concentrations of N-chloroanilides were varied, are given in Tables A38, A39, A40, A41, A42, A43, A44, and A45, and Fig. 51, 53, 55 and 57. Fig. 52, 54, 56 and 58 show the corresponding logarithmic plots.

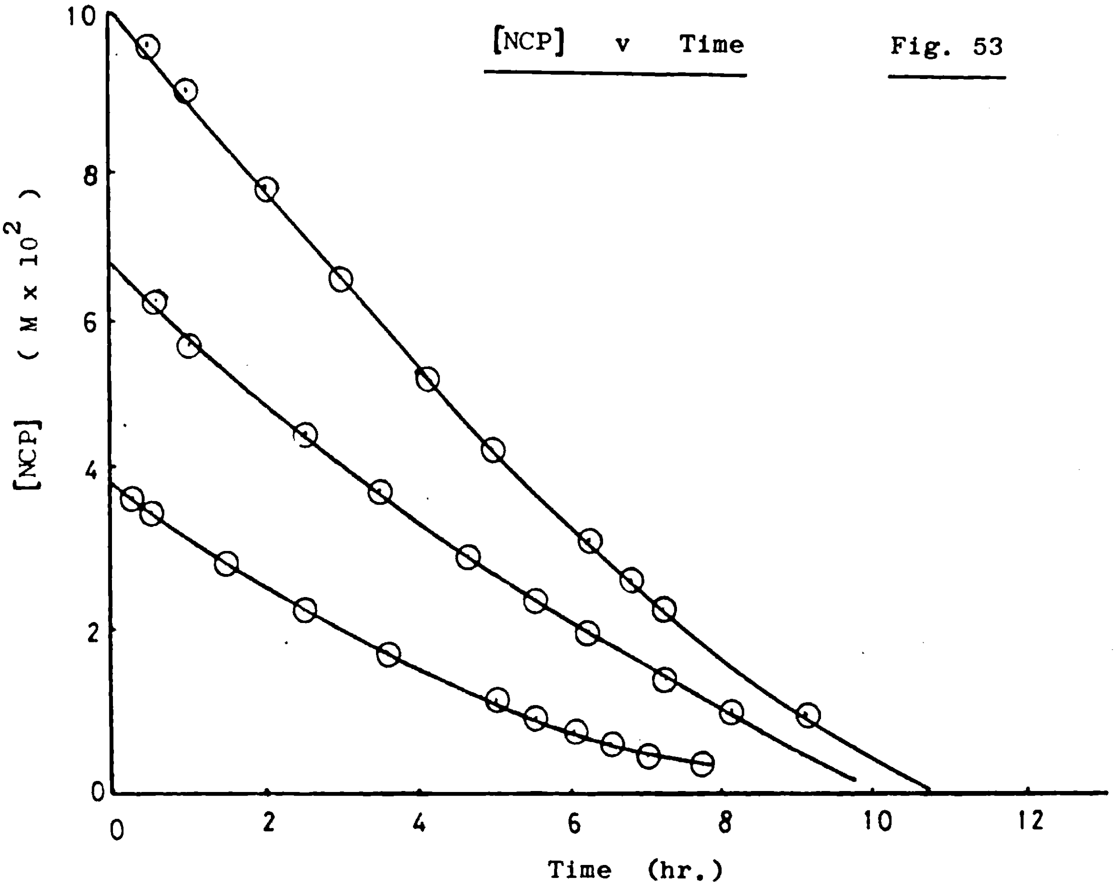
The rate of reaction of N-chlorophenylacetanilide and N-chlorodiphenylacetanilide appear to be higher in the latter part of the reaction, than it would have been if the reaction was of the first-order throughout. Consequently further experiments were performed in order to discover whether or not hydrogen chloride was formed during these reactions, since the increase in rate during the analogous photolysis of N-chloroacetanilide has been

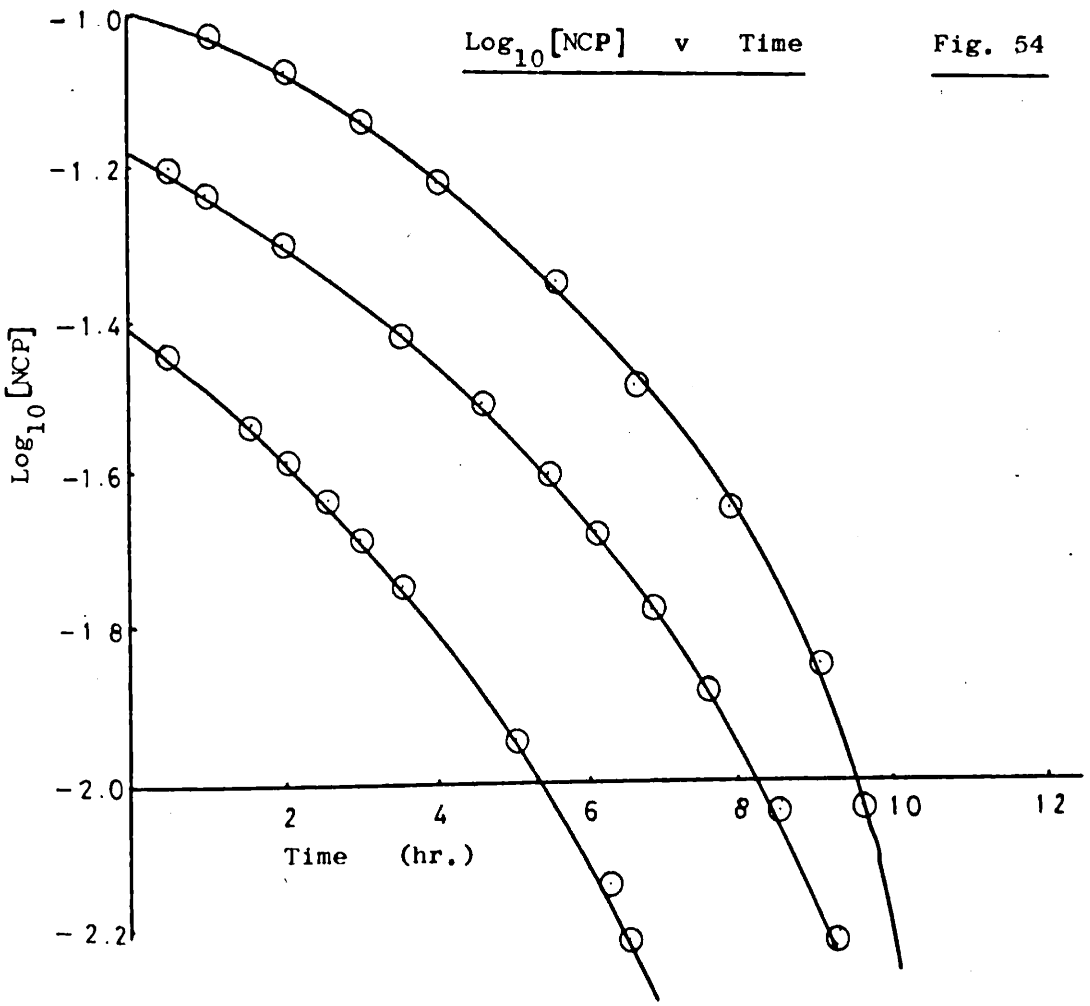
Photolysis of N-Chlorobenzanilide.



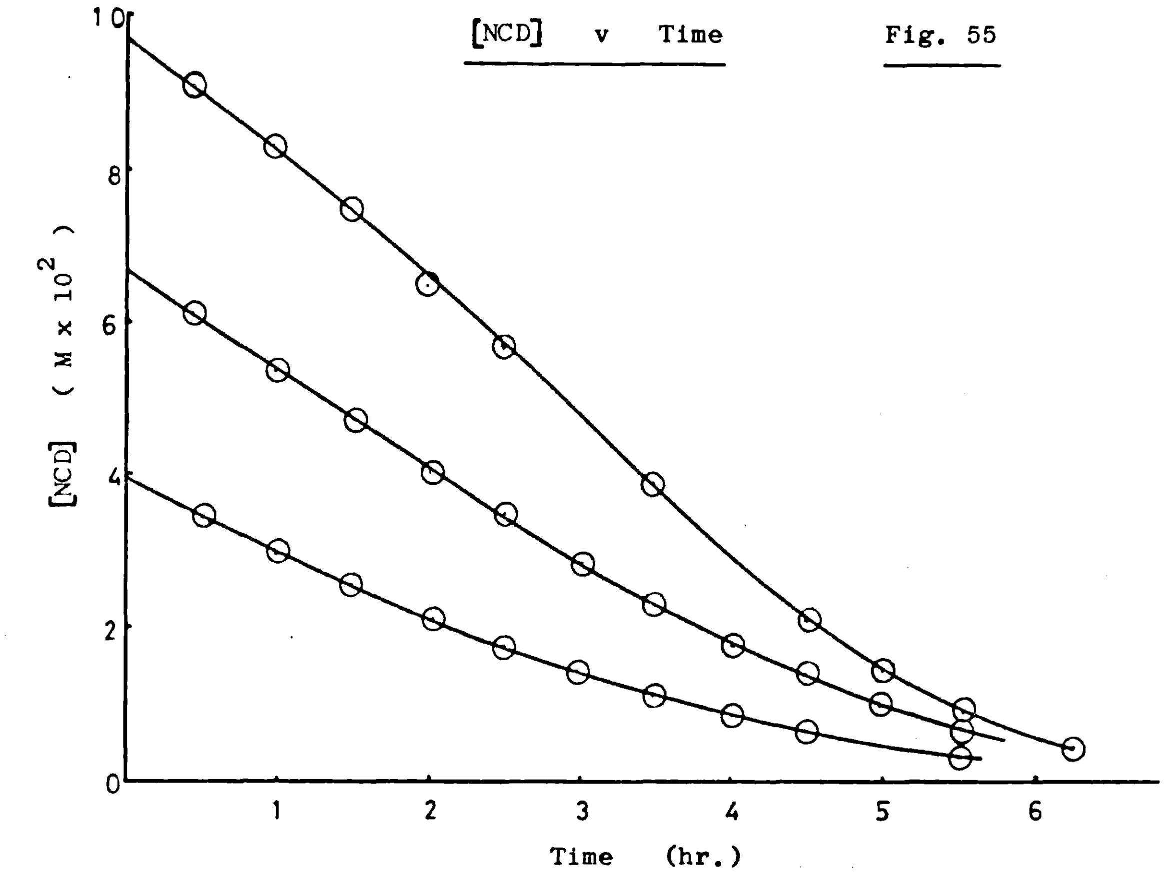


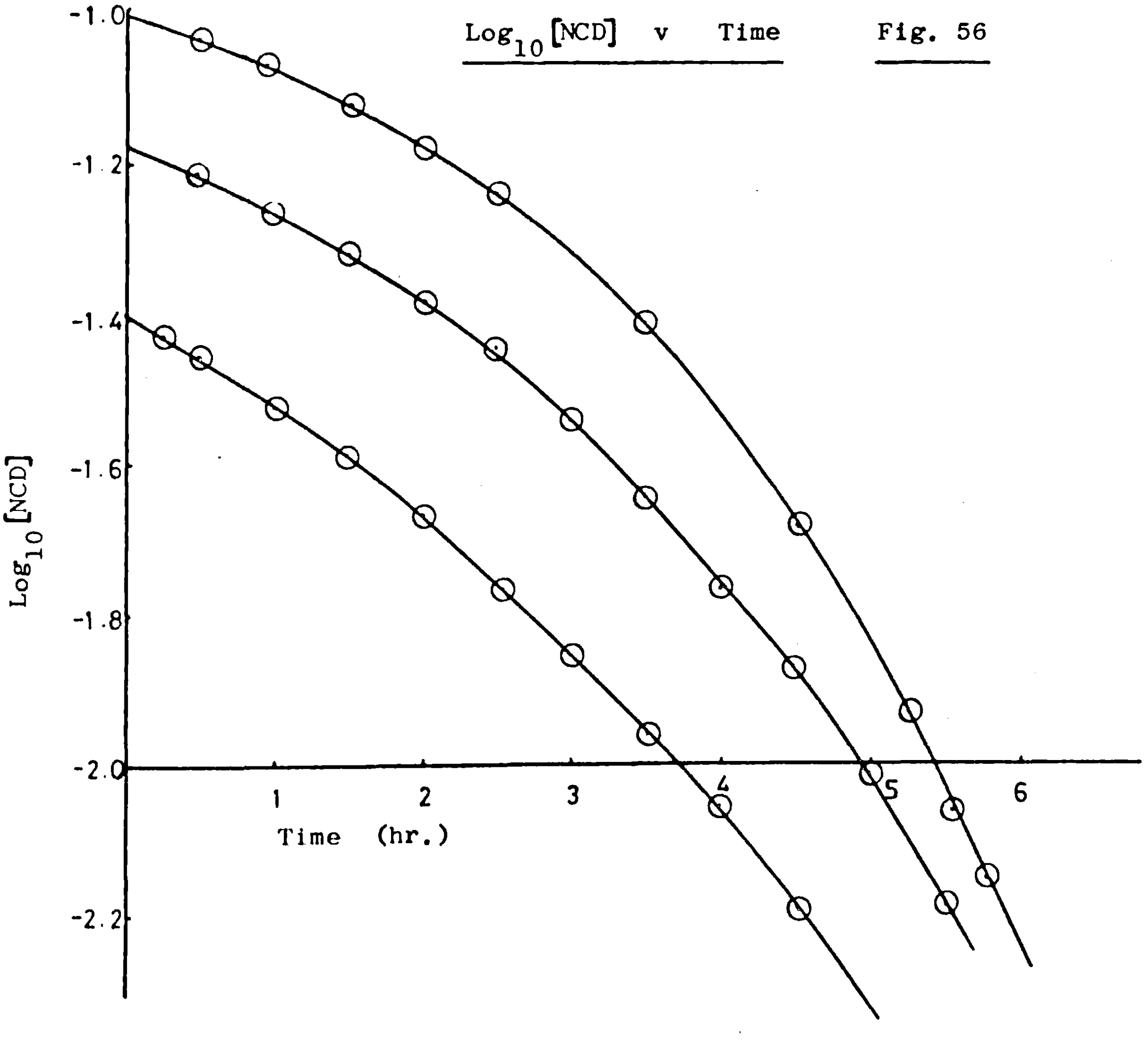
Photolysis of N-Chlorophenylacetanilide.



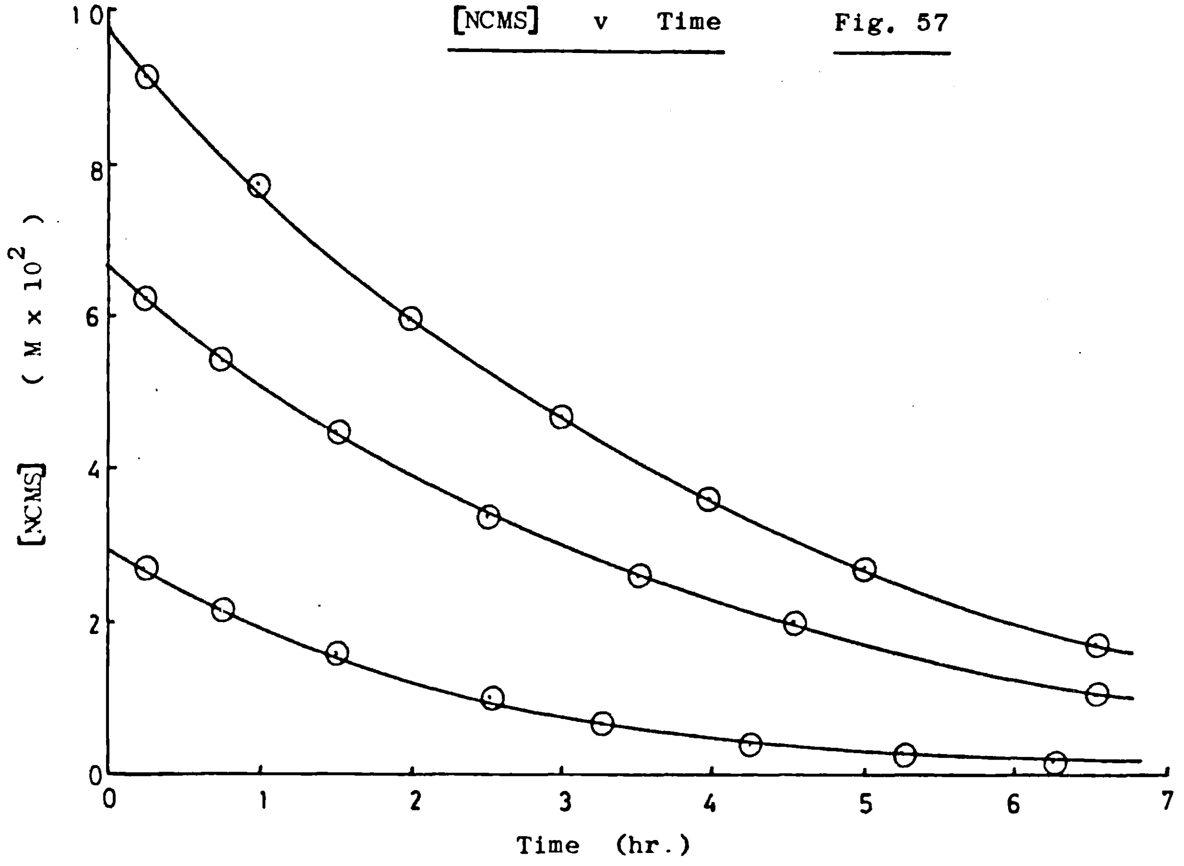


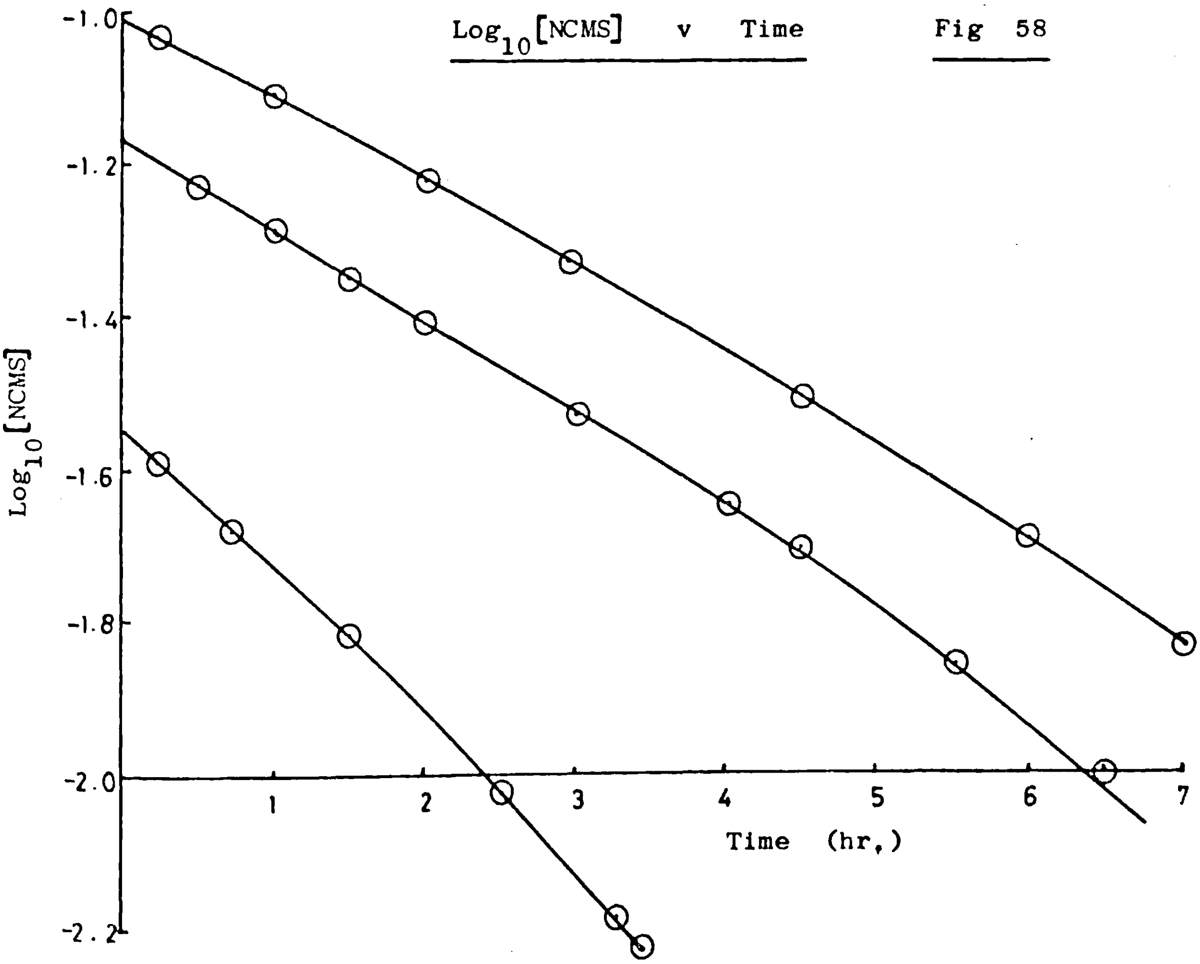
Photolysis of N-Chlorodiphenylacetanilide.





Photolysis of N-Chloromethanesulphonanilide.





shown to be related to the presence of hydrogen chloride in solution. Nitrogen was passed, in turn, through solutions of each N-chloroanilide (0.0085 mole), in carbon tetrachloride (85 ml.), and the solutions were irradiated as before. Dry nitrogen, saturated with carbon tetrachloride, was passed through the solution of the N-chloroanilide, and then through a standard solution of sodium hydroxide (50 ml., 0.100 M). When the rearrangement was complete, the aqueous solution was analysed as before (section 2.5.2.1.). The results are given in Table 27.

A study was also made of the kinetics of the photolysis of each of the N-chloroanilides, when nitrogen was passed through the solutions, throughout the reaction. The results are given in Tables A46, A47, A48 and A49, and Fig. 59, 61, 63 and 65. The corresponding logarithmic plots are also given (Fig. 60, 62, 64 and 66). For comparison the curves for the corresponding reactions without the passage of nitrogen, and the curves which would have been obtained if the reaction had been of the first-order throughout are included.

2.7.2. The Kinetics of the Rearrangement of N-Chlorobenzanilide in the Presence of Added Anilides.

In four experiments, benzanilide, acetanilide, benzenesulphonanilide and methanesulphonanilide (0.00595 mole), in turn, were added to solutions of N-chlorobenzanilide (0.00595 mole) in carbon tetrachloride (85 ml.), which were then irradiated. Samples were removed at intervals and the concentration of the N-chlorobenzanilide was estimated in the usual way. The results obtained are given in Tables A52, Fig. 67 and 68. The corresponding graph for the rearrangement of N-chlorobenzanilide alone is included.

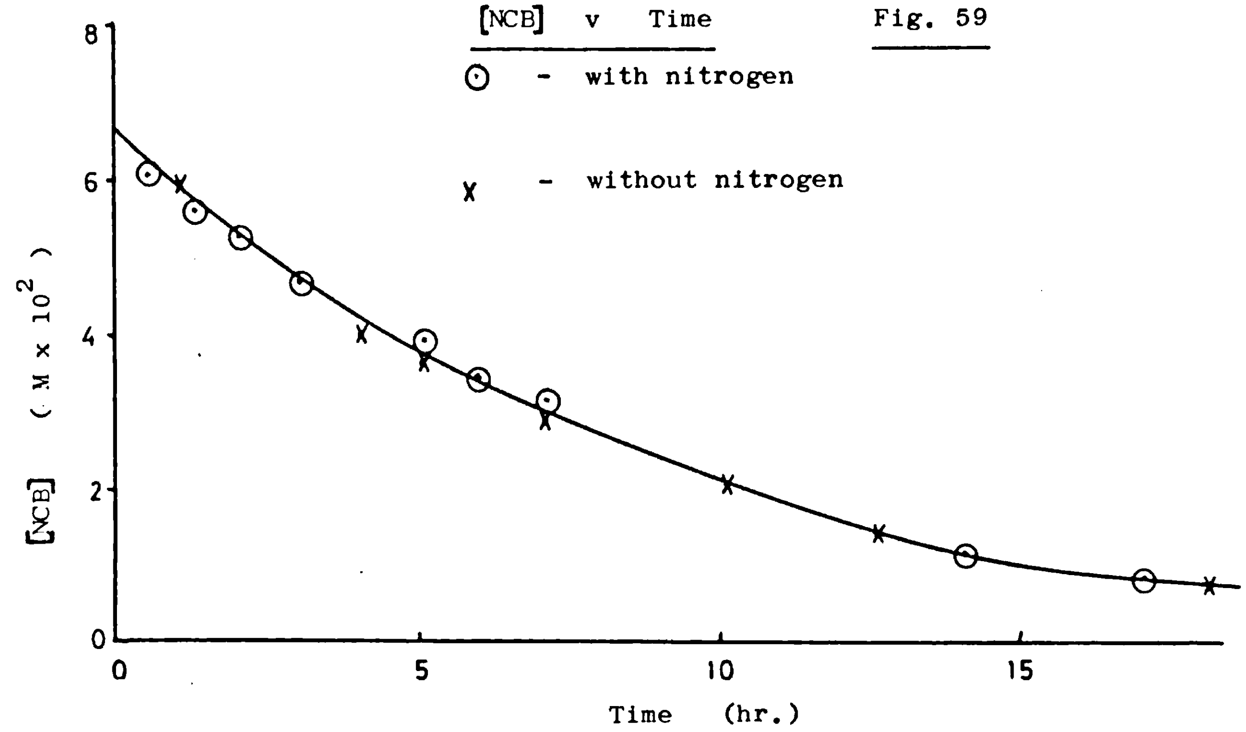
Experiments were also carried out in which solutions of N-chlorobenzanilide and each anilide in turn were heated at 77.7° in the dark. The results obtained, Table A51, show that there was no appreciable

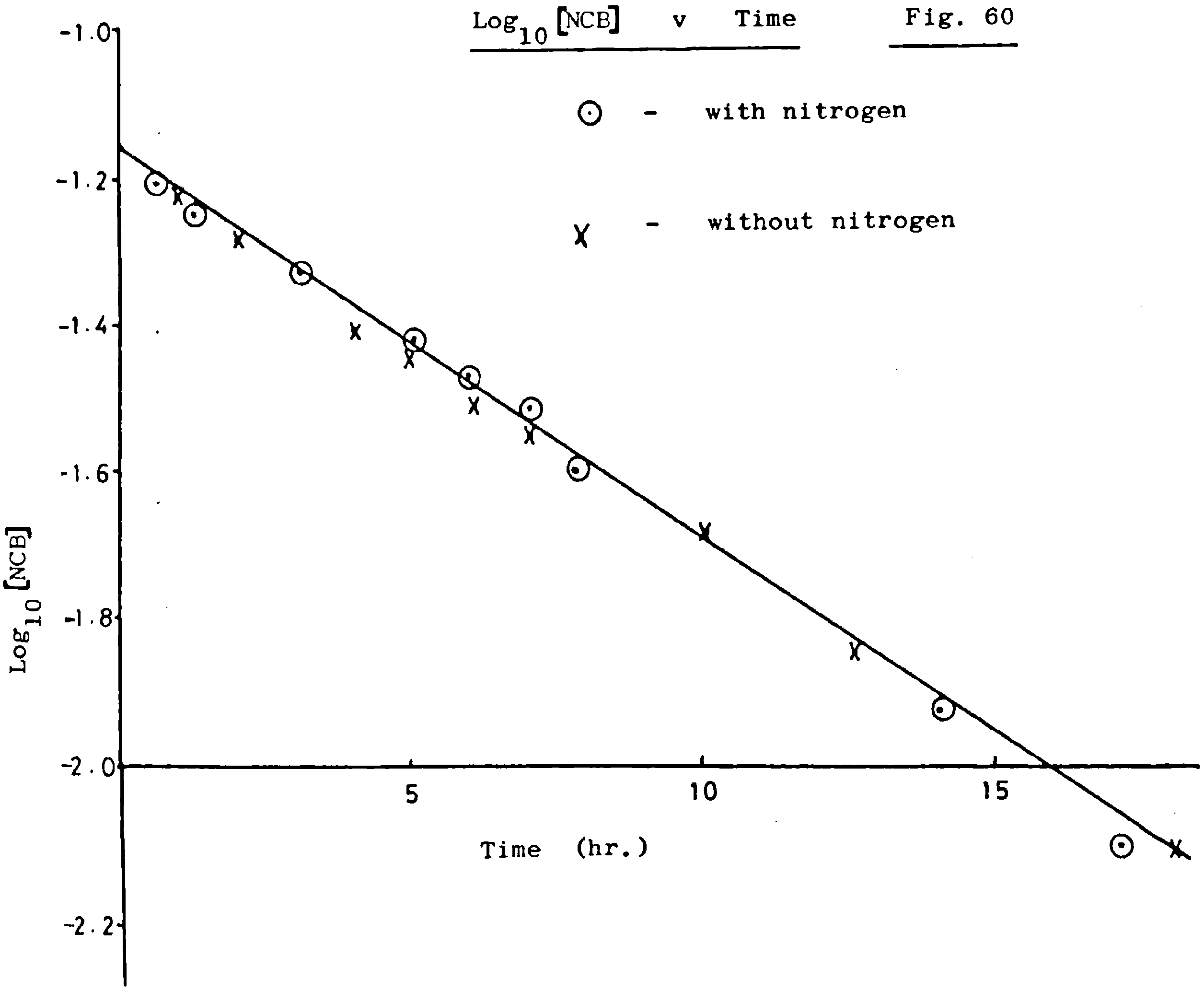
Table 27

The Volatile Products of the Photolysis of N-Chloroanilides in Carbon Tetrachloride.

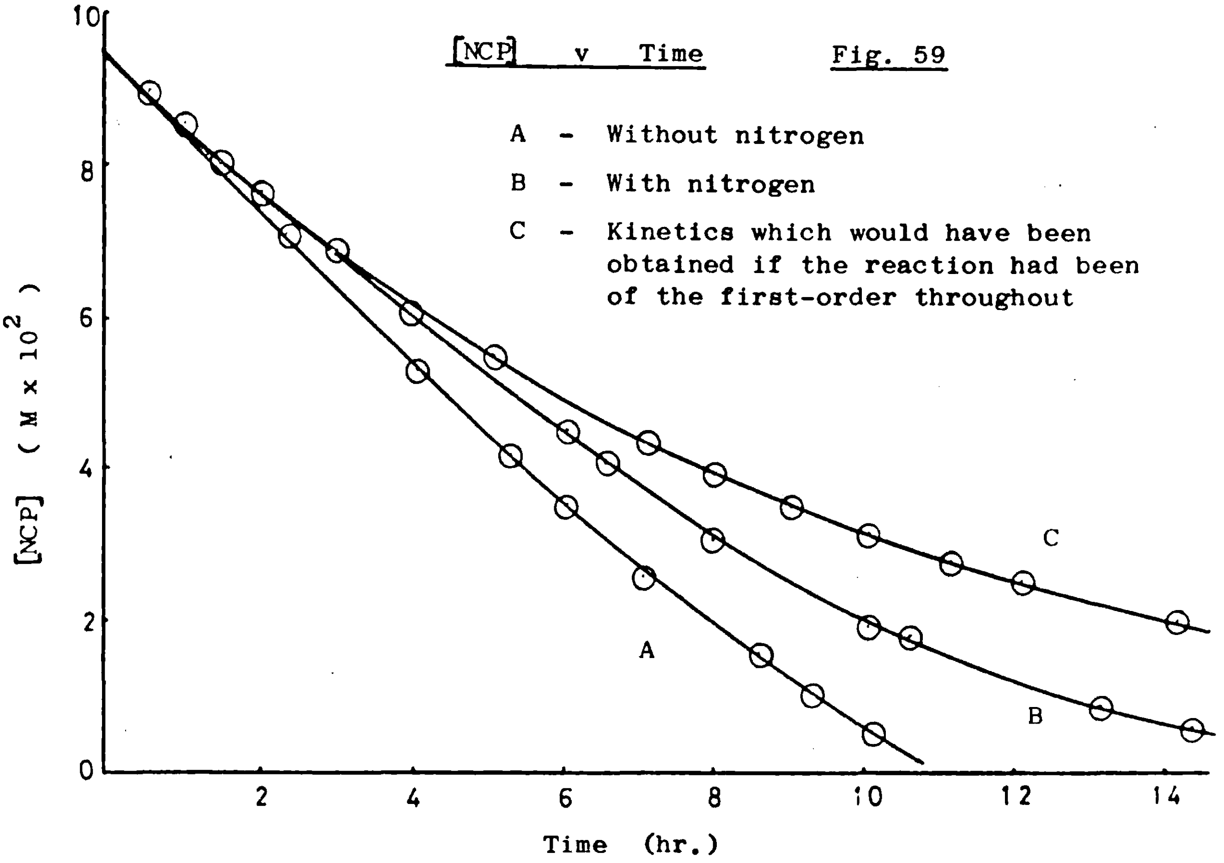
	N-Chloro-benzanilide		N-Chlorophenyl-acetanilide			N-Chlorodiphenyl-acetanilide		N-Chloromethane-sulphonanilide	
	1	2	1	2	3	1	2	1	2
Nitrogen Flow-rate (l. hr.$^{-1}$)	1.0	1.0	1.0	1.0	1.5	1.0	1.0	1.0	1.0
N-Chloroanilide (mole x 10^{-3})	8.5	8.5	8.5	8.5	8.5	2.5	2.5	2.5	8.5
Hydrogen Chloride evolved (mole x 10^{-5})	1.93	1.58	17.0	17.2	22.8	9.1	7.9	14.8	38.0
Chlorine evolved (mole x 10^{-5})	0.57	0.45	6.7	5.9	2.5	3.2	2.8	0.32	0.86
Total Chlorine evolved (mole x 10^{-5})	3.07	2.48	30.4	28.0	27.7	15.5	13.6	15.4	39.7
Total Chlorine evolved as a percentage of the available chlorine	0.36	0.29	3.6	3.4	3.2	6.2	5.4	6.1	4.7

Photolysis of N-Chlorobenzanilide, in Carbon Tetrachloride, aspirated with Nitrogen.

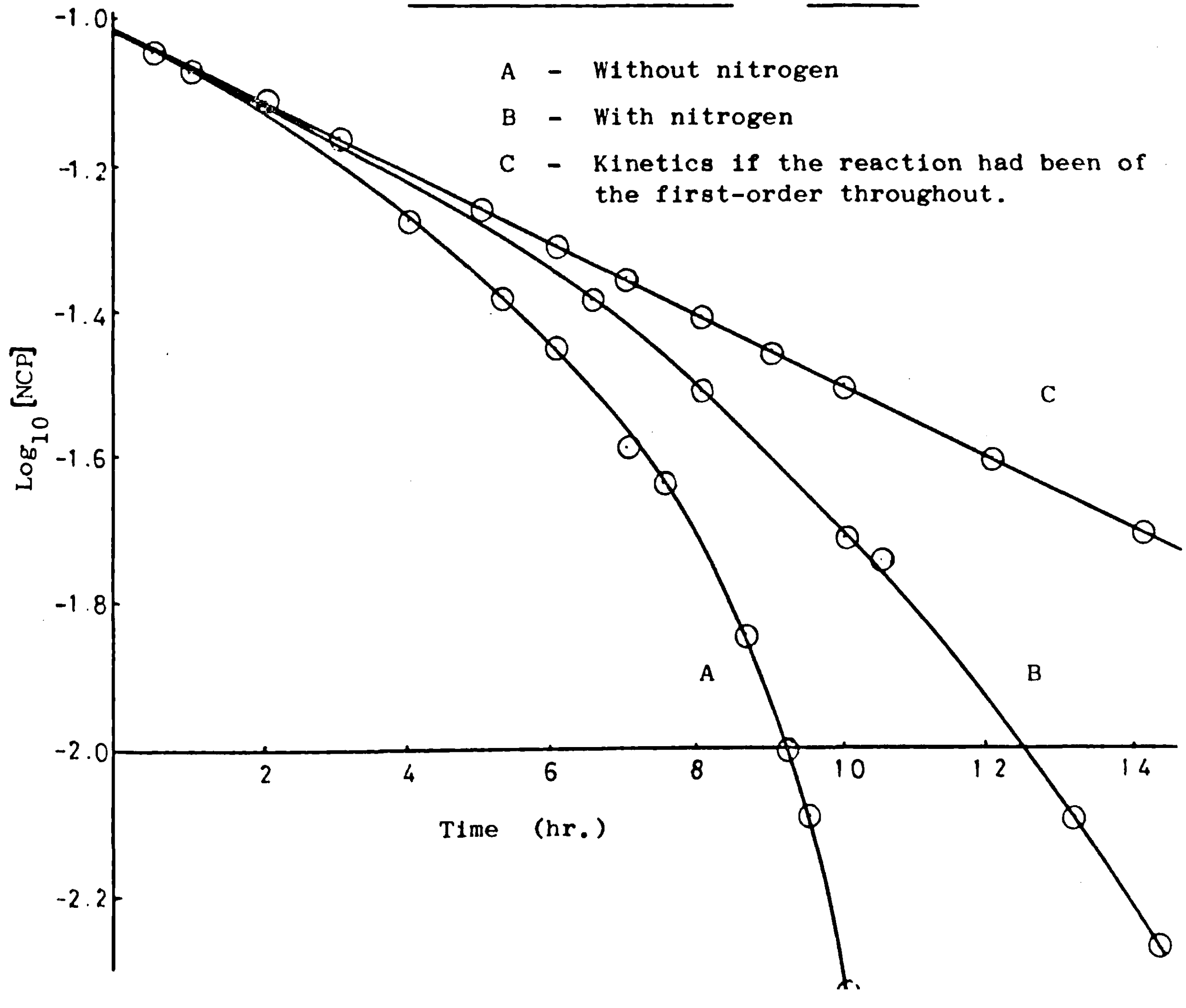

[NCB] v Time Fig. 59


Log_{10} [NCB] v Time Fig. 60

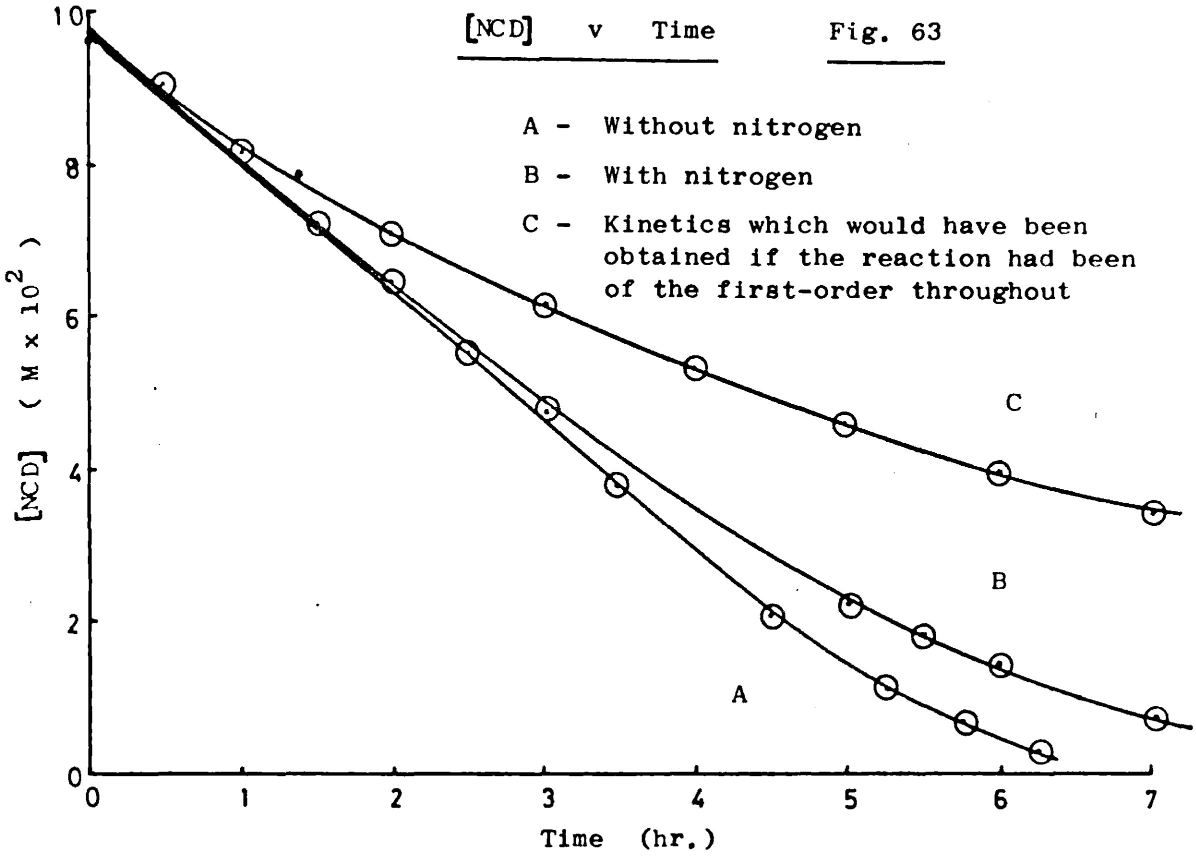
Photolysis of N-Chlorophenylacetanilide, aspirated with Nitrogen.


[NCP] v Time Fig. 59

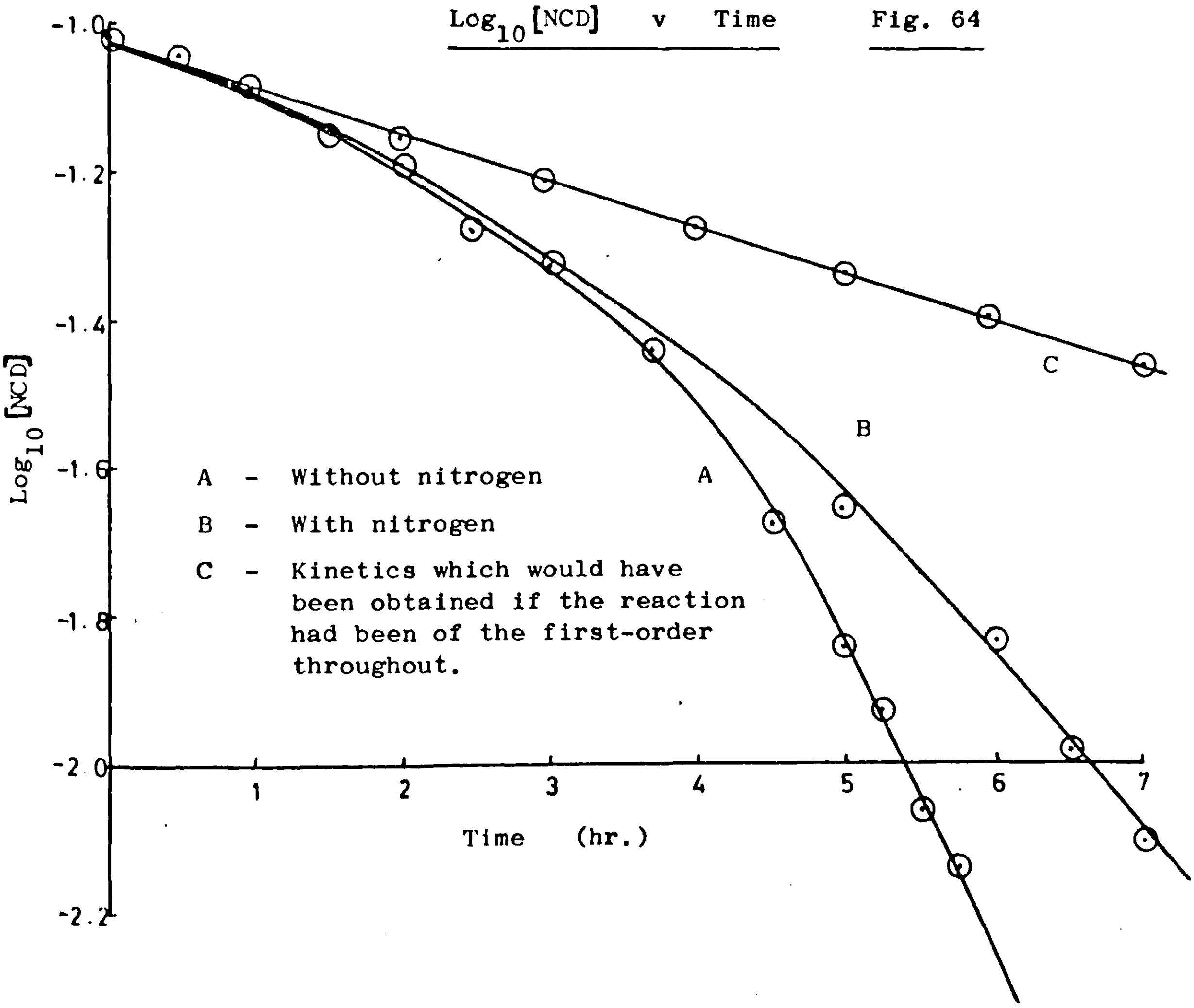
Log$_{10}$[NCP] v Time Fig. 60



Photolysis of N-Chlorodiphenylacetanilide, aspirated with Nitrogen.



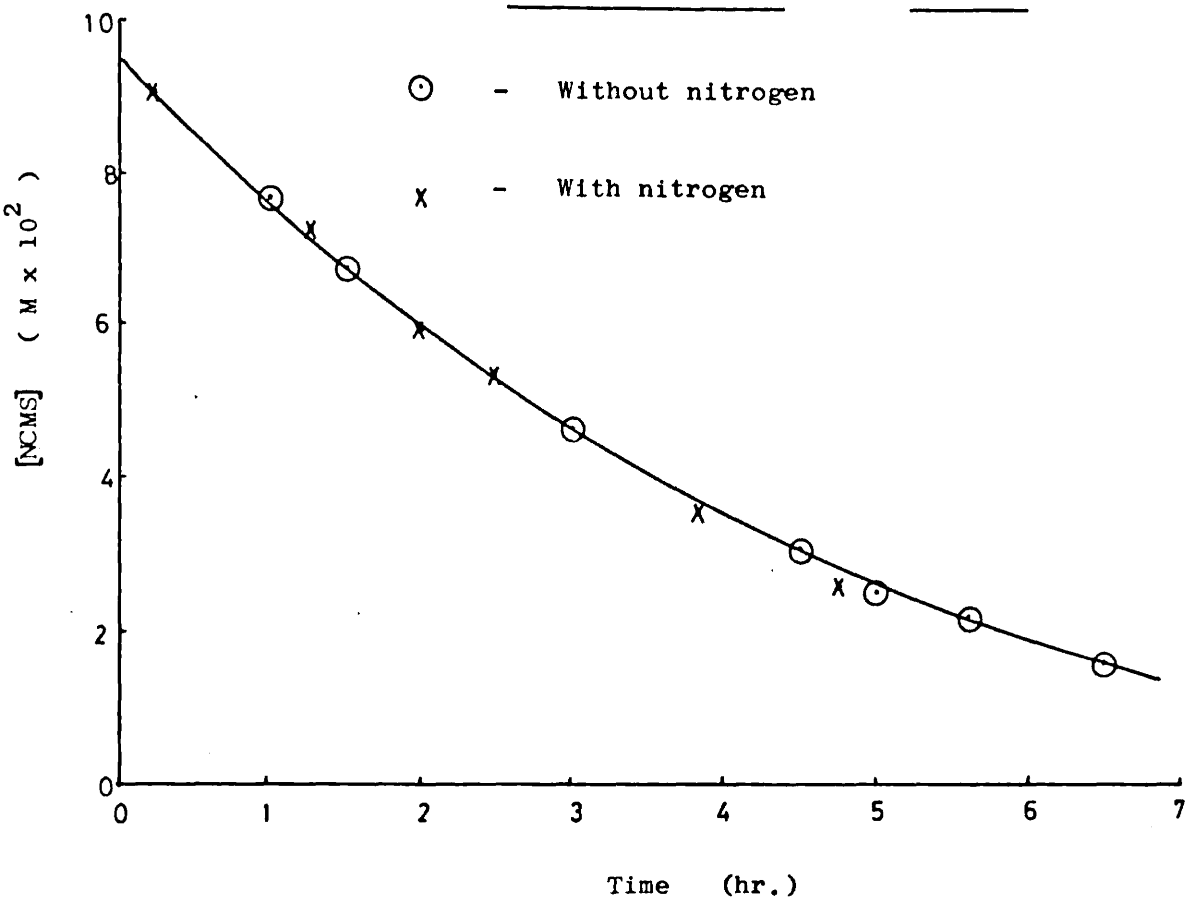
[NCD] v Time Fig. 63



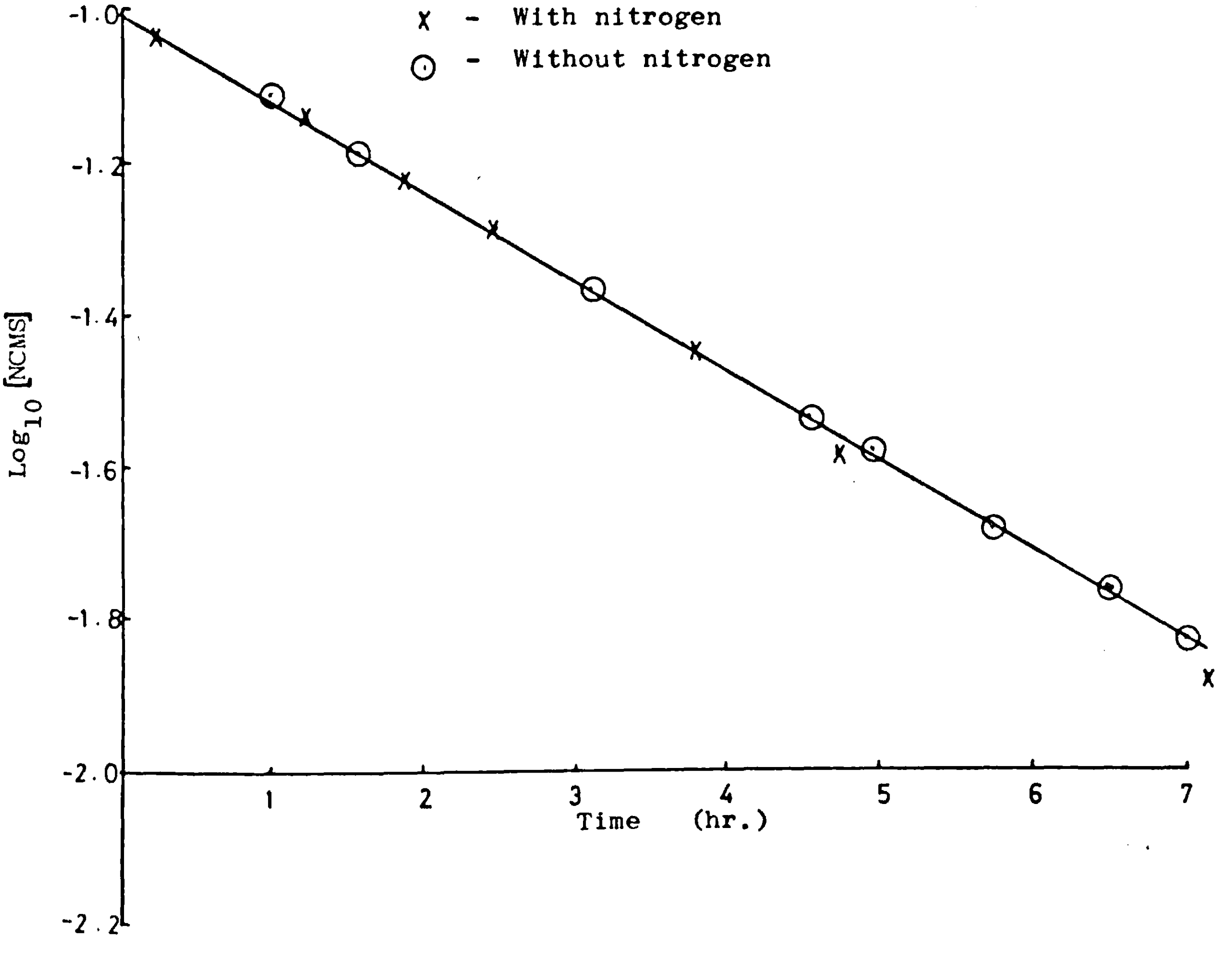
Log$_{10}$[NCD] v Time Fig. 64

Photolysis of N-Chloromethanesulphonanilide, aspirated with Nitrogen.

[NCMS] v Time Fig. 65



Log$_{10}$ [NCMS] v Time Fig. 66



reaction in the dark at this temperature.

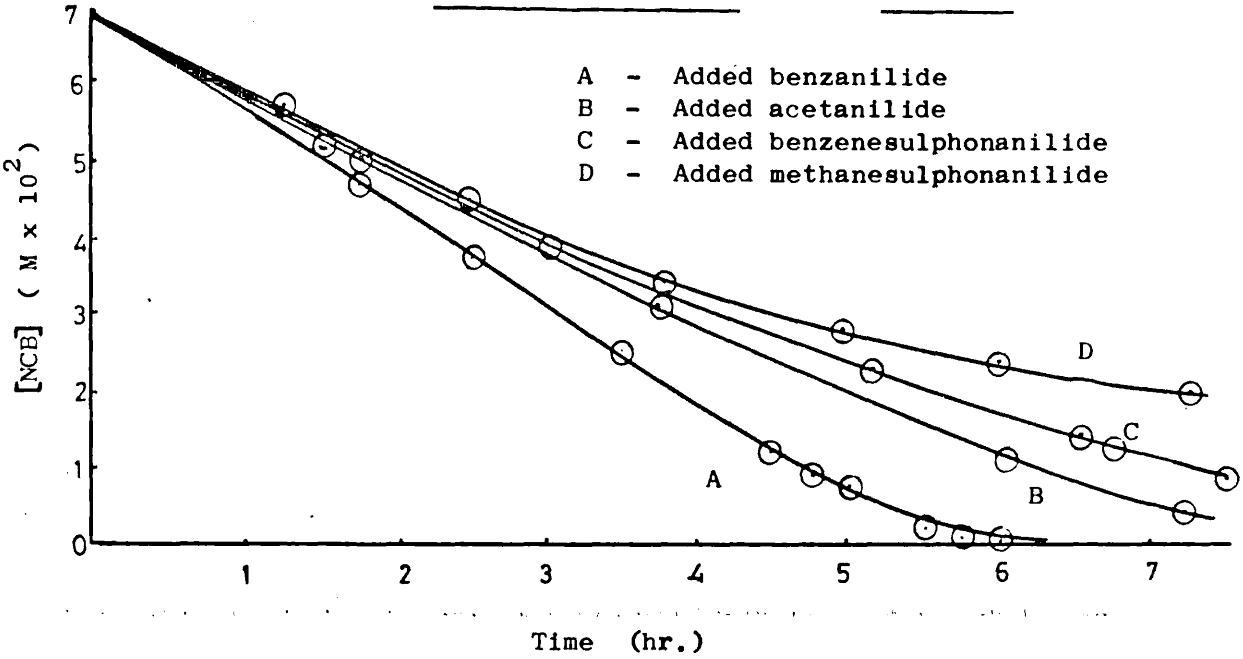
Dry nitrogen, saturated with carbon tetrachloride, was passed through a solution of N-chlorobenzanilide (1.43 g., 0.00595 mole) and methanesulphonanilide (0.449 g., 0.00298 mole) in carbon tetrachloride (85 ml.) which was irradiated. The kinetics of this reaction were studied for two different nitrogen flow-rates, and the results are given in Table A53 and Fig. 69. The logarithmic plot is also given in Fig. 70. For comparison, the curve for the same reaction without the passage of nitrogen is included and also a rate-graph which is based on the initial rate of reaction and shows what the rate would have been if the reaction was of the first-order throughout. In further experiments the emergent gas was passed through a standard solution of sodium hydroxide (50 ml., 0.1 M) and, when the rearrangement, this solution was analysed in the usual way (section 2.5.2.1.) to estimate the quantity of hydrogen chloride and chlorine evolved. The experiments were performed for each of the four anilides so that the total number of moles of chlorine lost from solution could be correlated with the extent of the deviation from first-order kinetics. The results obtained are set out in Table 28.

2.7.3. Analysis of the products formed in the reaction.

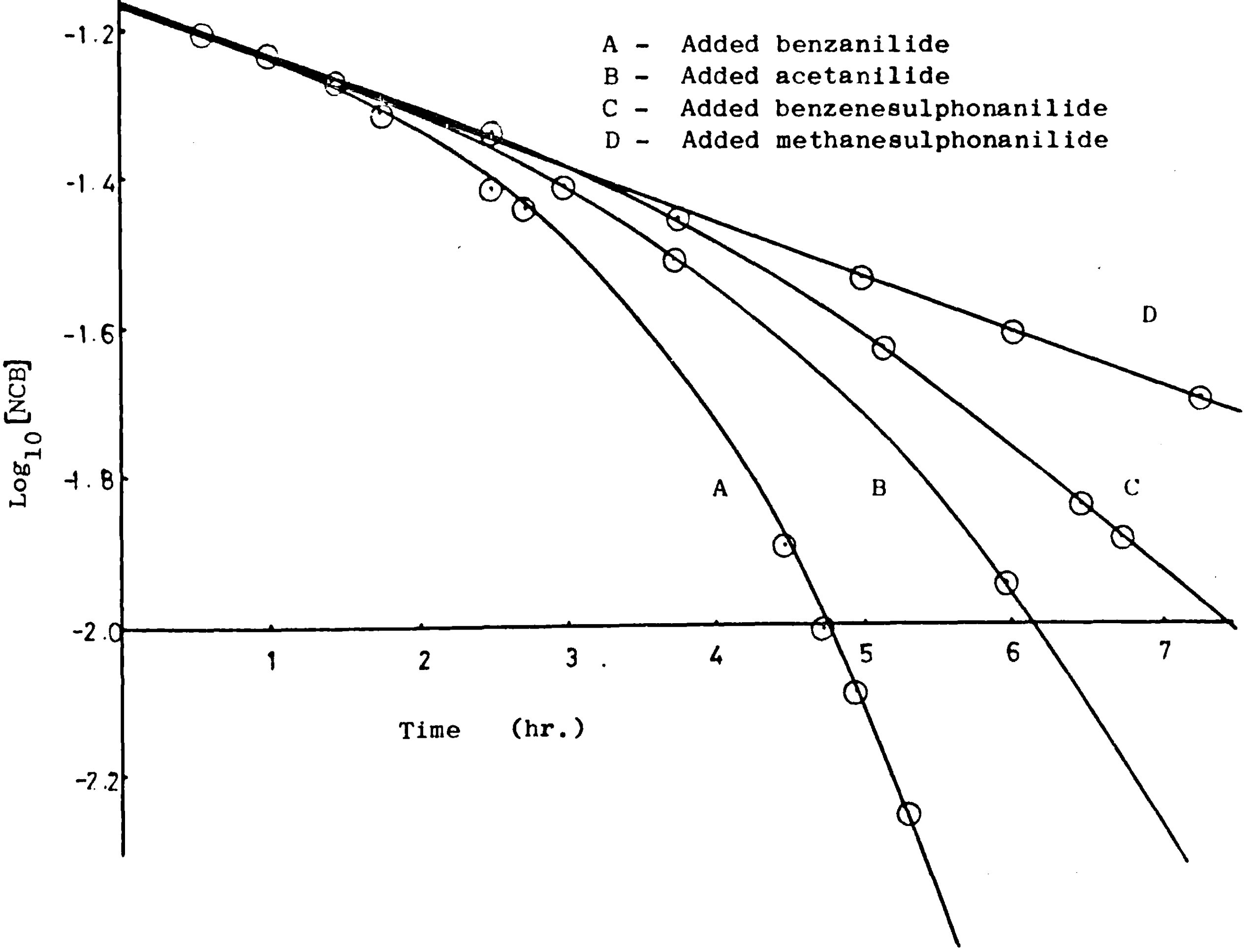
N-Chlorobenzanilide (2.04 g., 0.0085 mole) was dissolved in carbon tetrachloride (85 ml.) and the solution was irradiated for thirty-six hours. When the transformation was complete, the solvent was removed from the dark red solution by distillation under reduced pressure, and the residue was hydrolysed and the hydrolysate was analysed by the standard procedure (section 2.2.). The results are given in Table 29. A further experiment was carried out to determine the proportions of products formed by photolytic rearrangement of N-chlorobenzanilide, when dry nitrogen was passed slowly (1.0 l. hr.$^{-1}$) through the solution throughout the reaction.

The Photolytic Rearrangement of N-Chlorobenzanilide in the presence of added Anilides.

[NCB] v Time Fig. 67

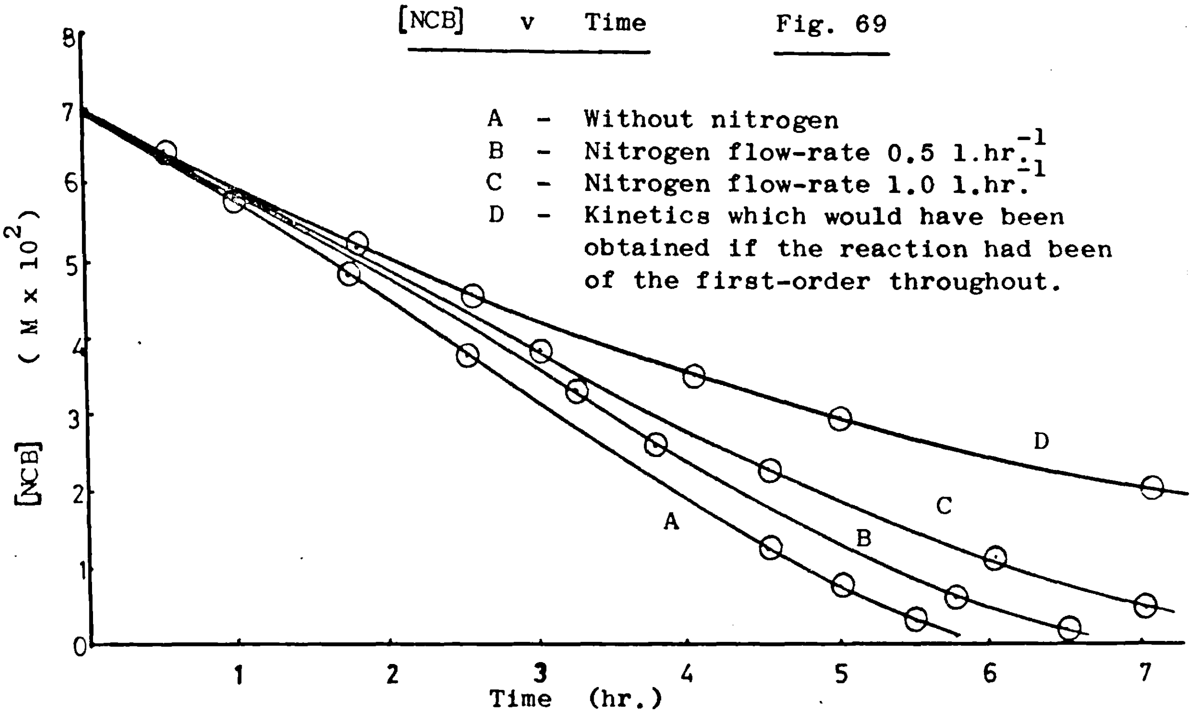


Log$_{10}$[NCB] v Time Fig. 68



The Photolytic Rearrangement of N-Chlorobenzanilide in the presence of added methanesulphonanilide, aspirated with nitrogen.

[NCB] v Time Fig. 69



Log$_{10}$[NCB] v Time Fig. 70

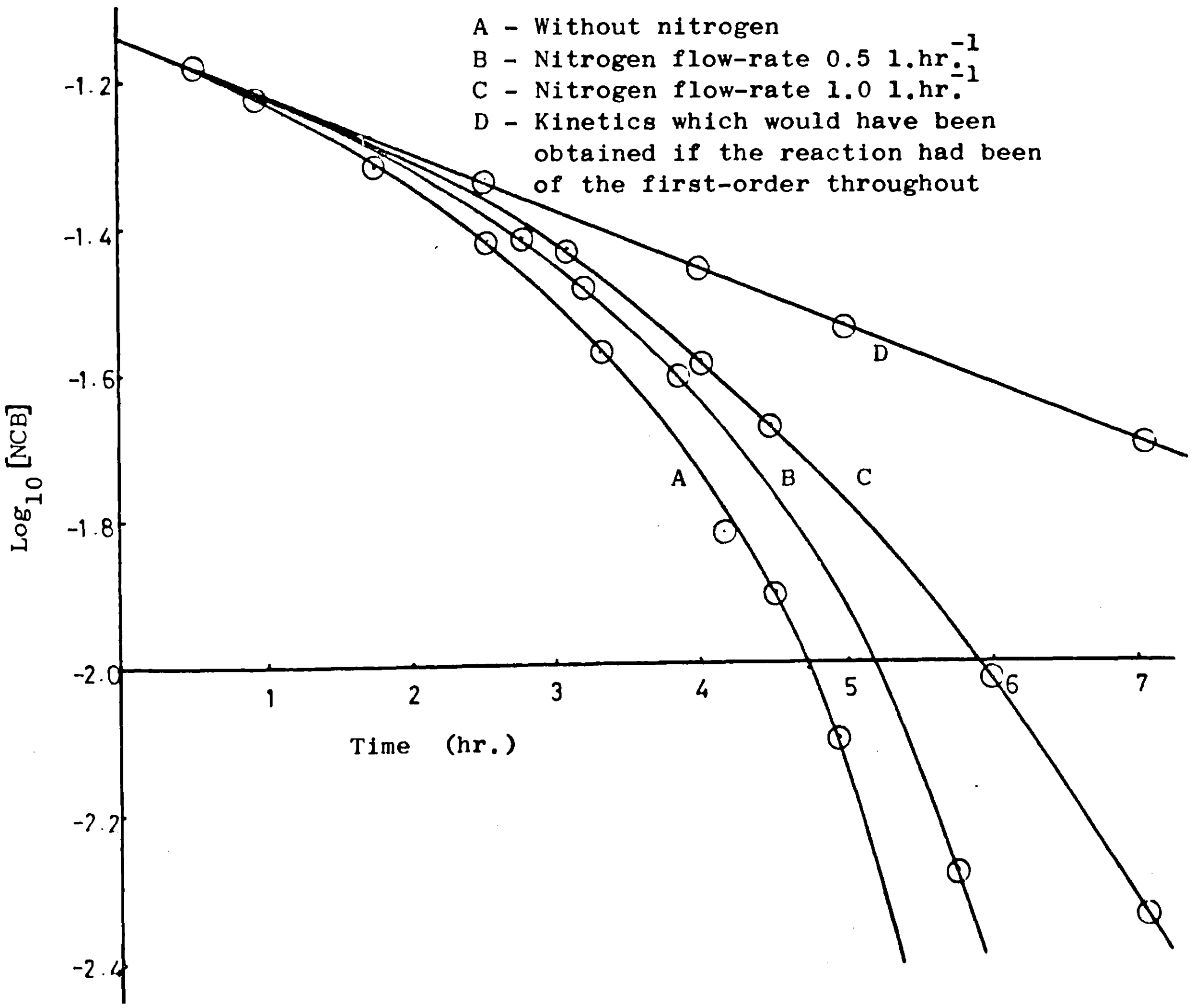


Table 28

Analysis of the Gases Removed from the Solution of *N*-Chlorobenzanilide in Carbon Tetrachloride Undergoing Irradiation.

	Benzanilide		Acetanilide		Benzenesulphonanilide		Methanesulphonanilide		
	1	2	1	2	1	2	1	2	3
Nitrogen flow-rate (l./hr.)	1.0	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0
N-Chlorobenzanilide (mole x 10^{-3})	5.95	5.95	5.95	5.95	5.95	5.95	5.95	5.95	5.95
Chlorine removed (mole x 10^{-5})	3.6	3.1	3.9	4.3	7.4	7.8	6.5	6.6	7.6
Hydrogen Chloride removed (mole x 10^{-5})	1.2	0.9	2.1	4.6	11.1	7.8	6.3	11.6	2.35
Total Chlorine removed (mole x 10^{-5})	8.4	7.1	9.9	12.2	25.9	23.4	19.3	24.8	36.7
Total Chlorine removed as a percentage of the available chlorine	1.3	1.1	1.7	2.0	4.3	4.0	3.2	4.2	6.2

Further experiments were performed to investigate the products of the photolysis of N-chlorophenylacetanilide and N-chloromethanesulphonanilide, both with and without the passage of dry nitrogen through the solution during the reaction. The results of all these experiments are given in Table 29.

Table 29

Products of the Photolytic Rearrangement of *N*-Chloroanilides in Carbon Tetrachloride.

N-Chloroanilide	N_2 Flow-rate	%		Molar % of Amines					
	$l.hr^{-1}$	Distillate	Residue	a	o	p	d	t	o:p
N-Chlorobenzanilide	-	40	35	19.6	34.4	41.1	4.7	0.1	1:1.19
N-Chlorobenzanilide	-	77	12.5	33.6	28.6	32.6	4.8	0.3	1:1.14
N-Chlorobenzanilide	-	74	13.4	33.4	29.0	32.2	4.9	0.3	1:1.12
N-Chlorobenzanilide	1	74	14.5	34.2	28.2	32.4	4.5	0.3	1:1.15
N-Chlorophenylacetanilide	-	62	-	37.5	32.4	26.5	3.6	0.03	1:0.81
N-Chlorophenylacetanilide		64	-	40.0	31.4	25.7	3.0	0.05	1:0.82
N-Chlorophenylacetanilide	2	52	-	45.7	26.9	38.2	4.1	0.08	1:1.42
N-Chlorophenylacetanilide	2	53	-	40.7	23.9	33.0	3.6	0.05	1:1.38
N-Chloromethanesulphonanilide	-	-	-	5.6	46.7	47.5	-	-	1:1.02
N-Chloromethanesulphonanilide	-	-	-	8.6	48.6	42.4	-	-	1:0.87
N-Chloromethanesulphonanilide	-	-	-	8.2	45.8	45.8	-	-	1:1.00
N-Chloromethanesulphonanilide	1	-	-	14.2	44.4	41.3	-	-	1:0.93

2.8. The Rearrangement of N-Chloroanilides in Carbon Tetrachloride, in the Presence of Benzoyl Peroxide.

2.8.1. The Kinetics of the Reaction.

It has been shown that rearrangement of certain N-haloanilides in aprotic solvents is catalysed by carboxylic acids[29]. As benzoic acid was a possible product of the decomposition of benzoyl peroxide, it was considered necessary to determine whether or not rearrangement of N-chloroanilides, under the conditions to be employed for the reaction, would be brought about by benzoic acid.

In four experiments, N-chlorobenzanilide, N-chlorophenylacetanilide, N-chlorodiphenylacetanilide and N-chloromethanesulphonanilide (0.0085 mole), in turn, together with benzoic acid (0.0085 mole), were dissolved in carbon tetrachloride (85 ml.) and the solution was maintained at 77.7 ± 0.2°, in the dark. The concentration of N-chloroanilide remaining in solution, was estimated in the usual way, and the results obtained, given in Tables A54, A56, A58 and A60, and Fig. 71, 73, 75, and 77, show that benzoic acid caused no significant rearrangement of the N-chloroanilides under the reaction conditions.

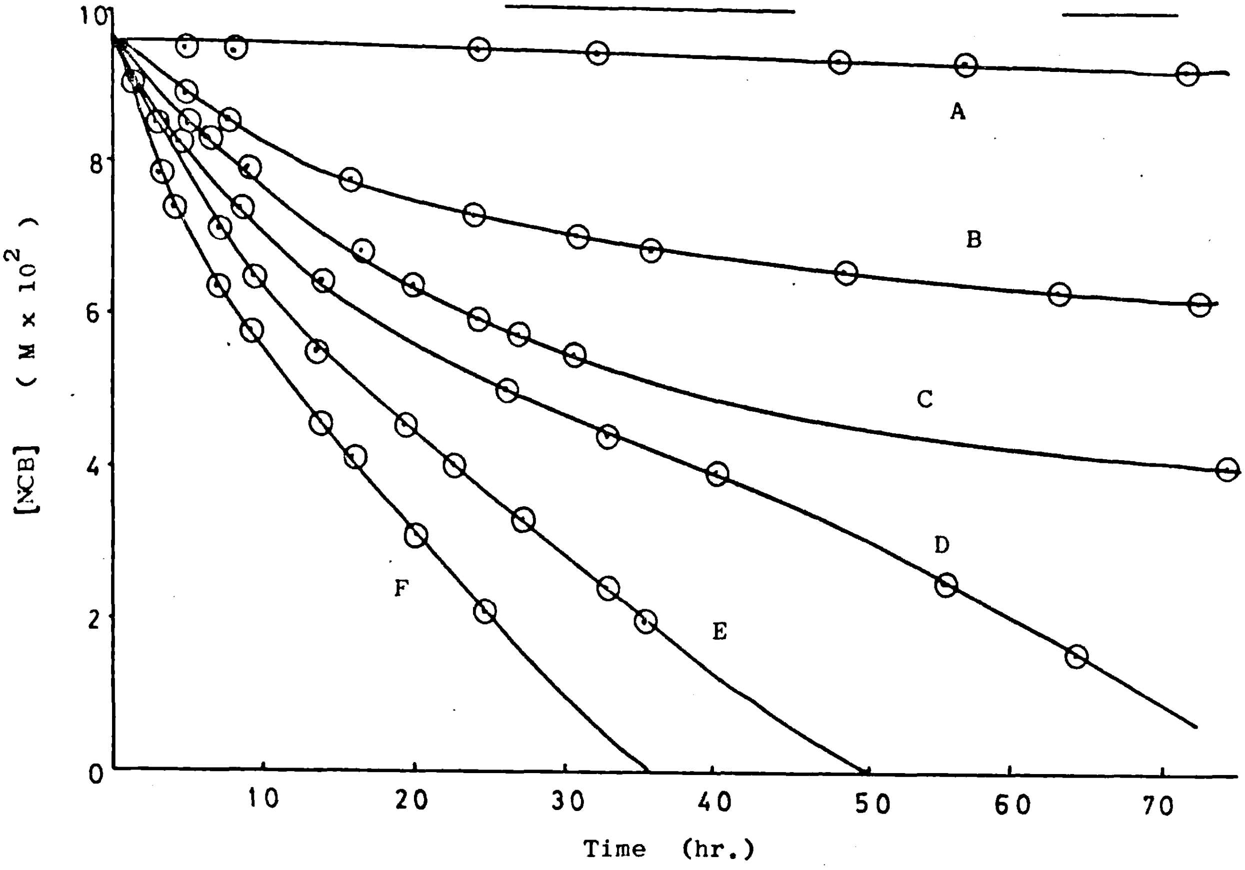
The isomerisation of N-chlorobenzanilide, N-chlorophenylacetanilide, N-chlorodiphenylacetanilide and N-chloromethanesulphonanilide, in turn, in the presence of benzoyl peroxide was followed by iodometric titration. In each series of experiments, the initial concentration of N-chloroanilide was the same, but varying initial concentrations of benzoyl peroxide were employed. The results are given in Tables A54, A55, A56, A57, A58, A59, A60 and A61, and Fig. 71, 73, 75, and 77. Fig. 72, 74, 76 and 78 show the corresponding plot of the initial rates of decomposition of each N-chloroanilide against the initial concentration of benzoyl peroxide.

In a further series of experiments, the initial concentration of benzoyl peroxide was the same, but varying initial concentrations of

The Rearrangement of N-Chlorobenzanilide in the presence of Benzoyl Peroxide, at 77.7°.

[NCB] v Time

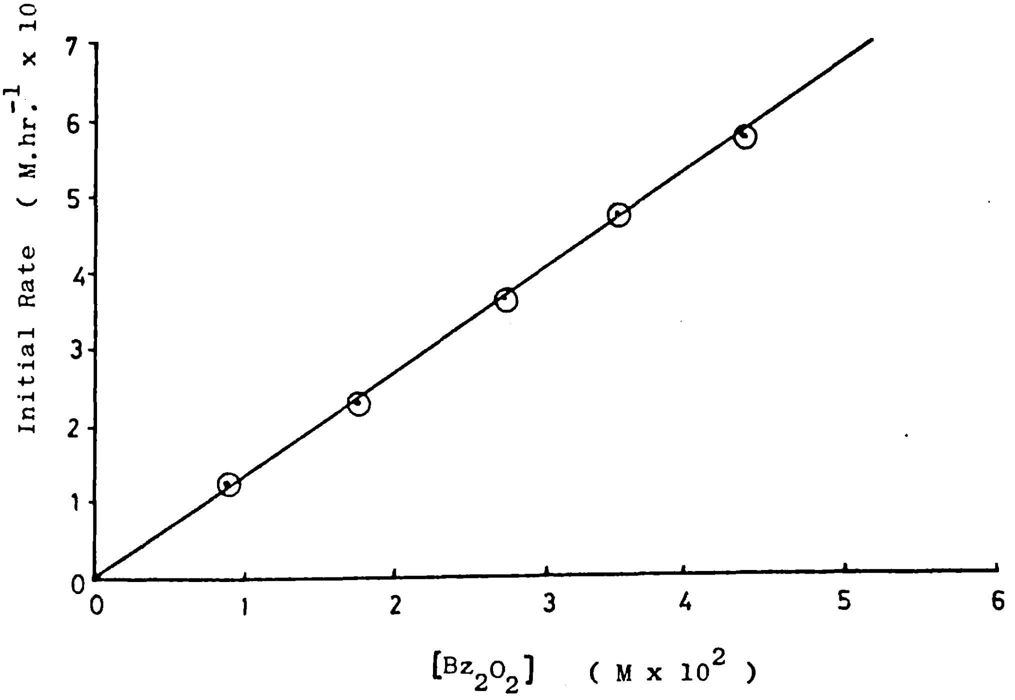
Fig. 71



A - $[Bz_2O_2]$ = 0.000M
B - $[Bz_2O_2]$ = 0.0086M
C - $[Bz_2O_2]$ = 0.0172M
D - $[Bz_2O_2]$ = 0.0258M
E - $[Bz_2O_2]$ = 0.0344M
F - $[Bz_2O_2]$ = 0.0430M

Initial Rate v $[Bz_2O_2]$

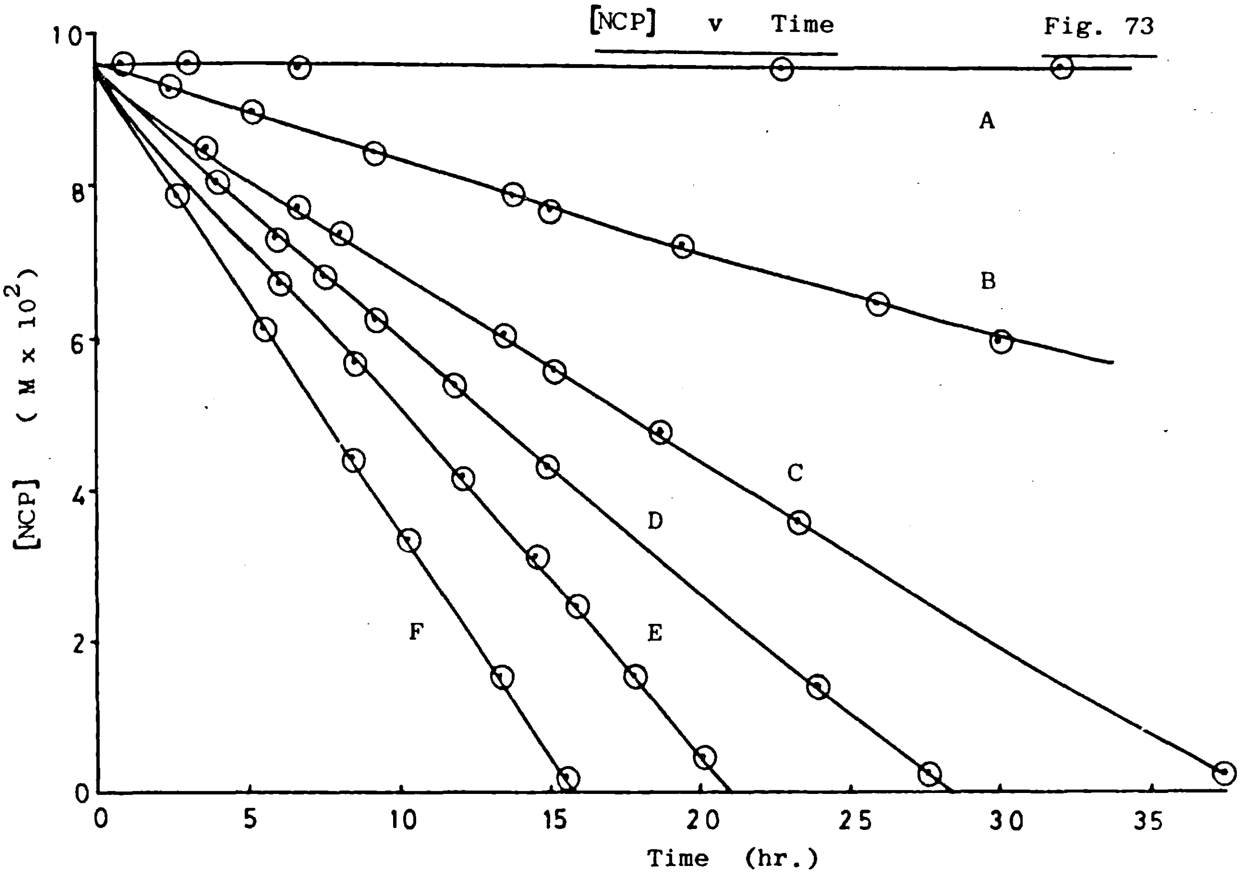
Fig. 72



The Rearrangement of N-Chlorophenylacetanilide in the presence of Benzoyl Peroxide, at 77.7°.

[NCP] v Time

Fig. 73



A - $[Bz_2O_2]$ = 0.000M

B - $[Bz_2O_2]$ = 0.0086M

C - $[Bz_2O_2]$ = 0.0172M

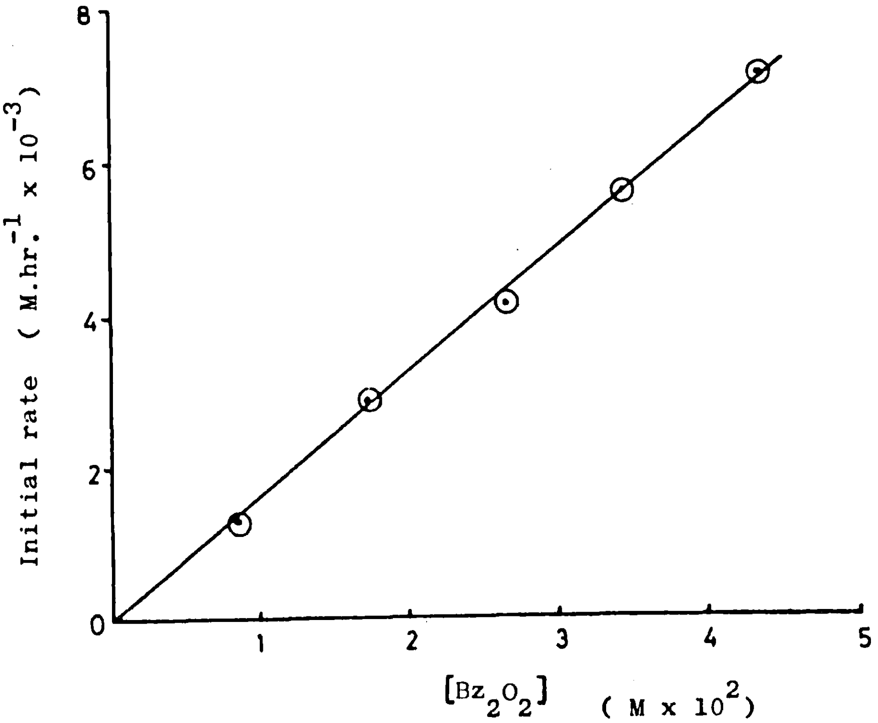
D - $[Bz_2O_2]$ = 0.0258M

E - $[Bz_2O_2]$ = 0.0344M

F - $[Bz_2O_2]$ = 0.0430M

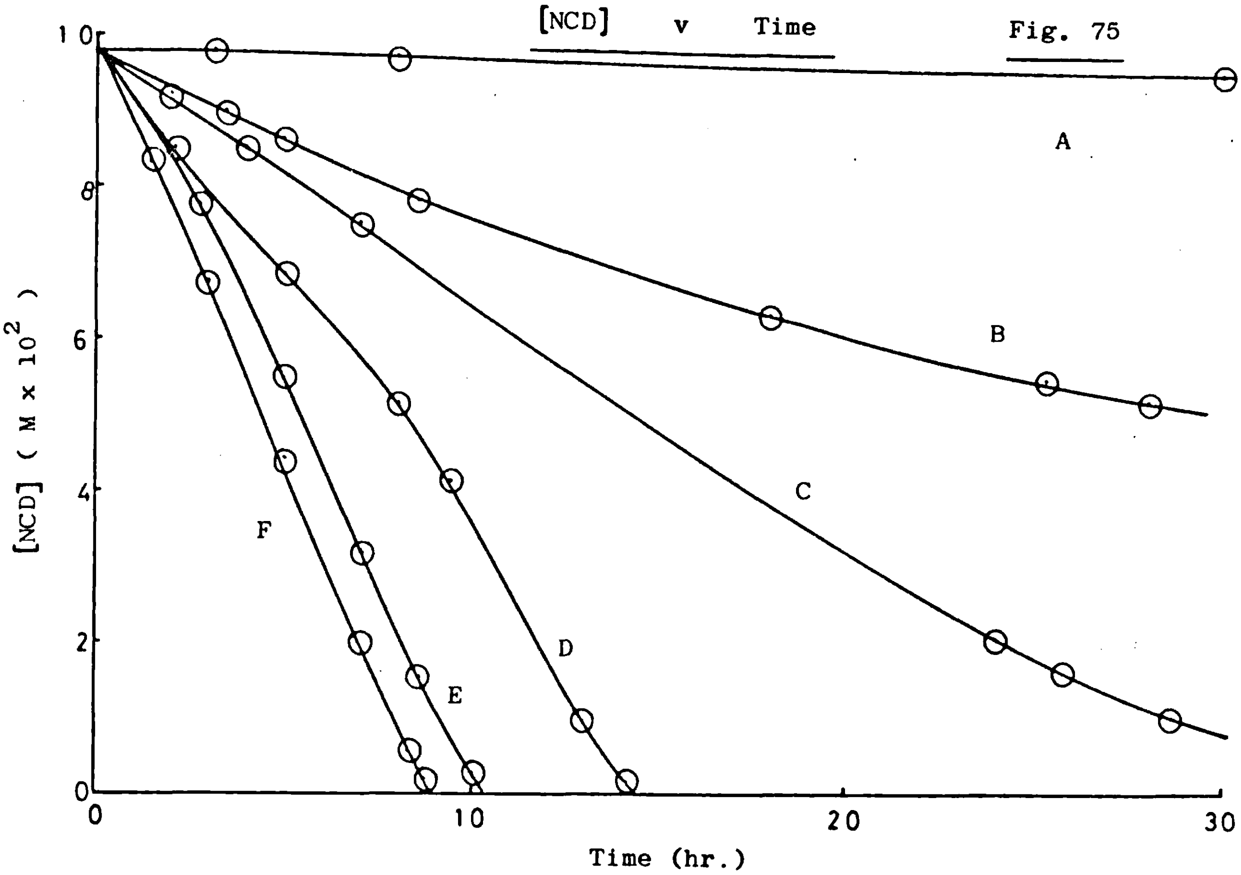
Initial rate v $[Bz_2O_2]$

Fig. 74



The Rearrangement of N-Chlorodiphenylacetanilide in the presence of Benzoyl Peroxide at 77.7°.

[NCD] v Time **Fig. 75**



A - $[Bz_2O_2]$ = 0.000M

B - $[Bz_2O_2]$ = 0.0043M

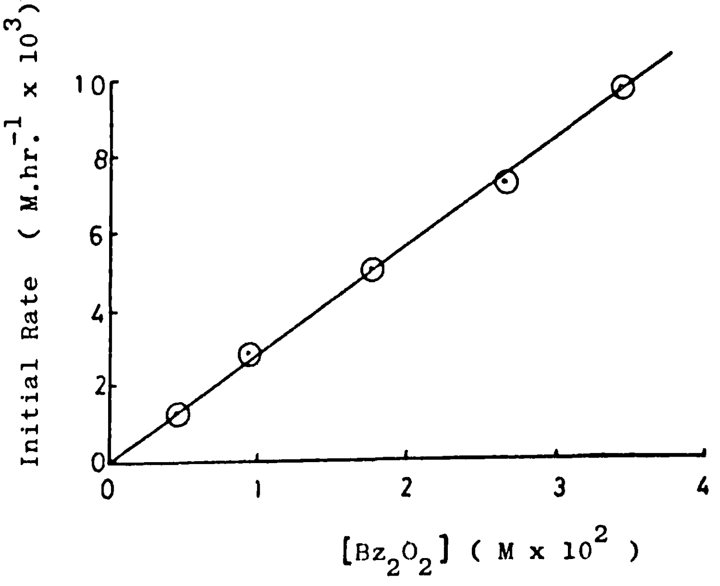
C - $[Bz_2O_2]$ = 0.0086M

D - $[Bz_2O_2]$ = 0.0172M

E - $[Bz_2O_2]$ = 0.0258M

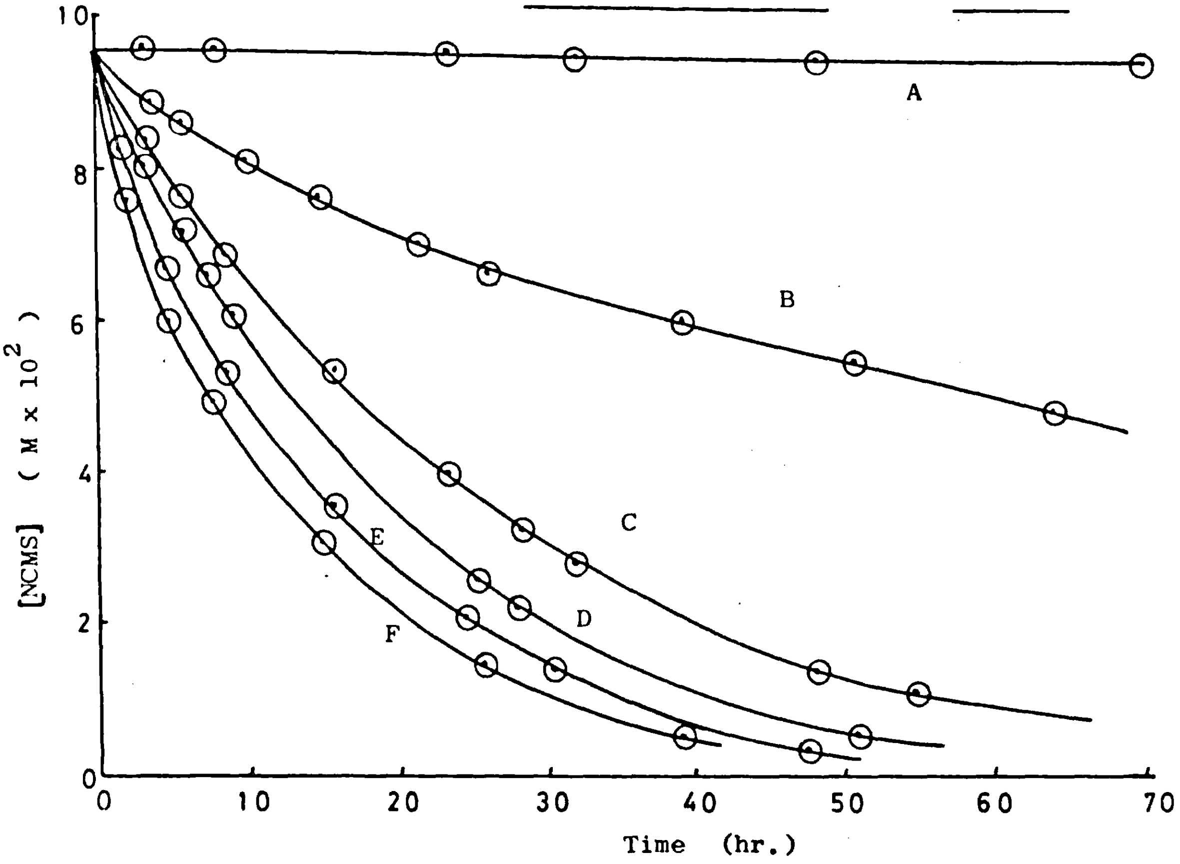
F - $[Bz_2O_2]$ = 0.0344M

Initial Rate v $[Bz_2O_2]$ Fig. 76



The Rearrangement of N-Chloromethanesulphonanilide in the presence of Benzoyl Peroxide at 77.7°.

[NCMS] v Time Fig. 77



A - $[Bz_2O_2]$ = 0.000M

B - $[Bz_2O_2]$ = 0.0086M

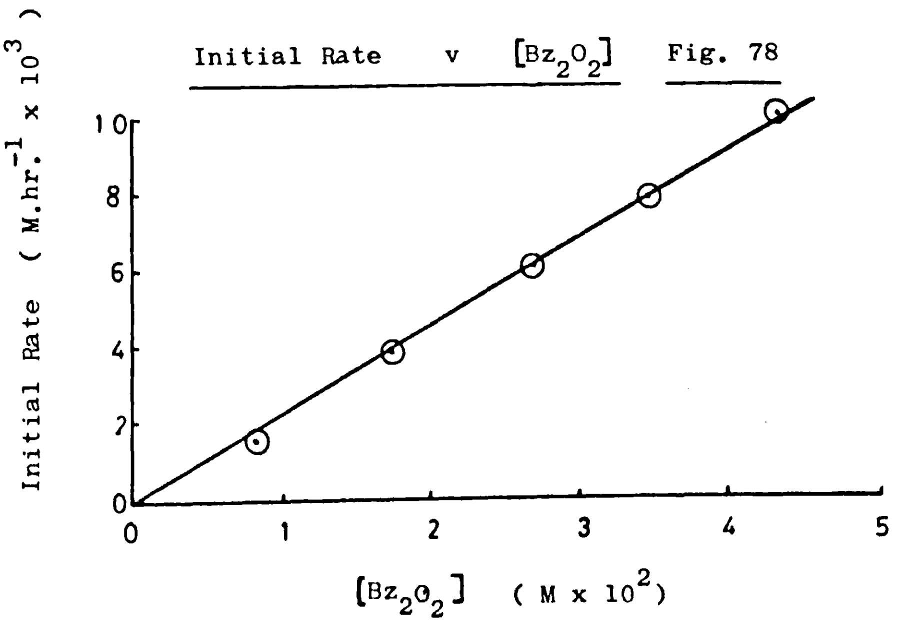
C - $[Bz_2O_2]$ = 0.0172M

D - $[Bz_2O_2]$ = 0.0258M

E - $[Bz_2O_2]$ = 0.0344M

F - $[Bz_2O_2]$ = 0.0430M

Initial Rate v $[Bz_2O_2]$ Fig. 78



The Rearrangement of N-Chlorobenzanilide at 77.7° in the presence of Benzoyl Peroxide.

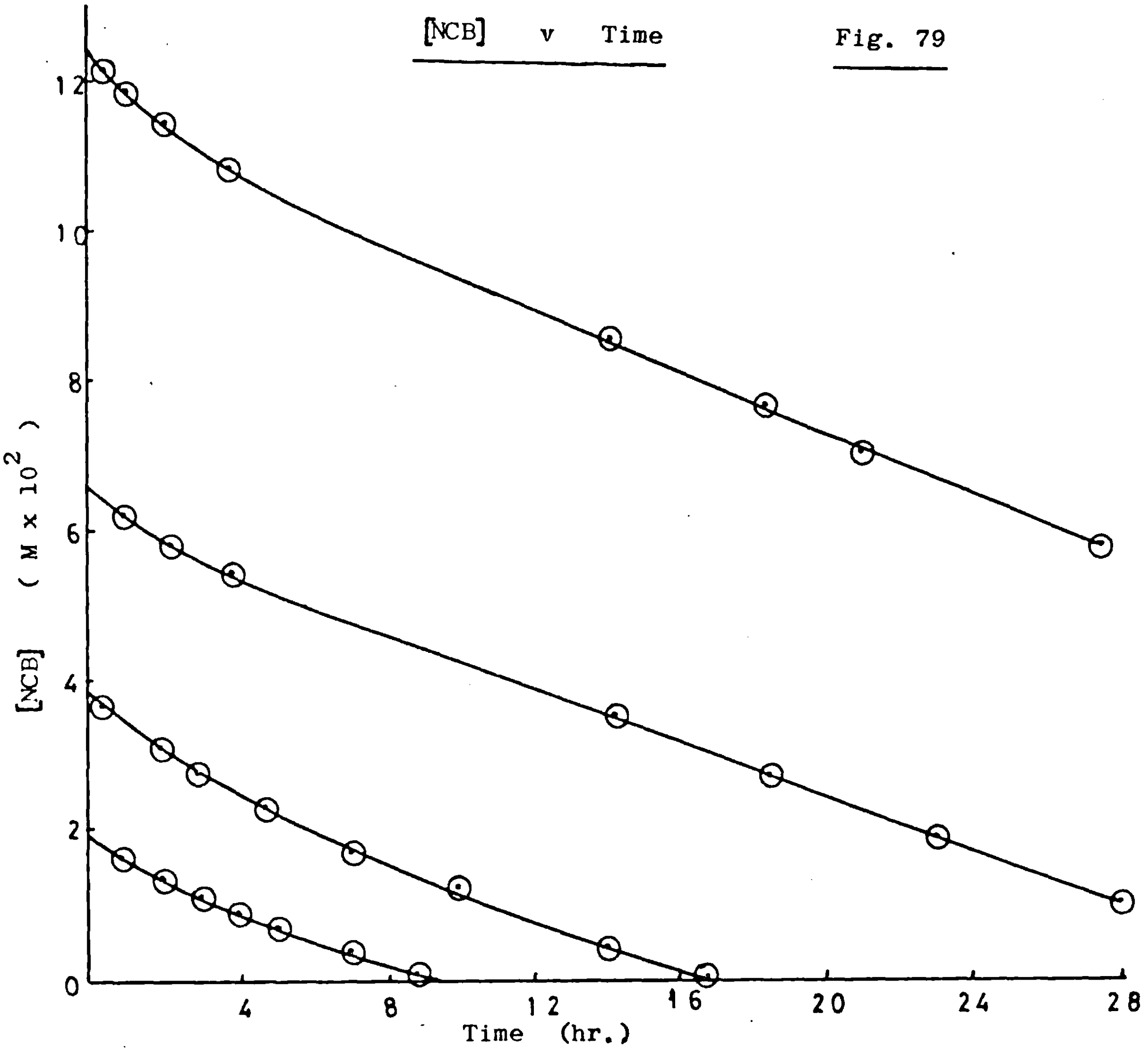

[NCB] v Time

Fig. 79

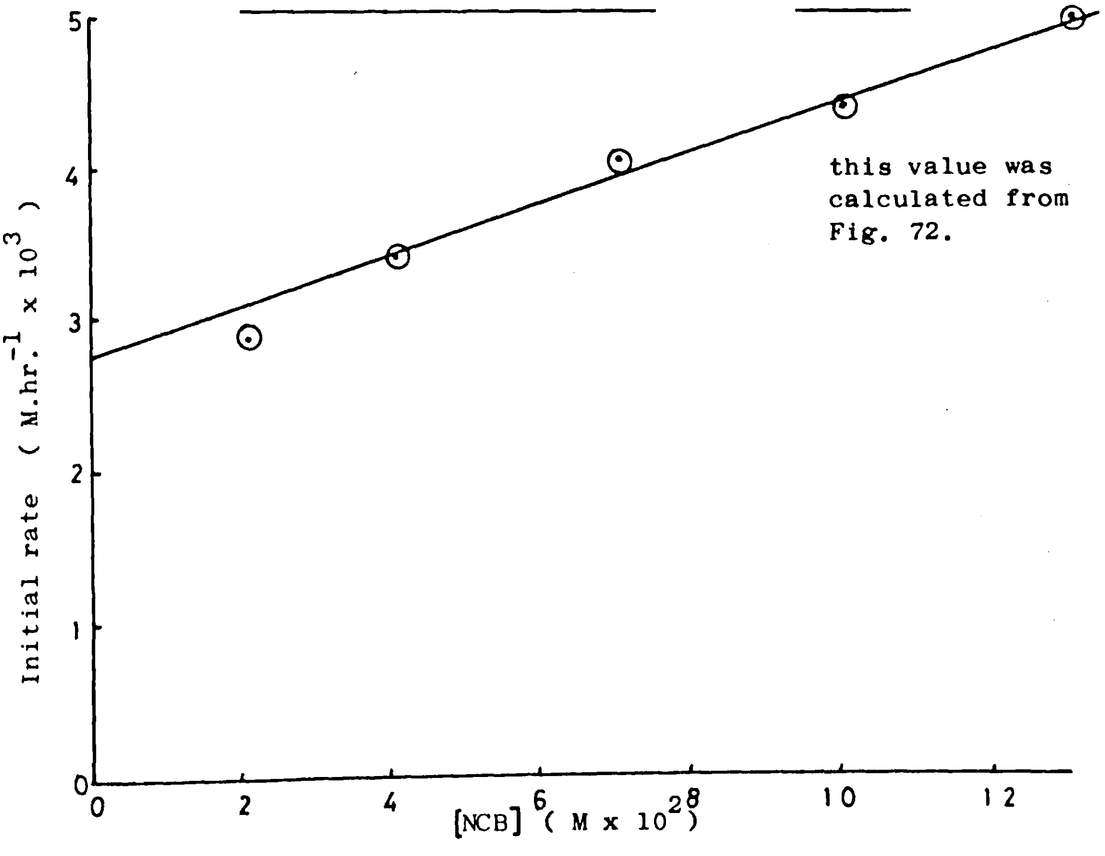

Initial Rate v [NCB]

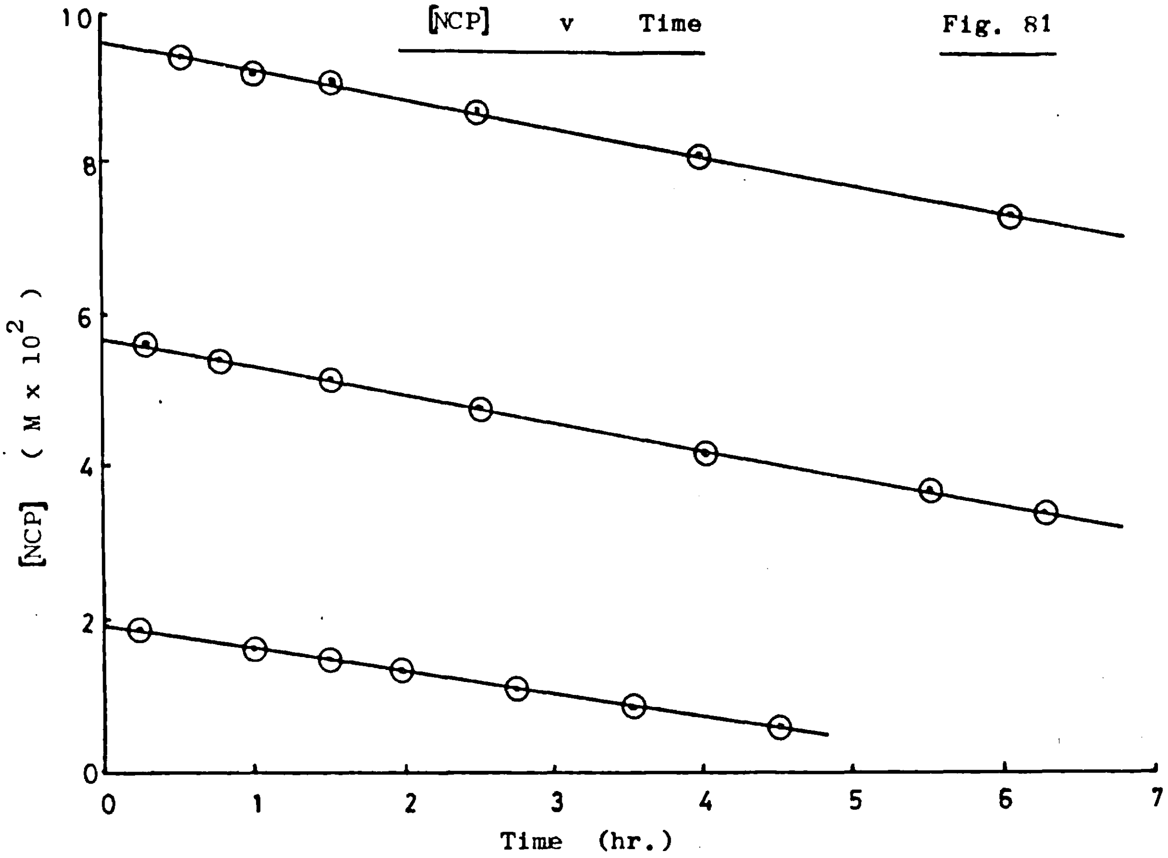
Fig. 80

this value was calculated from Fig. 72.

The Rearrangement of N-Chlorophenylacetanilide at 77.7°, in the presence of Benzoyl Peroxide.

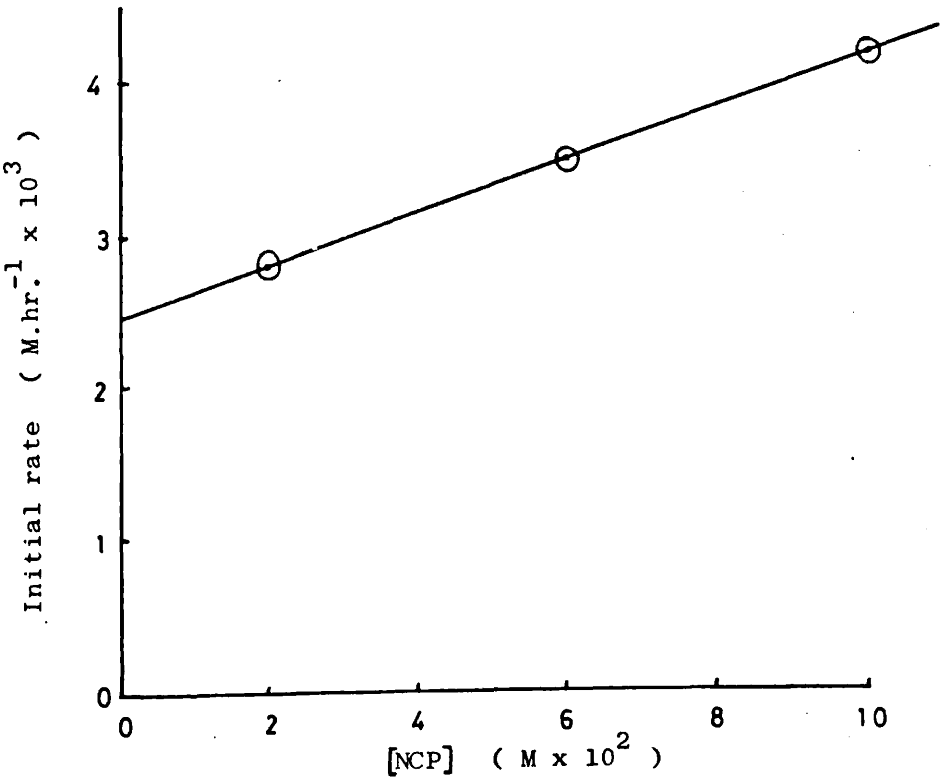
[NCP] v Time

Fig. 81



Initial Rate v [NCP]

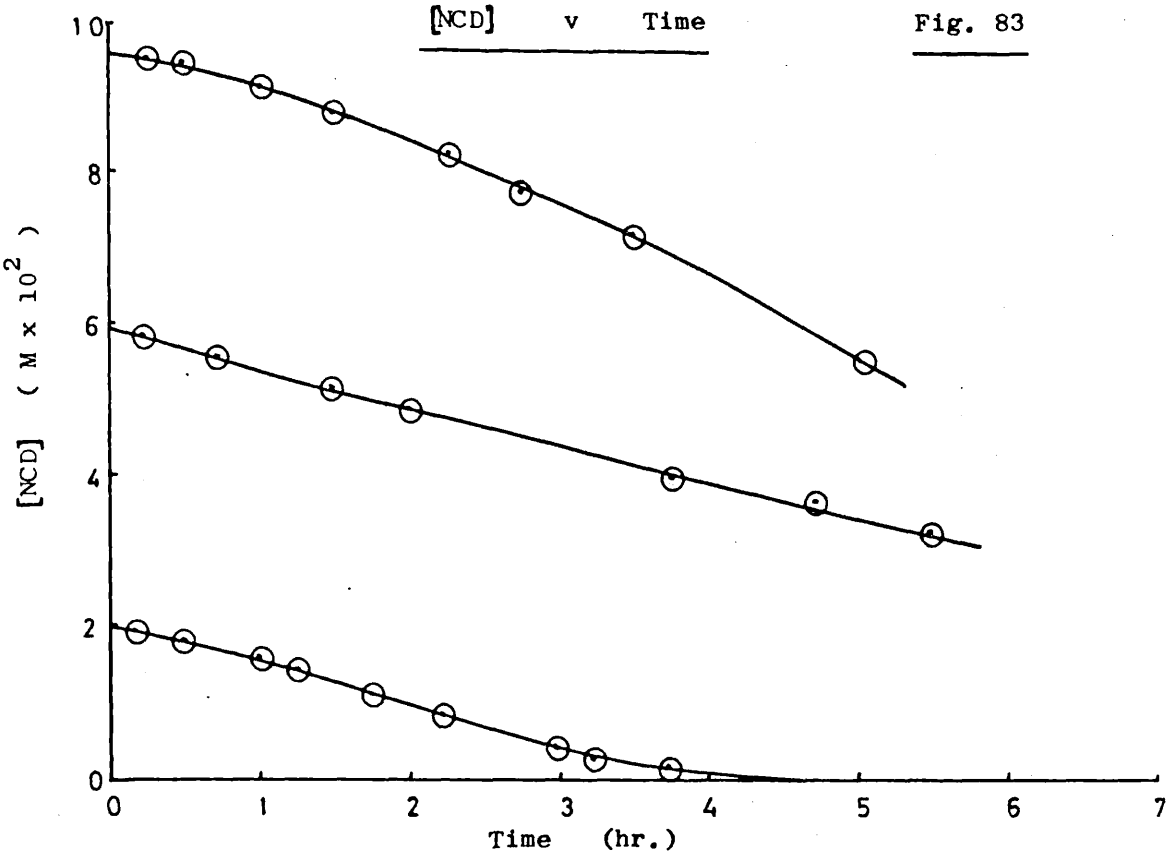
Fig. 82



The Rearrangement of N-Chlorodiphenylacetanilide at 77.7° in the presence of Benzoyl Peroxide.

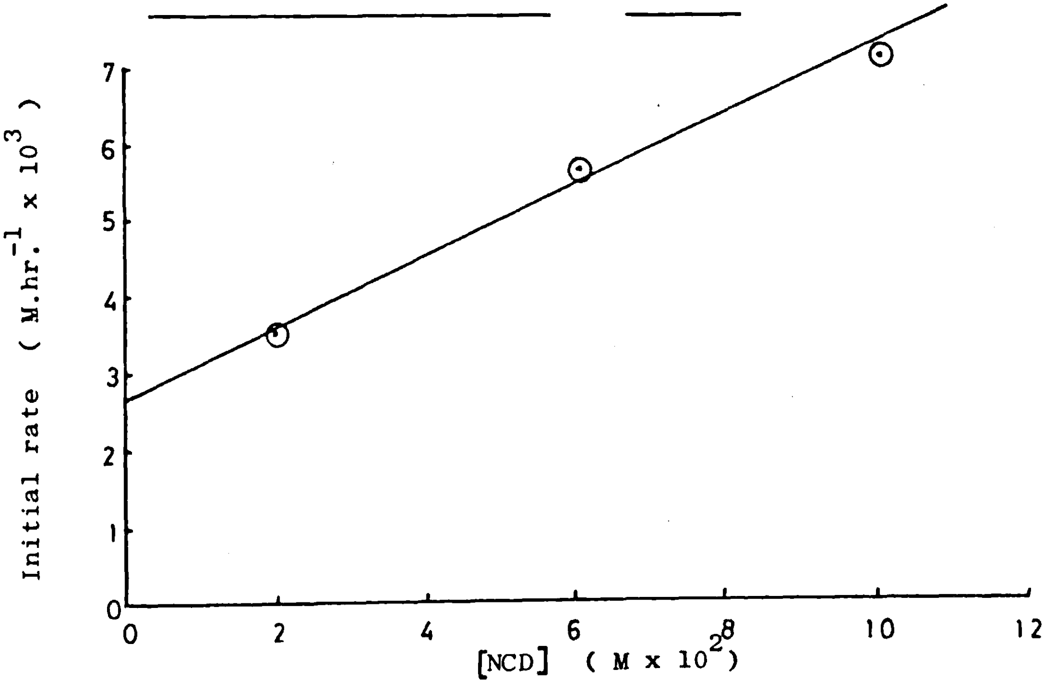
[NCD] v Time

Fig. 83



Initial Rate v [NCD]

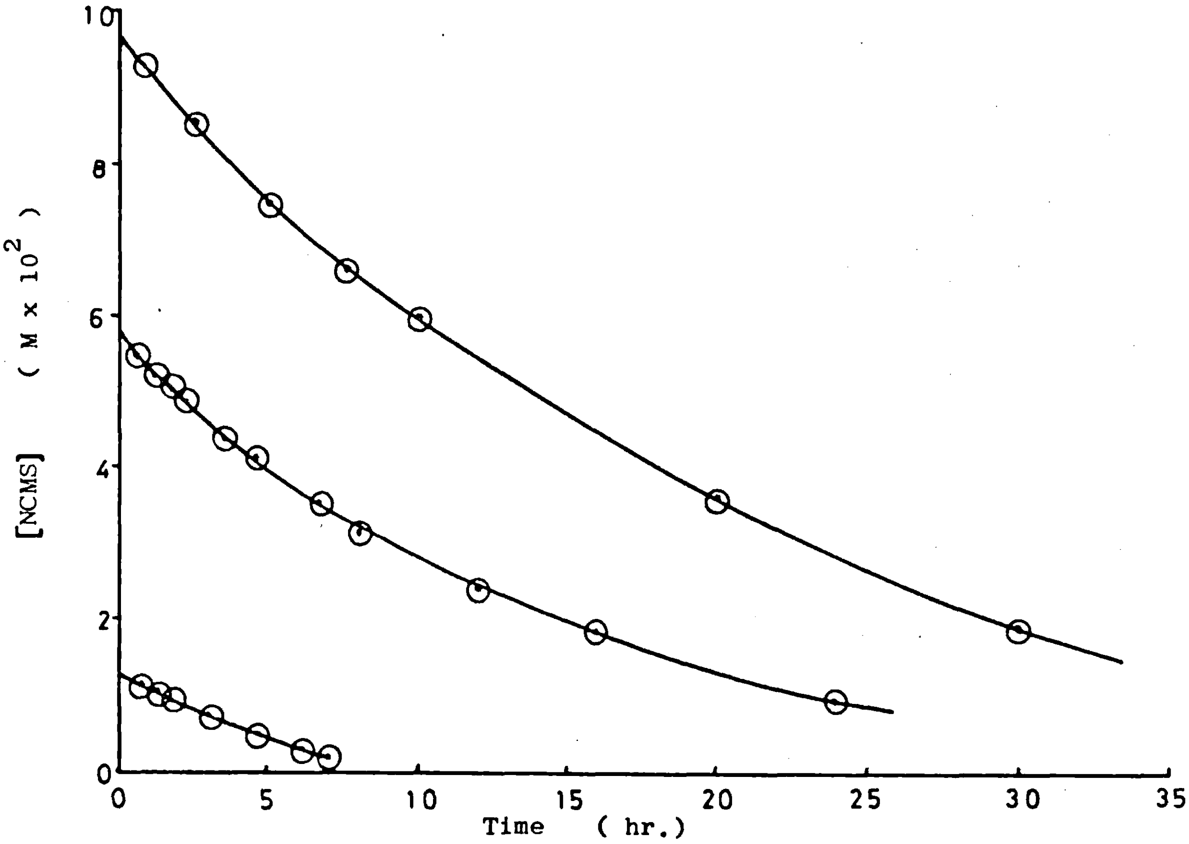
Fig. 84



The Rearrangement of N-Chloromethanesulphonanilide at 77.7° in the presence of Benzoyl Peroxide.

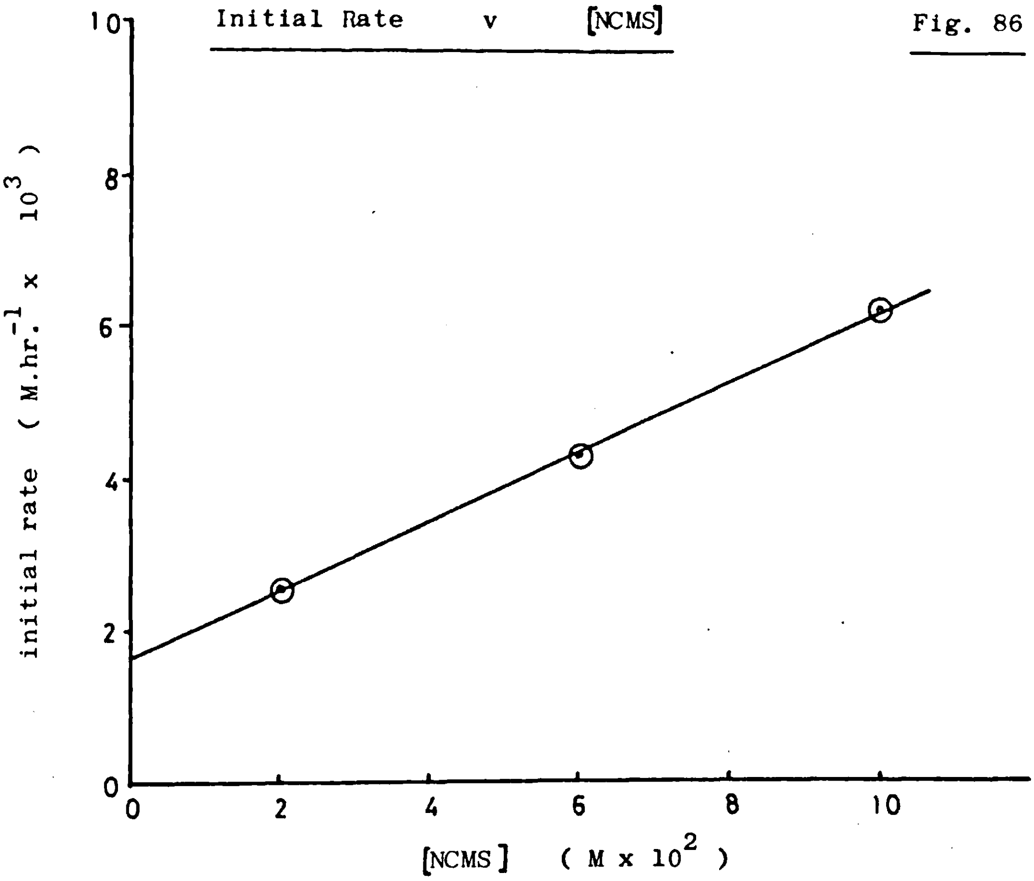
[NCMS] v Time

Fig. 85

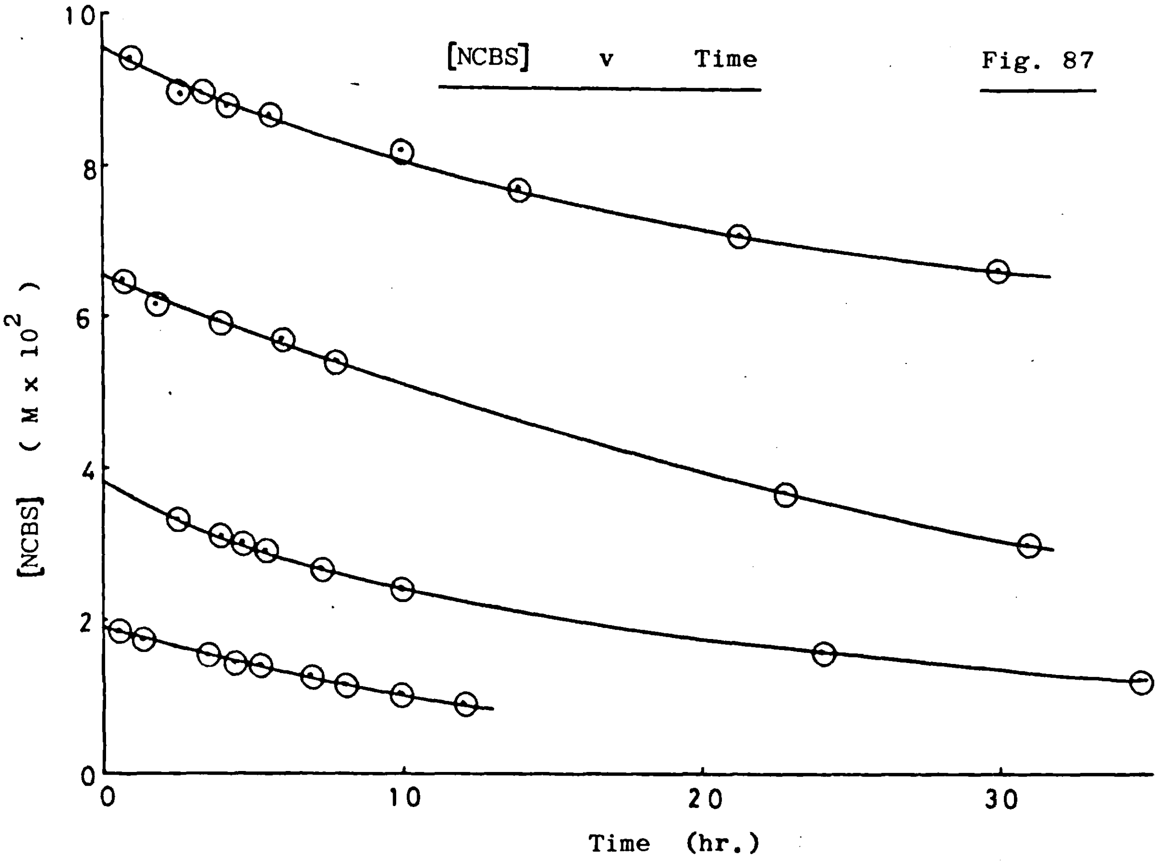


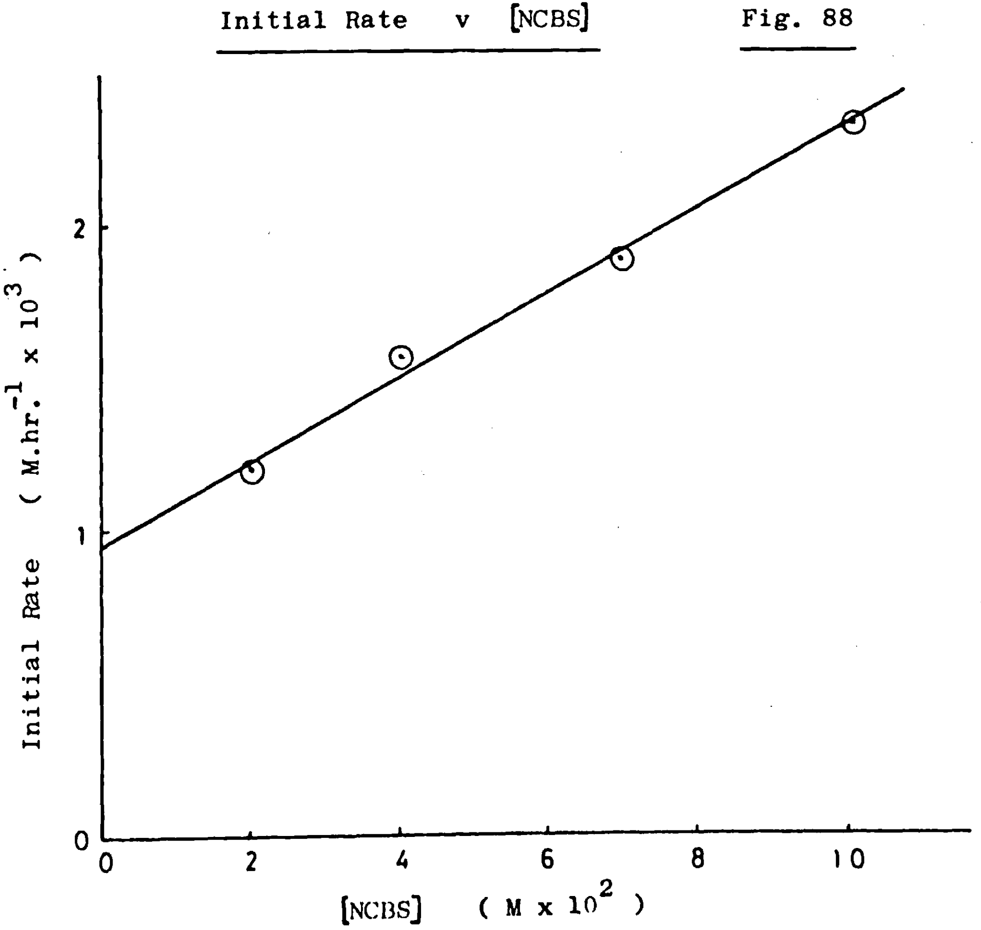
Initial Rate v [NCMS]

Fig. 86



The Rearrangement of N-Chlorobenzenesulphonanilide at 77.7° in the presence of Benzoyl Peroxide.





each N-chloroanilide were employed. The results are given in Tables A62, A63, A64, A65, A66 and A67, and Fig. 79, 81, 83, 85 and 87. Fig. 80, 82, 84, 86, 88 show the corresponding plot of the initial rate of decomposition of N-chloroanilide against the initial concentration of each N-chloroanilide.

2.8.2. The Effect of the Passage of Nitrogen During the Rearrangement.

Dry nitrogen, saturated with carbon tetrachloride, was passed through solutions of N-chlorobenzanilide, N-chlorophenylacetanilide, N-chlorodiphenylacetanilide, and N-chloromethanesulphonanilide (0.0085 mole), in turn, and benzoyl peroxide (0.00365 mole) in carbon tetrachloride (85 ml.), maintained at 77.7°, in the dark, and through a standard solution of sodium hydroxide (50 ml., 0.100 M) using the conditions described previously (section 2.5.2.1.). After rearrangement of the N-chloroanilide was complete, the sodium hydroxide was analysed as before (section 2.5.2.3.) and the number of moles of chlorine and hydrogen chloride removed from the reaction mixture was calculated. The results obtained are given in Table 30.

2.8.3. The Analysis of the Products of the Rearrangement.

After the N-chloroanilide (0.0085 mole) had dissolved in hot carbon tetrachloride (85 ml.), benzoyl peroxide (0.0042 mole) was added and the resultant solution was maintained at 77.7° in the dark. When the rearrangement was complete, and the solvent had been distilled off from the dark red solution, the solid residue was hydrolysed and the hydrolysate was analysed in the usual way. The results are given in Table 31.

Further experiments were performed in which each N-chloroanilide was allowed to rearrange in the presence of benzoyl peroxide while dry nitrogen was passed slowly through the solution, at a flow-rate of approximately 1 l. hr.$^{-1}$, throughout the reaction. The products were analysed as before and the results are given in Table 31.

Table 30

Analysis of the Volatile Products of the Rearrangement of N-Chloroanilides, Catalysed by Benzoyl Peroxide.

	N-Chlorobenzanilide		N-Chlorophenylacetanilide			N-Chlorodiphenylacetanilide		N-Chloromethanesulphonanilide	
	1	2	1	2	3	1	2	1	2
Nitrogen Flow-rate (l. hr^{-1})	1.0	1.0	1.0	1.2	1.2	1.0	1.0	1.5	1.5
N-Chloroanilide (mole x 10^{-3})	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Chlorine evolved (mole x 10^{-5})	3.8	4.9	1.3	5.5	7.9	5.4	4.0	0.16	0.14
Hydrogen chloride evolved (mole x 10^{-5})	13.8	12.9	25.0	15.2	16.2	59.2	61.7	3.9	2.9
Total chlorine evolved (mole x 10^{-5})	21.4	22.7	27.5	26.2	32.2	67.2	71.8	4.2	3.2
Total chlorine evolved as as a percentage of the available chlorine	2.5	2.6	3.2	3.1	3.8	7.9	8.4	0.8	0.6

Table 31

Products of the Rearrangement of N-Chloroanilides Catalysed by Benzoyl Peroxide in Carbon Tetrachloride at 77.7^{o}.

N-Chloroanilides	Nitrogen Flow-rate	%		Molar % of Products					
	$l.hr^{-1}$	Distillate	Residue	a	o	p	d	t	o:p
N-Chlorobenzanilide	-	68	16	30.2	6.5	57.6	4.0	1.7	1:8.85
N-Chlorobenzanilide	-	66	13.5	28.0	5.8	51.1	14.1	1.3	1:8.77
N-Chlorobenzanilide	1	64	19.6	36.4	5.4	48.2	8.8	1.2	1:8.91
N-Chlorobenzanilide	1	65	24	35.8	4.9	45.0	14.0	0.6	1:9.30
N-Chlorophenylacetanilide	-	61	17	43.3	7.47	45.4	3.4	0.4	1:6.07
N-Chlorophenylacetanilide	-	62	14	42.7	7.50	43.3	5.1	0.5	1:5.80
N-Chlorophenylacetanilide	1	-	-	47.5	7.4	41.4	3.2	0.3	1:5.58
N-Chloromethanesulphonanilide	-	-	-	49.7	10.5	39.8	-	-	1:3.80
N-Chloromethanesulphonanilide	-	-	-	48.5	10.5	41.0	-	-	1:3.90
N-Chloromethanesulphonanilide	1	-	-	50.7	10.0	39.3	-	-	1:3.95

3. DISCUSSION

3.1. The Rearrangements of N-Chloroanilides in Acetic Acid.

3.2. The Rearrangement of N-Chloroanilides in Carbon Tetrachloride Catalysed by Hydrogen Chloride.

3.3. The Thermal Rearrangement of N-Chloroanilide in Nitrobenzene.

3.4. The Thermal Rearrangement of N-Chloroanilides in the presence of Added Anilides.

3.5. The Photolytic Rearrangement.

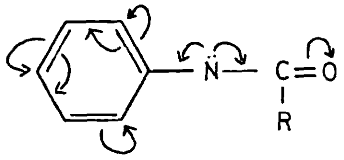
3.6. The Rearrangement of N-Chloroanilide in Carbon Tetrachloride in the presence of Benzoyl Peroxide.

3.1. The Rearrangements of N-Chloroanilides in Acetic Acid.

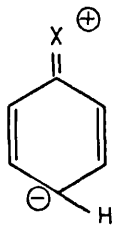
3.1.1. The Products of the Rearrangement

It has been shown that the rearrangement of N-haloanilides in acetic acid involves formation of intermediate halogenating species, which react with the anilides to give nuclear-substituted products. The laws which govern such electrophilic aromatic substitution are well established, and will only be mentioned briefly, with regard to the reactions under discussion.

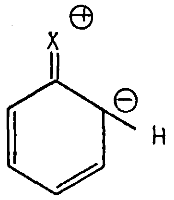
An amino-group present in the nucleus exerts a directing influence, activating the ortho-and para-positions by transfer of electrons from the nitrogen to these positions (the mesomeric effect). No activation of the meta-sites can occur by this effect and, as has already been observed (section 2.3.), there is no indication of meta-substitution in the reactions of N-chloroanilides in acetic acid. As Ingold[1] has observed, in anilides, the acyl group attached to the nitrogen atom diminished the ortho- and para-directing influence, as compared with unsubstituted amino-group. This is due to mesomerism within the acylamino-group, conflicting with the conjugation of the nitrogen atom with the aryl system.



Solely on a statistical basis, it would be expected that substitution in the ortho-position of an anilide would be twice as extensive as in the para-position. However, Waters[85] and de la Mare[86] have stressed that the mesomeric effect favours the formation of p-substituted products as the dipolar structure (a) has been shown to be more stable than (b), and consequently, (a) would make a greater contribution to the mesomeric state.



a



b

The presence of a bulky substitutuent has been shown by Cohn, Hughes and Jones[87], to favour *p*-substitution, although the relative importance of this steric effect depends on the size of both the original substituent and the entering group.

There are also certain data which indicate that inductive effects influence the relative reactivity of the *ortho*- and *para*-positions. Holleman[88] has reported that the nitration of fluorobenzene gives 12% *ortho*-substitution, chlorobenzene 30%, bromobenzene 30% and iodobenzene 41%. This is the reverse of the order that would be expected from steric considerations, but it can be explained on the basis of the inductive effect, for this would be strongest in the case of fluorine and most marked at the *ortho*-position, since the inductive effect decreases rapidly with distance from the substituent.

The nature of the entering group has also been shown to play a considerable part in determining the products of aromatic substitution. Studies of halogenation of toluene[89, 90] have indicated that there is a considerable steric effect, as bromination gives rise to a relatively higher yield of *p*-substituted product (*o*:*p* 1:0.49) than chlorination (*o*:*p* 1:1.50). The electrophilicity of the entering group has also been shown to influence the proportions of products[91]. The chlorination of chlorobenzene, in the presence of aluminium chloride, gave 68% of the *p*-substituted products whereas when ferric chloride was the catalyst only 55% of the p-substituted product was formed. Since the chlorinating species in the former reaction would be expected to be less bulky, the lower o:p ratio must be due to the greater electrophilicity of the intermediate.

The effect of solvent on the proportions of products obtained from chlorination of toluene at 25° has been investigated by Stock and Himoe[92]. The variation in o:p ratios (1:0.45 to 1:1.94) could not be correlated with any simple physical parameter, such as dielectric constant. It was therefore suggested that the variation was partly due to the differences in reactivity between the complexes formed from the molecular chlorine and the solvent, and partly to the differences in the extent of solvation of the components of the transition state.

In order to relate the factors, which affect the products of the rearrangement to the proportions of products formed, the results obtained in the present work, and those of previous workers are summarised in Table 32.

If the rearrangement of N-chloroanilides, catalysed by hydrogen chloride, involves the "Orton" mechanism (equation 2), then the proportions of products obtained from this reaction should be similar to those from the chlorination of the corresponding anilide. The products of the chlorination of benzanilide, at 76.8°, have been analysed in the present study, and the proportions of products for the analogous reaction at 20°, have been determined by Chattaway and Orton[26] (Table 32). Orton and King[14] have also investigated the products of this reaction; however, their results appear anomalous, for they have shown that the rate of chlorination of either o- or p-chlorobenzanilide is 800 times lower than that of the chlorination of benzanilide, and yet they reported that both benzanilide and 2,4-dichlorobenzanilide

Table 32

Products of the Rearrangement of N-Chloroanilides and of the Chlorination of Benzanilide, in Glacial Acetic Acid.

Reactant(s)	Temp. (°)	Yield (%)	o:p ratio
N-Chloroacetanilide, HCl[6]	20	87	1:2.75
N-Chloroacetanilide[6]	100	90	1:1.65
N-Chlorophenylacetanilide, HCl	77.7	90	1:1.96
N-Chlorophenylacetanilide	77.7	96	1:1.87
N-Chlorobenzanilide, HCl	20	92	1:2.86
N-Chlorobenzanilide, HCl	77.7	93	1:1.89
N-Chlorobenzanilide	77.7	94	1:2.00
N-Chlorobenzanilide, N_2	77.7	90	1:2.38
N-Chlorobenzanilide	100	97	1:1.79
Benzanilide, Cl_2	76.8	94	1:1.87
N-Chloromethanesulphonanilide, HCl	77.7	-	1:1.59
N-Chlorobenzenesulphonanilide, HCl[5]	20	91	1:1.95
N-Chlorobenzenesulphonanilide[5]	100	92	1:1.53

formed in considerable yield in the chlorination of benzanilide. The proportions of products obtained from the rearrangement of N-chlorobenzanilide, catalysed by hydrogen chloride, at both 77.7° and 20°, are similar to those obtained from chlorination of benzanilide, and this is consistent with the reaction scheme proposed by Orton (equation 2). The low yields of 2,4-dichloro-, and 2,4,6-trichlorobenzanilide, and of involatile residue obtained after hydrolysis of the products of each of these reactions, were found to be associated with reactions which involve heterolytic mechanisms. Similar studies have indicated that the rearrangement of N-chloro-2,5-dimethylacetanilide[93], N-chlorobenzenesulphonanilide[94] and diphenyl N-chloro-N-phenylphosphoramidate[25], catalysed by hydrogen chloride, involve chlorination of the parent anilide by molecular chlorine.

Thus the products of the rearrangement, in acetic acid, of N-chloroanilides catalysed by hydrogen chloride, are formed by electrophilic aromatic chlorination of the anilide, and must be considered in relation to the factors which are known to affect the products of this type of substitution. The results show that an increase in the temperature of the reaction gives rise to a higher proportion of the ortho-substituted anilide, and that the temperature coefficients are of a similar magnitude for each N-chloroanilide.

The o:p ratios for the rearrangements of N-chloroacetanilide, N-chlorophenylacetanilide and N-chlorobenzanilide are closely similar. The o:p ratios for the corresponding reactions of N-chloromethanesulphonanilide and N-chlorobenzenesulphonanilide resemble one another but are appreciably higher than those obtained for the rearrangements of the other N-chloroanilides. This difference in o:p ratios may well be due to the considerable difference in the electron-withdrawing power between the sulphonyl-groups and the other acyl groups. The extent of delocalisation of the lone-pair of electrons on the nitrogen atom in the aromatic nucleus would be expected to be much smaller in sulphonanilides than in the other anilides. The selective mesomeric effect, which has been shown to favour p-substitution, would therefore be less important in the rearrangements of N-chlorosulphonanilides than in those of the other N-chloroanilides.

Coulson, Williams and Johnston[6] suggested that the rearrangements of N-chloroanilides in glacial acetic acid alone, commenced with a slow reaction, but hydrogen chloride, formed in a side-reaction, caused the incursion of the far more rapid "Orton" rearrangement. If this were so, the major part of the product would be formed by the "Orton" mechanism and the proportions of the constituents would be expected to be similar to those for the reaction carrier out in the presence of added hydrogen chloride, under similar conditions. In the present work, this was, in fact, found to be the case (Table 32). It appears likely that a relatively low o:p ratio is characteristic of the slow initial reaction since the yield of p-chloroanilide was higher than in the presence of added hydrogen chloride, and higher still when hydrogen chloride, produced during the reaction, was removed by aspiration with nitrogen.

In the present and previous work a method of removing hydrogen chloride from the solution other than by passing nitrogen was sought in the use of a solution of silver acetate in glacial acetic acid as solvent. However, it became apparent that the silver acetate not only inhibited the "Orton" reaction, by removing chloride ions as silver chloride, but also acted as a catalyst for rearrangement by yet another mechanism, which was characterised by a high o:p ratio (Table 33), high yields of 2,4-dichloro- and 2,4,6-trichloro-anilide and involatile residue, and a low total yield.

Table 33

Products of the Rearrangement of N-Chloroanilides in Glacial Acetic Acid, in the presence of Silver Acetate.

	Temperature (o)	% Yield	o:p ratio
N-Chloroacetanilide[6]	100	73	1:0.40
N-Chlorophenylacetanilide	77.7	70	1:0.42
N-Chlorobenzanilide	77.7	74	1:0.15
N-Chlorobenzanilide	100	75	1:0.09
N-Chlorobenzenesulphonanilide[5]	100	55	1:0.37

3.1.2. The Kinetics of the Rearrangements.

The rate-graphs for the decomposition of N-chlorobenzanilide and of N-chlorophenylacetanilide, in hot glacial acetic acid, show characteristics of autocatalysis (Fig 2 and 4) similar to those for the rearrangement of N-chloroacetanilide and N-chlorobenzenesulphonanilide[5]. It therefore seems probable that a rate-equation for this reaction involves two terms. One term would correspond to the rate of the initial reaction and be expected to be of the first-order with respect to the N-chloroanilide, because the rearrangement of N-chlorobenzanilide when the solution was aspirated with nitrogen, closely followed first-order kinetics. The second term, relating to the reaction catalysed by hydrogen chloride, would be expected to be first-order with respect to the N-chloroanilide and must also involve a function of the concentration of products since the total rate increases as the reaction progresses. The experimental data were found to fit the following rate-equation closely.

$$\frac{d[NCX]}{dt} = k_i[NCX] + k_{ii}[NCX]([NCX]_o - [NCX])^2 \quad ......(33)$$

$[NCX]_o$ = The initial concentration of the N-chloroanilide

$[NCX]_o - [NCX]$ = The concentration of the products.

The rate constant (k_i) for the slow reaction was calculated from the initial slope of the graph for the decomposition of the N-chloroanilide. Tangents were also drawn at various points, and the corresponding rates and concentrations of N-chloroamide and product were calculated. The values for a typical reaction, the decomposition of N-chlorophenylacetanilide alone in acetic acid at 77.7° (Fig. 4) are given in Table 34. A plot of:

$$\frac{d[NCX]}{dt}\Big/[NCX] \quad \text{against} \quad ([NCX]_o - [NCX])^2$$

was drawn (Fig 89) and indicated that these terms were related linearly. The slope of this line gave the rate constant k_{ii}. This procedure was carried out for each rearrangement. The values of k_i and k_{ii} were checked by carrying out a similar procedure using a computer. The programme is given in Appendix 2. Good agreement was obtained for the rate constants using these methods of calculation.

Table 34

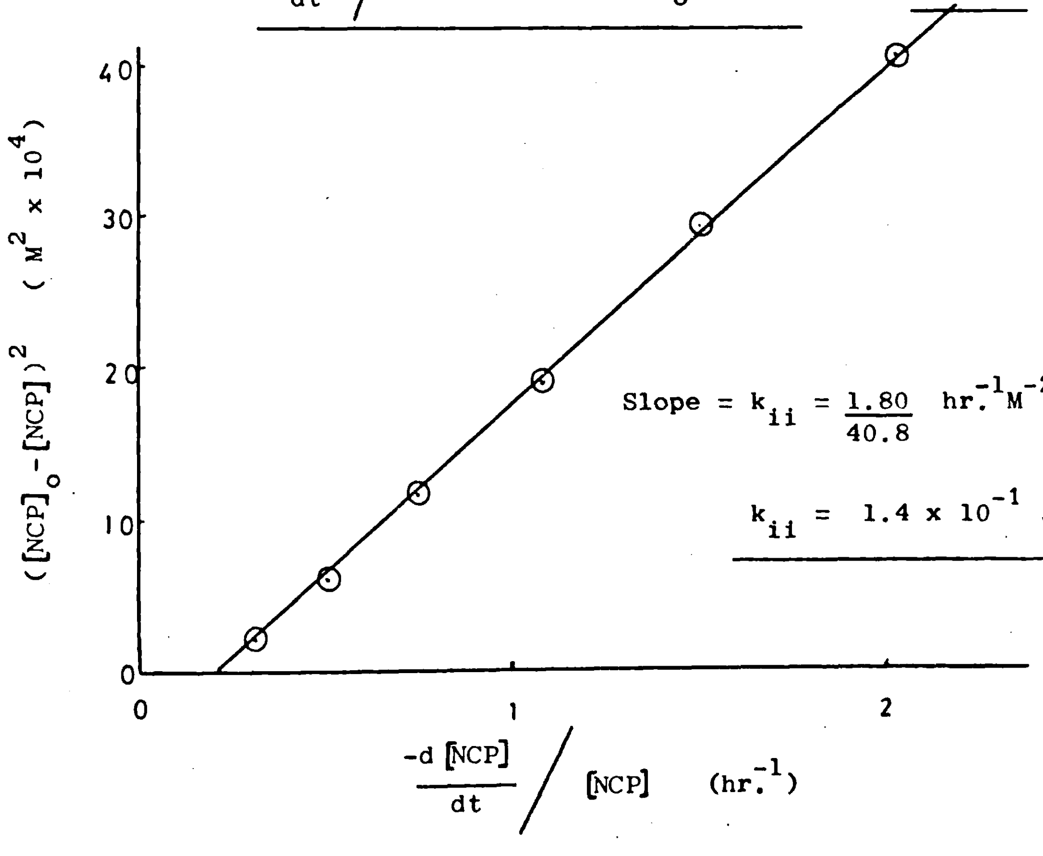
The Rearrangement of N-Chlorophenylacetanilide in Acetic Acid at 77.7^0.

$[NCP]_o$ = 0.094M (Fig. 4, page 57)

$\frac{-d[NCP]}{dt}$ M x 10^2 hr^{-1}	$[NCP]$ M x 10^2	$\frac{-d[NCP]}{dt} / [NCP]$ $hr.^{-1}$	$[NCP]_o - [NCP]$ M x 10^2	$([NCP]_o - [NCP])^2$ M^2 x 10^4
2.50	8.0	0.31	1.4	2.0
3.60	7.0	0.51	2.4	5.7
4.50	6.0	0.75	3.4	11.5
5.50	5.0	1.09	4.4	19.3
5.92	4.0	1.48	5.4	29.2
6.02	3.0	2.00	6.4	40.8

$\frac{d[NCP]}{dt} / [NCP]$ v $([NCP]_o - [NCP])^2$

Fig. 89



Slope = k_{ii} = $\frac{1.80}{40.8}$ $hr.^{-1}M^{-2}$ x 10^4

k_{ii} = 1.4 x 10^{-1} $sec^{-1}M^{-2}$

Values of the rate constants k_i and k_{ii} are given in Table 35 for the rearrangement of each N-chloroanilide studied, in acetic acid alone. The rate constants for the reactions of N-chloroacetanilide[6] and N-chlorobenzenesulphonanilide[5] under similar conditions are included for comparison.

Table 35

Rate Constants for the Reactions of N-Chloroamides in Acetic Acid.

N-Chloroanilide	$[NCX]_o$ M x 10^2	Temp. (^{o})	k_i sec^{-1} x 10^{-5}	k_{ii} $sec^{-1}M^{-2}$ x 10^{-1}
N-Chloroacetanilide	6.9	77.5	7.6	0.85
N-Chloroacetanilide	1.7	100	3.3	83.
N-Chlorophenylacetanilide	10.0	77.7	0.86	1.4
N-Chlorobenzanilide	4.0	77.7	0.88	2.3
N-Chlorobenzanilide	10.0	77.7	0.51	0.85
N-Chlorobenzanilide *	10.0	77.7	0.45	0.01
N-Chlorobenzanilide	4.0	100	3.1	98.
N-Chlorobenzenesulphonanilide	6.9	77.5	0.20	0.43
N-Chlorobenzenesulphonanilide	1.7	100	0.14	18.

* The solution was aspirated with dry nitrogen throughout this experiment.

Longmaid[25] has shown that the water content of the acetic acid affects not only the features of autocatalysis but also the initial rate. In the present work, the water content was constant for all reactions, but rate constants obtained from the results of other workers may not be strictly comparable as the water content for those reactions may well have been slightly different. The kinetics of each reaction were found to be closely similar to those predicted by the rate-equation, and the values of k_i were similar for each of the N-chloroanilides. However, the agreement for values of rate constants using different initial concentrations was not very good, and this may indicate that the rate equation (Equation 33) does not, in fact, fully express the kinetics of these reactions. It is apparent from the values of k_{ii} for N-chlorobenzanilide that the rate constant is dependent on the initial concentration of the N-chloroanilide, and that an increase in temperature causes a large increase in the rate constant. This large temperature effect is also observed for the reactions of other N-chloroanilides.

The passage of nitrogen through the solution of N-chlorobenzanilide had no significant effect on the initial rate of reaction but caused a considerable decrease in the value of k_{ii}, compared with the reaction in the absence of nitrogen, indicating that the ratio of hydrogen chloride to products had decreased, hydrogen chloride had been removed by the nitrogen, and the "Orton" reaction had been suppressed.

Although the silver acetate was found to be effective in inhibiting the reaction catalysed by hydrogen chloride, in some experiments, the initial rate of rearrangement was in fact found to be higher than in the absence of this acetate (Table 36).

Table 36

The Rearrangements of N-Chloroanilides in Acetic Acid in the presence of Metal Acetates

N-Chloroanilide	Catalyst	[NCX] M x 10	Temp. (o)	k_A sec^{-1} x 10^{-5}
N-Chloroacetanilide	-	0.17	100	3.3
N-Chloroacetanilide	AgOAc	0.47	100	1.2
N-Chlorophenylacetanilide	-	1.0	77.7	0.86
N-Chlorophenylacetanilide	AgOAc	1.0	77.7	0.52
N-Chlorobenzanilide	-	1.0	77.7	0.51
N-Chlorobenzanilide	AgOAc	1.0	77.7	
N-Chlorobenzanilide	-	0.40	100	3.1
N-Chlorobenzanilide	AgOAc	0.40	100	14.0
N-Chlorobenzenesulphonanilide	-	0.17	100	0.14
N-Chlorobenzenesulphonanilide	AgOAc	0.17	100	16.8

where $\frac{d[NCX]}{dt} = k_A [NCX]$

k_A was calculated for the initial rate of reaction.

It therefore seemed likely that the silver acetate was catalysing the reaction by another mechanism, since the reaction appeared to be of the first order with respect to the N-chloroanilide. A further investigation of the kinetics revealed that the reaction was of the first-order with respect to both the N-chloroanilide and the silver acetate. The rate-equation may be written as follows:-

$$\frac{-d\,[\mathrm{NCX}]}{dt} = k_x\,[\mathrm{NCX}]\,[\mathrm{AgOAc}] \qquad \ldots\ldots\ (34)$$

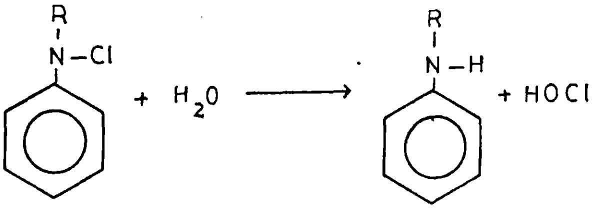
The values of k_x as determined from two sets of experiments (section 2.3., Figs. 4 and 5) show good agreement ($k_x = 6.6$ $hr.^{-1}$ M^{-1} for the experiments in which the concentration of silver acetate was varied, and $k_x = 6.9$ $hr.^{-1}$ M^{-1} for the experiments in which the concentration of N-chlorobenzanilide was varied.) Since the graph of the initial rate of reaction against the initial concentration of silver acetate for the series of experiments in which the concentration of silver acetate was varied, passed through the origin, it appears likely that in the presence of silver acetate, the only reaction of any significance taking place is that catalysed by this acetate.

3.1.3. The Mechanisms of the Rearrangements

The mechanism of the rearrangement of N-Chloroanilides, catalysed by hydrogen chloride, has been well established, although no conclusive evidence has been obtained to show if hydrogen chloride reacts in molecular or ionic form, though the latter seems more reasonable in a polar medium. The results of the present study (sections 2.3.3.1. and 2.3.3.5.) confirm that the rearrangement of N-chlorobenzanilide, catalysed by hydrogen chloride, involves chlorination of the anilide by molecular chlorine.

It has been suggested that the rearrangement of N-chloroanilides in acetic acid alone involves two reactions. The faster reaction, which is responsible for the major part of the product of the reaction, has been shown by product analysis and kinetic studies (sections 3.1.1. and 3.1.2.) to be the "Orton" rearrangement. However, the mechanism of the slow initial isomerisation and of the formation of hydrogen chloride have not been elucidated. This reaction could involve acetyl hypochlorite as an intermediate as proposed by Israel, Tuck and Soper[29]. However the presence of silver acetate, a source of acetate ions, would be expected to cause an increase in initial rate, and yet in some cases, a decrease in the initial rate was observed for the reaction in the presence of silver acetate. An intramolecular reaction such as that proposed by Dewar[32] is conceptually attractive, yet it does not explain how chloride ions could be formed, why the water content of the acetic acid is so critical, and why such a large yield of p-chloroanilide was formed when nitrogen was passed through the solution. A further possible mechanism, suggested by Cadogan and Foster[4] involved free radical intermediates, and, although abstraction of hydrogen by chlorine atoms provides a feasible route to hydrogen chloride, it is unlikely that a homolytic thermal decomposition of the N-chloroanilide would occur in acetic acid but not in carbon tetrachloride (at the same temperature), for no appreciable rearrangement occurred in this solvent after several hours, especially as free radical reactions are not usually very sensitive to solvent effects[95].

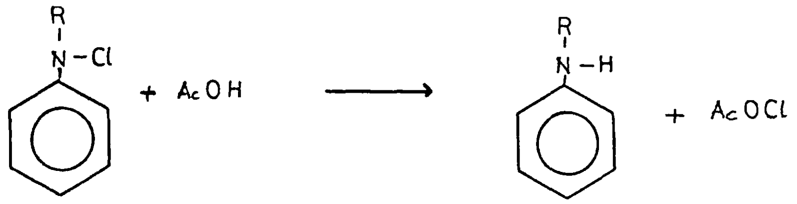
As it has been shown that the initial rate is dependent on the water content of the acetic acid, hydrolysis of the N-chloroanilide is a possible step in the mechanism (equation 35) as this process has been shown to occur in water.



.... (35)

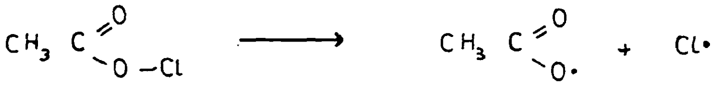
Hypohalous acid is known to decompose to oxygen and hydrogen chloride, which could be responsible for the autocatalysis. The products of the slow initial reaction could be those formed by chlorination of the anilide by hypochlorous acid.

A reaction, similar to equation 35 in which acetic acid replaced the water could also occur (equation 36)



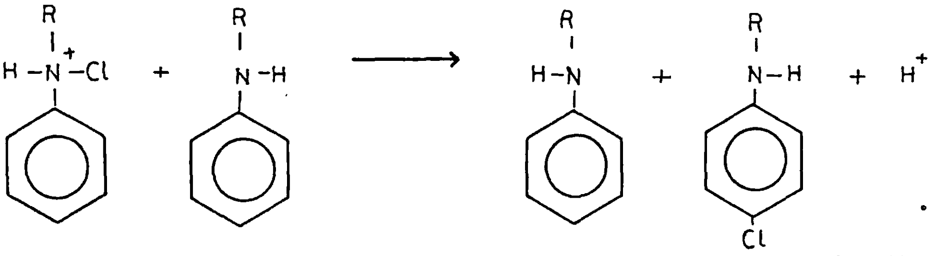
.... (36)

Acetyl hypochlorite is a well characterised intermediate. It is possible that it would decompose to give chlorine atoms which could abstract hydrogen to form hydrogen chloride



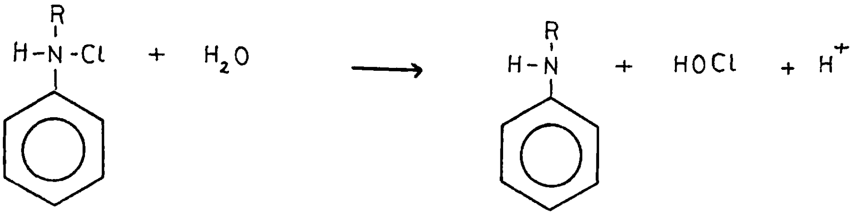
.... (37)

Another possible chlorinating species is the protonated N-chloroanilide.



.... (38)

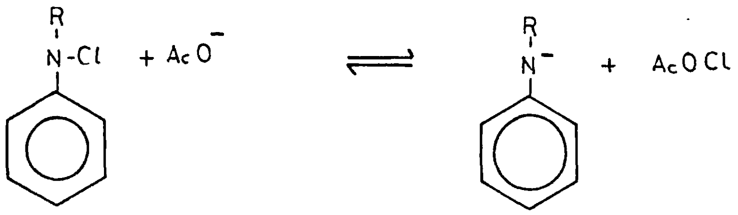
Protonation of the N-chloroanilide would be expected to be the rate-determining step[96], consequently the reaction would be of the first-order with respect to the N-chloroanilide and experiments showed that this was the case. Hydrolysis of the protonated N-chloroanilide would give rise to hypochlorous acid (equation 39) which is a potential source of hydrogen chloride.



.... (39)

In view of the size of the protonated N-chloroanilide it would be expected to give a relatively low o:p ratio, which is consistent with the ratio of monochloroanilides obtained for the reaction carried out with nitrogen passing through the solution.

In the reaction catalysed by silver acetate, there is a relatively powerful nucleophile in the solution (the acetate ion), and an equilibrium could be set up as follows:-



.... (40)

Chlorination of this acylamino-anion would be expected to lead to a high o:p ratio, firstly because the negative charge would be concentrated on the amino-end of the molecule (the more electronegative end) and secondly because chlorine acetate is known to give rise to high o:p ratios.[97] It would also explain the high proportion of 2,4-dichloro- and 2,4,6-trichloro-anilide in the products because the anions derived from p-chloro-, o-chloro- and 2,4-dichloro-anilide are more stable than that derived from the anilide itself. The formation of the anion would be expected to be the rate determining step, and consequently, in agreement with the experimental results the reaction would be of the first-order with respect to both the acetate and N-chloroanilide.

3.2. The Rearrangement of N-Chloroanilides in Carbon Tetrachloride Catalysed by Hydrogen Chloride.

3.2.1. The Products of the Rearrangement.

The results of the study of the products of the rearrangement of several N-chloroanilides in the presence of hydrogen chloride are summarised in Table 37. The values obtained by previous workers in experiments with certain other N-chloroamides are included for comparison.

Table 37

Products of the Rearrangement of N-Chloroanilides, catalysed by Hydrogen Chloride in Carbon Tetrachloride.

N-Chloroanilide	Temperature (°)	Yield (%)	o:p
N-Chloroacetanilide[6], aq	20	82	1:2.75
N-Chloroacetanilide[6], aq	80	78	1:2.30
N-Chlorophenylacetanilide, aq	80	96	1:2.09
N-Chlorophenylacetanilide, an	77		1:3.45
N-Chlorobenzanilide, aq	20	82	1:8.05
N-Chlorobenzanilide, aq	77	90	1:4.86
N-Chlorobenzanilide, an	77	-	1:5.32
N-Chloromethanesulphonanilide[5], an	77	-	1:1.45
N-Chlorobenzenesulphonanilide[5], aq	20	90	1:0.78

aq the reaction was catalysed by aqueous hydrogen chloride

an the reaction was catalysed by anhydrous hydrogen chloride

The rearrangement of N-chlorobenzanilide, catalysed by concentrated hydrochloric acid acid, was carried out so that the ratio of products from this reaction could be compared with those determined by previous workers for other N-chloroanilides. The products of the rearrangement in which the catalyst was anhydrous hydrogen chloride, were also analysed, and a comparison of the products of the isomerisations catalysed by aqueous and anhydrous hydrogen chloride shows that water has only a relatively small effect on the composition of the products.

It can be seen that temperature had a considerable influence on the proportions of the products formed. As in the case of the rearrangement in glacial acetic acid, the o:p ratio was found to be greater at higher temperatures, although this effect was less marked with carbon tetrachloride as solvent.

The results show that the nature of the acyl group of the N-chloroanilide has a marked influence on the product ratios when carbon tetrachloride is used as the solvent. This is in contrast to the results obtained when glacial acetic acid was used, when there was only a small variation in the proportions of products for different N-chloroanilides. However, in both solvents, the proportion of o-isomer was greater for the N-chlorosulphonanilides than for the other N-chloroanilides studies. Another difference between the reactions in the two solvents is the considerably higher yield of 2,4-dichloro- and 2,4,6-trichloro-anilides obtained when carbon tetrachloride is used. Since molecular chlorine was detected in the effluent gas, it seems reasonable to assume that the rearrangement in carbon tetrachloride proceeded by essentially the same mechanism as in glacial acetic acid. However, the differences in the proportions of products indicate that marked solvent effects are involved.

The difference in the o:p ratio of monochloroanilides formed by the chlorination of benzanilide and that for the rearrangement of N-chlorobenzanilide catalysed by hydrogen chloride under comparable conditions, indicates that the mechanism of the chlorination step is not the same in the two cases. Dewar[32] has suggested that, in non-polar solvents, ionic reactions take place within aggregates of polar molecules. The reaction between hydrogen chloride and N-chlorobenzanilide in carbon tetrachloride would be expected to take place in such aggregates of molecules. It is possible that not all the chlorine formed by the reaction would become entirely free from the anilide but would be retained within the aggregate. Such chlorine would be expected to be associated with the "polar" region of the anilide molecules and hence to attack the o-position preferentially. This would account for the percentage of o-chloroanilide obtained from the reaction between N-chlorobenzanilide and hydrogen chloride, which is higher than that formed by intermolecular chlorination of the anilide. The percentage of o-isomer formed by the rearrangement of N-chlorobenzanilide catalysed by aqueous hydrogen chloride was somewhat higher than that obtained by the rearrangement catalysed by anhydrous hydrogen chloride. This is consistent with the involvement of aggregates of molecules, since the water would be expected to stabilize such aggregates and to favour the retention of chlorine within them.

3.2.2. The Kinetics of the Rearrangements

Longmaid[25] showed that the reaction between hydrogen chloride and diphenyl N-chloro-N-phenylphosphoramidate, carried out in a sealed vessel to prevent loss of chlorine and hydrogen chloride, was first-order with respect to the N-chloroamide, whereas the kinetics did not follow a simple rate equation when the reaction was carried out in an open vessel. Because of the difficulties involved in following the kinetics using a closed vessel at 77°, hydrogen chloride was passed through the solution throughout the reaction. In this way the solution was saturated with hydrogen chloride and so the concentration of gas was kept constant throughout the experiment. The results (section 2.4.4.) confirm those obtained by Longmaid[25], since each of the reactions follows first-order kinetics. The rate constants for the rearrangement of each N-chloroanilide are given in Table 38.

Table 38

Rate constants for the Rearrangements of N-Chloroanilides in Carbon Tetrachloride catalysed Hydrogen Chloride.

N-Chloroacetanilide	k_o sec^{-1} M^{-2}
N-Chloroacetanilide	250
N-Chlorophenylacetanilide	120
N-Chlorodiphenylacetanilide	90
N-Chlorobenzanilide	50
N-Chloromethansesulphonanilide	0.80
N-Chlorobenzenesulphonanilide	0.10

The relatively low rate of reaction of the N-chlorosulphonanilides with hydrogen chloride can be explained on the basis of a reduction of electron-density on the nitrogen atom caused by the electron-withdrawing effect on the sulphonyl group. This would retard the attack by electrophiles, such as hydrogen chloride or the hydrogen ion.

3.3. The Thermal Rearrangement of N-Chloroanilides in Nitrobenzene.

3.3.1. The Kinetics of the Reactions.

The rate-graphs and the corresponding logarithmic plots (section 2.3.2.) for the rearrangements of the eight N-chloroanilides studied each show characteristics of autocatalysis, similar to those observed for the reactions in acetic acid (section 2.3.) and for the photolyses (section 2.7.). The passage of nitrogen through the reaction mixture removed appreciable quantities of hydrogen chloride and chlorine, and suppressed the features of autocatalysis, so that the decomposition of each N-chloroanilide then closely followed first-order kinetics. Thus it was considered probable that the rate-equation for thermal decomposition, in this solvent, was similar to that for the reaction in acetic acid, being made up of two terms; one term corresponding to the initial reaction and of the first-order with respect to the N-chloroanilide, and the second corresponding to the reaction catalysed by hydrogen chloride, and of the first-order with respect to the N-chloroanilide but dependent also on the concentration of the products. Each reaction was, in fact, found to obey the same rate-equation (equation 33) as for the decompositions in acetic acid. The rate constants (k_i and k_{ii}), which were determined as described previously (section 3.1.2.) are given in Table 39.

The nature of the acyl group of the N-chloroanilide influences the rate constant of the initial reaction (k_i) and it appears that the more electron withdrawing the acyl group, the greater the rate constant.

Table 39

Rate Constants of the Thermal Rearrangement of N-Chloroanilides alone, in Nitrobenzene, at 156° in the dark

$NCX_o = 0.0100M$

N-Chloroanilide	k_i $sec^{-1} \times 10^{-4}$	k_{ii} $sec^{-1}M^{-2}$	k_o $sec^{-1}M^{-2}$	m
N-Chlorobenzanilide	0.74	0.15	50	2.9×10^{-3}
N-Chloroacetanilide	0.016	4.4	250	1.8×10^{-3}
N-Chlorodiphenylacetanilide	0.67	0.66	90	7.3×10^{-3}
N-Chlorophenylacetanilide	0.29	0.29	120	2.4×10^{-3}
N-Chloromethanesulphonanilide	1.1	0.42	0.8	0.53
N-Chlorobenzenesulphonanilide	4.5	0.10	0.10	1.03
N-Chloro-4'-nitrobenzanilide	1.12	0.13	-	-
N-Chloro-4-nitrobenzanilide	0.92	0.10	-	-

The latter term in the rate-equation (equation 33), which corresponds to the hydrogen chloride catalysed reaction, is of a similar form to the rate-equation for the "Orton" rearrangement (equation 3). Since both terms represent the same reaction, they may be equated

$$k_o\ [NCX]\ [HCl]^2 = k_{ii}\ [NCX]\ ([NCX]_o - [NCX])^2 \qquad \ldots.\ (41)$$

therefore $$k_{ii} = \frac{k_o\,[\mathrm{HCl}]^2}{([\mathrm{NCX}]_o - [\mathrm{NCX}])^2} = k_o\,m^2 \qquad \ldots.\ (42)$$

where k_o is the rate constant for the "Orton" rearrangement (equation 3)

and $$m = \frac{[\mathrm{HCl}]}{[\mathrm{NCX}]_o - [\mathrm{NCX}]}$$

thus m is a measure of the ease of formation of hydrogen chloride in the side reaction.

As it was not possible to determine values of the rate constant for the rearrangement, catalysed by hydrogen chloride, of each N-chloroanilide, in nitrobenzene at 156°, values for the corresponding reaction in carbon tetrachloride at 77° (section 2.4.), were used to calculate m for each N-chloroanilide, and these values are given in Table 39. It must be remembered that the relative magnitudes of k_o for the reactions of the various N-chloroanilides, in nitrobenzene, at 156° might be significantly different from those determined in carbon tetrachloride at 77°. All the values of k_{ii} are of the same order of magnitude. However, the N-chlorosulphonanilides, in fact, react more slowly with hydrogen chloride, but this is compensated by the more rapid production of hydrogen chloride from the products of their rearrangements, as is indicated by the relatively high values of m for these N-chloroanilides.

Analysis of the gases removed by the passage of nitrogen revealed that chlorine and hydrogen chloride were present, and that the total number of moles of chlorine removed was greater for the reaction of N-chloroacetanilide than for the reaction of N-chlorobenzanilide. This would be expected since the autocatalytic effect was greater for N-chloroacetanilide than for N-chlorobenzanilide. For the rearrangement of each N-chloroanilide, the molar ratio of chlorine to hydrogen chloride, removed from the solution by the passage of nitrogen, indicated that the reaction between hydrogen chloride and the N-chloroanilide is slower, under these conditions, than chlorination of the anilide.

The rate-curves for the thermal rearrangement of four N-chloroanilides, in nitrobenzene, with nitrogen passing through the solutions, show first-order kinetics for a considerable part of the total reaction . These reactions were carried out at five temperatures and the values of k_1 obtained were used to calculate the energies of activation (Fig. 90 Table 41)

Table 40

The Energy of Activation and the Pre-exponential factor of the Thermal Rearrangement of N-Chloroamides in Nitrobenzene

N-Chloroanilide	E_a kcals/mole	A
N-Chloroacetanilide	35.5	18.4
N-Chlorobenzanilide	32.0	12.5
N-Chlorobenzenesulphonanilide	31.5	13.4
N-Chloromethanesulphonanilide	23.3	8.0

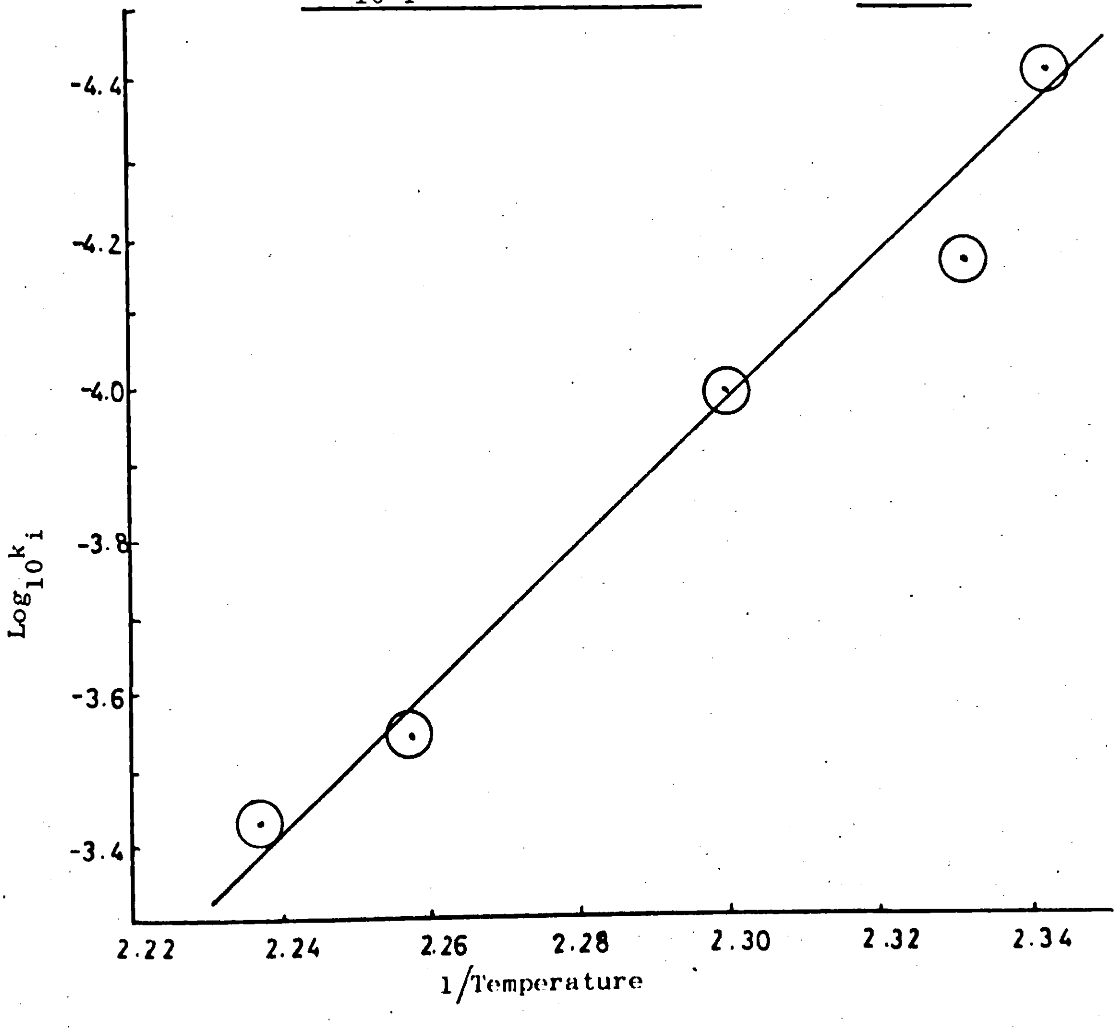
The relatively low energy of activation of the reaction of N-Chloromethanesulphonanilide may well be due to the strongly electron-withdrawing methanesulphonyl group weakening the N-Cl bond.

The Thermal Rearrangement of N-Chlorobenzanilide in Nitrobenzene.

Table 41

Temperature of the Reaction (°C)	(°K)	$\frac{1}{T} \times 10^3$	$-k_i$	$\mathrm{Log}_{10} k_i$
174	447	2.237	3.70×10^{-4}	-3.43
170	443	2.257	2.88×10^{-4}	-3.54
162	435	2.299	1.02×10^{-4}	-3.99
156	429	2.331	6.98×10^{-5}	-4.16
154	427	2.342	6.01×10^{-5}	-4.22

$\mathrm{Log}_{10} k_i$ v 1/Temperature Fig. 90



3.3.2. The Products of the Rearrangement.

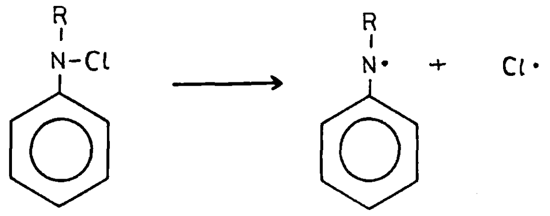
The kinetics of the decomposition of each *N*-chloroanilide have indicated that two reactions are involved, a homolytic process, and a heterolytic reaction which is catalysed by hydrogen chloride. The results of the analysis of the products of the rearrangements (Table 24, page 91) are consistent with this view, since the *o*:*p* ratio was considerably reduced by the passage of nitrogen, which is known to suppress the reaction catalysed by hydrogen chloride, and this latter reaction has been shown to give rise to a relatively high *o*:*p* ratio. Relatively high yields of 2,4-dichloro- and 2,4,6-trichloro-anilide and residue were obtained when nitrogen was passed through the solution, indicating that the rearrangement was then proceeding almost entirely by a homolytic mechanism. In contrast, the products of the reaction, catalysed by hydrogen chloride, contained only small proportions of di- and tri-chloroanilides and residue.

3.3.3. The Mechanism of the Thermal Rearrangement of N-Chloroanilides.

Beard, Boocock and Hickinbottom[3] have obtained evidence that the rearrangement takes place by a homolytic mechanism. In the present work it was found that the rate-curves for the thermal and photolytic reactions were similar and, as the latter reaction has been shown by several workers[2,4,6] to involve free radicals, it can be assumed that the thermal reaction, in the initial stages at least, proceeds homolytically. The following mechanistic scheme for the photolytic reaction has been proposed by Hodges[43], and modified by Tanner and Protz[44], Coulson, Williams and Johnston[6], and Atkins[46], and is also the most probable scheme for the thermal rearrangement.

(i) Chain Initiation.

This reaction involves homolytic cleavage of the N-Cl bond (equation 42)



.... (42)

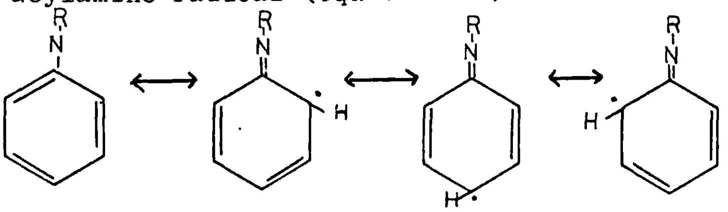
Robertson and Waters[38] have commented on the symmetrical nature of this bond, and have shown that it is susceptible to homolytic fission. A strongly electron-withdrawing group (R) would be expected to weaken the N-Cl bond, thus making it more susceptible to thermal cleavage. This is the probable reason for the relatively low energy of activation of the thermal rearrangement of the N-chloroanilides.

(ii) Chain Propogation.

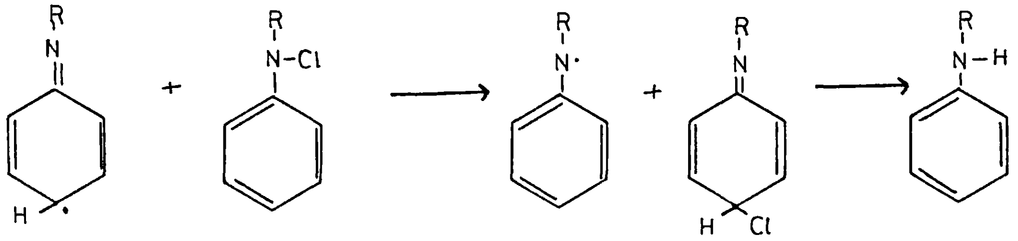
Four chain propogation reactions have been suggested:-

(a) The acylamino-radical as the chain carrier.

The acylamino-radical, which is a product of the homolytic cleavage of the N-Cl bond, is stabilized by mesomerism (equation 43), and can abstract chlorine from a molecule of the N-chloroanilide, generating a new acylamino-radical (equation 44)



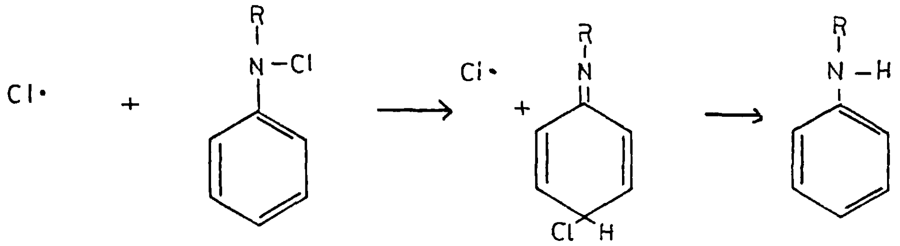
.... (43)



.... (44)

(b) The chlorine atom as the chain carrier.

This involves a 1.5 displacement of the chlorine atom of the N-chloroanilide in the following manner:-

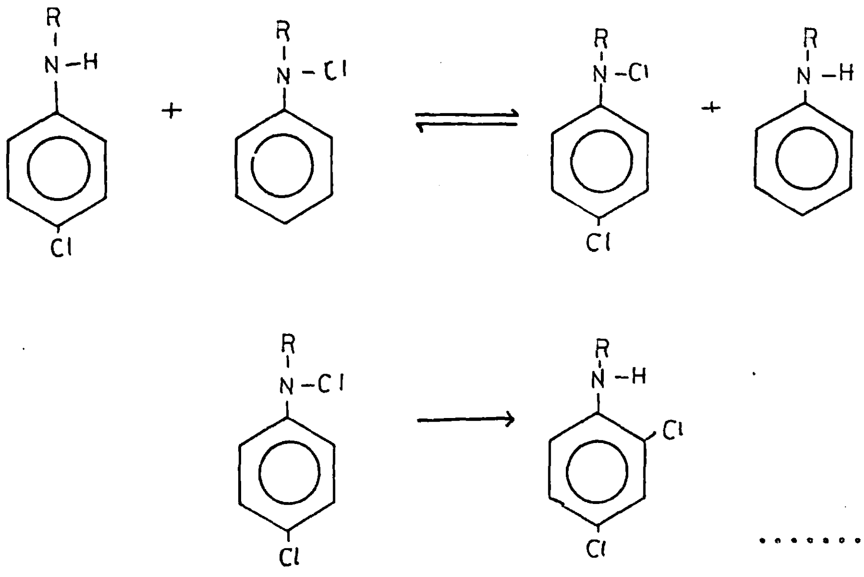


.........(45)

The displacement could be a one-step process involving a concerted addition-elimination reaction, or it could be a two stage reaction. An analogous 1.3 displacement could give the 2-chloroanilide, but the 3-chloroisomer could not be obtained by this mechanism.

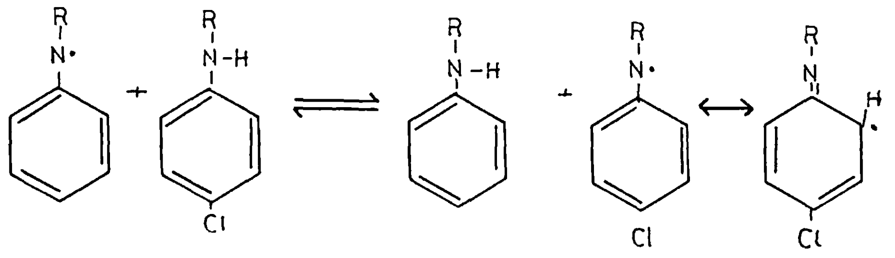
(c) An exchange mechanism

A mechanism of this type is required to explain the presence of 2,4-dichloro- and 2,4,6-trichloro-anilide in the products of the rearrangement. Two mechanisms are: firstly an exchange between the chlorine of the N-chloroamide and the hydrogen of the mono-nuclear-chlorinated anilide (equation 46)

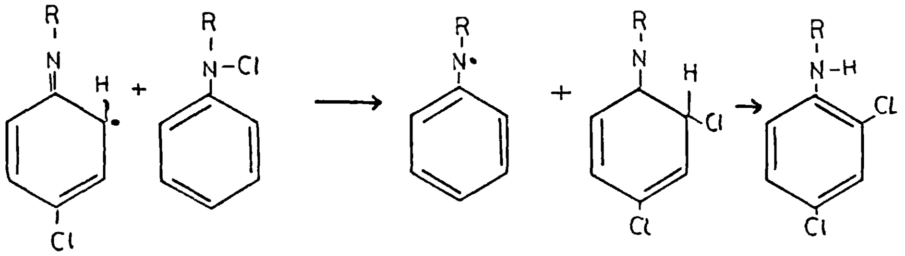


............(46)

and secondly abstraction of the N-hydrogen of a monochloroanilide by an acylamino-radical, yielding a chlorinated acylamino radical, which could then give rise to the dichloroanilide (equations 47 and 48)



.............(47)

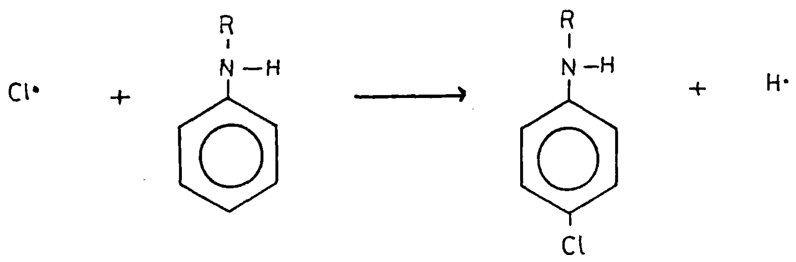


.............(48)

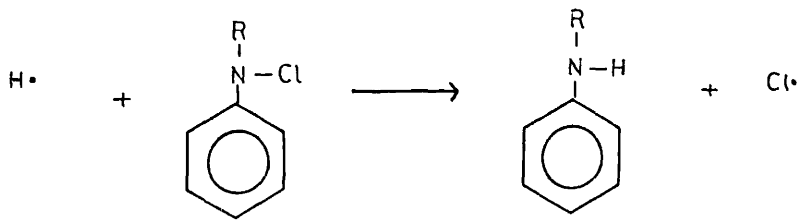
The latter mechanism appears the more reasonable. A similar reaction scheme can be postulated to explain the presence of 2,4,6-trichloroanilide in the products of the reaction.

(d) Chlorine and hydrogen atoms as chain carriers.

Hodges[43] has suggested a mechanism which involved free hydrogen and chlorine atoms (equations 49 and 50)



.............(49)

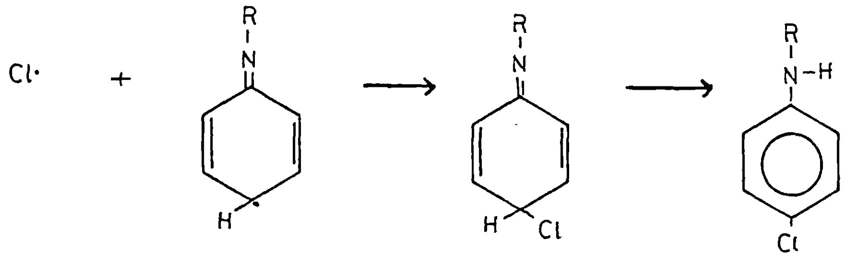


.............(50)

This scheme must be discounted as it involves a strongly endothermic reaction (equation 49) and would also be expected to give rise to some 3-chloroanilides, which were never detected among the products of the rearrangements.

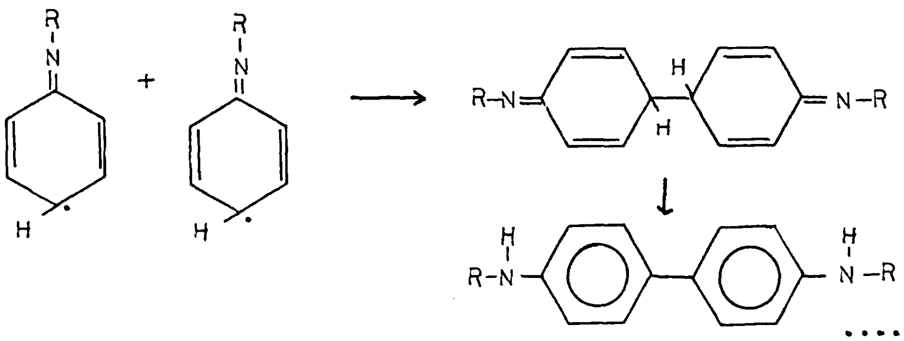
(iii) Chain Termination.

Radical-radical reactions, such as coupling or disproportionation, could occur between any of the free radical intermediates which are involved in the reaction, for example:-



.............(51)

An analogous reaction could occur to give 2-chloro- or N-chloro-anilide. Reactions between two acylamino-radicals are the most probable chain termination steps as the acylamino-radical is a less reactive intermediate than the chlorine atoms.



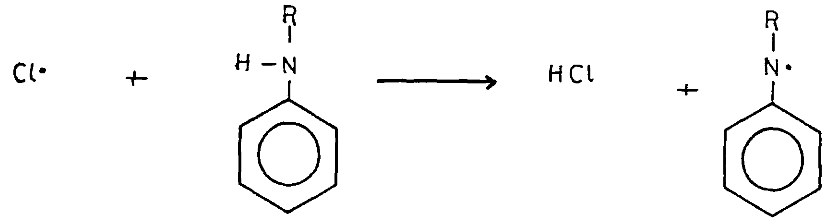
............(52)

The acylamino-radical can react as though the odd electron were at the N-, or the ortho-, or the para-position. Thus all the permutations of coupling (N-o, o-p etc.) are possible and several have been isolated by Hodges[43], from the photolytic reaction. Evidence for the nitrogen-nitrogen dimer being a product of the photolytic reaction has been criticised by later workers[106].

(iv) The Origin of the Hydrogen Chloride

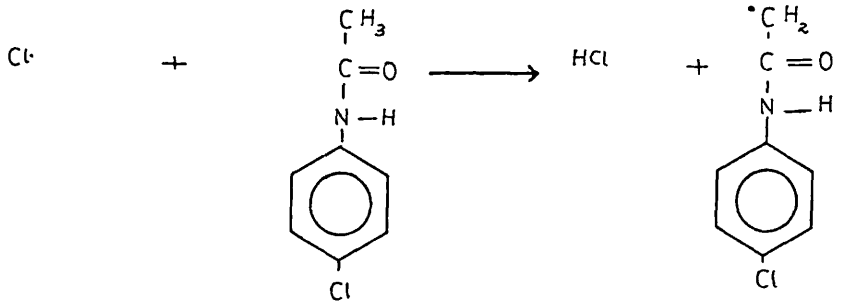
Coulson, Williams and Johnston[6] have shown that for the photolyses of N-chloroacetanilide, the products of the rearrangement appear to be involved in the formation of hydrogen chloride. The rate equation (equation 33) and studies of the photolytic and thermal rearrangements in the presence of added anilides confirm this view. Abstraction by a chlorine atom, of either the N-hydrogen of the product of the rearrangement (equation 53)

e.g.



.............(53)

or a hydrogen from the acyl group, for example the acyl group in p-chloroacetanilide (equation 54),



.............(54)

is the most probable mode of formation of hydrogen chloride. Abstraction of an aromatic hydrogen atom by a chlorine atom would be unlikely as it would not be highly endothermic.

The relative ease of formation of hydrogen chloride, from the products of the thermal rearrangement, has been deduced for each N-chloroanilide (Table 39). Since both N-chlorosulphonanilides have similar high values of m, it would seem likely that abstraction of the

N-hydrogen from the products of the rearrangement of N-chlorobenzenesulphonanilide was the more important reaction, as the chlorobenzenesulphonanilide have no abstractable hydrogen atoms in the acyl group. The strongly electron-withdrawing sulphonyl group would be expected to weaken the N-hydrogen bond of the products of the reaction, making it more susceptible to abstraction by chlorine atoms.

3.4. The Thermal Rearrangement of N-Chloroanilides in the presence of of Added Anilides.

3.4.1. The Kinetics of the Rearrangement.

Each of the reactions studied exhibited autocatalysis, and closely obeyed the same rate equation (equation 33) as the thermal rearrangement. Values of the rate constant (k_{ii}) and of the approximate total time of the thermal rearrarrangement of N-chlorobenzanilide, in the presence of added anilides, are given in Table 42. The results clearly indicate that the structural features of the anilides have a profound effect on the kinetics of the reaction.

In order to demonstrate that hydrogen chloride was formed in a side reaction and was at least partly responsible for the increase in rate, experiments were carried out, in which dry nitrogen was passed through the solution, throughout the reaction. The results (Table 25, page 101) show that appreciable quantities of hydrogen chloride and chlorine were formed during the reaction. Bell and Danckwerts[28], and Coulson[5] have observed that the presence of only a small quantity of hydrogen chloride would cause a marked increase in rate, owing to incursion of rearrangement by the "Orton" mechanism. It is therefore probable that the presence of hydrogen chloride is responsible for the autocatalysis. In agreement with this conclusion, the rate of rearrangement of the N-chlorobenzanilide was found to be considerably reduced by the passage of nitrogen (fig. 47), and to be dependent on the nitrogen flow-rate, though for each experiment, the nitrogen had no significant effect on the initial rate of reaction or on the temperature of the reaction mixture. It is interesting to note that analysis of the volatile products (Table 25) shows that a larger quantity of hydrogen chloride was removed than chlorine. This indicates that the reaction between hydrogen chloride and N-chlorobenzanilide is probably rate determining, and hence the rate of chlorination of the

Table 42

The Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114° in the presence of Added Anilides, in the dark.

$[NCB]_o$ = 0.070M $[X]_o$ = 0.035M

Added Anilide (X)	k_{ii} $sec^{-1}M^{-2} \times 10^{-2}$	Time of Reaction hr.
-	0.18	290
Acetanilide	2.12	31
Acetanilide*	0.33	72
N-Methylacetanilide	0.42	120
N-Phenylacetanilide	0.38	130
2-Phenylacetanilide	1.29	47
2,2-Diphenylacetanilide	1.34	49
2,2,2-Trichloroacetanilide	0.29	200
Formanilide	1.97	28
Benzanilide	0.70	85
N-Phenylbenzanilide	0.26	220
2'-Chlorobenzanilide	0.34	210
4'-Chlorobenzanilide	0.60	102
4'-Fluorobenzanilide	0.71	80
4'-Bromobenzanilide	0.61	105
4'-Iodobenzanilide	22.4	3
4'-Phenylbenzanilide	0.73	82
4'-Phenoxybenzanilide	1.09	57
4'-Nitrobenzanilide	0.43	118
4'-Benzoylbenzanilide	0.74	69
4-Nitrobenzanilide	1.94	32
4-Chlorobenzanilide	1.34	51
Methanesulphonanilide	17.7	6
Methanesulphonanilide*	7.11	35
N-Methylmethanesulphonanilide	0.38	140
Benzenesulphonanilide	1.83	39
Diphenyl N-phenylphosphoramidate	1.78	40

* Nitrogen was passed through the solution throughout the reaction.

anilides in solution has little effect on the rate of rearrangement.

The proportions of products of the rearrangement are consistent with the view that the increase in rate is due to incursion of the "Orton" rearrangement, and will be discussed at length in a later section (section 3.4.2.).

The effects of the structure of the added anilide on its efficiency as a catalyst may be discussed in terms of the mechanism of formation of the autocatalyst, hydrogen chloride, during the rearrangement. The conclusion has already been reached (section 3.3.4.) in respect of the thermal and photolytic reaction, that the abstraction of the N-hydrogen and to a lesser extent the hydrogen atoms in the acyl group of the products of the rearrangement, was the most probable source of hydrogen chloride. Indeed, it was primarily to test this hypothesis that the experiments were performed in which acetanilide, benzanilide and some of their N-substituted derivatives respectively were added at the start of the reactions.

Since the presence of N-phenylbenzanilide had the smallest effect on the decomposition of the N-chlorobenzanilide, it is probable that abstraction by chlorine atoms of aliphatic hydrogen atoms is a more favourable process than abstraction of aromatic hydrogen atoms. The relative effects of the presence of benzanilide and N-phenylbenzanilide, and acetanilide and N-phenylacetanilide on the kinetics, indicates that abstraction of the N-hydrogen is the most important mode of formation of hydrogen chloride, though a comparison of the rate constants for the experiments in which N-phenylacetanilide and N-phenylbenzanilide were present indicates that abstraction of the hydrogen in the acyl group does take place to a lesser extent. As the rate constants which correspond to the presence of N-phenylacetanilide and N-methylacetanilide are similar, it is probable that abstraction of the hydrogen atoms of the N-methyl group is a relatively insignificant process, and that neither the electron-donating N-methyl group, nor the more bulky, electron-withdrawing N-phenyl group greatly affects the ease of abstraction of hydrogen atoms from the acyl group.

A comparison of the rate constants for added acetanilide, 2-phenylacetanilide and 2,2-diphenylacetanilide indicates that tertiary hydrogen atoms in the acyl group are more easily abstracted than secondary or primary hydrogen atoms. It is probable that the phenyl rings in the acyl groups would donate electrons to the C-hydrogen, increasing the electron density around this atom, making it more easily abstractable by the electrophilic chlorine atom. Tedder[98] and Russell and Brown[99] have shown this to be the case and have also shown that the stability of the resultant radical and the strength of the C-H bond are not major factors in determining the ease of formation of hydrogen chloride, through hydrogen abstraction by chlorine atoms.

The relations between the values of the rate constant (k_{ii}) for the reactions in which acetanililide, 2-phenylacetanilide, 2,2-diphenylacetanilide, benzanilide, methanesulphonanilide and benzenesulphonanilide were added, are closely similar to those between values of m, determined for the photolytic and thermal rearrangements of the corresponding N-chloroanilides. Table 43 gives values for these constants, normalised to acetanilide = 1 for each series. The relatively high values of m for the thermal rearrangement of the N-chlorosulphonanilides (Table 43) may well be due to the use of values of k_o for the reaction in carbon tetrachloride at 77°, in calculating m for the rearrangement in nitrobenzene at 156°. Thus the kinetics of the photolytic and thermal rearrangements may be related, not only to the quantity of hydrogen chloride and chlorine formed during the reactions, but also to the relative ease of abstraction of hydrogen from the parent anilide.

Since abstraction of the N-hydrogen of the products of the

Table 43

Rate Constants for the Thermal Rearrangement of N-Chlorobenzanilide in the presence of Added Anilide, and Values of m for the Photolytic and Thermal Rearrangements.

Values for each reaction are normalised to acetanilide = 1.

Anilide	k_{ii} for the thermal rearrangement of N-chlorobenzanilide in the presence of added anilides at 114°. Table	m for the photolytic rearrangement of N-chlorobenzanilide in the presence of added anilides at 76°. Table	m for the thermal rearrangement of the corresponding N-chloroanilide in nitrobenzene at 156°. Table	m for the photolytic rearrangement of the corresponding N-chloroanilide in carbon tetrachloride at 76° Table
Acetanilide	1	1	1	1
Benzanilide	0.46	0.08	1.6	0.09
2-Phenylacetanilide	0.73	-	1.2	1.1
2,2-Diphenylacetanilide	1.3	-	4.0	2.2
Benzenesulphonanilide	1.6	1.5	570.	9.
Methanesulphonanilide	13.	2.4	290.	11.

products of the rearrangement, by chlorine atoms, appears to be the most important process in the formation of hydrogen chloride during photolyses or thermal reactions, the electronic features which affect this process were investigated in a series of experiments in which derivatives of benzanilide were added at the start of the experiment. Benzanilide was chosen as the standard because it has no abstractable hydrogen atoms in the acyl group. Electron-withdrawing substituents in the aniline ring were found to reduce the value of the rate constant (k_{ii}) as compared with benzanilide, presumably by reducing the electron density on the _N_-hydrogen, for this has been shown to be the most important factor in determining the ease of abstraction[97,98]. Conversely, electron donating substituents caused increases in the values of the rate constant, by increasing the electron density around the _N_-hydrogen. The results are correlated by the Hammett $\sigma\rho$ relationship (Table 44, Fig. 91) . The value of ρ (-0.90) is similar to that obtained by Walling and Miller[100] for the photochlorination of substituted toluenes at 69° by molecular chlorine ($\rho = -0.76$), but somewhat smaller than that obtained by Kooyman[101] for the free-radical chlorination of substituted toluenes by sulphuryl chloride ($\rho = -1.50$). This indicates that the rate limiting step in each of these reactions are similar, that is they involve abstraction of a hydrogen by electrophilic chlorine atoms. The variation in relative reactivities for these reactions may be partly due to the effect of temperature, and partly to solvent effects[100]. The influence of polar forces on the rate of abstraction is thus clearly indicated.

The relatively low value of k_{ii}, obtained for the reaction in which 2'-chlorobenzanilide was present could have been due to steric blocking of the _N_-hydrogen, or to hydrogen bonding between the _N_-hydrogen and the chlorine, both of which would be expected to reduce the ease of abstraction of the _N_-hydrogen by a chlorine atom. Benzanilide and 4'-chlorobenzanilide were more effective in causing the formation of

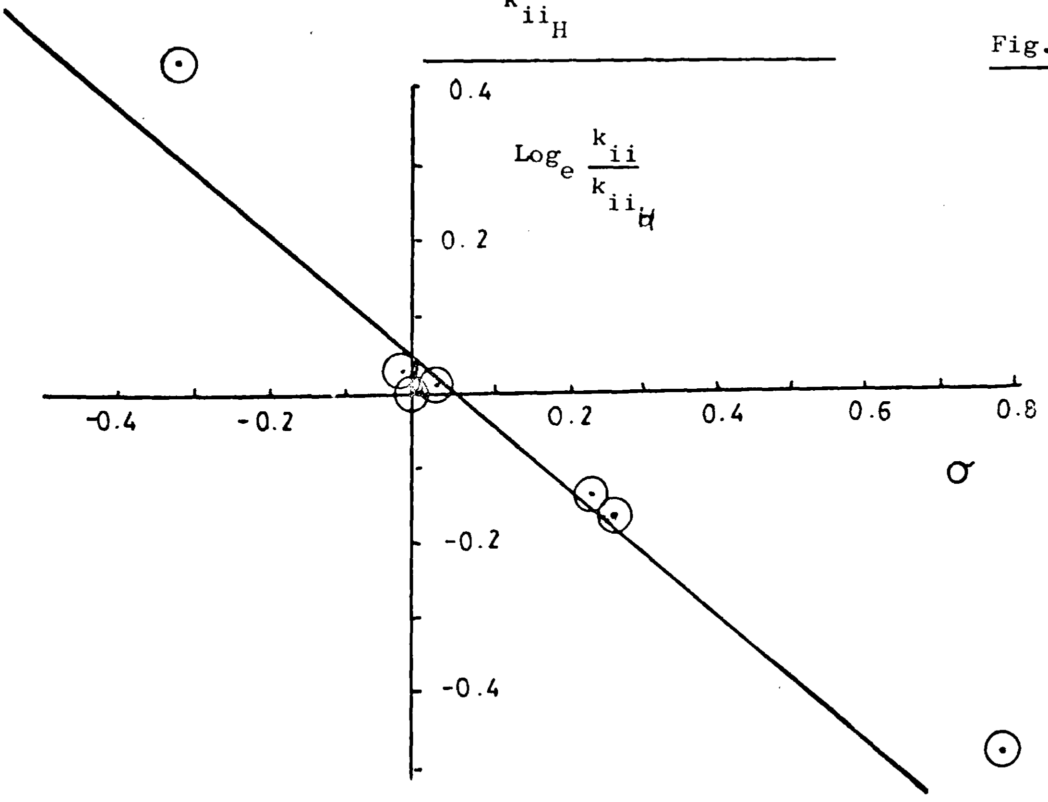
Correlation of the Rate Constants for the Rearrangement of N-Chlorobenzanilide in the presence of Added 4'-Substituted Benzanilides by the Hammett Equation.

Table 44

Substituent	k_{ii} $\sec^{-1}M^{-2} \times 10^{-2}$	$\frac{k_{ii}}{k_{ii_H}}$	$\log_e \frac{k_{ii}}{k_{ii_H}}$	σ
H	0.70			0.0
NO_2	0.43	0.62	-0.484	+0.78
PhO	1.09	1.56	0.447	-0.32
Ph	0.73	1.04	0.039	-0.01
F	0.71	1.01	0.010	+0.06
Cl	0.60	0.85	-0.163	+0.237
Br	0.61	0.87	-0.140	+0.232

$\text{Log}_e \frac{k_{ii}}{k_{ii_H}}$ v σ

Fig. 91

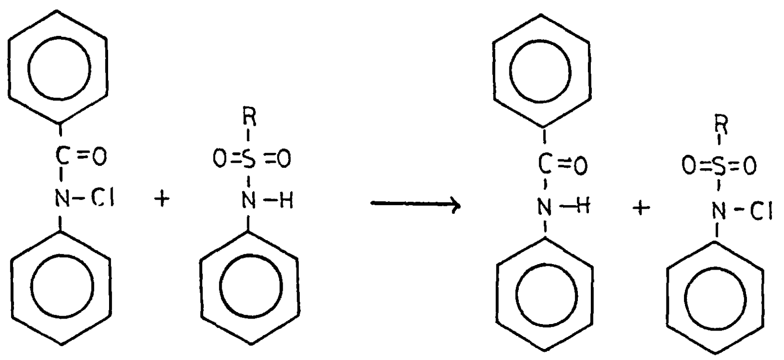


hydrogen chloride than 2'-chlorobenzanilide. Since hydrogen chloride has been shown to be partly responsible for the features of autocatalysis observed in the free-radical initiated rearrangement of several N-chloroanilides, it would be expected that those reactions which give rise to a relatively low o:p ratio, such as the reaction catalysed by benzoyl peroxide, would show autocatalysis to a greater extent.

The presence of added anilides with strongly electron-withdrawing acyl groups, such as the sulphonanilides, formanilide, and 4-nitrobenzanilide, brought about relatively fast reactions. However, it would be expected that such an acyl group would reduce the electron density around the N-hydrogen, making it less susceptible to abstraction. In these somewhat anomalous cases, the increased ease of formation of hydrogen chloride may be due to weakening of the N-hydrogen bond.

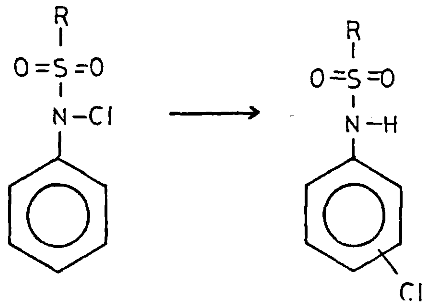
Although 2,2,2-trichloroacetanilide has an extremely powerful electron-withdrawing acyl group, the rearrangement of N-chlorobenzanilide in the presence of this anilide was extremely slow. This was probably due to the fact that abstraction of the N-hydrogen, by the chlorine atom, was hindered not only by the bulky acyl group, but also by hydrogen bonding between the N-hydrogen and the chlorine atoms of the acyl group.

The relative values of the rate constants for the experiments in which methanesulphonanilide and N-methylmethanesulphonanilide were present during the reaction, clearly indicate that the N-hydrogen was involved in this increase in rate. In view of the very rapid reaction when the sulphonanilides were present, and the fact that the rate of each of these reactions was similar to that of the thermal decomposition of the corresponding N-chloroanilide, in nitrobenzene, (section 2.6.2.), it was thought possible that a rapid exchange reaction may have taken place (equation 55) similar to that suggested by Ford, Hunt and Waters[47] for the reaction of p-N-chloroacetamidotoluene, in the presence of free radicals.



................(55)

The kinetics which were being followed could then have been those of the decomposition of the N-chlorosulphonanilides (equation 56).



...............(56)

However, the shape of the rate curves for the rearrangement of the two N-chlorosulphonanilides, in chlorobenzene, at 114°, were different from those of the reactions of N-chlorobenzanilide, in the presence of the corresponding sulphonanilide (Fig.50). Since no significant reaction occurred when benzanilide and N-chloroacetanilide were heated at 114° in chlorobenzene in the dark (Fig. 49), little exchange could have occurred between these anilides, and consequently, it is unlikely that exchange between the N-chlorobenzanilides was rate limiting. The passage of nitrogen through a solution of N-chlorobenzanilide and methanesulphonanilide not only removed appreciable quantities of hydrogen chloride and chlorine, but also caused a decrease in the rate constant (k_{ii}), and it was therefore concluded that hydrogen chloride, which appeared to be responsible for the autocatalysis, was formed in a similar way for all the added anilides studied, that is by abstraction of the non-aromatic hydrogen atoms by free chlorine atoms.

3.4.2. The Products of the Rearrangements of N-Chlorobenzanilide, in Chlorobenzene, at 114°.

The kinetics of the rearrangement of N-chlorobenzanilide in the presence of added benzanilide indicates that two mechanisms are involved. The proportion of chloroanilides formed in this reaction (o:p 1:7.10) is a little lower than that obtained for the reaction catalysed by hydrogen chloride (o:p 1:6.98), and slightly higher than that obtained for the photolytic reaction (o:p 1:6 69) during which nitrogen was passed through the solution, for this latter reaction has been shown to proceed predominantly by the homolytic mechanism. The high yields of 2,4-dichloro- and 2,4,6-trichloro-anilide and of tarry material, obtained in the photolyses, are characteristic of reactions which involve free radicals. The products of the other reactions contained relatively low yields of each of these substances, indicating that the thermal rearrangement, in the presence of added anilides, proceeds predominantly by a heterolytic mechanism.

3.5. The Photolytic Rearrangement

The photolytic rearrangement of N-chloroacetanilide was found, by Coulson, Williams and Johnston[6], to be subject to autocatalysis and hydrogen chloride and was shown to be responsible for the deviation from first-order kinetics. However, the corresponding reaction of N-chlorobenzenesulphonanilide[5] appeared to closely follow a simple first-order law.

N-Chloroanilides were chosen for the present studies in order to discover whether there was a relationship between the nature of the acyl group in the anilide and the extent of autocatalysis during the reaction.

3.5.1. The Kinetics of the Rearrangement.

The rate-curves and the corresponding logarithmic plots for the photolytic rearrangement of N-chlorophenylacetanilide and N-chlorodiphenylacetanilide clearly exhibit autocatalysis, whereas the rearrangements of N-chlorobenzanilide and N-chloromethanesulphonanilide showed only a small deviation from simple first-order kinetics. Each kinetic run followed the rate equation which had been deduced for the thermal rearrangement, and values of the rate constants, which were calculated as described previously (section 3.1.2.), are given in Table 45. The corresponding rate constants for N-chloroacetanilide[6] and N-chlorobenzenesulphonanilide[5] are also given for comparison.

The kinetics of each reaction were found to be closely similar to those predicted by the rate-equation, and the values of k_i were similar for all of the N-chloroanilides. However, the agreement for values of rate constants using different initial concentrations was not very good, and this may indicate that the rate equation (equation 33) does not, in fact, fully express the kinetics of these reactions.

The initial rate constants (k_i) decrease with increasing initial concentration of the N-chloroanilide, for each N-chloroanilide studied in the present work. In contrast to these results, Coulson, Williams and Johnston[6] have observed that the rate constant for the analogous reaction of N-chloroacetanilide increases with increasing initial concentration of this N-chloroanilide, and have suggested that this may be due to induced decomposition of the N-chloroanilide by radicals, in addition to the primary scission of the N-Cl bond. However, this does not explain the present results. The decrease in rate constant must be caused by either a decrease in the rate of cleavage of the N-Cl bond, or a decrease in the length of the radical chain, caused by the presence of a greater concentration of anilides, by chain propagation steps becoming less favourable with respect to chain termination steps. It would therefore be expected that the presence of an added anilide would decrease the initial rate of rearrangement of the N-chloroanilide. In the present work, the presence of added anilides appears to have little significant effect on the initial rate of reaction for the photolysis, although Coulson, Williams and Johnston[6] observed that the presence of added p-chloroacetanilide caused a significant decrease in the initial rate of reaction for the photolysis of N-chloroacetanilide.

The rate curves for the photolytic rearrangements of N-chlorophenylacetanilide and N-chlorodiphenylacetanilide showed obvious features of autocatalysis, and when nitrogen was passed through the solutions of these N-chloroanilides during the photolyses, the reactions were slower and some chlorine and hydrogen chloride were removed from the solutions. Hence it appears that some rearrangement by the "Orton" mechanism occurred during these reactions.

Table 45

Rate-Constants for the Photolyses of N-Chloroanilides.

N-Chloroanilide	Conc. M x 10	k_i sec^{-1} x 10^{-5}	k_{ii} $sec^{-1}M^{-2}$	k_o $sec^{-1}M^{-2}$	m
N-Chloroacetanilide[6]	0.95	7.93	2.6 x 10^{-2}	2.5 x 10^{2}	1.0 x 10^{-4}
N-Chloroacetanilide[6]	0.69	7.61	2.7 x 10^{-2}	2.5 x 10^{2}	1.1 x 10^{-4}
N-Chloroacetanilide[6]	0.56	7.16	3.4 x 10^{-2}	2.5 x 10^{2}	1.4 x 10^{-4}
N-Chlorobenzanilide	1.00	3.10	1.0 x 10^{-3}	5.0 x 10	2.0 x 10^{-5}
N-Chlorobenzanilide	0.70	3.52	5.0 x 10^{-4}	5.0 x 10	1.0 x 10^{-5}
N-Chlorobenzanilide	0.40	4.72	5.0 x 10^{-4}	5.0 x 10	1.0 x 10^{-5}
N-Chlorophenylacetanilide	1.00	3.20	1.1 x 10^{-2}	1.2 x 10^{2}	9.3 x 10^{-5}
N-Chlorophenylacetanilide	0.70	4.86	1.5 x 10^{-2}	1.2 x 10^{2}	1.2 x 10^{-4}
N-Chlorophenylacetanilide	0.40	4.96	5.4 x 10^{-3}	1.2 x 10^{2}	4.5 x 10^{-5}
N-Chlorodiphenylacetanilide	1.00	6.18	2.0 x 10^{-2}	9.0 x 10	2.2 x 10^{-4}
N-Chlorodiphenylacetanilide	0.70	6.49	2.2 x 10^{-2}	9.0 x 10	2.5 x 10^{-4}
N-Chlorodiphenylacetanilide	0.40	6.91	7.4 x 10^{-2}	9.0 x 10	8.2 x 10^{-4}
N-Chloromethanesulphonanilide	1.00	5.88	1.5 x 10^{-3}	8.0 x 10^{-1}	1.8 x 10^{-3}
N-Chloromethanesulphonanilide	0.70	7.72	1.0 x 10^{-3}	8.0 x 10^{-1}	1.2 x 10^{-3}
N-Chloromethanesulphonanilide	0.40	12.4	5.0 x 10^{-4}	8.0 x 10^{-1}	0.6 x 10^{-4}
N-Chlorobenzenesulphonanilide[5]	0.70	4.01	1.0 x 10^{-4}	1.0 x 10^{-1}	1.0 x 10^{-3}

The rate constant, k_{ii} (equation 33), has been shown to be related to the rate constant of the "Orton" reaction (equation 3), and the values of m calculated from k_{ii} and k_o for all these reactions are given in Table 45. Although the rate curves for the rearrangement of the N-chlorosulphonanilides show little deviation from first-order kinetics, the values m determined for the N-chlorosulphonanilides are higher than those for other N-chloroanilides. However, it must be remembered that considerable errors were involved in the calculation of m for these reactions. Thus the products of rearrangement of the N-chlorosulphonanilides must have been more effective in giving rise to hydrogen chloride. This fits in with the evidence obtained from the studies of the thermal rearrangement of N-chlorobenzanilide in chlorobenzene, at 114°, in the presence of added anilides (section 3.4.). The relative magnitudes of m for each N-chloroanilide in this reaction are similar to those for the thermal rearrangement when the parent anilides were added at the beginning of the reaction (Table 43). This indicates that hydrogen chloride is formed by the same mechanism in each case. Values of m increase slightly with decreasing initial concentration of N-chloroanilide in each case.

Aspiration with nitrogen partially suppressed the "Orton" rearrangement, by removal of chlorine and hydrogen chloride, and considerably reduced the values of m (Table 46), indicating that the ratio of hydrogen chloride to products in the solution has decreased. In each case, the initial rate was unaffected by the passage of nitrogen. The kinetics of the rearrangement of N-chlorobenzanilide, in which the "Orton" reaction was of little importance were unaffected by the flow of nitrogen. It is therefore probably that the passage of nitrogen has no other significant effect, other than removal of hydrogen chloride and chlorine.

Table 46

Rate Constants for the Photolytic Rearrangement of N-Chloroanilides, aspirated with Nitrogen.

N-Chloroanilide	[NCX] M x 10	N_2 flow $l.hr.^{-1}$	k_i $sec^{-1} \times 10^{-5}$	k_{ii} $sec^{-1}M^{-2}$	k_o $sec^{-1}M^{-2}$	m
N-Chloroacetanilide[6]	0.69	-	7.8	2.7×10^{-2}	2.5×10^{2}	1.1×10^{-4}
N-Chloroacetanilide[6]	0.69	2.	2.8	1.6×10^{-2}	2.5×10^{2}	6.5×10^{-5}
N-Chlorobenzanilide	1.00	-	3.1	1.0×10^{-3}	5.0×10	2.0×10^{-5}
N-Chlorobenzanilide	1.00	1.0	3.1	1.0×10^{-3}	5.0×10	2.0×10^{-5}
N-Chlorophenylacetanilide	1.00	-	3.2	1.1×10^{-2}	1.2×10^{2}	9.4×10^{-5}
N-Chlorophenylacetanilide	1.00	1.0	3.2	6.51×10^{-3}	1.2×10^{2}	5.4×10^{-6}
N-Chlorodiphenylacetanilide	1.00	-	4.9	2.0×10^{-2}	9.0×10	2.2×10^{-4}
N-Chlorodiphenylacetanilide	1.00	1.0	4.9	1.5×10^{-2}	9.0×10	1.8×10^{-4}
N-Chloromethanesulphonanilide	1.00	-	5.9	1.5×10^{-3}	8.0×10^{-1}	1.8×10^{-3}
N-Chloromethanesulphonanilide	1.00	1.0	7.0	1.0×10^{-3}	8.0×10^{-1}	1.2×10^{-3}

The quantities of hydrogen chloride and chlorine removed by the nitrogen, are given in Table 47.

Table 47

Quantities of Hydrogen Chloride and Chlorine Removed by Nitrogen.

N-Chloroanilide	Molar % based on the available chlorine		
	Hydrogen chloride	Chlorine	Total Chlorine
N-Chloroacetanilide[6]	2.4	3.5	9.3
N-Chlorobenzanilide	0.2	0.05	0.3
N-Chlorophenylacetanilide	2.1	1.2	3.4
N-Chlorodiphenylacetanilide	3.4	1.2	5.8
N-Chloromethanesulphonanilide	3.2	1.1	5.4

The high yield of "total chlorine" for the rearrangement of N-Chloromethanesulphonanilide would be expected in view of the high values of m. There is reasonable agreement between the values of m and the quantity of chlorine and hydrogen chloride removed from the photolytic rearrangement.

3.5.2. The Kinetics of the Photolytic Rearrangement in the Presence of Added Anilides.

It can be seen that the presence of added anilides increased the deviation from first-order kinetics for the photolyses (section 2.7.2.) although the initial rate of rearrangement was not affected significantly. Each of these reactions obeyed the rate-equation (equation 33) and the values of the rate constants are given in Table 48. When the anilides are arranged according to their effectiveness in causing an increase in rate, the series is the same as that for the thermal rearrangement in the presence of added anilides, and for the photolysis of the corresponding N-chloroanilides. It therefore seems likely that a similar mechanism for the formation of hydrogen chloride is involved in each of these reactions.

Experiments in which the solutions of N-chlorobenzanilide and added anilides were aspirated with nitrogen indicated that the "Orton" reaction was responsible for the deviation from first-order kinetics. The rate of reaction of N-chlorobenzanilide was considerably reduced, and appreciable quantities of chlorine and hydrogen chloride were removed from the solution (Table 48). As would be expected from equation, the quantities of hydrogen chloride and chlorine were approximately proportional to m, as determined from the kinetics.

3.5.3. The Products of the Rearrangement.

A summary of the ratios of isomers obtained from the photolytic rearrangement of N-chloroanilides is given in Table 49. It can be seen that the o:p ratios are lower in each case than for the corresponding "Orton" rearrangement in glacial acetic acid (Table 32) or carbon tetrachloride (Table 37). Evidence from the kinetics indicates that at least two mechanisms are involved. As the kinetics of the photolyses of N-chlorobenzanilide, N-chloromethanesulphonanilide and N-chlorobenzenesulphonanilide indicate that these reactions take place almost entirely by a homolytic mechanism, it follows that this mechanism favours high o:p ratios. The photolyses of the other N-chloroanilides studied involve also the heterolytic "Orton" reaction, which gives rise to lower o:p ratios (Table 49) and this is reflected in the lower o:p ratios for these photolyses.

Aspirating the solution with nitrogen, which has the effect of suppressing the "Orton" rearrangement, gave rise to a higher o:p ratio, lower yield of distillate, and a higher proportion of dark brown tar, which blackened on hydrolysis to give a high yield

Table 48

The Photolyses of N-Chlorobenzanilide, in the Presence of Added Anilides in Carbon Tetrachloride .

k_i - 5.23 x 10^{-5} sec^{-1}

[NCB] = 0.070M

k_o - 5.0 x $sec^{-1}M^{-2}$

[X] = 0.070M

Added Anilide (X)	N_2 flow-rate $l.hr^{-1}$	k_{ii} $sec^{-1}M^{-2}$	m	% chlorine and HCl removed by the passage of nitrogen
-	-	1.0×10^{-3}	2.0×10^{-4}	0.3
Benzanilide	-	2.0×10^{-3}	4.0×10^{-4}	1.2
Acetanilide	-	2.3×10^{-2}	4.6×10^{-3}	1.9
Benzenesulphonanilide	-	3.4×10^{-2}	6.7×10^{-3}	4.2
Methanesulphonanilide	-	5.7×10^{-2}	1.1×10^{-2}	5.2
Methanesulphonanilide	0.5	4.8×10^{-2}	9.6×10^{-3}	-
Methanesulphonanilide	1.0	3.3×10^{-2}	6.6×10^{-3}	-

of involatile residue in each case. High proportions of 2,4-dichloro- and 2,4,6,trichloro-anilide and tar, and a relatively low yield of monochlorinated products appear to be characteristic of this homolytic reaction.

Table 49

Products of the Photolyses of N-Chloroanilide in Carbon Tetrachloride at 77.7°.

N-Chloroanilide	% Yield	Mean o:p
N-Chloroacetanilide[6]	75	1:2.15
N-Chloroacetanilide[6]	68	1:1.45
N-Chlorophenylacetanilide	63	1:0.81
N-Chlorophenylacetanilide	52	1:1.40
N-Chlorobenzanilide	76	1:1.15
N-Chlorobenzanilide	74	1:1.19
N-Chloromethanesulphonanilide	-	1:0.96
N-Chloromethanesulphonanilide	-	1:0.93
N-Chlorobenzenesulphonanilide[5]	67	1:1.25

3.5.4. The Mechanism of the Photolytic Rearrangement.

The results of the studies of photolyses of the N-chloroanilides indicate that both homolytic and heterolytic mechanisms are involved. The latter mechanism has been discussed previously (section 3.2.). Since the kinetics of both the thermal and photolytic rearrangements of each of the N-chloroanilides studied fit the same rate-equation, the same mechanism (section 3.3.) is probably involved in each reaction.

Tanner and Protz[44] have suggested a radical cage mechanism for the photolytic rearrangement of N-bromoacetanilide. However, the relatively high quantum efficiency, as determined by Hodges[43], for the photolysis of N-chloroacetanilide in carbon tetrachloride, indicates that a chain mechanism is probably involved in the photolyses of the N-chloroanilides studied. Both chlorine atoms (equation 45) and acylamino-radicals (equation 43 and 44) probably act as chain carriers in the chain propagation. These processes have been shown to occur in the metal-ion catalysed reactions of N-chloroamides[102] and analogous processes were shown to occur in the photolysis of N-bromoacetanilide[43]. In this latter reaction, the bromine radical chain was shown to be the more important chain propagation process. As the chlorine atom is relatively small and formally electrically neutral, the position of attack of this radical at the o- and p-positions of the N-chloroanilide should not be greatly affected by the polar or steric influence of the acyl group, and therefore the proportions of the products obtained should tend towards that expected solely on a statistical basis. Thus the chlorine atom chain reaction would be expected to give rise to a relatively high o:p ratio, which would be similar for each N-chloroanilide. However, the acylamino-radical chain would be expected to give rise to a lower o:p ratio, as the ease of attack by this bulky radical would be affected by the size of the acyl group. Williams[103] has, in fact, shown that these acylamino-radicals react to give predominately p-substituted product. Since the photolytic rearrangement gave rise to a higher o:p ratio than the "Orton" reaction in either acetic acid or carbon tetrachloride, for each N-chloroanilide, it is probably that the chlorine atom chain (equation 45) is the more important chain propagation process. The similar proportions of products of the rearrangements of N-chlorobenzanilide and N-chloromethanesulphonanilide, both of which have been shown to proceed almost entirely by a homolytic process, support this view of the relative importance of the two chain propagation processes.

Chain termination processes would involve radical coupling and disproportionation, and products of dimerisation of acylamino-radicals have been characterised for the photolysis of N-chloroacetanilide by Hodges[43].

A comparison of the values of m determined for the photolytic and thermal rearrangements of the N-chloroanilides, and for the photolytic and thermal reactions of N-chlorobenzanilide, in the presence of added anilides, indicate that hydrogen chloride, which is responsible for the deviations from first-order kinetics, is formed in an analogous manner in each of these reactions, that is, by abstraction of protons by the chlorine radical.

Incursion of the "Orton" rearrangement is the probable cause of the anomalous quantum efficiencies, determined by Hodges[43], for the photolyses of N-chloroacetanilide in certain solvents. High quantum efficiencies were obtained for solvents which contained abstractable hydrogen (e.g., cyclohexane Φ =180) whereas considerably lower values were obtained for solvents which did not contain abstractable hydrogen atoms (e.g., carbon tetrachloride Φ =6). It is also significant that the quantum efficiency of the photolyses in cyclohexane (Φ =180) was higher than that of the corresponding reaction in toluene (Φ =108), since Russell and Brown[99] have shown that chlorine radicals abstract hydrogen rapidly in the case of cyclohexane even though attack of these radicals on toluene yields the relatively stable benzyl radical.

Tanner and Protz[44] have shown that if the photolytic rearrangement of N-bromoacetanilide is stopped after 15% reaction, little further reaction occurs if the solution is then heated in the dark at the same temperature. Although they inferred from this that the "Orton" rearrangement does not play a significant part in this photolysis, their deductions may be criticised on two counts. Firstly, although the "Orton" rearrangement does not play an important part in these early stages of the reaction, its importance increases as the reaction progresses. Secondly, any hydrogen bromide formed would be lost from the refluxing solution very rapidly, as it would be the most volatile component. Consequently, it would seem likely that continuous generation of the hydrogen halide is necessary for the features of autocatalysis to be observed.

3.6. The Rearrangement in Carbon Tetrachloride, in the Presence of Benzoyl Peroxide.

The rate-graphs for the rearrangement, in the presence of benzoyl peroxide, of each N-chloroanilide studied (Figs. 73-89) show that the initial rate of reaction is dependent on the initial concentrations of both the peroxide and the N-chloroanilide. Since graphs of the initial rate against the initial concentrations of both the peroxide and N-chloroanilide are linear, the rate-determining step is of the first-order with respect to each of these reactants. Before considering this reaction further, it is, therefore, necessary to review previous relevant studies of the thermal decomposition of benzoyl peroxide itself.

3.6.1. The Thermal Decomposition of Benzoyl Peroxide in Carbon Tetrachloride.

The thermal breakdown of benzoyl peroxide in aliphatic solvents, such as carbon tetrachloride, has been studied less extensively than the reactions in aromatic solvents. The reaction in most solvents has been shown to follow an approximately first-order law, and to involve the following mechanism:

$$(\,PhCOO\,)_2 \longrightarrow 2\ PhCOO\cdot \qquad .....(53)$$

$$PhCOO\cdot \longrightarrow Ph\cdot + CO_2 \qquad .....(54)$$

However, Nozaki and Bartlett[104] showed that the rate constant increased with increasing concentration of peroxide, and suggested that this induced decomposition was due to attack of solvent radicals on the peroxide. The reaction was shown to obey the following rate equation:

$$\frac{-\,d[P]}{dt} = k_3\,[P] + k_4\,[P]^{\frac{3}{2}} \qquad .....(55)$$

where the k_3 P applies to the unimolecular thermal dissociation of the peroxide, and the term $k_4\,[P]^{\frac{3}{2}}$ to the induced chain process.

The decomposition of benzoyl peroxide in carbon tetrachloride at 77.5° has been shown to obey equation 55 , thus

$$\frac{-d[P]}{dt} = k_{total}[P] = k_3[P] + k_4[P]^{\frac{3}{2}} \qquad \ldots(56)$$

and hence

$$k_{total} = k_3 - k_4[P]^{\frac{1}{2}} \qquad \ldots(57)$$

Coulson, Williams and Johnston[6] obtained values for k_3 of 1.56 x 10^{-5} sec^{-1}, and for k_4 of 2.5 x 10^{-5} $mole^{-\frac{1}{2}}$ $litre^{-1}$ sec^{-1}, which are closely similar to those obtained by Nozaki and Bartlett[104] for the decomposition at 80°.

3.6.2. The Kinetics of the Rearrangement of N-Chloroanilides in the Presence of Benzoyl Peroxide.

3.6.2.1. The Kinetics of the Initial Reaction.

The autocatalysis, which is a feature of the rearrangement of some *N*-chloroanilides, will be discussed later, and the present discussion will be confined to the initial reaction, before the increase in rate takes place.

Ayad, Beard, Garwood and Hickinbottom's mechanism[2] for the rearrangement of *N*-chloroanilides, catalysed by benzoyl peroxide, involved chain propagation by acylamino-radicals (equation 43 and 44).

Chain Initiation

$$(\mathrm{PhCOO})_2 \longrightarrow 2\ \mathrm{PhCOO}\cdot \qquad \ldots\ldots(58)$$

$$\mathrm{PhCOO}\cdot \longrightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \qquad \ldots\ldots(59)$$

Chain Propagation

$$\mathrm{Ph}\cdot + \mathrm{Ph.NCl.R} \longrightarrow \mathrm{PhCl} + \mathrm{Ph.}\dot{\mathrm{N}}\mathrm{.R.} \qquad \ldots\ldots(60)$$

$$\mathrm{Ph.}\dot{\mathrm{N}}\mathrm{.R} + \mathrm{Ph.NCl.R} \longrightarrow (\underline{o},\underline{p})\mathrm{Cl.C_6H_4.NH.R} + \mathrm{Ph.}\dot{\mathrm{N}}\mathrm{.R} \qquad \ldots\ldots(61)$$

Assuming that, in the first stages of the reaction, the same proportion of the phenyl radicals derived from the peroxide react with the *N*-chloroanilide, irrespective of the *N*-chloroanilide used, and neglecting the induced decomposition of the benzoyl peroxide, application of the steady state hypothesis to the phenyl radicals gives an equation for the rate of decomposition of the N-chloroanilide, as follows. The initial rate is given by:

$$\frac{-d[\mathrm{NCX}]}{dt} = k_a\, n\, [\mathrm{Ph}\cdot]\, [\mathrm{NCX}] + k_b [\mathrm{Ph.\dot{N}.R}][\mathrm{NCX}] \quad ..(62)$$

where n is the proportion of phenyl radicals which react with the N-chloroanilides, and k_a and k_b are the appropriate rate constants.

From equation 58 and 59,

Rate of formation of phenyl radicals which react with N-chloroanilide $= 2\, k_i\, n\, [\mathrm{P}]$ ...(63)

From equation 60

Rate of disappearance of phenyl radicals which have reacted with the N-chloroanilide

$$= k_a\, n\, [\mathrm{Ph}\cdot]\, [\mathrm{NCX}] \quad ...(64)$$

At the stationary state these rates are equal, therefore

$$k_a\, [\mathrm{Ph}\cdot][\mathrm{NCX}]\, n = 2\, k_i\, [\mathrm{P}]\, n \quad ...(65)$$

Substituting for Ph· in equation 62 gives:

$$\frac{-\,d[\mathrm{NCX}]}{dt} = 2k_i n\, [\mathrm{P}] + k_b\, [\mathrm{Ph{\cdot}\dot{N}.R}]\, [\mathrm{NCX}] \quad ...(66)$$

For this equation to be consistent with the experimental data, the second term must be either small or independent of the N-chloroanilide concentration. If the acylamino-radicals are removed by reaction with another reagent, Z, for example by combination with a phenyl radical, of which the concentration can be regarded as constant, the value of the second term in equation 66 can be calculated as follows:

From equation 60

Rate of formation of $\mathrm{Ph.\dot{N}.R} = k_a\, [\mathrm{Ph}\cdot][\mathrm{NCX}]\, n$ ...(67)

Rate of consumption of $\mathrm{Ph.\dot{N}.R} = k_c\, [\mathrm{Ph.\dot{N}.R}][\mathrm{Z}]$ ...(68)

where k_c is the appropriate rate constant.

Reaction 61 makes no contribution to these rates, as the rate of consumption of acylamino radicals is equal to the rate of formation for this reaction.

$$k_a\,[\mathrm{Ph}\cdot][\mathrm{NCX}]\,n \;=\; k_c\,[\mathrm{Ph.\dot{N}.R}][\mathrm{Z}] \qquad \ldots.(69)$$

but from equation 65

$$[\mathrm{Ph}\cdot] = \frac{2_i\,k_i\,[\mathrm{P}]\,n}{k_a\,[\mathrm{NCX}]} \qquad \ldots.(70)$$

substitution for $[\mathrm{Ph}\cdot]$ in equation 69 gives

$$2.k_i\,[\mathrm{P}]n^2 \;=\; k_c\,[\mathrm{Ph.\dot{N}.R}][\mathrm{Z}] \qquad \ldots.(71)$$

therefore $$[\mathrm{Ph.\dot{N}.R}] = \frac{2\,k_i\,[\mathrm{P}]\,n^2}{k_c\,[\mathrm{Z}]} \qquad \ldots.(72)$$

substituting for Ph.N.R in equation 66

$$\frac{-\,d\,[\mathrm{NCX}]}{dt} = 2\,k_i\,[\mathrm{P}] - \frac{2k_b k_i n^2\,[\mathrm{P}][\mathrm{NCX}]}{k_c\,[\mathrm{Z}]} \qquad \ldots.(73)$$

let $$\frac{2\,k_b\,k_i}{k_c\,[\mathrm{Z}]} = k_{iii} \qquad \ldots.(74)$$

then $$\frac{-\,d\,[\mathrm{NCX}]}{dt} = 2\,k_i\,n\,[\mathrm{P}] + k_{iii}\,n^2\,[\mathrm{P}][\mathrm{NCX}] \qquad \ldots.(75)$$

Coulson, Williams and Johnston[6] have shown that this relationship holds for the rearrangement of N-chloroacetanilide, since the graph of the initial rate of disappearance of the N-chloroanilide against the initial concentration of benzoyl peroxide was a straight line.

The graph of the initial rate of disappearance of each N-chloroanilide against the initial concentration of N-chloroanilide for a constant concentration of peroxide, was a straight line for each N-chloroanilide. The intercept gave a value of $2\,k_i n$ and as k_i has been found[6] to be 1.56×10^{-5} sec^{-1}, a value of n was obtained. The slope of the graph was $k_{iii} n^2$, and from this k_{iii} may be calculated. The graph of the initial rate of disappearance of each N-chloroanilide against the initial concentration of benzoyl peroxide, for a constant concentration of N-chloroanilide, was also a straight line for each N-chloroanilide studied. The slope of this graph gave a value of $k_{iii}n^2$ and hence this estimate of k_{iii} was obtained. The values of $2\ k_i n$, and n and k_{iii} are given in Table 50. The close agreement between the two sets of values of k_{iii} suggests that the assumptions made for the deduction of equation 75 were justified.

3.6.2.2. The Autocatalysis observed in the Reaction between Benzoyl Peroxide and N-Chloroanilides.

The rate-graphs for the rearrangement of N-chlorobenzanilide, N-Chlorophenylacetanilide and N-chlorodiphenylacetanilide, in the presence of benzoyl peroxide, exhibit the characteristics of autocatalysis (Figs. 73, 75 and 77) as did those obtained by Coulson, Williams and Johnston[6] for the rearrangement of N-chloroacetanilide under similar conditions. Moreover, the kinetics of the transformation of N-chloromethanesulphonanilide (Fig. 79) resemble those obtained by Coulson[5] for N-chlorobenzanesulphonanilide, and show no increase in rate as the reaction progresses.

Coulson, Williams and Johnston[6] found that the passage of nitrogen through a solution of N-chloroacetanilide and benzoyl peroxide in carbon tetrachloride, at 77.5°, not only caused a marked increase in the total time of reaction, but also removed appreciable quantities of hydrogen chloride and chlorine, which were detected and estimated in the effluent gas. They therefore concluded that the rearrangement of the N-chloroanilide took place to a considerable extent by the "Orton" mechanism and that this accounted for the features of autocatalysis.

In the analogous isomerisation of N-chlorobenzenesulphonanilide[5], the passage of nitrogen had little effect on the kinetics, and this was taken to indicate that reaction by the "Orton" mechanism was negligible for this N-chloroanilide. In agreement with

Table 50

The Rearrangement of N-Chloroanilides catalysed by Benzoyl Peroxide in Carbon Tetrachloride at 77.7^{o} in the dark.

N-Chloroanilide	$k_i\ n$ * sec^{-1} x 10^{-5}	n *	$k_{iii}\ n^{2*}$	k_{iii} * M^{-1} sec^{-1}	$k_{iii}n^{2+}$ x 10^{-4}	k_{iii} +
N-Chloroacetanilide[6]	3.03	0.97	1.15	1.22	1.04	1.08
N-Chlorobenzanilide	2.57	0.82	1.49	2.19	1.20	1.76
N-Chlorophenylacetanilide	2.70	0.87	1.86	2.48	1.83	2.44
N-Chlorodiphenylacetanilide	2.90	0.94	5.07	5.76	5.19	5.89
N-Chloromethanesulphonanilide	1.77	0.57	4.72	14.75	4.70	14.68
N-Chlorobenzenesulphonanilide[5]	1.27	0.41	1.91	11.23	1.63	9.48

*These values were calculated from experiments in which NCX was constant.

+These values were calculated from experiments in which P was constant.

this, very small quantities of chlorine and hydrogen chloride were removed from solution.

In the present work, the passage of nitrogen was found to reduce the initial rate of reaction of each N-chloroanilide appreciably. It was not therefore considered possible to investigate the relative importance of the "Orton" mechanism in the rearrangement of any of the N-chloroanilides by studying the effect of the passage of nitrogen on the kinetics.

The quantities of chlorine and hydrogen chloride removed by the passage of nitrogen (Table 50) appear to be related to the extent of autocatalysis, since in the present work, those N-chloroanilides which exhibit little autocatalysis produced small quantities of chlorine and hydrogen chloride. It is therefore probable that in the reactions of N-chlorodiphenylacetanilide, N-chlorophenylacetanilide, and, to a lesser extent, those of N-chlorobenzanilide, the "Orton" rearrangement was responsible for the formation of a considerable proportion of the products. In agreement with this, aspirating with nitrogen had a large effect on the products of the rearrangement of N-chlorophenylacetanilide, little effect on those of N-chlorobenzanilide and virtually no effect on those of N-chloromethanesulphonanilide. By analogy, nitrogen aspiration would be expected to have a large effect on the products of rearrangement of N-chlorodiphenylacetanilide, although this was not checked.

No rate equation could be found to fit the kinetics of the reactions of the N-chloroanilides in the presence of benzoyl peroxide, and therefore the extent of autocatalysis could not be put on a numerical basis. It was thought possible that the value of n varied as the reaction progresses, since in the later stages of the reaction, a significant proportion of the radicals derived from benzoyl peroxide probably react with the products of the rearrangement, and consequently the total reaction could not be expected to follow a simple rate law.

3.6.3. The Products of the Rearrangement.

A summary of the o:p ratios for the rearrangement of each N-chloroanilide studied, together with the results of the previous workers, is given in Table 51.

Table 51

Products of the Rearrangement of N-Chloroanilides Catalysed by Benzoyl Peroxide in Carbon Tetrachloride at 77.7° in the dark.

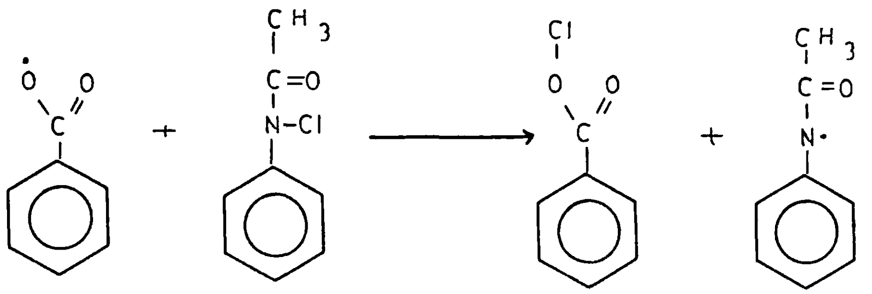
N-Chloroanilide	Yield	o:p
N-Chloroacetanilide[6]	79	1:3.7
N-Chloroacetanilide[6], N_2	73	1:2.9
N-Chlorophenylacetanilide	62	1:5.9
N-Chlorophenylacetanilide, N_2	-	1:5.6
N-Chlorobenzanilide	67	1:8.8
N-Chlorobenzanilide, N_2	65	1:9.1
N-Chloromethanesulphonanilide	-	1:3.9
N-Chloromethanesulphonanilide, N_2	-	1:3.9
N-Chlorobenzenesulphonanilide[5]	44	1:1.8
N-Chlorobenzenesulphonanilide[5], N_2	39	1:1.7

N_2 - These experiments had nitrogen passing through the solution solution throughout the reaction.

It is apparent that the passage of nitrogen causes a change in the yields and proportions of the products of the rearrangement of N-chloroacetanilide, and N-chlorophenylacetanilide, and to a lesser extent N-chlorobenzanilide and N-chloromethanesulphonanilide. These results support the view, expressed previously (section 3.6.3.) that the rearrangement catalysed by hydrogen chloride plays a much more significant part in the reactions of N-chloroacetanilide and N-chlorophenylacetanilide, catalysed by benzoyl peroxide, than in the reactions of the other N-chloroanilides studied. For each of the N-chloroanilides, the o:p ratio for the reaction with benzoyl peroxide was considerably lower than that for the photolytic rearrangement of the corresponding N-chloroanilide. The relatively high yields of 2,4-dichloro- and 2,4,6-trichloro-anilides, and residue, and relatively low yields of monochloroanilides obtained in these reactions indicate that the reaction proceeds to a large extent by a homolytic mechanism.

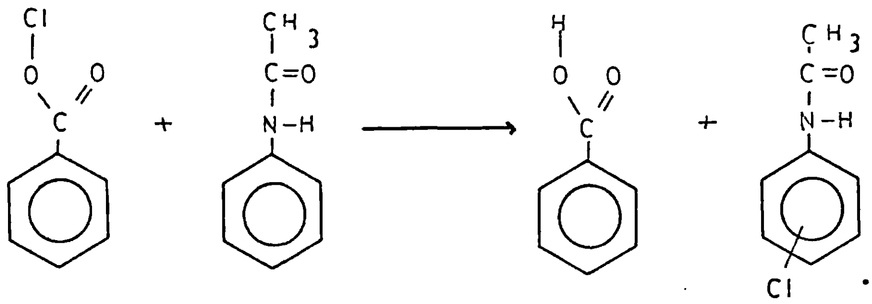
3.6.4. The Mechanism of the Rearrangement catalysed by Benzoyl Peroxide.

Coulson, Williams and Johnston[6] obtained a higher yield of p-chloroacetanilide from the rearrangement of N-chloroacetanilide catalysed by benzoyl peroxide, than in the corresponding photolytic reaction, even when the "Orton" rearrangement had been suppressed by the passage of nitrogen. To account for this observation, they suggested that a third mechanism was involved, in addition to the "Orton" rearrangement and the acylamino radical chain (equations 43 and 44) which was thought to be the mechanism of the photolytic rearrangement[6]. Since the rearrangement catalysed by benzoyl peroxide gave rise to a lower o:p ratio than chlorination by molecular chlorine (the "Orton" rearrangement), a more highly electrophilic chlorinating agent was thought to be involved. They considered that the most likely such intermediate was benzoyl hypochlorite, and suggested that it was formed by a benzoxy radical, a product of the decomposition of benzoyl peroxide, abstracting the N-chlorine of N-chloroacetanilide (equation 76).



.........(76)

They suggested that this intermediate then chlorinated the parent anilide.



...........(77)

However, it is not obvious that this hypochlorite would be highly electrophilic, for it might be expected to be similar to hypochlorous acid, which is known to be a relatively weak electrophile. If this third mechanism (equations 76 and 77) were responsible for the relatively low o:p ratio, then it must be the major reaction under these conditions, and consequently one would expect similar o:p ratios for each N-chloroanilide, as has been found for the heterolytic "Orton" rearrangement (Table 32). On the contrary, however, the ratio of products formed in the reactions catalysed by benzoyl peroxide has now been found to be strongly dependent on the nature of the N-chloroanilide. Thus, although some of the benzoyl hypochlorite might possibly react in the way suggested by Coulson, Williams and Johnston[6], it is unlikely that this process accounts for a large proportion of the products.

The major difference between the mode of formation of the products from the photolyses and the reaction catalysed by benzoyl peroxide lies in the chain propagation process. In the photolysis, the chlorine atom chain (equation 45) and the acylamino-radical chain (equation 43) are the major propagation processes, although, as has been mentioned before, the former is probably the more important. It would be expected that the chlorine radical chain would give rise to a relatively high proportion of 2-chloroanilides, from steric considerations, and this is reflected in the product ratios for the photolytic rearrangement (e.g. N-chlorobenzanilide o:p - 1:1.16). However, in the rearrangement catalysed by benzoyl peroxide, The major chain propagation process appears to involve the acylamino-radical (Hickenbottom's mechanism, equation 43) since the chain initiation reaction gives rise to the acylamino-radical only, whereas in the photolytic rearrangement the chain initiation reaction gives rise to both chlorine and acylamino radicals. A small quantity of chlorine atoms may be formed by thermal decomposition of benzoyl hypochlorite, and these atoms could abstract aliphatic hydrogen atoms from the products of the reaction to give hydrogen chloride, which has been shown to be responsible for the features of autocatalysis observed in the rate curves, and could also initiate the chlorine atom chain. It would be expected that the proportion of available chlorine which would form chlorine atoms would be considerably smaller in the reaction catalysed by benzoyl peroxide than in the corresponding photolytic reaction, consequently the chlorine atom chain propagation process would be less important in the former reaction. The formation of hydrogen chloride would be relatively easier in the reaction catalysed by peroxide, since the products of this reaction would be a richer source of abstractable hydrogen atoms. Thus the most important process involved in the formation of products would be the acylamino-radical chain, and from both mesomeric and steric considerations, it would be expected to react preferentially in the "para-form" and hence give rise to a relatively low o:p ratio and this was found to be the case (e.g. N-chlorobenzanilide o:p 1:8.8).

The high proportions of di- and tri-chloroanilides in the products of the reactions catalysed by benzoyl peroxide provide further evidence to support this view of the mechanism, for the exchange reaction (equation 46) necessitates the involvement of the acylamino-radical. The high yields of di- and tri-chloroanilides compared with those obtained in the corresponding photolyses indicate that the acylamino-radicals are the more important chain propagating agents in the former reaction. The high proportion of unsubstituted anilide in the product of the rearrangement catalysed by benzoyl peroxide, is probably due to the fact that a considerable proportion of the chlorine is abstracted from the N-Cl bond, by phenyl radicals to form chlorobenzene (equation 28).

The mechanism of this reaction may be summarised as follows. The rearrangement of N-chloroanilides is initiated by benzoyl peroxide, which decomposes into phenyl and to a lesser extent benzoxy radicals. Abstraction of the N-chlorine of the N-chloroanilide by phenyl radicals gives chlorobenzene and initiates the acylamino-radical chain reaction (equations 43 and 44), and this process is thought to be responsible for the formation of the major part of the product. The benzoxy radicals can also abstract the N-chlorine initiating the acylamino-radical chain reaction. The product of the abstraction of the N-chlorine, benzoyl hypochlorite, is thought to decompose giving chlorine atoms, though a smaller proportion of the available chlorine forms chlorine atoms than in the corresponding photolytic reaction. The chlorine atoms could initiate the chlorine atom chain reaction, combine with free radicals or abstract an aliphatic hydrogen atom to give hydrogen chloride. This latter process would be more favourable than in the corresponding photolytic rearrangement since the proportion of the available hydrogen in the product would be greater and this would explain the features of autocatalysis observed in the rate curves of the rearrangement of some of the N-chloroanilides studied.

REFERENCES

1. E.D. Hughes and C.K. Ingold, Q. Rev., 1952, 6, 34.

2. K.N. Ayad, C. Beard, R.F. Garwood and W.J. Hickinbottom, J. Chem. Soc., 1957, 2981.

3. C.C. Beard, J.R.B. Boocock and W.J. Hickinbottom, J. Chem. Soc., 1960, 520.

4. J.I.G. Cadogan and W.R. Foster, J. Chem. Soc., 1961, 3076.

5. J. Coulson, Ph.D., thesis, London University,

6. J. Coulson, G.H. Williams, and K.M. Johnston, J. Chem. Soc., 1967, 174.

7. G. Bender, Ber., 1886, 19, 2272.

8. E.E. Slosson, Ber., 1895, 28, 3265.

9. F.D. Chattaway and K.J.P. Orton, J. Chem. Soc., 1899, 75, 1046.

10. H.E. Armstrong, J. Chem. Soc., 1900, 77, 1047.

11. K.J.P. Orton and W.J. Jones, J. Chem. Soc., 1909, 95, 1456.

12. F.G. Soper, J. Phys. Chem., 1927, 31, 1192.

13. K.J.P. Orton and H. King, J. Chem. Soc., 1911, 99, 1185.

14. K.J.P. Orton and H. King, J. Chem. Soc., 1911, 99, 1377.

15. K.J.P. Orton and A.E. Bradfield, J. Chem. Soc., 1927,

16. A.R. Olson, C.W. Porter, F.A. Long and A.S. Halford, J. Amer. Chem. Soc., 1936, 58, 2467.

17. A.R. Olson, R.S. Halford and J.C. Hornel, J. Amer. Chem. Soc., 1937, 59, 1613.

18. J.J. Blanksma, Proc.K. Akad. Wetensch. Amsterdam., 1902, 5, 178.
    Proc.K. Akad. Wetensch. Amsterdam., 1902, 5, 359.
    Abstract. J. Chem. Soc., 1902, 82.2, 646.
    Abstract. J. Chem. Soc., 1903, 84.2, 137.

19. S.F. Acree amd J.M. Johnson, Am. Chem. J., 1907, 37, 410.
    Am. Chem. J., 1907, 38, 258.

20. M. Richardson and F.G. Soper, *J. Chem. Soc.*, 1929, 1873.

21. J.W. Belton, *J. Chem. Soc.*, 1930, 116.

22. H.M. Dawson and H. Miller, *J. Chem. Soc.*, 1932, 1920.

23. F.G. Soper and D.R. Pryde, *J. Chem. Soc.*, 1927, 2761.

24. W.J. Jones and K.J.P. Orton, *J. Chem. Soc.*, 1909, 1056.

25. F.M. Longmaid, personal communication.

26. F.D. Chattaway and K.J.P. Orton, *Proc. Chem. Soc.*, 1902, *18*, 200.

27. F.D. Chattaway, *J. Chem. Soc.*, 1902, *101*, 816.

28. R.P. Bell, *Proc. Roy. Soc. A*, 1934, *143*, 377.

R.P. Bell and R.V.H. Levinge, *Proc. Roy. Soc. A*, 1935, *151*, 211.

R.P. Bell, *J. Chem. Soc.*, 1936, 1154.

R.P. Bell and J.F. Brown, *J. Chem. Soc.*, 1936, 1520.

R.P. Bell and O.M. Lidwell, *J. Chem. Soc.*, 1939, 1096.

R.P. Bell and P.V. Danckwerts, *J. Chem. Soc.*, 1939, 1700.

29. G.C. Israel, A.W.N. Tuck and F.G. Soper, *J. Chem. Soc.*, 1945, 547.

30. W.J. Hickinbottom, *J. Chem. Soc.*, 1934, 1700.

31. M.J.S. Dewar, Electronic Theory of Organic Chemistry, Oxford Univ. Press, 1949, page 225.

32. M.J.S. Dewar, I.U.P.A.C. Kekule Symposium, "Aromatic Rearrangements", London, 1958.

33. P.J. Couzens, Ph.D. Thesis, London University, 1960.

34. J.M.W. Scott and J.G. Martin, *Canad. J. Chem.*, 1965, *43*, 732.

35. J.M.W. Scott and J.G. Martin, *Canad. J. Chem.*, 1966, *44*, 2901.

36. C.W. Porter and P. Wilbur, *J. Amer. Chem. Soc.*, 1927, *49*, 2145.

37. A.E. Bradfield, *J. Chem. Soc.*, 1929, 351.

38. A. Robertson and W.A. Waters, *J. Chem. Soc.*, 1947, 492.

39. J.J. Blanksma, *Rec. Trav. Chim.*, 1902, *21*, 366.

40. J.J. Blanksma, *Rec. Trav. Chim.*, 1903, *22*, 296.

41. F.D. Chattaway and K.J.P. Orton, *Proc. Chem. Soc.*, 1902, *18*, 200.

42. J. H. Matthews and R.V. Williamson, J. Amer. Chem. Soc., 1923, 45, 2574.

43. F.W. Hodges, J. Chem. Soc., 1933, 240.

44. D.D. Tanner and E. Protz, Canad. J. Chem., 1966, 44, 1555.

45. G.A. Russell and K.M. Desmond, J. Amer. Chem. Soc., 1963, 85, 3139.

46. T. Atkins, Ph.D. Thesis, University of London, in preparation.

47. M.C. Ford, L.J. Hunt and W.A. Waters, J. Chem. Soc., 1953, 3529.

48. O. Schmidt, Ber., 1903, 36, 2474.

49. J.F. Durand and R. Naves, Bull. Soc. chim. France, 1925, 37, 722.

50. L.M.F. van de Lande, Rec. Trav. chim., 1932, 51, 98.

51. G.H. Dyson, H.J. George and R.F. Hunter, J. Chem. Soc., 1926, 3043.

52. M.P.J. Montagne, Rec. Trav. chim., 1902, 21, 384.

53. A.J. von Peski, Rec. Trav. chim., 1921, 40, 114.

54. W. Staedel, Ber., 1846, 19, 1947.

55. O. Wallach, Annalen, 1882, 214, 235.

56. A. Reissert and A. More, Ber., 1906, 39, 3307.

57. J.F. Bunnett, T. Kato, R.R. Flynn and J.A. Skorcz, J. Org. Chem., 1963, 28, 1.

58. H. Staudinger, Ber., 1911, 44, 546.

59. R. Anschutz and A.R. Haslam, Annalen, 1889, 253, 129.

60. M.P. Freundler, Bull. Soc. chim. France, 1904, 31, 630.

61. A. Claus, Ber., 1881, 14, 2368.

62. F. Meinecke, Ber., 1875, 8, 564.

63. F.D. Chattaway and A.B. Constable, J. Chem. Soc., 1914, 126.

64. B.F. Fortinsky, J. Russ. Phys. Chem. Soc., 1912, 44, 781.

65. O.L. Brady and R.P. Mehta, J. Chem. Soc., 1924, 125, 2297.

66. O. Doebner, Annalen, 1908 , 210, 271.

67. R. von Walther and A. Grossmann, J. prakt. Chem., 1908 , 78, 493.

68. R. von Walther and A. Grossmann, J. prakt. Chem., 1908 , 78, 486.

69. R. von Walther, J. prakt. Chem., 1903 , 67, 453.

70. H.L. Wheeler and B.B. Boltwood, Amer. Chem. J., 1896, 18, 386.

71. F.D. Chattaway, K.J.P. Orton and W.H. Hurtley, Ber., 1899, 32, 3637.

72. G. Schiemann and R. Pillarsky, Ber., 1929, 62, 3041

73. A. Hantzch, Ber., 1891, 24, 56.

74. H. Weil and P. Wasserman, Ber., 1922, 55, 2533.

75. R.G. Shepherd, J. Org. Chem., 1947, 12, 275.

76. M. Dugeut, Rec. Trav. chim., 1902, 21, 76.

77. C.S. Marvel, M.D Helfrick and J.P. Belsley, J. Amer. Chem. Soc., 1929, 51, 1273.

78. R.A. Abramovitch, J.Roy and V. Uma, Canad. J. Chem., 1965, 43, 3407.

79. A.G. Kostova, Zhur. Obshchei. Khim., 1954, 24, 618.

80. J.S. Chalsty and S.S. Israelstam, J. S. African Chem. Inst., 1956, 9, 30.

81. H.M. Tetter, R.C. Bachman, E.W. Bell and J.C. Cowan, Ind. Eng. Chem., 1949, 41, 849.

82. D.R. Augood, D.H. Hey and G.H. Williams, J. Chem. Soc., 1952, 2094.

83. R. von Walther, J. prakt. Chem., 1911 , 78, 483.

84. H. Staudinger, Ber., 1905, 38, 1737.

85. W.A. Waters, J. Chem. Soc., 1948, 727.

86. P.D. de la Mare, J. Chem. Soc., 1949, 287.

87. H. Cohn, E.D. Hughes, M.H. Jones and M.G. Peeling, Nature, 1952, 169, 291.

88. M.A.F. Holleman, Chem. Rev., 1925, 1, 218

89. H.C. Brown and L.M. Stock, J. Amer. Chem. Soc., 1957, 76, 1421.

90. H.C. Brown and L.M. Stock, J. Amer. Chem. Soc., 1957, 76, 5175.

91. P.D. de la Mare, J.T. Harvey, M. Hassan and S. Varma, J. Chem. Soc., 1957, 2756.

92. L.M. Stock and A. Himoe, J. Amer. Chem. Soc., 1961, 83, 4605.

93. C. Beard and W.J. Hickenbottom, Chem. and Ind., 1957, 1421.

C. Beard and W.J. Hickenbottom, J. Chem. Soc., 1958, 2982.

94. S.M Verma and R.C. Srivastava, J. Indian Chem. Soc., 1964, 3(6), 266.

95. C.J.M. Stirling, Radicals in Organic Chemistry, Oldbourne Press, London.

96. P.B.D. de la Mare and J.H. Ridd, Aromatic Substitution, Butterworth Press, 1959.

97. P.B.D. de la Mare, I.C. Hilton and S. Varma, J. Chem. Soc., 1960, 4044.

98. J.M. Tedder, Quart. Rev.(London), 1960, 14, 336.

99. G.A. Russell and H.C. Brown, J. Amer. Chem. Soc., 1955, 77, 4578.

100. C. Walling and B. Miller, J. Amer. Chem. Soc., 1957, 79, 4181.

101. R. van Helden and E.C. Kooyman, Rec. Trav. chim., 1954, 73, 269.

102. D.D. Tanner and M.W. Mosher, Canad. J. Chem., 1969, 47, 715.

F. Minisci, G.P. Gardini and F. Bertini, Canad. J. Chem., 1970, 48, 544.

103. H.J. Williams, Ph.D. Thesis, London University, 1964.

104. K. Nazaki and P.D. Bartlett, J. Amer. Chem. Soc., 1946, 68, 1686.

105. J-M. Geneste amd A. Kergomad, Bull. Soc. chim. France, 1963, 470.

106. K.M. Johnston, G.H. Williams and H.J. Williams, J. Chem. Soc., 1960, B, 1114.

APPENDIX A

Table A1

The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid alone at 77.7^{o}.

A

$[\mathrm{NCB}]_o$ = 0.040M

B

$[\mathrm{NCB}]$ = 0.100M

Time (hr.)	$[\mathrm{NCB}]$ M x 10^2	Time (hr.)	$[\mathrm{NCB}]$ M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCB}]$
0.25	3.87	0.75	9.52	-1.021
0.50	3.82	1.50	9.06	-1.043
0.75	3.76	2.00	8.36	-1.078
1.25	3.64	2.50	7.30	-1.137
2.00	3.37	2.83	6.30	-1.201
2.25	3.29	3.00	5.75	-1.240
2.75	3.14	3.25	4.61	-1.336
3.25	3.04	3.50	3.21	-1.494
4.00	2.74	3.75	2.21	-1.656
4.75	2.43	3.92	1.37	-1.863
5.75	1.88	4.00	0.90	-2.046
6.75	1.37	4.08	0.46	-2.337
7.75	0.77	4.16	0.23	-2.638
8.75	0.10	4.25	0.11	-2.958

Table A2

The Rearrangement of N-Chlorophenylacetanilide in Glacial Acetic Acid at 77.7° .

A

$[NCB]_o$ = 0.100M
$[AgOAc]_o$ = 0.000M

B

$[NCB]_o$ = 0.100M
$[AgOAc]_o$ = 0.050M

Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]	Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
0.50	9.28	-1.033	0.5	9.66	-1.015
0.75	9.15	-1.039	4.5	8.94	-1.048
1.00	9.06	-1.043	6.5	8.58	-1.064
1.20	8.91	-1.050	9.0	8.20	-1.086
1.75	8.04	-1.095	10.0	8.02	-1.096
2.50	4.93	-1.307	14.0	7.53	-1.123
2.75	3.27	-1.485	20.0	6.90	-1.161
2.83	2.44	-1.613	25.5	6.56	-1.183
3.05	1.33	-1.877	30.5	6.13	-1.213
3.17	0.32	-2.498	33.0	5.83	-1.235
3.25	0.06	-3.231	38.0	5.16	-1.287
3.30	0.01	-3.951	41.0	4.98	-1.303
			45.0	4.68	-1.321
			48.5	4.29	-1.347
			62.0	3.61	-1.443
			73.0	2.89	-1.539

Table A3

Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid at 77.7°, Aspirated with Nitrogen

Nitrogen Flow-rate = 4 l/hr.

$[NCB]_o$ = 0.100M

Time (hr.)	[NCB] M x 10^2	$\mathrm{Log}_{10}[NCB]$
1.00	9.65	-1.015
2.00	9.48	-1.023
3.75	9.25	-1.034
6.50	8.70	-1.061
15.50	7.38	-1.132
17.00	6.89	-1.162
22.25	6.48	-1.188
24.25	6.23	-1.205
28.33	5.28	-1.277
39.25	4.19	-1.378
43.00	3.60	-1.444
47.50	3.04	-1.517
63.75	1.64	-1.785
68.00	1.33	-1.876

Table A4

The Rearrangement of N-Chlorobenzanilide at 77.7°, in Acetic Acid, with added Silver Acetate

A		B		C		D	
$[NCB]_o$ = 0.100M		$[NCB]_o$ = 0.100M		$[NCB]_o$ = 0.100M		$[NCB]_o$ = 0.100M	
$[AgOAc]$ = 0.0013M		$[AgOAc]$ = 0.0026M		$[AgOAc]$ = 0.0052M		$[AgOAc]$ = 0.0122M	
Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$
1.00	9.56	0.50	9.51	0.50	9.48	1.25	8.84
1.75	9.43	1.25	9.39	0.75	9.32	2.00	8.31
2.00	9.50	4.50	8.93	1.25	9.18	4.50	7.37
2.25	9.45	5.50	8.81	1.50	9.06	7.00	6.54
2.50	9.46	7.00	8.67	1.75	8.99	8.00	6.22
3.25	9.35	8.00	8.49	2.00	8.90	15.00	5.14
4.00	9.26	24.00	0.12	2.75	8.66	21.50	4.40
4.50	9.22			3.75	8.42	28.33	3.66
5.00	9.19			4.00	8.32	39.50	3.06
				4.50	8.21	47.75	2.37
Initial Rate = 0.7×10^{-3} M.hr.$^{-1}$		Initial Rate = 1.5×10^{-3} M.hr.$^{-1}$		Initial Rate = 3.3×10^{-3} M.hr.$^{-1}$		Initial Rate = 6.9×10^{-3} M.hr.$^{-1}$	

Table A5

The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid at 77.7°

A		B		C		D	
$[NCB]_o = 0.010M$ $[AgOAc] = 0.0052M$		$[NCB]_o = 0.020M$ $[AgOAc] = 0.0052M$		$[NCB]_o = 0.040M$ $[AgOAc] = 0.0052M$		$[NCB]_o = 0.070M$ $[AgOAc] = 0.0052M$	
Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$	Time (hr.)	$[NCB]$ $M \times 10^2$
0.50	0.929	0.50	1.91	0.25	3.80	0.25	6.44
1.25	0.917	1.25	1.80	0.50	3.82	0.50	6.34
1.50	0.901	1.50	1.78	1.00	3.66	1.00	6.28
2.00	0.873	2.00	1.74	1.50	3.56	1.50	6.12
2.75	0.857	2.75	1.70	2.00	3.48	2.00	6.02
4.50	0.810	4.50	1.61	2.50	3.40	2.50	5.87
				3.00	3.36	3.00	5.80
				3.50	3.38	3.50	5.74
Initial Rate = 0.40×10^{-3} M.hr.$^{-1}$		Initial Rate = 0.27×10^{-3} M.hr.$^{-1}$		Initial Rate = 1.75×10^{-3} M.hr.$^{-1}$		Initial Rate = 2.50×10^{-3} M.hr.$^{-1}$	

Table A6

The Rearrangement of N-Chlorobenzanilide in Glacial Acetic Acid, at 100°.

A

$[NCB]_o$ = 0.040M

$[AgOAc]_o$ = 0.000M

B

$[NCB]_o$ = 0.040M

$[AgOAc]_o$ = 0.150M

Time (hr.)	[NCB] M x 10^2	$Log_{10}[NCB]$	Time (hr.)	[NCB] M x 10^2	$Log_{10}[NCB]$
0.25	3.74	-1.428	0.08	3.11	-1.507
0.50	3.57	-1.448	0.25	2.10	-1.677
0.75	3.12	-1.506	0.34	1.46	-1.834
1.00	2.48	-1.606	0.42	1.28	-1.892
1.25	1.52	-1.818	0.50	1.04	-1.985
1.50	0.72	-2.142	0.75	0.43	-2.362
1.75	0.12	-2.941	1.00	0.23	-2.636
1.83	0.02	-3.770	1.25	0.10	-3.004
			1.50	0.06	-3.242

Table A7

The Rearrangement of N-Chloroanilide in Carbon Tetrachloride, catalysed by Hydrogen Chloride.

N-Chlorobenzanilide						N-Chloroacetanilide			N-Chlorophenylacetanilide		
A			B			C			D		
[Diphenyl Ether] = 0.00M $[NCB]_o$ = 0.070M			[Diphenyl Ether] = 0.20M $[NCB]_o$ = 0.070M			$[NCA]_o$ = 0.070M			$[NCP]_o$ = 0.70M		
Time (min.)	[NCB] $M\times10^2$	$\log_{10}[NCB]$	Time (min.)	[NCB] $M\times10^2$	$\log_{10}[NCB]$	Time (min.)	[NCA] $M\times10^2$	$\log_{10}[NCA]$	Time (min.)	[NCP] $M\times10^2$	$\log_{10}[NCP]$
0.3	4.96	-1.304	0.5	3.70	-1.432	0.25	1.74	-1.768	0.25	3.90	-1.408
0.5	3.45	-1.467	1.0	2.14	-1.670	0.50	0.03	-3.540	0.50	1.89	-1.723
1.0	2.39	-1.621	1.5	0.97	-2.011	0.75	0.00		0.75	0.77	-2.110
1.5	1.12	-1.950	2.0	0.51	-2.291				1.00	0.29	-2.541
2.0	0.45	-2.350	2.5	0.19	-2.722				1.25	0.18	-2.730
2.5	0.19	-2.720	3.0	0.09	-3.036				1.50	0.09	-3.078
3.0	0.10	-2.998	3.5	0.06	-3.222				1.75	0.07	-3.140
3.5	0.05	-3.266	4.0	0.04	-3.421						

Table A8

The Rearrangement of N-Chloroanilide in Carbon Tetrachloride
Catalysed by Hydrogen Chloride.

N-Chlorodiphenylacetanilide			N-Chlorobenzenesulphonanilide			N-Chloromethanesulphonanilide		
Time (min.)	[NCD] M x 10^2	Log$_{10}$[NCD]	Time (min.)	[NCBS] M x 10^2	Log$_{10}$[NCBS]	Time (min.)	[NCMS] M x 10^2	Log$_{10}$[NCMS]
0.25	4.69	-1.330	0.5	6.75	-1.171	1.0	6.59	-1.181
0.50	2.97	-1.528	1.5	6.75	-1.171	3.0	6.28	-1.202
0.75	1.42	-1.846	4.0	6.65	-1.177	12.0	5.36	-1.271
1.00	0.90	-2.045	6.0	6.62	-1.179	20.0	4.48	-1.349
1.25	0.47	-2.331	30.0	6.43	-1.192	30.0	3.83	-1.417
1.50	0.26	-2.586	54.0	6.11	-1.214	40.0	3.14	-1.503
1.75	0.13	-2.887	110.0	5.08	-1.294	55.0	2.36	-1.627
2.00	0.08	-3.119	135.0	4.48	-1.349	80.0	1.58	-1.802
2.25	0.04	-3.350	210.0	3.08	-1.519	100.5	1.12	-1.951
2.50	0.02	-3.586	270.0	1.79	-1.747	135.0	0.56	-2.246
			285.0	1.45	-1.837	165.0	0.34	-2.473

Table A9

The Thermal Rearrangement of N-Chlorobenzanilide at 156°in Nitrobenzene

$[NCB]_o = 0.100M$

A			B		
Without Nitrogen.			Aspirated with Nitrogen.		
Time (hr.)	[NCB] $M \times 10^2$	Log_{10}[NCB]	Time (hr.)	[NCB] $M \times 10^2$	Log_{10}[NCB]
0.01	9.15	-1.038	0.01	9.20	-1.036
0.10	9.09	-1.041	0.15	9.03	-1.045
0.20	8.89	-1.050	1.20	6.79	-1.168
0.40	8.63	-1.064	1.50	6.32	-1.199
0.60	7.83	-1.106	2.00	5.59	-1.253
0.75	7.13	-1.147	2.50	5.14	-1.289
0.90	6.36	-1.195	3.00	4.48	-1.348
1.00	5.83	-1.235	3.66	3.74	-1.427
1.15	4.84	-1.315	4.33	3.30	-1.482
1.30	3.75	-1.425	5.33	2.49	-1.613
1.50	1.52	-1.817	5.66	2.30	-1.638
1.60	0.73	-2.365	6.66	1.73	-1.763
1.65	0.19	-2.723	8.00	1.20	-1.928
1.70	0.00				

Table A10

The Thermal Rearrangement of N-Chlorobenzanilide, in Nitrobenzene, Aspirated with Nitrogen.

$[NCB]_o$ = 0.100M

T = 154° T = 162°

Time (hr.)	[NCB] M x 10^2	$Log_{10}[NCB]$	Time (hr.)	[NCB] M x 10^2	$Log_{10}[NCB]$
0.75	7.97	-1.100	0.25	8.26	-1.083
1.25	7.02	-1.154	0.50	7.54	-1.123
1.75	6.36	-1.196	0.75	7.08	-1.150
2.25	5.60	-1.252	1.10	6.22	-1.206
3.50	4.31	-1.366	1.83	4.92	-1.308
4.25	3.81	-1.419	2.59	3.87	-1.411
5.50	3.01	-1.522	3.35	2.75	-1.560
7.0	2.04	-1.691	4.50	1.87	-1.729
9.25	1.30	-1.868			
10.70	0.91	-2.041			

Table A11

The Thermal Rearrangement of N-Chlorobenzanilide in Nitrobenzene.

$[NCB]_o = 0.100M$

T = 170°			T = 177°		
Time (hr.)	[NCB] $M \times 10^2$	$Log_{10}[NCB]$	Time (hr.)	[NCB] $M \times 10^2$	$Log_{10}[NCB]$
0.25	6.73	-1.169	0.10	7.96	-1.099
0.50	5.47	-1.262	0.35	5.85	-1.233
0.75	4.40	-1.357	0.40	5.39	-1.269
1.00	3.35	-1.475	0.55	4.77	-1.321
1.25	2.70	-1.569	0.80	3.49	-1.457
1.50	2.07	-1.684	1.35	1.71	-1.765
2.00	1.21	-1.917	1.55	1.23	-1.909
2.75	0.61	-2.213	1.80	0.88	-2.057
			2.05	0.65	-2.184
			3.0	0.20	-2.704

Table A12

Thermal Rearrangement of N-Chlorobenzanilide in Nitrobenzene

Aspirated with Nitrogen

Temperature = 170°

[NCB] = 0.100M

Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
0.25	7.49	-1.125
0.50	5.85	-1.233
0.75	4.69	-1.328
1.00	3.12	-1.506
1.20	2.62	-1.582
1.40	2.09	-1.680
1.60	1.70	-1.770
1.80	1.30	-1.887
2.00	1.09	-1.960
2.25	0.84	-2.078
2.50	0.62	-2.207
2.75	0.46	-2.338
3.00	0.38	-2.452
3.50	0.18	-2.748
4.25	0.08	-3.100

Table A13

The Thermal Rearrangement of N-Chloroacetanilide at 156°

in Nitrobenzene

$[\text{NCA}]_o = 0.100\text{M}$

A Without Nitrogen			B With Nitrogen		
Time (hr.)	[NCA] M x 10^2	Log_{10}[NCA]	Time (hr.)	[NCA] M x 10^2	Log_{10}[NCA]
0.35	8.92	-1.050	0.25	8.91	-1.050
0.50	8.86	-1.053	0.50	8.89	-1.052
0.90	8.77	-1.057	0.75	8.73	-1.059
1.00	8.54	-1.068	1.00	8.71	-1.060
1.20	8.22	-1.085	1.50	8.59	-1.066
1.40	7.56	-1.122	2.00	8.43	-1.074
1.50	7.32	-1.136	2.25	8.38	-1.077
1.65	6.45	-1.190	3.00	8.12	-1.090
1.75	5.54	-1.257	3.50	7.71	-1.113
1.85	4.35	-1.361	4.50	7.15	-1.146
1.95	2.63	-1.570	6.00	5.48	-1.261
2.00	1.50	-1.832	6.50	5.24	-1.281
2.05	0.11	-2.960	7.50	3.81	-1.419
2.10	0.00		9.00	2.62	-1.682

Table A14

The Thermal Rearrangement of N-Chloroacetanilide in Nitrobenzene, with Nitrogen

$[\mathrm{NCA}]_o = 0.100\mathrm{M}$

A T = 161°			B T = 169°		
Time (hr.)	$[\mathrm{NCA}]$ M x10^2	$\mathrm{Log}_{10}[\mathrm{NCA}]$	Time (hr.)	$[\mathrm{NCA}]$ M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCA}]$
0.05	8.91	-1.050	0.20	8.60	-1.065
0.20	8.80	-1.055	0.50	8.15	-1.089
0.50	8.61	-1.065	0.75	7.85	-1.105
1.25	8.27	-1.083	1.25	7.12	-1.148
2.25	7.24	-1.138	2.15	4.51	-1.346
3.00	7.04	-1.153	2.60	1.67	-1.778
3.50	6.19	-1.209	2.75	0.96	-2.065
5.00	3.44	-1.463	2.90	0.09	-3.035
5.50	2.70	-1.568	3.00	0.06	-3.200
6.00	1.86	-1.731	3.20	0.00	
7.00	0.72	-2.150			
7.50	0.26	-2.585			
8.00	0.00				

Table A15

The Rearrangement of N-Chloroacetanilide in Nitrobenzene with Nitrogen Aspirating the Solution

$[NCA]_o$ = 0.100M
T = 182°

Time (hr.)	[NCA] $M \times 10^2$	$\mathrm{Log}_{10}[NCA]$
0.10	8.72	-1.060
0.15	8.63	-1.064
0.25	8.29	-1.081
0.35	8.06	-1.094
0.45	7.79	-1.109
0.50	7.62	-1.118
0.60	6.83	-1.165
0.75	6.27	-1.203
0.88	5.72	-1.243
0.95	5.02	-1.299
1.05	4.39	-1.357
1.20	3.51	-1.455
1.35	0.54	-2.268
1.40	0.14	-2.850

Table A16

The Thermal Rearrangement of N-Chlorophenylacetanilide in Nitrobenzene at 156°.

$[NCP]_o = 0.100M$

A

no nitrogen

B

nitrogen was bubbled through the solution, throughout the reaction.

Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$	Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$
0.10	8.91	-1.050	0.25	8.86	-1.053
0.20	8.81	-1.054	0.33	8.70	-1.060
0.30	8.65	-1.063	0.5	8.51	-1.070
0.40	8.31	-1.080	0.75	8.15	-1.079
0.50	8.10	-1.091	0.83	8.10	-1.081
0.66	7.72	-1.112	1.16	7.85	-1.105
0.83	6.74	-1.171	1.25	7.47	-1.127
1.00	5.40	-1.267	1.66	6.94	-1.158
1.10	4.34	-1.363	2.15	5.96	-1.225
1.20	3.41	-1.467	3.00	4.17	-1.381
1.40	0.05	-3.334	3.42	3.32	-1.478
1.50	0.01	-3.911	4.16	1.21	-1.918

Table A17

The Thermal Rearrangement of N-Chlorodiphenylacetanilide in Nitrobenzene at 156°.

$[\text{NCD}]_o = 0.100\text{M}$

A — no nitrogen.

B — nitrogen was bubbled through the solution throughout the reaction.

A: Time (hr.)	A: $[\text{NCD}]$ M x 10^2	A: $\text{Log}_{10}[\text{NCD}]$	B: Time (hr.)	B: $[\text{NCD}]$ M x 10^2	B: $\text{Log}_{10}[\text{NCD}]$
0.05	8.93	-1.049	0.10	8.95	-1.046
0.10	8.79	-1.056	0.20	8.83	-1.054
0.15	8.37	-1.073	0.33	8.53	-1.070
0.20	7.80	-1.108	0.40	8.47	-1.072
0.30	5.97	-1.224	0.50	8.20	-1.085
0.35	4.78	-1.321	0.66	7.56	-1.121
0.40	3.38	-1.471	1.00	5.88	-1.231
0.45	2.24	-1.657	1.20	4.56	-1.340
0.50	0.81	-2.003	1.40	3.05	-1.516
0.55	0.09	-3.054	1.60	1.52	-1.819
0.60	0.02	-3.700	1.85	0.25	-2.598
			1.95	0.03	-3.623

Table A18

The Thermal Rearrangement of N-Chlorobenzenesulphonanilide in Nitrobenzene at 156°

$[NCBS]_o = 0.100M$

Without Nitrogen			With Nitrogen		
Time (hr.)	$[NCBS]$ M x 10^2	$Log_{10}[NCBS]$	Time (hr.)	$[NCBS]$ M x 10^2	$Log_{10}[NCBS]$
0.05	8.30	-1.080	0.10	7.41	-1.131
0.10	7.69	-1.114	0.20	5.91	-1.117
0.20	6.14	-1.212	0.30	4.88	-1.312
0.30	4.68	-1.331	0.40	3.63	-1.443
0.40	4.07	-1.392	0.50	2.82	-1.551
0.45	3.45	-1.462	0.60	2.50	-1.613
0.55	2.43	-1.614	0.70	1.85	-1.723
0.60	2.14	-1.668	0.80	1.45	-1.837
0.70	1.66	-1.782	0.90	1.17	-1.931
0.85	1.14	-1.940	1.00	0.97	-2.012
1.10	0.52	-2.278	1.20	0.56	-2.249
1.30	0.19	-2.712	1.40	0.40	-2.401
1.45	0.08	-3.119	1.75	0.11	-2.958

Table A19

The Thermal Rearrangement of N-Chlorobenzenesulphonanilide in Nitrobenzene aspirated with nitrogen

$[\mathrm{NCBS}]_o = 0.100\mathrm{M}$

B			C		
T = 150.5°			T = 137°		
Time (hr.)	[NCBS] M x 10^2	Log_{10} [NCBS]	Time (hr.)	[NCBS] M x 10^2	Log_{10} [NCBS]
0.20	7.14	-1.146	0.25	7.26	-1.139
0.25	6.83	-1.165	0.40	6.31	-1.203
0.75	3.27	-1.485	0.60	5.33	-1.273
1.25	1.90	-1.721	1.00	3.53	-1.453
1.50	1.22	-1.913	1.20	2.84	-1.537
1.75	0.86	-2.064	2.10	1.11	-1.954
2.00	0.58	-2.236	2.45	0.80	-2.096
2.25	0.37	-2.435	2.65	0.62	-2.207
3.00	0.15	-2.818	2.95	0.29	-2.531
3.50	0.07	-3.155	3.25	0.23	-2.632
3.75	0.04	-3.408	3.60	0.10	-2.994

Table A20

The Thermal Rearrangement of N-Chlorobenzenesulphonanilide in Nitrobenzene aspirated with Nitrogen

$[\mathrm{NCBS}]_o = 0.100\mathrm{M}$

D

$T = 132^{\circ}$

Time (hr.)	$[\mathrm{NCBS}]$ M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCBS}]$
0.50	7.30	-1.137
1.00	5.93	-1.227
1.30	5.12	-1.291
1.70	4.47	-1.350
2.10	3.67	-1.435
2.50	2.90	-1.528
3.10	2.37	-1.625
3.50	1.88	-1.725
4.75	1.09	-1.962
5.50	0.79	-2.101
6.00	0.71	-2.149
7.00	0.51	-2.311

E

$T = 126^{\circ}$

Time (hr.)	$[\mathrm{NCBS}]$ M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCBS}]$
0.50	8.06	-1.084
1.00	7.19	-1.143
1.25	6.81	-1.167
1.75	6.05	-1.218
2.10	5.50	-1.259
2.50	5.08	-1.294
3.00	4.35	-1.362
4.00	3.69	-1.433

Table 21

The Thermal Rearrangement of N-Chloromethanesulphonanilide in Nitrobenzene at 156°.

$[\mathrm{NCMS}]_o = 0.100\mathrm{M}$

A without Nitrogen			B with Nitrogen		
Time (hr.)	[NCMS] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCMS}]$	Time (hr.)	[NCMS] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCMS}]$
0.05	7.75	-1.111	0.05	7.67	-1.115
0.10	6.46	-1.190	0.10	6.25	-1.204
0.15	5.02	-1.289	0.20	4.40	-1.356
0.20	3.85	-1.415	0.30	3.16	-1.500
0.25	2.36	-1.627	0.40	2.22	-1.653
0.30	1.49	-1.825	0.50	1.51	-1.821
0.35	0.57	-2.245	0.60	1.05	-1.979
0.38	0.24	-2.624	0.70	0.76	-2.124
0.40	0.03	-2.588	0.80	0.50	-2.296
0.45	0.00		0.90	0.32	-2.481
			1.00	0.20	-2.705

Table A22

The Thermal Rearrangement of N-Chloromethanesulphonanilide in Nitrobenzene, Aspirated with Nitrogen

$[\mathrm{NCMS}]_o = 0.100\mathrm{M}$

Nitrogen Flow-rate = 2.0 $\mathrm{l.hr.}^{-1}$

A			B		
T = 118^o			T = 126^o		
Time (hr.)	[NCMS] M x 10^2	Log_{10}[NCMS]	Time (hr.)	[NCMS] M x 10^2	Log_{10}[NCMS]
0.25	8.87	-1.052	0.10	8.97	-1.047
0.50	8.84	-1.079	0.20	8.61	-1.065
0.75	7.64	-1.117	0.40	7.80	-1.108
1.00	7.32	-1.135	0.60	7.38	-1.132
1.50	6.22	-1.205	1.00	5.83	-1.234
2.05	5.31	-1.274	1.35	5.20	-1.280
3.00	4.37	-1.360	1.56	5.00	-1.303
5.85	2.06	-1.684	2.10	3.54	-1.452
7.00	1.43	-1.842	3.60	1.90	-1.722
8.00	1.11	-1.954	4.00	1.65	-1.782
			5.25	0.85	-2.063
			6.00	0.56	-2.248
			7.00	0.31	-2.505

Table A23

The Thermal Rearrangement of N-Chloromethanesulphonanilide in Nitrobenzene, Aspirated with Nitrogen

$[\mathrm{NCMS}]_o$ = 0.100M

Temperature = 132°

Nitrogen Flow-rate = 2 l. hr.$^{-1}$

Time (hr.)	[NCMS] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCMS}]$
0.10	8.65	-1.063
0.15	7.90	-1.098
0.20	7.69	-1.113
0.30	7.40	-1.129
0.50	6.89	-1.162
0.75	5.88	-1.231
1.00	5.31	-1.275
1.50	3.76	-1.425
2.00	2.74	-1.562
3.00	1.61	-1.792
4.00	0.90	-2.047

Table A24

The Thermal Rearrangement of N-Chloro- 4'- nitrobenzanilide, in Nitrobenzene at 156°.

[NC4'nB] = 0.100M

A Without Nitrogen			B Aspirated with Nitrogen		
Time (hr.)	[NC4'nB] M x 10^2	Log$_{10}$[NC4'nB]	Time (hr.)	[NC4'nB] M x 10^2	Log$_{10}$[NC4'nB]
0.10	8.77	-1.057	0.35	7.78	-1.109
0.20	8.49	-1.080	0.70	7.08	-1.150
0.30	8.20	-1.086	1.75	4.24	-1.372
0.45	7.82	-1.107	2.50	2.58	-1.589
0.55	7.05	-1.152	3.00	1.77	-1.754
0.70	6.64	-1.178	3.25	1.28	-1.891
0.85	6.01	-1.221	3.75	0.65	-2.188
1.10	4.43	-1.354	4.00	0.41	-2.389
1.20	4.10	-1.387	4.40	0.20	-2.700
1.35	3.25	-1.486	5.00	0.00	
1.50	2.27	-1.645			
1.75	0.60	-2.216			
1.80	0.25	-2.604			
1.85	0.02	-3.700			

Table A25

Thermal Rearrangement of N-Chloro-4-nitrobenzanilide

A			B		
Without Nitrogen			Aspirated with Nitrogen		
Time (hr.)	[NC4nB] M x 10^2	Log$_{10}$[NC4nB]	Time (hr.)	[NC4nB] M x 10^2	Log$_{10}$[NC4nB]
0.1	9.14	-1.040	0.13	8.57	-1.067
0.3	8.60	-1.066	0.30	8.57	-1.070
0.5	7.96	-1.099	0.75	7.53	-1.123
0.75	6.92	-1.160	1.20	6.38	-1.195
0.95	6.32	-1.199	1.75	5.32	-1.275
1.20	5.23	-1.292	2.0	4.50	-1.347
1.40	4.23	-1.374	2.5	3.01	-1.522
1.60	3.51	-1.455	2.8	2.05	-1.689
1.90	1.79	-1.748	3.1	1.43	-1.845
2.05	1.13	-1.946	3.75	0.59	-2.254
2.10	1.08	-1.068	4.25	0.28	-2.548
2.35	0.20	-2.700	4.5	0.16	-2.800

Table A26

Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114°.

$[NCB]_o = [A]_o = 0.070M$

A No added anilide		B Added benzanilide		C Added N-phenylbenzanilide	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
5.5	6.37	1.00	6.37	5.00	6.43
23.5	6.31	6.75	6.30	14.75	6.36
44.5	6.15	10.25	6.30	18.75	6.30
55.5	5.93	15.25	6.15	23.50	6.24
71.0	5.68	20.50	6.11	28.75	6.08
79.5	5.55	23.50	5.99	42.75	5.93
95.0	5.27	25.80	5.90	48.75	5.85
116.0	4.84	29.00	5.70	62.75	5.59
143.0	4.27	39.25	5.30	67.5	5.51
168.0	3.82	46.75	4.94	71.25	5.22
215.0	2.46	50.50	4.55	84.75	4.87
239.0	1.97	68.00	2.96	88.50	4.67
264.0	1.22	71.25	2.51	93.50	4.43
288.0	0.58	75.50	1.84	108.50	3.69
		79.50	1.45	152.00	0.68
		87.25	0.33	163.00	0.46
		89.25	0.20		

Table A27

Thermal Rearrangement of N-Chlorobenzanilide, in Chlorobenzene, in 114°, in the Presence of Derivatives of Acetanilide

$[NCB]_o$ = 0.070M

A With acetanilide		B With N-methylacetanilide		C With N-phenyl-acetanilide	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
1.00	6.44	0.75	6.24	0.50	6.49
2.00	6.37	20.0	6.28	18.75	6.36
3.00	6.24	23.5	6.16	23.50	6.26
7.00	5.98	31.2	6.03	38.75	6.09
9.50	5.58	44.0	5.64	46.75	5.88
15.75	4.19	50.7	5.67	62.75	5.52
19.0	3.34	57.0	5.27	71.30	5.20
25.25	1.63	71.3	4.48	87.50	4.67
26.00	1.43	80.5	3.73	91.50	4.47
26.50	1.33	97.0	1.52	95.50	4.07
27.00	1.14	100.0	1.20	110.50	2.98
29.50	0.49	105.0	0.67	117.00	2.35

Table A28

Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114°, (A) in the Presence of 2-Phenylacetanilide, and (B) in the Presence of 2,2-Diphenylacetanilide

A

$[NCB]_o$ = 0.070M

$[A]_o$ = 0.070M

B

$[NCB]_o$ = 0.070M

$[A]_o$ = 0.070M

Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$
2.5	6.42	3.5	6.47
4.5	6.28	7.0	6.38
6.5	6.22	9.0	6.13
13.5	6.08	13.5	6.01
16.5	5.92	15.5	5.86
18.5	5.58	16.5	5.77
20.5	5.36	20.5	5.51
22.5	5.05	23.5	5.24
30.5	3.79	29.0	4.58
40.0	2.12	38.0	2.97
41.5	1.72	42.0	1.79
43.5	1.09	49.0	0.36
46.5	0.02	51.0	0.19

Table A29

Thermal Rearrangement of N-Chlorobenzanilide in the Presence of Added (A) Formanilide and (B) Trichloroacetanilide

[NCB] = 0.070M

[Anilide] = 0.070M

A		B	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
0.5	6.40	2.0	6.36
1.5	6.35	7.5	6.25
2.5	6.32	16.0	6.16
4.0	6.20	25.5	5.98
6.5	5.53	31.5	5.74
8.5	5.00	40.0	5.66
15.5	3.34	47.0	5.40
16.5	2.99	55.0	5.27
19.5	2.18	63.0	5.12
21.5	1.25	71.5	4.92
23.0	1.16	92.0	4.39
28.0	0.42	100.5	4.11
30.0	0.15	115.0	3.53
		122.0	3.24
		151.0	2.22
		175.0	1.25
		197.0	0.20

Table A30

Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114°, (A) with added 2'-Chlorobenzanilide and (B) with added 4'-Chlorobenzanilide

$[\text{NCB}]_o$ = 0.070M

[Anilide] = 0.070M

A		B	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
3.75	6.34	5.50	6.36
23.50	6.13	15.75	6.23
29.25	5.99	23.00	6.05
34.00	5.89	27.00	6.04
53.00	5.74	40.00	5.77
71.00	5.06	47.50	5.60
80.00	4.92	55.50	4.99
96.50	4.46	72.00	3.76
144.00	2.82	75.00	3.48
151.00	2.49	79.50	2.78
174.00	1.67		
200.00	0.40		

Table A31

Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114^{o} (A) with 4'-Fluorobenzanilide, (B) with 4'-Bromobenzanilide, and (C) with 4'-Iodobenzanilide

$[NCB]_o = 0.070M$ $[A] = 0.070M$

A		B		C	
Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$
2.0	6.48	7.0	6.53	0.5	6.06
7.0	6.46	15.0	6.38	1.0	5.68
18.0	6.27	23.0	6.27	1.5	4.72
23.0	6.05	47.0	5.17	2.0	2.73
41.0	4.86	50.0	4.95	2.2	1.99
44.5	4.51	55.5	4.41	2.3	1.39
50.5	4.17	72.5	2.77	2.5	0.75
64.0	2.49	77.5	2.32	2.7	0.48
68.5	1.85	82.5	2.01	2.8	0.22
71.5	1.14	95.5	0.71	3.0	0.14
75.0	0.80	98.0	0.48	3.3	0.07
78.0	0.43	102.0	0.22	3.5	0.02

Table A32

Thermal Rearrangement of N-Chlorobenzanilide in Chlorobenzene at 114° with Added (A) 4'-Phenoxybenzanilide (B) 4'-Phenylbenzanilide (C) 4'-Nitrobenzanilide and (D) 4'-Benzoylbenzanilide.

$[NCB]_o$ = 0.070M $[Anilide]_o$ = 0.070M

A		B		C		D	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
3.5	6.48	4.5	6.41	5.0	6.42	1.0	6.41
8.5	6.24	9.5	6.41	16.5	6.21	4.0	6.48
14.0	6.01	9.5	6.20	25.0	6.22	7.0	6.34
22.5	5.43	23.5	5.99	27.0	6.14	9.0	6.23
27.5	4.91	26.3	5.88	40.0	5.66	24.0	4.39
32.0	4.51	33.0	5.38	42.0	5.47	28.5	3.61
39.0	4.00	40.0	5.10	46.0	5.11	32.5	3.09
43.5	3.35	43.0	4.74	52.0	4.86	47.5	1.12
48.0	2.74	47.8	4.44	63.5	2.36	52.5	0.37
50.5	2.26	53.5	4.05	67.5	2.03	59.0	0.05
56.0	1.38	63.0	2.67	73.5	1.56		
58.5	0.92	68.5	1.75	90.0	0.50		
		72.0	1.20	95.0	0.30		
		87.0	0.05				

Table A33

Thermal Rearrangement of N-Chlorobenzanilide, in Chlorobenzene at 114°, with added (A) 4-Nitrobenzanilide (B) 4-Chlorobenzanilide

$[NCB]_o$ = 0.070M

$[Anilide]_o$ = 0.070M

A		B	
Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$
2.0	6.48	1.0	6.42
4.5	6.41	7.0	6.19
6.0	6.34	8.5	6.18
7.5	6.17	17.5	5.46
9.0	5.99	22.5	5.05
14.8	5.10	24.0	4.71
16.5	5.04	25.5	4.43
21.8	3.76	32.0	3.62
23.3	3.38	39.7	2.46
27.0	1.83	42.3	1.99
29.0	1.05	45.5	1.05
31.0	0.11	48.0	0.58

Table A34

Thermal Rearrangement of N-Chlorobenzanilide at 114°, with Added (A) Methanesulphonanilide, (B) N-Methylmethanesulphonanilide, (C) Benzenesulphonanilide and (D) Diphenyl N-Phenylphosporamidate

$[\mathrm{NCB}]_o = 0.070\mathrm{M}$ $[\mathrm{A}]_o = 0.070\mathrm{M}$

Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
0.50	6.27	0.5	6.49	3.0	6.49	3.0	6.29
1.00	6.20	4.0	6.47	7.0	6.36	7.0	6.11
2.00	5.77	7.5	6.35	9.0	6.22	9.0	5.96
2.60	5.44	16.0	6.30	16.5	6.00	15.0	5.61
3.30	4.62	24.0	6.25	23.0	5.18	18.0	5.44
3.85	3.87	27.0	6.07	27.0	3.83	27.0	3.85
4.50	2.54	34.0	5.88	30.0	2.92	30.0	2.76
4.75	1.99	40.0	5.82	32.0	2.26	32.0	2.30
5.00	1.37	45.0	5.38	33.0	1.88	33.0	1.88
5.25	0.89	53.0	5.18	40.0	0.10		
5.50	0.20	58.0	5.00	45.0	0.02		
5.75	0.09	68.0	4.20				
		89.0	3.10				
		93.0	2.73				

Table A3.5

Thermal Rearrangement of N-Chlorobenzanilide, in Chlorobenzene, at 114°, in the presence of (A), (B) Acetanilide and (C) Methanesulphonanilide, aspirated with Nitrogen.

$[NCB]_o$ = 0.070M

[Anilide] = 0.070M

A		B		C	
Nitrogen Flow-rate = 2.0 l.hr.$^{-1}$		Nitrogen Flow-rate = 0.5 l.hr.$^{-1}$		Nitrogen Flow-rate = 1.0 l.hr.$^{-1}$	
Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
3.50	6.38	3.5	6.33	0.50	6.40
15.50	6.12	7.0	5.82	1.00	6.42
20.00	6.11	22.0	4.72	1.50	6.28
23.50	5.85	23.0	4.43	3.00	6.03
39.75	4.52	25.5	4.35	5.50	5.34
44.25	4.16	28.0	3.69	7.50	4.67
48.25	3.33	29.0	3.30	9.50	4.34
65.00	1.24	48.0	0.30	23.75	2.10
72.00	0.10			27.75	1.62

Table A36

Thermal Rearrangement of N-Chloroacetanilide in Chlorobenzene at 114°, (A) alone, (B) in the Presence of Added Benzanilide (B)

$[NCA]_o = 0.070M$

$[B]_o = 0.070M$

A		B	
Time (hr.)	[NCA] M $\times 10^2$	Time (hr.)	[NCA] M $\times 10^2$
1.0	6.41	4.0	6.45
15.0	6.38	8.0	6.30
24.0	6.38	23.5	6.39
39.0	6.46	32.0	6.44
48.0	6.50	71.5	6.29
61.0	6.35	80.5	6.32
74.0	6.42	96.0	6.22
85.0	6.36		
99.0	6.32		

Table A37

Thermal Rearrangement of (A) N-Chloromethanesulphonanilide and (B) N-Chlorobenzenesulphonanilide, in Chlorobenzene at 114°.

A

$[\text{NCMS}]_o$ = 0.070M

B

$[\text{NCBS}]_o$ = 0.070M

Time (hr.)	[NCMS] M x 10^2	Time (hr.)	[NCBS] M x 10^2
1.0	5.95	0.5	5.42
2.0	5.67	1.5	6.37
3.0	5.17	2.0	6.18
4.0	4.77	3.5	5.87
4.75	4.55	4.75	5.61
5.75	4.05	12.5	4.04
7.0	3.43	14.0	3.75
8.75	2.96	16.0	3.41
		18.0	3.08
		20.5	2.68
		43.5	0.58
		45.5	0.48
		47.0	0.34

Table A38

Photolysis of N-Chlorobenzanilide

$[NCB]_o = 0.100M$

A

Control Experiment

B

Time (hr.)	[NCB] M x 10^2	Log$_{10}$[NCB]	Time (hr.)	[NCB] M x 10^2	Log$_{10}$[NCB]
18.0	9.56	-1.020	0.5	8.81	-1.055
43.5	9.68	-1.014	1.5	7.87	-1.104
68.5	9.64	-1.016	2.5	7.31	-1.136
92.2	9.56	-1.020	3.5	6.24	-1.205
138.0	9.98	-1.001	4.5	5.54	-1.253
189.0	9.93	-1.003	6.5	4.47	-1.350
			8.0	3.79	-1.422
			9.0	3.31	-1.480
			13.0	2.16	-1.665
			14.0	1.93	-1.715
			16.0	1.49	-1.826
			17.0	1.30	-1.885
			18.0	1.15	-1.937
			20.0	0.98	-2.006
			25.0	0.57	-2.248

Table A39

Photolysis of N-Chlorobenzanilide

A			B		
$[NCB]_o$ = 0.070M			$[NCB]_o$ = 0.040M		
Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]	Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
0.50	6.15	-1.211	0.5	3.53	-1.452
1.00	5.95	-1.226	1.5	3.07	-1.513
1.50	5.53	-1.257	2.5	2.54	-1.595
2.00	5.14	-1.289	4.0	2.16	-1.665
3.00	4.55	-1.342	5.0	1.87	-1.729
4.00	3.90	-1.409	6.0	1.63	-1.781
5.00	3.57	-1.447	7.0	1.43	-1.843
6.00	3.08	-1.512	7.5	1.28	-1.893
7.00	2.81	-1.552	8.5	1.15	-1.937
7.75	2.57	-1.590	9.5	1.04	-1.983
10.00	2.08	-1.682	10.5	0.94	-2.023
12.50	1.42	-1.847	12.0	0.71	-2.148
18.00	0.77	-1.111			
20.00	0.53	-1.278			
23.50	0.35	-2.462			

Table A40

Photolysis of N-Chlorophenylacetanilide

$[NCP]_o = 0.100M$

Control Experiment

Solution was not irradiated | Solution was irradiated

Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$	Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$
1	9.62	-1.017	0.50	8.86	-1.053
25	9.59	-1.018	1.00	8.37	-1.076
49	9.67	-1.015	1.50	7.93	-1.101
73	9.64	-1.016	2.00	7.31	-1.136
101	9.53	-1.021	3.00	6.34	-1.198
			4.00	5.21	-1.283
			5.25	4.16	-1.381
			6.00	3.51	-1.455
			7.00	2.56	-1.592
			7.50	2.32	-1.634
			8.50	1.53	-1.815
			9.25	0.99	-2.003
			9.50	0.81	-2.092
			10.00	0.49	-2.322
			10.50	0.23	-2.045

Table A41

Photolysis of N-Chlorophenylacetanilide

$[NCP]_o = 0.070M$ $[NCP]_o = 0.040M$

Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$	Time (hr.)	[NCP] M x 10^2	$Log_{10}[NCP]$
0.50	6.25	-1.204	0.25	3.77	-1.423
1.00	5.77	-1.239	0.50	3.61	-1.443
2.00	4.97	-1.303	1.00	3.28	-1.484
2.50	4.54	-1.347	1.50	2.91	-1.535
3.50	3.81	-1.419	2.00	2.58	-1.588
4.60	3.07	-1.513	2.50	2.34	-1.630
5.50	2.49	-1.604	3.00	2.04	-1.690
6.10	2.09	-1.680	3.50	1.79	-1.748
7.25	1.45	-1.827	5.00	1.14	-1.943
8.10	1.08	-1.967	5.50	0.98	-2.008
8.50	0.90	-2.045	6.00	0.72	-2.145
9.00	0.68	-2.166	6.50	0.59	-2.227
9.25	0.60	-2.222	7.00	0.48	-2.317
9.50	0.48	-2.316	7.75	0.32	-2.496
10.50	0.22	-2.661	9.00	0.13	-2.860

Table A42

Photolysis of N-Chlorodiphenylacetanilide

$[\mathrm{NCD}]_o = 0.100\mathrm{M}$

Control Experiment

Solution was not irradiated			Solution was irradiated		
Time (hr.)	[NCD] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCD}]$	Time (hr.)	[NCD] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCD}]_o$
0	9.58	-1.019	0.50	9.16	-1.038
25	9.62	-1.017	1.00	8.32	-1.080
35	9.60	-1.018	1.50	7.51	-1.124
49	9.61	-1.017	2.00	6.45	-1.190
56	9.60	-1.018	2.50	5.66	-1.247
72	9.62	-1.017	3.50	3.89	-1.411
120	9.74	-1.011	4.50	2.10	-1.677
			5.00	1.43	-1.844
			5.25	1.16	-1.934
			5.50	0.88	-2.064
			5.75	0.72	-2.142
			6.25	0.35	-2.454
			7.25	0.07	-3.152
			7.75	0.04	-3.400

Table A43

Photolysis of N-Chlorodiphenylacetanilide

$[NCD]_o = 0.040M$ $[NCD]_o = 0.070M$

Time (hr.)	$[NCD]$ M x 10^2	$\log_{10}[NCD]$	Time (hr.)	$[NCD]$ M x 10^2	$\log_{10}[NCD]$
0.25	3.65	-1.437	0.50	6.05	-1.218
0.50	3.48	-1.458	0.75	5.70	-1.254
0.75	3.24	-1.489	1.00	5.38	-1.270
1.00	2.99	-1.524	1.50	4.77	-1.321
1.50	2.58	-1.387	2.00	4.07	-1.391
2.00	2.15	-1.668	2.50	3.54	-1.448
2.50	1.76	-1.754	3.00	2.85	-1.545
3.00	1.40	-1.853	3.50	2.32	-1.655
3.50	1.10	-1.953	4.00	1.68	-1.776
4.00	0.88	-2.057	4.50	1.37	-1.865
4.50	0.62	-2.209	5.00	0.99	-2.003
5.50	0.34	-2.572	5.50	0.65	-2.183
6.50	0.16	-2.756	5.75	0.56	-2.252
7.50	0.08	-3.091	7.00	0.28	-2.545

Table A44

Photolysis of N-Chloromethanesulphonanilide

$[\text{NCMS}]_0 = 0.100\text{M}$

Control Experiment

Solution was not irradiated / Solution was irradiated

Time (hr.)	[NCMS] M x 10^2	Log_{10} [NCMS]	Time (hr.)	[NCMS] M x 10^2	Log_{10} [NCMS]
1.00	9.59	-1.018	0.25	9.10	-1.041
9.00	9.66	-1.015	0.50	8.67	-1.062
24.00	9.60	-1.018	1.00	7.69	-1.114
34.50	9.55	-1.021	1.50	6.78	-1.169
			2.00	5.94	-1.226
			2.50	5.25	-1.280
			3.00	4.62	-1.335
			3.50	4.06	-1.392
			4.00	3.56	-1.449
			4.50	3.10	-1.509
			5.00	2.68	-1.572
			5.50	2.31	-1.637
			6.00	1.98	-1.699
			6.50	1.69	-1.772
			7.00	1.51	-1.831
			8.00	1.09	-1.971

Table A45

Photolysis of N-Chloromethanesulphonanilide

$[NCMS]_o$ = 0.030M			$[NCMS]_o$ = 0.070M		
Time (hr.)	[NCMS] M x 10^2	Log$_{10}$ [NCMS]	Time (hr.)	[NCMS] M x 10^2	Log$_{10}$ [NCMS]
0.25	2.57	-1.599	0.25	6.15	-1.211
0.50	2.28	-1.642	0.50	5.87	-1.231
0.75	2.06	-1.686	0.75	5.39	-1.268
1.00	1.85	-1.722	1.00	5.05	-1.297
1.50	1.51	-1.821	1.25	4.75	-1.323
2.00	1.31	-1.947	1.50	4.41	-1.356
2.50	0.94	-2.025	2.00	3.86	-1.413
3.25	0.64	-2.194	2.50	3.37	-1.472
3.75	0.48	-2.319	3.00	2.96	-1.529
4.25	0.39	-2.414	3.50	2.56	-1.592
4.75	0.32	-2.489	4.00	2.24	-1.649
5.25	0.23	-2.636	4.50	1.96	-1.708
5.50	0.21	-2.660	5.50	1.39	-1.858
5.75	0.17	-2.757	6.50	1.01	-1.995
6.25	0.14	-2.847	7.50	0.72	-2.143

Table A46

Photolysis of N-Chlorobenzanilide

Solution Aspirated with Nitrogen

$[NCB]_o = 0.070M$

Time (hr.)	[NCB] M x 10^2	$Log_{10}[NCB]$
0.5	6.04	-1.219
1.3	5.57	-1.254
3.0	4.64	-1.333
5.0	3.87	-1.412
6.0	3.48	-1.464
7.0	3.10	-1.508
8.1	2.84	-1.585
9.75	2.40	-1.656
12.00	1.57	-1.805
14.0	1.19	-1.924
17.0	0.81	-2.101
20.0	0.62	-2.207
22.5	0.54	-2.272
25.0	0.44	-2.361

Table A47

Photolysis of N-Chlorophenylacetanilide

$[NCP]_o = 0.100M$

Reaction mixture was aspirated with Nitrogen.

Kinetics which would have been obtained if the reaction had been of the first-order throughout.

Time (hr.)	[NCP] $M \times 10^2$	$Log_{10}[NCP]$	Time (hr.)	[NCP] $M \times 10^2$	$Log_{10}[NCP]$
0.50	8.77	-1.057	0.0	9.55	-1.020
1.00	8.44	-1.074	1.0	8.51	-1.070
1.90	7.73	-1.112	2.0	7.60	-1.119
4.00	6.03	-1.220	3.0	6.79	-1.168
6.00	4.55	-1.342	4.0	6.08	-1.216
6.50	4.04	-1.384	5.0	5.46	-1.263
8.00	3.02	-1.520	6.0	4.89	-1.311
10.00	1.93	-1.714	7.0	4.37	-1.360
10.50	1.82	-1.739	8.0	3.91	-1.408
13.00	0.84	-2.075	9.0	3.49	-1.457
14.25	0.54	-2.270	10.0	3.11	-1.508
14.75	0.45	-2.355	11.0	2.79	-1.553
15.50	0.39	-2.415	12.0	2.51	-1.600
16.50	0.15	-2.795	14.0	2.00	-1.699
17.50	0.07	-3.104	16.0	1.60	-1.795

Table A48

Photolysis of N-Chlorodiphenylacetanilide

$[\mathrm{NCD}]_o = 0.100\mathrm{M}$

Reaction mixture was aspirated with Nitrogen.

N_2 flow-rate = 4 l. hr.$^{-1}$

Kinetics which would have been obtained if the reaction had been of the first-order throughout.

Time (hr.)	[NCD] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCD}]$	Time (hr.)	[NCD] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCD}]$
1.0	8.07	-1.094	0.0	9.60	-1.018
1.5	7.21	-1.143	1.0	8.18	-1.087
2.0	6.50	-1.187	2.0	7.10	-1.149
3.0	4.76	-1.323	3.0	6.19	-1.208
5.0	2.22	-1.653	4.0	5.33	-1.273
5.5	1.81	-1.743	5.0	4.60	-1.338
6.0	1.45	-1.838	6.0	3.99	-1.399
6.5	1.05	-1.977	7.0	3.46	-1.461
7.0	0.79	-2.104	8.0	3.06	-1.522
7.5	0.58	-2.234	9.0	2.59	-1.587
8.0	0.36	-2.447	10.0	2.24	-1.649
8.5	0.27	-2.568	12.0	1.70	-1.770
9.0	0.16	-2.790	14.0	1.26	-1.900
9.8	0.08	-3.091	16.0	0.96	-2.028

Table A-49

Photolysis of N-Chloromethanesulphonanilide

$[\mathrm{NCMS}]_o = 0.100M$

Solution was aspirated with nitrogen.

N_2 Flow-rate = 0.5 l./hr.

Time (hr.)	[NCMS] M x 10^2	$\mathrm{Log}_{10}[\mathrm{NCMS}]$
0.25	8.96	-1.048
0.50	8.70	-1.061
1.25	7.23	-1.140
2.00	5.86	-1.232
2.50	5.12	-1.280
3.85	3.55	-1.450
4.50	3.02	-1.520
5.00	2.55	-1.593
5.75	2.04	-1.690
7.35	1.29	-1.890
8.06	1.06	-1.975
9.15	0.77	-2.112
9.56	0.64	-2.193
23.25	0.01	-3.835

Table A50

The Decomposition of N-Chlorobenzanilide, in the presence of Added Anilides, in Carbon Tetrachloride at 77.7°, in the dark.

[NCB] = 0.070M [Anilide] = 0.035M

A		B		C		D	
with added benzanilide		with added acetanilide		with added benzenesulphonanilide		with added methanesulphonanilide	
Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$	Time (hr.)	[NCB] $M \times 10^2$
8.0	6.60	8.0	6.70	1.0	6.75	2.0	6.75
26.0	6.72	26.0	6.77	18.0	6.69	32.0	6.70
72.0	6.93	72.0	6.81	66.0	6.73	53.0	6.84
120.5	6.89	120.5	6.89	114.0	6.82	120.0	6.95

Table A51

Photolysis of N-Chlorobenzanilide in the presence of Added Anilides in Carbon Tetrachloride

[NCB] = 0.070M

A			B		
[Benzanilide] = 0.035M			[Acetanilide] = 0.035M		
Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]	Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
1.00	5.87	-1.239	0.75	6.41	-1.193
1.50	5.32	-1.274	1.50	5.47	-1.262
3.00	3.91	-1.408	2.50	4.66	-1.332
5.00	2.90	-1.536	3.75	3.52	-1.453
6.00	2.46	-1.608	5.12	2.34	-1.631
7.25	2.04	-1.697	6.50	1.44	-1.843
8.50	1.58	-1.801	6.75	1.29	-1.887
10.00	1.20	-1.919	7.50	0.86	-2.067
11.00	0.83	-2.080	8.50	0.65	-2.186
			9.00	0.41	-2.382

Table A52

Photolysis of N-Chlorobenzanilide in the Presence of Added Anilides in Carbon Tetrachloride

[NCB] = 0.070M

C

[BS] = 0.035M

D

[MS] = 0.035M

Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]	Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
0.75	6.14	-1.211	0.50	6.47	-1.189
1.25	5.87	-1.244	1.00	5.87	-1.231
1.75	5.07	-1.295	1.75	4.80	-1.320
3.00	3.88	-1.413	2.50	3.79	-1.421
3.75	3.13	-1.504	3.50	2.59	-1.587
6.00	1.14	-1.943	4.50	1.29	-1.899
7.25	0.40	-2.400	4.75	0.98	-2.010
8.00	0.16	-2.783	5.00	0.81	-2.090
			5.50	0.24	-2.613
			5.75	0.13	-2.868
			6.25	0.03	-3.563

Table A53

The Photolylic Rearrangement of N-Chlorobenzanilide in Carbon Tetrachloride, in the Presence of (added) Methanesulphonanilide Aspirated with Nitrogen

[NCB] = 0.070M

[Methanesulphonanilide] = 0.035M

B			C		
Nitrogen Flow-rate 1.0 l.hr.$^{-1}$			Nitrogen Flow-rate 0.5 l.hr.$^{-1}$		
Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]	Time (hr.)	[NCB] M x 10^2	Log_{10}[NCB]
0.75	6.12	-1.213	0.50	6.36	-1.197
1.50	5.48	-1.261	1.00	5.95	-1.225
2.0	4.93	-1.307	1.75	5.20	-1.284
2.5	4.66	-1.332	2.50	4.39	-1.358
3.0	3.72	-1.430	3.00	3.74	-1.427
4.0	2.60	-1.585	3.25	3.33	-1.477
4.5	3.39	-1.665	3.75	2.48	-1.605
5.5	1.26	-1.898	4.25	1.96	-1.708
6.0	0.99	-2.022	5.00	1.20	-1.921
7.0	0.45	-2.349	5.75	0.50	-2.284
			6.50	0.12	-2.905
			6.75	0.09	-3.024

Table A54

The Rearrangement of N-Chlorobenzanilide, in Carbon Tetrachloride at 77.7°, Catalysed by Benzoyl Peroxide

A

$[NCB]_o$ = 0.100M
$[BzOH]$ = 0.100M
$[Bz_2O_2]$ = 0.000M

B

$[NCB]_o$ = 0.100M
$[Bz_2O_2]$ = 0.0086M

C

$[NCB]_o$ = 0.100M
$[Bz_2O_2]$ = 0.0172M

Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
0.10	9.61	0.50	9.50	0.25	9.53
0.50	9.64	1.10	9.38	1.00	9.41
0.75	9.59	2.20	9.16	1.75	9.23
3.00	9.58	5.00	9.00	4.00	8.80
4.75	9.54	7.50	8.62	6.00	8.49
6.75	9.41	9.66	8.27	7.00	8.39
24.00	9.56	11.66	8.06	9.00	8.19
32.00	9.52	15.50	7.76	15.75	7.63
48.00	9.44	23.80	7.56	23.50	6.95
56.50	9.40	30.60	7.21	24.00	6.92
71.50	9.27	33.00	7.09	26.50	6.82
79.50	9.38	48.50	6.73	30.50	6.62
		53.50	6.68	32.00	6.54
		63.00	6.47	40.00	6.09
		74.00	6.26	74.00	4.14
		79.00	6.18	97.00	3.64
		89.00	6.01		

	B	C
	Initial Rate = 1.3×10^{-3} M.hr.$^{-1}$	Initial Rate = 2.3×10^{-3} M.hr.$^{-1}$

Table A55

The Rearrangement of N-Chlorobenzanilide, in Carbon Tetrachloride at 77.7°, Catalysed by Benzoyl Peroxide

D: $[Bz_2O_2]$ = 0.0258M

E: $[Bz_2O_2]$ = 0.0344M

F: $[Bz_2O_2]$ = 0.0430M

Time (hr.)	$[NCB]$ M x 10^2	Time (hr.)	$[NCB]$ M x 10^2	Time (hr.)	$[NCB]$ M x 10^2
0.25	9.51	0.50	9.42	0.5	9.27
0.50	9.45	1.50	9.18	1.0	8.90
2.00	8.72	2.50	8.22	1.5	8.65
4.00	8.21	4.50	7.96	2.0	8.29
6.00	7.86	7.00	7.23	3.0	7.92
7.75	7.35	9.00	6.88	4.0	7.49
10.25	6.97	13.00	5.54	7.0	6.33
14.00	6.56	17.00	4.86	7.5	6.22
19.00	5.97	19.00	4.58	9.0	5.84
26.50	5.19	22.50	4.02	12.0	4.86
32.75	4.57	27.25	2.74	14.0	4.64
40.00	4.11	30.50	3.43	16.0	4.20
48.00	3.35	32.25	2.53	17.3	3.78
55.75	2.59	35.00	2.08	20.0	3.19
64.00	1.52	38.30	1.55	22.5	2.84
72.00	0.80	49.25	0.05	23.1	2.67
80.00	0.25	50.30	0.02	24.5	2.24

D: Initial Rate = 3.7×10^{-3} M.hr.$^{-1}$

E: Initial Rate = 4.85×10^{-3} M.hr.$^{-1}$

F: Initial Rate = 5.8×10^{-3} M.hr.$^{-1}$

Table A56

The Rearrangement of N-Chlorophenylacetanilide, in Carbon Tetrachloride, at 77.7°, Catalysed by Benzoyl Peroxide

A	B	C
$[NCP]_o$ = 0.100M	$[NCP]_o$ = 0.100M	$[NCP]_o$ = 0.100M
[Bz OH] = 0.100M		
$[Bz_2O_2]$ = 0.000H	$[Bz_2O_2]$ = 0.0086M	$[Bz_2O_2]$ = 0.0172M

Time (hr.)	[NCP] M x 10^2	Time (hr.)	[NCP] M x 10^2	Time (hr.)	[NCP] M x 10^2
1.0	9.51	1.5	9.37	0.50	9.42
3.0	9.66	2.5	9.21	1.75	9.09
8.0	9.45	4.1	8.88	2.50	8.89
32.0	9.68	5.0	8.80	3.75	8.55
47.0	9.79	7.5	8.50	6.75	7.71
56.0	9.85	9.2	8.43	7.75	7.39
71.0	9.84	15.0	7.61	13.75	6.09
80.0	9.91	19.5	7.35	15.25	5.62
		23.5	6.88	16.50	5.35
		26.0	6.53	18.75	4.79
		30.0	5.96	20.25	4.41
		40.0	5.51	23.50	3.60
		44.8	5.10	37.50	0.22
		54.0	4.20		
		87.0	1.49		
		95.0	0.59		

	B	C
	Initial Rate = 1.3×10^{-3} M.hr.$^{-1}$	Initial Rate = 2.9×10^{-3} M.hr.$^{-1}$

Table A57

The Rearrangement of N-Chlorophenylacetanilide, in Carbon Tetrachloride, at 77.7 °, Catalysed by Benzoyl Peroxide

D		E		F	
$[Bz_2O_2]$	= 0.0268M	$[Bz_2O_2]$	= 0.0344M	$[Bz_2O_2]$	= 0.0430M
[NCP]	= 0.100M	[NCP]	= 0.100M	[NCP]	= 0.100M
Time (hr.)	[NCP] $M \times 10^2$	Time (hr.)	[NCP] $M \times 10^2$	Time (hr.)	[NCP] $M \times 10^2$
0.10	9.60	0.50	9.43	0.25	9.51
0.25	9.51	1.00	9.10	1.00	8.01
0.50	9.38	1.50	8.99	1.50	8.65
1.00	9.16	2.00	8.52	2.00	8.22
1.50	9.10	3.00	8.01	2.50	7.85
2.50	8.53	4.00	7.49	3.00	7.62
4.00	8.07	6.00	6.63	3.50	7.11
6.00	7.29	7.00	6.22	5.50	6.03
7.50	6.87	8.50	5.62	7.00	5.10
8.50	6.58	9.00	5.34	7.50	4.88
9.25	6.24	9.50	5.15	8.50	6.40
12.00	5.39	12.00	4.14	10.25	3.36
15.00	4.31	14.50	3.07	11.63	2.59
17.50	3.40	16.00	2.47	13.50	1.48
19.75	2.51	17.00	1.90	16.25	0.74
24.00	1.42	17.75	1.511	15.00	0.31
26.00	0.92	18.25	1.312	15.50	0.15
27.00	0.39	20.00	0.48		
28.00	0.33				
27.50	0.36				
Initial Rate = 4.1×10^{-3} M.hr.$^{-1}$		Initial Rate = 5.65×10^{-3} M.hr.$^{-1}$		Initial Rate = 7.2×10^{-3} M.hr.$^{-1}$	

Table A58

The Rearrangement of N-Chlorodiphenylacetanilide, in Carbon Tetrachloride at 77.7°, Catalysed by Benzoyl Peroxide

A

$[Bz_2O_2]$ = 0.000M
$[Bz.OH]$ = 0.100M
$[NCD]_o$ = 0.100M

B

$[Bz_2O_2]$ = 0.0043M
$[NCD]$ = 0.100M

C

$[Bz_2O_2]$ = 0.0086M
$[NCD]$ = 0.100M

Time (hr.)	[NCD] M x 10^2	Time (hr.)	[NCD] M x 10^2	Time (hr.)	[NCD] M x 10^2
3.0	9.74	0.50	9.41	0.50	9.56
8.0	9.63	2.00	9.25	1.00	9.32
30.0	9.49	4.00	8.68	1.50	9.20
56.0	9.31	6.00	8.11	2.00	9.11
71.0	9.38	8.60	8.00	2.75	8.86
80.0	9.29	13.00	6.53	4.50	8.42
		25.50	5.55	5.00	8.11
		28.00	5.27	5.50	7.95
		32.25	4.93	7.00	7.57
		35.25	4.81	7.50	7.44
		48.25	4.47	24.00	2.04
		56.25	3.92	25.50	1.73
		59.75	4.04	26.50	1.47
		72.00	3.93	27.50	1.27
		80.00	3.62	28.50	1.07
		97.50	3.52	31.00	0.72
		145.00	3.40	33.00	0.37
		Initial Rate = 1.4×10^{-3} M.hr.$^{-1}$		Initial Rate = 2.88×10^{-3} M.hr.$^{-1}$	

Table A59

The Rearrangement of N-Chlorodiphenylacetanilide, in Carbon Tetrachloride at 77.7°, Catalysed by Benzoyl Peroxide

D

$[Bz_2O_2]$ = 0.0172M

$[NCD]$ = 0.100M

E

$[Bz_2O_2]$ = 0.0268M

$[NCD]$ = 0.100M

F

$[Bz_2O_2]$ = 0.0344M

$[NCD]$ = 0.100M

Time (hr.)	$[NCD]$ M x 10^2	Time (hr.)	$[NCD]$ M x 10^2	Time (hr.)	$[NCD]$ M x 10^2
0.50	9.26	0.25	9.47	0.50	9.36
0.75	9.14	0.50	9.44	1.00	8.68
1.00	9.05	1.00	9.09	1.50	8.31
1.50	8.89	1.50	8.73	2.50	7.21
2.00	8.53	2.25	8.23	3.00	6.78
2.50	8.48	2.75	7.74	3.50	6.24
3.50	7.85	3.50	7.20	4.50	5.24
5.00	6.83	4.00	6.31	5.00	4.41
6.00	6.27	5.00	5.54	6.00	3.46
7.00	5.56	6.00	4.36	6.50	3.13
8.00	5.18	7.00	3.19	6.75	2.27
9.50	4.19	7.75	2.61	7.00	1.94
13.00	0.74	8.25	2.03	7.50	1.25
14.00	0.30	8.75	1.48	8.50	0.35
15.00	0.05	9.50	0.60	9.25	0.18
16.75	0.01	10.00	0.30	9.50	0.06

Initial Rate = 5.1×10^{-3} M.hr.$^{-1}$

Initial Rate = 6.8×10^{-3} M. hr. $^{-1}$

Initial Rate = 9.8×10^{-3} M.hr.$^{-1}$

Table A60

The Rearrangement of N-Chloromethanesulphonanilide, at 77.7 °, in Carbon Tetrachloride, Catalysed by Benzoyl Peroxide.

A

$[\mathrm{NCMS}]_o = 0.100\mathrm{M}$
$[\mathrm{BzOH}] = 0.100\mathrm{M}$
$[\mathrm{Bz_2O_2}]_o = 0.000\mathrm{M}$

B

$[\mathrm{MCMS}]_o = 0.100\mathrm{M}$
$[\mathrm{Bz_2O_2}]_o = 0.0086\mathrm{M}$

C

$[\mathrm{NCMS}]_o = 0.100\mathrm{M}$
$[\mathrm{Bz_2O_2}]_o = 0.0172\mathrm{M}$

Time (hr.)	[NCMS] M x 10^2	Time (hr.)	[NCMS] M x 10^2	Time (hr.)	[NCMS] M x 10^2
3.0	9.61	0.50	9.30	0.50	9.30
8.0	9.67	1.00	9.19	1.00	9.01
23.5	9.58	2.00	9.12	1.50	8.93
32.0	9.55	4.25	8.74	2.25	8.57
48.0	9.51	5.75	8.61	3.50	8.05
56.0	9.54	7.25	8.25	5.00	7.73
72.5	9.46	10.00	8.15	6.00	7.28
		15.00	7.75	8.50	6.90
		21.50	7.02	16.00	5.37
		23.00	6.92	23.75	4.07
		26.25	6.61	25.75	3.77
		39.00	6.15	28.25	3.30
		50.25	5.53	32.00	2.89
		64.00	4.84	48.50	1.39
		71.50	4.29	54.50	1.20
		88.00	3.69	71.75	0.64

Initial Rate =
1.75×10^{-3} M.hr.$^{-1}$

Initial Rate =
3.85×10^{-3} M.hr.$^{-1}$

Table A61

The Rearrangement of N-Chloromethanesulphonanilide, at 77.7° in Carbon Tetrachloride, Catalysed by Benzoyl Peroxide

$[NCMS]_o$ = 0.100M $[Bz_2O_2]_o$ = 0.0268M		$[NCMS]_o$ = 0.100M $[Bz_2O_2]_o$ = 0.0344M		$[NCMS]_o$ = 0.100M $[Bz_2O_2]_o$ = 0.0430M	
Time (hr.)	[NCMS] M x 10^2	Time (hr.)	[NCMS] M x 10^2	Time (hr.)	[NCMS] M x 10^2
0.50	9.04	1.00	8.75	0.50	8.87
0.75	9.83	1.50	8.22	1.00	8.55
1.00	8.87	2.00	8.01	1.25	8.30
1.50	8.59	2.50	7.53	2.75	7.40
2.00	8.27	3.25	7.14	3.75	6.84
2.50	7.95	4.50	6.64	5.00	6.03
3.00	7.87	5.75	6.18	7.25	5.46
3.50	7.53	6.75	5.83	8.25	5.16
5.25	7.01	8.50	5.27	15.00	3.03
6.00	6.98	15.50	3.55	17.75	2.64
6.75	6.78	24.00	2.23	21.75	2.07
7.75	6.62	25.00	2.19	25.70	1.57
8.75	6.01	27.50	1.59	28.50	1.20
25.50	2.67	30.50	1.44	39.50	0.56
28.00	2.22	33.50	1.19	50.50	0.30
52.00	0.68	47.25	0.36	64.50	0.11
Initial rate = 6.12×10^{-3} M.hr.$^{-1}$		Initial rate = 7.95×10^{-3} M.hr.$^{-1}$		Initial rate = 10.1×10^{-3} M.hr.$^{-1}$	

Table A62

The Rearrangement of N-Chlorobenzanilide Catalysed by Benzoyl Peroxide at 77.7°

A

$[NCB]_o$ = 0.020M

$[P]$ = 0.030M

B

$[NCB]_o$ = 0.040M

$[P]$ = 0.030M

Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
0.25	1.88	0.25	3.72
1.00	1.58	0.50	3.60
1.25	1.56	1.00	3.39
1.50	1.44	1.25	3.33
2.00	1.35	1.50	3.30
2.50	1.28	2.00	3.02
3.00	1.12	3.00	2.67
3.50	1.10	4.13	2.47
4.00	0.95	4.75	2.32
5.00	0.75	7.00	1.61
5.75	0.62	10.00	1.19
7.00	0.40	14.00	0.38
8.75	0.02	16.75	0.05

Initial Rate 2.67 x 10^{-3} M.hr.$^{-1}$

Initial rate 3.36 x 10^{-3} M.hr.$^{-1}$

Table A63

The Rearrangement of N-Chlorobenzanilide Catalysed by Benzoyl Peroxide at 77.7°.

C

$[NCB]_o = 0.070M$

$[P]_o = 0.030M$

D

$[NCB]_o = 0.130M$

$[P]_o = 0.030M$

Time (hr.)	[NCB] M x 10^2	Time (hr.)	[NCB] M x 10^2
0.25	6.51	0.25	12.27
1.00	6.23	0.50	12.09
1.25	6.13	1.00	11.91
1.50	6.02	2.15	11.43
2.25	5.81	2.75	11.23
3.25	5.55	4.00	10.84
4.00	5.49	4.50	10.68
4.75	5.14	18.00	8.86
14.25	3.60	14.25	8.66
17.50	2.93	18.50	7.88
18.50	2.69	21.00	7.01
21.00	2.08	23.00	6.67
23.00	1.90	27.50	5.82
26.00	1.46	36.00	4.17
28.00	1.08	43.25	2.85
36.50	0.32	48.00	1.81

Initial rate 4.11×10^{-3} $M.hr.^{-1}$

Initial rate 4.98×10^{-3} $M.hr.^{-1}$

Table A64

The Rearrangement of N-Chlorophenylacetanilide Catalysed by Benzoyl Peroxide at 77.7°.

A

$[NCP]_o$ = 0.020M

$[P]_o$ = 0.0258M

B

$[NCP]_o$ = 0.060M

$[P]_o$ = 0.0258M

Time (hr.)	[NCP] M x 10^2	Time (hr.)	[NCP] M x 10^2
0.25	1.84	0.25	5.57
0.50	1.78	0.75	5.40
1.00	1.54	1.00	5.33
1.50	1.45	1.50	5.17
2.00	1.38	2.50	4.77
2.75	1.12	4.00	4.13
3.50	0.81	4.75	3.91
4.50	0.49	5.50	3.64
		6.25	3.47
		7.50	2.95
		8.75	2.60
		10.10	2.13

Initial Rate 2.82 x 10^{-3} M.hr.$^{-1}$

Initial Rate of Reaction 3.50 x 10^{-3} M.hr.$^{-1}$

Table A65

The Rearrangement of N-Chlorodiphenylacetanilide Catalysed by Benzoyl Peroxide at 77.7°.

A

$[NCD]_o$ = 0.020M

$[P]$ = 0.0258M

B

$[NCD]_o$ = 0.060M

$[P]$ = 0.0258M

Time (hr.)	[NCD] M x 10^2	Time (hr.)	[NCD] M x 10^2
0.25	1.91	0.25	5.81
0.50	1.86	0.75	5.55
0.75	1.72	1.00	5.46
1.00	1.60	1.50	5.06
1.25	1.45	2.00	4.84
1.75	1.12	3.75	3.99
2.25	0.90	4.75	3.66
3.00	0.42	5.50	3.27
3.25	0.25	7.00	2.49
3.75	0.02	8.25	1.73
		9.70	1.02

Initial Rate = 3.52×10^{-3} M.hr.$^{-1}$

Initial Rate = 5.66×10^{-3} M.hr.$^{-1}$

Table A66

The Rearrangement of N-Chloromethanesulphonanilide Catalysed by Benzoyl Peroxide at 77.7°.

A		B	
[NCMS] =	0.020M	[NCMS] =	0.060M
$[Bz_2O_2]$ =	0.0258M	$[Bz_2O_2]$ =	0.0258M

Time (hr.)	[NCMS] $M \times 10^2$	Time (hr.)	[NCMS] $M \times 10^2$
0.25	1.84	0.25	5.63
0.50	1.77	0.50	5.50
0.75	1.67	0.75	5.42
1.25	1.46	1.00	5.30
2.00	1.30	2.00	4.94
3.00	1.05	3.50	4.41
4.25	0.84	4.50	4.19
4.75	0.73	6.50	3.51
6.25	0.47	8.00	3.16
7.00	0.36	12.00	2.42
8.00	0.25	16.00	1.91
		24.00	1.06

Table A67

The Rearrangement of N-Chlorobenzenesulphonanilide, at 77.7° in Carbon Tetrachloride, catalysed by Benzoyl Peroxide.

A

$[NCBS]_o = 0.020M$
$[BzO_2]_o = 0.020M$

B

$[NCBS]_o = 0.040M$
$[Bz_2O_2]_o = 0.020M$

C

$[NCBS]_o = 0.100M$
$[Bz_2O_2]_o = 0.020M$

A		B		C	
Time (hr.)	[NCBS] M x 10^2	Time (hr.)	[NCBS] M x 10^2	Time (hr.)	[NCBS] M x 10^2
0.25	1.91	0.25	3.79	0.25	9.59
0.50	1.89	0.50	3.76	0.50	9.47
1.50	1.78	1.00	3.62	1.00	9.41
2.50	1.65	1.50	3.49	1.50	9.28
3.75	1.55	2.50	3.37	2.50	8.97
4.50	1.47	3.24	3.25	3.25	8.95
5.25	1.40	4.00	3.17	4.00	8.76
7.00	1.32	4.75	3.03	5.50	8.71
8.00	1.12	5.50	2.97	7.00	8.48
10.00	1.09	7.00	2.71	10.00	8.22
12.00	0.94	10.00	2.48	14.00	7.71
		24.00	1.62	21.25	7.08
		34.00	1.29	24.00	7.03
		48.00	1.23	30.00	6.70
		56.00	1.11	48.00	5.90

Initial rate = 1.20×10^{-3} M.hr.$^{-1}$

Initial rate = 1.57×10^{-3} M.hr.$^{-1}$

Initial rate = 2.35×10^{-3} M.hr.$^{-1}$

Appendix B

Computer Programme

```
      FORTRAN COMPILATION BY #XFAT MK 3E     RUN BY GEORGE 2/MK8E
      LIST (LP,50)
      PROGRAM (RATE)
      INPUT  1,5=CR0
      OUTPUT 2,6=LP0
      OUTPUT   3=CP0
      COMPACT DATA
      COMPRESS INTEGER AND LOGICAL
      TRACE 0
      END
```

```
      MASTER RATEPLOTTER
      INTEGER TEN,TSCALE
      LOGICAL ORD,ORIG
      DIMENSION CONC(100),TIME(100),SLOPE(100),IPRINT(6),XDUM(100),YDUM(
     1100)
C
C     N         = NUMBER OF PAIRS OF POINTS INCLUDING CO AT TIME=0,
C                 IF < 1 THE PROGRAM HALTS.
C     TITLE       INPUTS AND OUTPUTS A TITLE OF ANY LENGTH,
C                    TERMINATING WITH A ;
C     CO        = THE INITIAL CONCENTRATION AT TIME(1)=0
C     TEN       = THE POWER OF TEN MULTIPLYING THE CONCENTRATION
C     TSCALE    = FACTOR MULTIPLYING THE TIME TO CONVERT IT INTO SECONDS.
C     CONC(I)   = THE CONCENTRATION, I=2 TO N+1 , CONC(1)=CO
C     TIMF(I)   = THE TIME CORRESPONDING TO THE CONCENTRATION CONC(I).
C     IPRINT(I)= A SET OF 6 CONTROL PARAMETERS  I=1 TO 6,
C                  PUNCHED IN COLUMNS 1 TO 6
C                  SUCH THAT, IF IPRINT(I) IS NON-ZERO, FOR
C             I=1  A GRAPH OF CONCENTRATION AGAINST TIME IS OUTPUT,
C             I=2  A TABLE OF THE SLOPE (=CONC./TIME) AND
C                    CORRESPONDING TIME IS OUTPUT,
C             I=3  A TABLF OF SLOPE/CONCENTRATION  AND CORRESPONDING
C                    VALUES OF (INITIAL CONCENTRATION-CONCENTRATION
C                    AT SLOPE)↑2 IS OUTPUT
C             I=4 THE VALUES TABULATED WHEN I=3 ARE OUTPUT ONTO CARDS,
C             I=5  A GRAPH OF THE TABULATED VALUES OUTPUT WHEN I=3 IS
C                    DRAWN BY THE LINEPRINTER.
C             I=6  THE LINEAR PART OF THE TABULATION OF I=3 IS FOUND
C                    AND THE PROPERTIES OF THIS LEAST SQUARES LINE IS OP
C
    1 READ(1,100) N
  100 FORMAT(2I0)
      WRITE (2,101)
  101 FORMAT(1H1,//)
      IF (N.LE.0) STOP
      CALL TITLE
      READ(1,102) CO
  102 FORMAT(2F0.0)
      READ (1,100) TEN,TSCALE
      ORD=.FALSE.
      ORIG=.TRUE.
      LINES=100
      TIMF(1)=0.0
```

```
      WRITE (2,103) C0,N
  103 FORMAT(1H0,//,19X,'INITIAL CONCENTRATION =',F9.4,19X,'NUMBER OF PO
     1INTS =',I3,///)
      CONC(1)=C0
      READ (1,108) (IPRINT(I),I=1,6)
  108 FORMAT(6I1)
      WRITE (2,104) TEN
  104 FORMAT(1H0,44X,'CONCENTRATION*10↑',I2,10X,'TIME')
      WRITE (2,105) CONC(1),TIME(1)
      A=10.0**TEN
      C0=C0*A
      CONC(1)=C0
      DO 3 I=2,N
      READ (1,102) CONC(I),TIME(I)
      WRITE (2,105) CONC(I),TIME(I)
  105 FORMAT(49X,F9.4,13X,F9.4)
      CONC(I)=CONC(I)*A
      TIME(I)=TIME(I)*TSCALE
      IF (C0-CONC(I)) 0,3,3
      C0=C0/TEN
      WRITE (2,106) C0
  106 FORMAT(1H0,5X,'THE ABOVE CONCENTRATION IS GREATER THAN',F9.4,', TH
     1E INITIAL CONCENTRATION, THEREFORE IGNORED THIS SET OF DATA ')
      DO 2 J=I,N
      READ (1,102) CONC(J),TIME(J)
    2 CONTINUE
      GOTO 1
    3 CONTINUE
      IF (IPRINT(1).EQ.0) GOTO 4
      WRITE (2,107)
  107 FORMAT(1H1,42X,36HGRAPH OF CONCENTRATION AGAINST TIME.)
      CALL UL(43,36)
      O=0.0
      CALL PLOTXY(TIME,CONC,XDUM,YDUM,N,LINES,O,ORD,ORIG)
    4 DO 5 I=2,N
      J=I-1
      SLOPE(J)=(CONC(J)-CONC(I))/(TIME(J)-TIME(I))
      CONC(J)=(CONC(I)+CONC(J))*0.5
      TIME(J)=(TIME(I)+TIME(J))*0.5
    5 CONTINUE
      N=N-1
      IF (IPRINT(2).EQ.0) GOTO 7
      WRITE (2,109)
  109 FORMAT(1H0,////,50X,'SLOPE',10X,'TIME (SECS.)')
      DO 6 I=1,N
      WRITE (2,110) SLOPE(I),TIME(I)
    6 CONTINUE
  110 FORMAT(47X,E12.5,7X,E11.5)
    7 IF (IPRINT(3).EQ.0.AND.IPRINT(4).EQ.0.AND.IPRINT(5).EQ.0.AND.IPRIN
     1T(6).EQ.0) GOTO 1
      DO 8 I=1,N
      A=CONC(I)
      SLOPE(I)=SLOPE(I)/A
      CONC(I)=(C0-A)*(C0=A)
    8 CONTINUE
      IF (IPRINT(3).EQ.0) GOTO 10
      WRITE (2,111)
  111 FORMAT(1H0,////,36X,'SLOPE/CONCENTRATION',10X,'(C0=CONCENTRATION)↑
     12')
      DO 9 I=1,N
      WRITE (2,112) SLOPE(I),CONC(I)
  112 FORMAT(39X,E14.7,16X,E13.7)
    9 CONTINUE
```

```
 10 IF (IPRINT(4).EQ.0) GOTO 12
    DO 11 I=1,N
    WRITE (3,113) CONC(I),SLOPE(I)
113 FORMAT(2X,F12.9,4X,F12.9)
 11 CONTINUE
 12 IF (IPRINT(5).EQ.0) GOTO 13
    WRITE (2,114)
114 FORMAT(1H1,31X,'GRAPH OF SLOPE/CONCENTRATION AGAINST (CO-CONCENTRA
   1TION)↑2')
    CALL UL(32,57)
    ORD,ORIG=.FALSE.
    CALL PLOTXY(CONC,SLOPE,XDUM,YDUM,N,LINES,0,ORD,ORIG)
 13 IF (IPRINT(6).EQ.0) GOTO 1
    N1=N-3
    BESTSIG=5.0E75
    ISAVE=1
    KSAVE,K=N
 14 DO 16 I=1,N1
    C,CC,S,SS,CS=0.0
    DO 15 L=I,K
    C=C+CONC(L)
    S=S+SLOPE(L)
    CC=CC+CONC(L)*CONC(L)
    SS=SS+SLOPE(L)*SLOPE(L)
    CS=CS+CONC(L)*SLOPE(L)
 15 CONTINUE
    M=K-I+1
    A=M*CS-C*S
    SIG=SQRT(SS/(M-2)-(S*S+(A*A)/(M*CC-C*C))/(M*M-M+M))
    IF (SIG-BESTSIG) 0,16,16
    BESTSIG=SIG
    ISAVE=I
    KSAVE=K
 16 CONTINUE
    K=K-1
    N1=N1-1
    IF (N1.GT.2) GOTO 14
    C,S,CC,SS,CS=0.0
    DO 18 I=ISAVE,KSAVE
    C=C+CONC(I)
    S=S+SLOPE(I)
    CC=CC+CONC(I)*CONC(I)
    SS=SS+SLOPE(I)*SLOPE(I)
    CS=CS+CONC(I)*SLOPE(I)
 18 CONTINUE
    M=KSAVE-ISAVE+1
    A=M*CC-C*C
    B1=(M*CS-C*S)/A
    B0=(CC*S-C*CS)/A
    BESTSIG=SS/(M-2)-(S*S+B1*B1*A)/(M*M-M+M)
    SIG=SQRT(BESTSIG)
    CO=SQRT(BESTSIG*M/A)
    O=SQRT(BESTSIG/M+BESTSIG*C*C/(A*M))
    WRITE (2,117) SLOPE(ISAVE),CONC(ISAVE),SLOPE(KSAVE),CONC(KSAVE),B1
   1,CO,B0,O,SIG
117 FORMAT(1H0,////,13X,'THE LINEAR PART OF THE SLOPE/CONCENTRATION AG
   1AINST (CO-CONCENTRATION)↑2 GRAPH BY LEAST SQUARES.',//////,34X,'SL
   2OPE/CONCENTRATION  (CO-CONCENTRATION)↑2   SLOPE/CONCENTRATION',
   32X,'(CO-CONCENTRATION)↑2',/,7X,'LINEARITY OCCURING BETWEEN',4X,
   4E13.6,8X,E13.6,4X,'AND',3X,E13.6,8X,E13.6,////,38X,'SLOPE',14X,
   5'=',F11.6,' +-',F11.6,/,38X,'INTERCEPT',10X,'=',E11.5,' +-',E11.5,
   6/,38X,'STANDARD DEVIATION =',E13.6)
    GOTO 1
    END
    SUBROUTINE UL(I,J)
    INTEGER SP,ULN
```

```
      DATA SP/' '/,ULN/'-'/
      WRITE (2,100) (SP,K=1,I),(ULN,K=1,J)
  100 FORMAT(121A1)
      RETURN
      END
      SUBROUTINE TITLE
    THIS PROCEDURE INPUTS AND OUTPUTS A TITLE OF ANY LENGTH, STOPPING ON A
      INTEGER C,SP
      DIMENSION NAME(80)
      DATA C/1H;/
    1 READ (1,100) NAME
  100 FORMAT(80A1)
      L=0
      DO 2 K=1,80
      I=1
      IF (ICOMP(I,NAME(K),1,C,1).EQ.0) GOTO 3
    2 CONTINUE
      K=80
      L=1
    3 IF (L.NE.1) K=K-1
    4 WRITE (2,101) (NAME(I),I=1,K)
  101 FORMAT(1X,80A1)
      IF (L.EQ.1) GOTO 1
      RETURN
      END
      SUBROUTINE SORT(A,M,Y)
      DIMENSION A(M),Y(M)
C  SORTS A(I) INTO ASCENDING ORDER
      N=M
    1 K=2
    2 L=N-1
      N=0
      J=K-1
      DO 4 I=J,L
      I1=I+1
      IF (A(I1)-A(I)) 3,4,4
    3 STORE=Y(I)
      TEMP=A(I)
      A(I)=A(I1)
      Y(I)=Y(I1)
      Y(I1)=STORE
      A(I1)=TEMP
      IF (N.EQ.0) K=I
      N=I
    4 CONTINUE
      IF (N) 5,6,5
    5 IF (K.EQ.1) GOTO 1
      GOTO 2
    6 CONTINUE
      RETURN
      END
      SUBROUTINE PLOTXY(XX,YY,X,Y,N,LINES,O,ORDER,ORIGIN)
      INTEGER R,P,Q,P1,SP,STAR
      LOGICAL ORDER,ORIGIN,B
      REAL MINX,MAXX
      DIMENSION X(N),XX(N),Y(N),YY(N)
      DATA SP/' '/,STAR/'*'/
C  THIS SUBROUTINE PLOTS X(K) AGAINST Y(K) (K IS FROM 1 TO N).
C  LINES=NUMBER OF LINES DOWN A PAGE REQUIRED FOR THE RANGE OF Y-VALUES
C  O=THE ORIGIN (X-VALUE) UNLESS ORIGIN=.FALSE. WHEN THE MINIMUM VALUE
C       OF X(K) IS USED
C  IF THE Y-VALUES ARE ALREADY SORTED INTO ASCENDING ORDER THEN
C  ORDER=.TRUE.
      DO 11 I=1,N
      X(I)=XX(I)
      Y(I)=YY(I)
   11 CONTINUE
```

```
      IF (ORDER) GOTO 1
      CALL SORT (Y,N,X)
    1 SCALEY=Y(N)-Y(1)
      ABSS=ABS(SCALEY)
      IF (ABSS-0.00001) 2,3,3
    2 WRITE (2,100)
  100 FORMAT(1X,/,40X,28H Y IS INSUFFICIENTLY VARIED.)
      GOTO 19
    3 SCALEY=SCALEY/LINES
      MAXX=-1.0E75
      MINX=1.0E76
      DO 7 K=1,N
      IF (MAXX-X(K)) 4,5,5
    4 MAXX=X(K)
    5 IF (MINX-X(K)) 7,7,6
    6 MINX=X(K)
    7 CONTINUE
      IF (ORIGIN) SHIFTX=0
      IF (.NOT.ORIGIN) SHIFTX=MINX
      SCALEX=MAXX-SHIFTX
      ABSS=ABS(SCALEX)
      IF (ABSS-0.000001) 8,9,9
    8 WRITE (2,101)
  101 FORMAT(1X,/,40X,22H SCALE OF X TOO SMALL.)
      GOTO 19
    9 SCALEX=SCALEX/106
      J=N
      JJ=N
      B=.TRUE.
      WRITE (2,103) Y(N)
  103 FORMAT(1H ,G12.6,2H ;)
   10 Q1=(X(J)-SHIFTX)/SCALEX-0.5
      IF (Q1+1) 22,23,23
   23 Q=14+IFIX(Q1)
      WRITE (2,104) (SP,K=1,Q),STAR
  104 FORMAT (1H+,121A1)
   22 IF (J-1) 17,17,12
   12 J=J-1
      P=INT((Y(JJ)-Y(J))/SCALEY)
      IF (P) 14,13,14
   13 WRITE (2,106)
  106 FORMAT(15H+              )
      IF (B) JJ=J
      B=.FALSE.
      GOTO 16
   14 P1=P-1
      DO 15 K=1,P1
   15 WRITE (2,108)
  108 FORMAT(15H              ;)
      ABSY=ABS(Y(J))
      IF (ABSY-0.000001) 21,20,20
   21 WRITE (2,107)
  107 FORMAT(4H 0.0,9X,2H ;)
      GOTO 24
   20 WRITE (2,103) Y(J)
   24 B=.TRUE.
      JJ=J
   16 GOTO 10
   17 WRITE (2,109)
  109 FORMAT(1X,14X,106H-------------------------------------------------
     1---------------------------------------------------------)
      IF (ORIGIN) MINX=0
      WRITE (2,111) MINX,MAXX
  111 FORMAT(10X,G12.6,87X,G12.6,////)
   19 CONTINUE
      RETURN
      END
```