THE KINETICS AND MECHANISMS OF SOME REDOX REACTIONS INVOLVING NITROGEN(III)

by

Mahmoud Medhat Abdul-Jawad

A THESIS
presented for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Science of the
UNIVERSITY OF LONDON

Bedford College, London June, 1974

ABSTRACT

This work is concerned with the oxidation of nitrogen(III) by chlorate, bromate and iodate in aqueous solution.

The introduction reviews background information concerning the reactants in isolation, considers relevant speculations about their reactivities and surveys previously published work on the reactions. These earlier kinetic studies were made before many of the concepts now applied to solution kinetics were available.

It has been shown experimentally that the reactions proceed at conveniently measurable rates under acid conditions. Concerning the reduction of chlorate by "nitrite", which was examined in the pH range (1 - 2), the kinetics show that it is of the first order with respect to chlorate, nitrous acid and hydrogen ions. The reduction of bromate by "nitrite", which was examined in the pH range (2.4 - 3.2), is of first order with respect to bromate, nitrous acid and hydrogen ions. The reduction of iodate by "nitrite", which was examined in the acidity range (1.42 - 2.26M), is more complex in its kinetics.

The rate of decomposition of nitrous acid alone, under similar conditions, was also studied. The effects on reaction rate of change in ionic strength, temperature and addition of various simple salts and products have been studied and the stoichiometry of each reaction, under conditions similar to those used in the kinetic measurements, has been worked out. Efforts were made to identify intermediates and reaction products via use of mass, e.s.r., visible and ultraviolet spectroscopy besides qualitative analysis.

Possible mechanisms for the reactions with nitrous acid are discussed.

ACKNOWLEDGEMENTS

I would like to express my most sincere thanks to Dr. K. E. Howlett, for his kindly encouragement and helpful supervision and his assistance with the theoretical interpretation of the results.

My thanks are due to Professor G. H. Williams for offering me a place in the Department of Chemistry and providing facilities for the investigation.

Finally, I wish to thank the academic staff in the Department for their helpful suggestions and the technical staff for their assistance during the course of the work.

M.A.J.

CONTENTS

SECTION I

INTRODUCTION

INTRODUCTION

In aqueous solution, nitrite and halates do not react under neutral or alkaline conditions. On acidification with a mineral acid or other moderately strong acid, reactions are immediate and fast$^{(1-5)}$.

So it is necessary to assess the situation which will exist in acid solution. The acidification of a nitrite may give a stepwise reaction, producing first (and more certainly) nitrous acid, and then, at high acidities, the nitrous acidium ion $H_2NO_2^+$ (which can be considered as solvated nitrosonium ion NO^+). This protonated nitrous acid is reported$^{(7)}$ to be involved in various equilibria:

$$2HNO_2 \rightleftharpoons H_2NO_2^+ + NO_2^-$$

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

$$H_2NO_2^+ \rightleftharpoons H_2O + NO^+$$

Thus nitrogen(III) could be nitrite (NO_2^-), nitrous acid (HNO_2), nitrosonium ion (NO^+), dinitrogen trioxide (N_2O_3) etc., in the reaction mixture in solution.

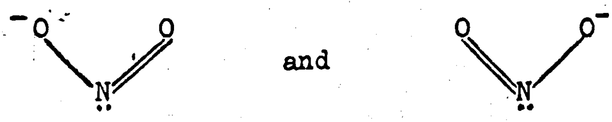
Nitrogen(III) lies in the middle of a range of oxidation states which exist for nitrogen. N(III) may act as an oxidising agent with the formation of N(I) or N(II), although powerful oxidising agents oxidise it to N(V).

Although a considerable amount of work has been done on nitrous acid, both in relation to organic and inorganic chemistry$^{(8)}$, there is some uncertainty as to many of its physical and chemical properties due to the unsuccessful attempts to isolate pure samples. This is because the acid undergoes decomposition. So before any kinetic investigation is started or any results interpreted, there are several points that must be mentioned and clarified.

In the gaseous phase nitrous acid exists in small quantity (about 10% at 1 atm.), in equilibrium with its dissociation products NO, NO_2 and H_2O together with N_2O_3, N_2O_4 and a trace of HNO_3 (9).

Although the actual molecular structure of nitrous acid is known, the nature of the bonding is still a problem. If we knew more about the nature of the chemical bonds, our understanding of reaction mechanisms and aspects that determine bonding in the transition state, would be considerably enhanced.

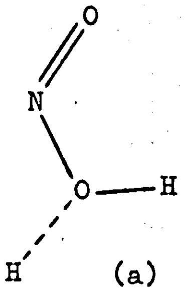
NO_2^- seems well understood structurally(7) as involving an electron distribution symmetrically disposed between two N - O bonds. One could, for example, regard the structure as involving equal participation of



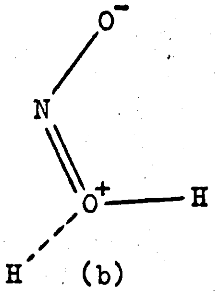
Alternatively one could assume that one nitrogen orbital is unhybridised and is occupied by two electrons; the other 6 electrons being associated with orbitals formed by overlapping sp^2 hybrids of the nitrogen with suitable oxygen atomic orbitals. These 6 will form the 2 sigma bonds and the lone pair. The unhybridised N-orbital may then overlap with p orbitals on the oxygen and since there are electrons in these orbitals this will give partial double bond character to both sigma bonds.

It has been shown by magnetic susceptibility measurements that the hydrogen in nitrous acid is bonded to oxygen rather than to nitrogen(10). It is well established by infra-red(11) and ultra-violet(12) spectroscopy that nitrous acid exists in cis and trans forms which are of comparable stability, the trans form being of lower energy by about 0.5 kcal mol^{-1}(16).

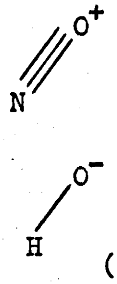
Nitrous acid, probably, is the smallest molecule for which cis/trans isomerism is considered to contribute to the structure of the acid. It has been suggested that, in the ground state, the possible structure (c) may be responsible for the greater stability of the trans form,(13,11a) though in view of the O - N - O interbond angles reported below, the effect of such a contributor would not be expected to favour the trans compound very much.



(a)

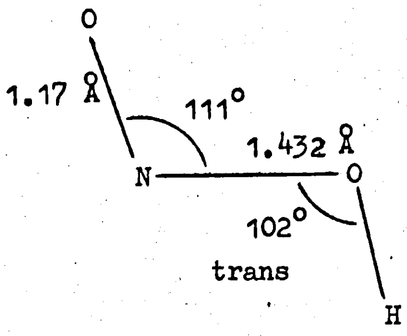


(b)

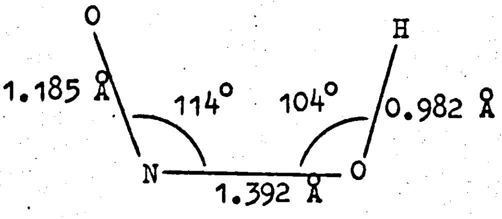


(c)

Recently, the microwave spectra of both isomers have been reported(14,15) and an accurate structure given. In these studies, the data are consistent with the expected planar configuration and the structural parameters of cis and trans nitrous acids are significantly different.



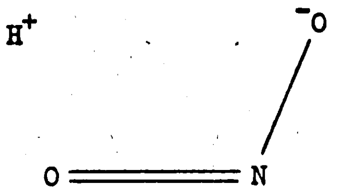
trans

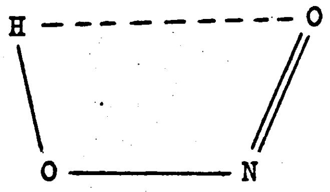


cis

Cox and his colleagues noticed that the increased bond angles in cis nitrous acid are accompanied by a shortening of the central N - O bond. They interpreted this decrease in bond length as being due to an increase in double bond character of the central N - O link at the expense of such character in the terminal N - O link. They also noticed that the O - H bond length is unusually long for a polyatomic molecule and surmised that this might be due to a weak hydrogen bond or dipole-dipole interaction.

These structural differences have been taken as evidence for electrostatic attraction between the hydrogen and the cis oxygen, suggesting the greater importance of one of the following contributors to the structure of the cis isomer(15b,c).



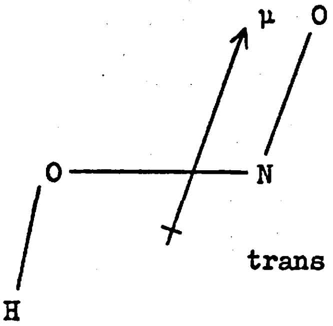


It seems likely from the reported barrier to rotation(11a,13), and thermodynamic free energies(16) for these forms of nitrous acid that rapid equilibration exists at room temperature between cis and trans forms, trans being favoured(17).

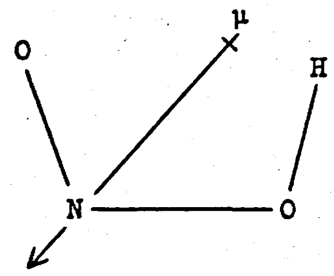
The N - O bond lengths in both species indicate a near localisation of the double bond towards the unprotonated oxygen.

There could be a point of interest in how the addition of the proton to nitrite has modified the charge distribution. Is it, for example, an alteration in the availability of the lone pair on the nitrogen which makes N(III) more resistant to oxidation under conditions where it is NO_2^-, than when it is HONO?

For the nitrite ion the dipole would be directed along the symmetry axis of the group. In trans nitrous acid the dipole (μ = 1.85 D) is directed nearly parallel with N = O, the hydrogen atom lying towards the positive end of the dipole. In the cis acid (μ = 1.39 D) again hydrogen is towards the positive end of the dipole(15b).



trans



cis

These facts would suggest that the electron density in the lone pair on the nitrogen is not diminished, but perhaps augmented on going from nitrite ion to nitrous acid. This could have the effect of making the nitrous acid a better potential reducing agent than the nitrite ion, at least consistent with the known facts.

Another point of practical significance is the instability of nitrous acid. As early as the turn of the century, the decomposition of nitrous acid in aqueous solution was a subject of interest.

The equilibrium constant of the decomposition

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O$$

can be expressed as

$$K = \frac{[H^+][NO_3^-]P_{NO}^2}{[HNO_2]^3}$$

and K has been found to have a value of about 30 at 25°C. P_{NO} is the partial pressure of nitric oxide over the solution, and K is expressed in $1\ mole^{-1}\ atm^2$.

The kinetics of the decomposition have been investigated by Abel and Schmid(18), and the rate was found to be proportional to the fourth power of the undissociated nitrous acid concentration and inversely proportional to the square of nitric oxide concentration as:

$$\mp \frac{d[HNO_2]}{dt} = \left\{ \pm \frac{k_1 a^3_{HNO_2}}{p^2_{NO}} \mp k_2 . a_{H^+} . a_{NO_3^-} \right\} . [HNO_2]$$

or:

$$\mp \frac{d[HNO_2]}{dt} = \pm k_1 \frac{[HNO_2]^4}{p^2_{NO}} \mp k_2[HNO_2][H^+][NO_3^-]$$

where k_1 has the value 46 and k_2 the value 1.6 at 25°C, concentrations being in moles per litre, pressure in atm., and time in min.

The effects of change of experimental conditions upon the reaction rate led to the suggestion of the following mechanism(19):

$$2HNO_2 \rightleftharpoons NO_2 + NO + H_2O$$

$$2NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 + H_2O \rightleftharpoons H^+ + NO_3^- + HNO_2 \quad \text{(rate-determining)}$$

Other aspects effecting the rate of the decomposition have been reported(7). Inert gases, air, agitation, light and hydrochloric acid accelerate it, whereas phthalic anhydride, potassium oxalate, molybdic acid, sucrose, glucose, glycerol, ethanol, diethyl ether, hydroquinone, phenol etc., and the use of hermetically sealed vessels reduce the rate. It has been said that the maximum rate of decomposition corresponds to that acid concentration at which nitrosonium ion and nitrous acid are present in approximately equal amounts(8).

Calculation based on the assumption that the bonds of nitrous acid are O - H, N - O, and N = O gives the standard heat of formation as -27.3 kcal/mole(20). Experimentally, the heat of formation of nitrous acid has been reported as -28.4 kcal/mole(21). These, and the following figures, all refer to 25°C.

It is also worth noting that the heat of formation of nitrite ion is -25.4 kcal/mole(21) (on the usual (solution) scale based on an assumed $\Delta H^o(f)$ for H^+ (aq) = 0). However it is common knowledge that nitrite ion is more stable than nitrous acid at ordinary temperatures. The standard free energies of formation of some species are:

$\Delta G^o(f)$ for HNO_2 (aq) is -13.3 kcal mol^{-1};

$\Delta G^o(f)$ for NO_2^- (aq) is -8.2 kcal mol^{-1}; whilst

$\Delta G^o(f)$ for NO_3^- (aq) and for HNO_3 are -26.4 kcal mol^{-1}.

It would seem reasonable to suggest that because the proton tends to destroy the symmetry of nitrite ion the stability is in some way reduced, and this appears to be a kinetic effect as far as the N(III) - N(V) change is concerned.

Moreover, isotopic exchange of oxygen atoms between water and the hydroxyl group of the nitrous acid molecule or of some entity derived from it, confirms the polarising power of the protons. The nitrite ion does not exchange its oxygen atoms with water at a measurable rate(22).

In dealing with nitrous acid, known to be a monobasic, one of the most important pieces of information needed is the dissociation constant of the acid. A review of previous determinations of the dissociation constant of nitrous acid has been given by Lumm and Tummavuori(23) who pointed out that due to the decomposition of nitrous acid, the previously reported values differ by about 0.2 - 0.4 pK unit from the values they obtained at about the same ionic strengths and at the same temperature.

In a recent paper(24), they extended their potentiometric measurements to determine the effect of neutral salts on the dissociation constant of the nitrous acid at different temperatures. The values of the thermodynamic dissociation constant at different temperatures were obtained by extrapolating the data to zero ionic strength, μ, using equations of the Debye-Hückel type.

For the process

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

the variation of pK with μ was interpreted by use of

$$pK = pK_o - 2A\sqrt{\mu}/(1 + \alpha\sqrt{\mu}) \quad + \beta\mu$$

and the results in nitrate media (approximately the conditions relevant to the present kinetic studies) are:

T °C	pK_o	α	β
15	3.220	1.852	0.0722
20	3.166	2.152	0.0660
25	3.136	2.074	0.0669
35	3.110	1.789	0.0708

These results have been accepted for the present work. When necessary, figures for other temperatures have been deduced by interpolation or short-extrapolation.

Oxidation by halates

The halates are strong oxidising agents in acid solution, and may therefore be reduced to a lower oxidation state of the halogen. Moreover, both thermodynamically and kinetically the oxidising powers of the halates are marked functions of the hydrogen ion concentration(16).

It may be judged by the redox potentials for ($XO_3^-/\frac{1}{2}X_2$) couples that the oxidising powers decrease in the order(25):

reduction potentials =	+ 1.51V	+ 1.46V	+ 1.2V
	bromate $\geqslant$	chlorate >	iodate

However, the rates of reaction with many substrates, the rate of exchange of oxygen atoms with water molecules and the size of central atoms follow the sequence(27):

iodate > bromate > chlorate

This latter sequence is paralleled by a shortening of the X - O bond from that expected for the single covalent bond distance, i.e. by an increase of double bond character. It has been suggested that the difference between the oxygen lability of iodate and of bromate and chlorate may lie in the tendency for iodine to assume co-ordination numbers greater than 3 or 4 in these compounds.

It is noteworthy that the iodate ion is appreciably hydrated, whereas the bromate and chlorate ions are less extensively hydrated perhaps because of the increase in bond order. Double bonding localises the negative charge on the central halogen atom thereby rendering the charge less accessible for bonding with the solvent molecules.

For the halic acids, chloric and bromic ($pK \leqslant 0$) are stronger than the iodic ($pK = 0.8$)(16), whereas the stability is greatest for iodic acid. Thus chloric and bromic acid can be obtained only in aqueous solution. Salts of all three acids are well known and stable to decomposition. The halate ion has a lone pair of electrons and a pyramidal structure.

The reactions of halates have been the subject of several reviews. Edwards has reviewed a number of mechanistic features common to oxyanion oxidations, in particular the dependence of rates on acid concentration. He supposes that the addition of protons to an oxide ion in an oxyanion should make it easier to break the bond between the oxygen and the central atom. Moreover, if breaking the oxide ion out of the oxyanion co-ordination sphere is an important part of the energetics of the reaction, then the influences of size and charge of the central atom and acidity on the rates, are on the way to being understood(26).

The Oxidation of Nitrogen(III) by Halate Ion

Certain aspects of the reactions between nitrite ion and chlorate, bromate and iodate in aqueous solution have been examined by several workers(1-6). The majority of these studies took place at the beginning of the century. Albin Kurtenacker reviewed some of these aspects and covered the literature published prior to 1913(5a). It can be seen from his publication that the reaction of nitrous acid with bromate and chlorate takes place quickly and quantitatively in cold aqueous solution, under acid conditions. Suitable conditions for the reaction with iodate are not so obvious.

Kurtenacker himself, examined the reactions kinetically. His studies began with the reduction of iodate by "nitrite ion", in the presence of sulphuric acid at 21°C(5a). He found the reaction to be of first order with respect to iodate, nitrite and hydrogen ions. In his original paper (1913) he gave the rate law as:

$$\frac{dx}{dt} = (k_1 + k_2\,[IO^-]).[H^+][IO_3^-][NO_2^-]$$

but in a later paper (1920), (comparing the reactions of halates with nitrite ion), he modified this to the following rate law:

$$\frac{dx}{dt} = (k_1 + k_2\,[IO^-][H^+])[IO_3^-][HNO_2]$$

so that k_1 and k_2 have different significances.

Kurtenacker interpreted his results to suggest the following mechanism:

$IO_3^- + NO_2^- \;=\; IO_2^- + NO_3^-$ (rate-determining)

$IO_2^- + NO_2^- \;=\; IO^- + NO_3^-$ (fast)

$2IO^- + NO_2^- + 2H^+ \;=\; I_2 + NO_3^- + H_2O$ (very slow)

Thus the last "step" can virtually be regarded as a subsequent reaction, and the products are regarded as IO^- and NO_3^-. It is relevant to note the method used by Kurtenacker to follow the reaction was as follows: nitrite solution and sulphuric acid were placed in one vessel apart from the iodate. After attaining the temperature of the thermostat the reactants were mixed and after a suitable time the reaction was stopped by means of a chemical quencher (in this case urea). The reaction mixture was boiled and cooled and the extent of reaction was measured iodometrically.

Kurtenacker observed that the addition of potassium iodide accelerates the rate of the reaction. He concluded that the iodide reacts with the iodate to produce hypoiodite which has the real accelerating effect. Thus he included it in the rate law. This however is difficult to reconcile with his assumption that the reaction with IO^- is very slow. He also observed that potassium chloride and bromide have an accelerating effect, this being stronger with the bromide.

He also found that the addition of potassium nitrate has a slight retarding effect on the reaction rate. Thus he concluded there was no need to consider it in the rate law.

Kurtenacker (1914) also examined the reaction between bromate and nitrite ion, in the presence of acetic acid at 21°C(5b). His most remarkable finding was that the order with respect to nitrite is zero. He considered that the nitrous acid decomposed to nitrate, nitric oxide and water, and that the nitric oxide reacted with bromate, though it is not immediately obvious how this accounts for the facts. He also found the order with respect to bromate to be one. The order with respect to hydrogen ion was found to be more than two. He justified the higher order as an accelerating effect of acetate on the reaction rate. With the results, Kurtenacker gave no rate law for the reaction, but in a later paper he gave the order with respect to hydrogen ion as two. He repeated his past conclusions and gave the following equation for the reaction:

$$\frac{dx}{dt} = (k_1 + k_2\,[H^+]^2).[BrO_3^-]$$

He interpreted his results to suggest the following equations:

$$3NO_2^- + 2H^+ = 2NO + NO_3^- + H_2O$$

$$BrO_3^- + 2NO + H_2O = Br^- + 2NO_3^- + 2H^+$$

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$$

$$Br_2 + NO_2^- + H_2O = 2Br^- + NO_3^- + 2H^+$$

It would seem however that if the first step is regarded as fast (to account for the zero order) then $[NO]_o$ would be directly proportional (in a closed system) to $[NO_2^-]_0$ and hence the rate of the second step would be dependent indirectly on HNO_2. This argument can be continued to indicate that this mechanism cannot account for the zero order observed in NO_2^-.

The method used to follow the reaction was similar to the one used to follow the iodate reaction, except in using sodium hydroxide and bromine water instead of urea to quench the reaction. Sodium thiosulphate was added to the reaction mixture until a colourless solution was obtained. Then the extent of the reaction was measured iodometrically.

The last reaction of the halates (the reduction of chlorate by nitrite ion) was also studied by Kurtenacker (1920)$^{(5c)}$. He examined the reaction using a solution of potassium hydrogen sulphate as an acid medium at 20°C. He found the reaction to be of first order with respect to chlorate and nitrite ions. He suggested that the acidity has a little effect on the reaction rate and it might be that HSO_4^- ion has a catalytic effect. He gave the following rate law:

$$\frac{dx}{dt} = (k_1 + k_2\,[H^+])[ClO_3^-][HNO_2]$$

and suggested the mechanism:

$$ClO_3^- + HNO_2 = HClO_2 + NO_3^-$$

$$HClO_2 + HNO_2 = HClO + NO_3^- + H^+$$

$$HClO + HNO_2 = Cl^- + NO_3^- + 2H^+$$

The method which Kurtenacker used to follow this reaction was again similar to the one used in following the bromate and iodate reactions. After a suitable time the reaction was neutralised with sodium hydroxide and boiled with ammonium sulphate then reacidified with sulphuric acid and the extent of reaction was measured titrimetrically using potassium permanganate solution.

Unfortunately the mixing of nitrite with acid well before the start of all Kurtenacker's experiments inevitably led to some decomposition of nitrous acid to varying and unknown degrees before reaction began; so that detailed results from this source are suspect.

In 1935 Lowe and Brown published a short paper on the reactions of chlorate and bromate with nitrous acid acidified with nitric acid but unbuffered at 25°C(6). They followed the reactions gravimetrically using silver nitrate as a precipitant. Concerning the chlorate reaction with nitrous acid they found that it follows second order kinetics and that the rate constant is directly proportional to hydrogen ion concentration. Few results were published. They found that there is no significant change in the rate constant when the chloride concentration is altered. Concerning the bromate reaction with nitrite no reaction rate equation was proposed nor any order with respect to any of the reactants. They seem to assume that the reactions are overall:

$$XO_3^- + 3HNO_2 \longrightarrow X^- + 3NO_3^- + 3H^+$$

They also inferred that the bromide ion has little effect on the mechanism and that the oxidation of bromide ion to bromine plays no part in it. Lowe and Brown concluded that an increase in the value of the rate constant as reaction proceeds is due to rise in hydrogen ion concentration as nitrous acid is oxidised to the strongly ionised nitric acid. The paper is a rather unsatisfactory one.

Finally, Gyani and Prasad examined the stoichiometry of the reduction of halate by nitrous acid potentiometrically in the presence of mineral acids(27). They found that bromate consumed 2.5 - 3 moles of nitrite, depending on the concentration of the acid used; higher concentration favouring 2.5 moles. The chlorate consumed three moles of nitrite under all conditions they applied. The iodate required about five moles of nitrite. They interpreted their results to suggest reaction mechanisms.

It could, however, be suggested that neglect of the possibility of decomposition of nitrous acid during the very long periods over which their potentiograms were obtained makes their numerical results of doubtful value. They report, for instance, that it was necessary to wait for 1 or 2 hours after addition of titrant before steady readings were obtained. Each titration was therefore presumably conducted over a matter of days.

Since the halates and nitrous acid are common materials, it is surprising that so little reliable work has been done in order to establish the rate law and the mechanism of their reactions together.

Few tentative ideas for mechanism have been produced, none of them giving proven indication as to the nature of the intermediates. Whatever is involved, nitrogen or halogen must at some time exist in an unusual valency state perhaps with unusual stereochemistry, nitrogen being possibly in oxidation state IV and halogen possibly involving X(IV), X(III), X(II), X(I) and X(O). For example in some reactions it has been suggested that X(IV) may be involved, as ClO_2 or BrO_2. However, of course, reactions between two non-transitional elements have long been recognised as normally proceeding in 2-electron steps(28).

The intermediates which are formed by reactions of oxyanions with protons and subsequent dehydration are acceptors or as otherwise called, cationic particles. Edwards(29) and Turney and Wright(8) in their reviews have assumed that IO^+, IO_2^+, BrO^+, ClO^+, Cl^+, NO^+ and others are intermediates.

They also have given valuable summaries of the reactions of nitrous acid with a large number of substrates. It has been suggested that the electrophilic activity of nitrosating agents decreases in the following order:

$$NO^+, H_2NO_2^+, NOX, N_2O_4, N_2O_3, HNO_2.$$

The voluminous literature on the nitrosation mechanism is highly argumentative and the situation is still not resolved. But there is general agreement that active entities, NO^+, N_2O_3 and N_2O_4 are of interest in considering the reactivity of nitrous acid in acid media.

Therefore it is of practical importance to report the equilibrium constants of these entities. Turney and Wright (30,31) have estimated two of them by considering thermodynamic cycles:

$$HNO_2(aq) + H^+(aq) \overset{K_1}{\rightleftharpoons} NO^+(aq) + H_2O\ (l) \qquad \Delta G = 5.7\ \text{kcal mol}^{-1}$$

$$2HNO_2(aq) \overset{K_2}{\rightleftharpoons} N_2O_3(aq) + H_2O\ (l) \qquad \Delta G = 2.8\ \text{kcal mol}^{-1}$$

Thus $K_1 = 7 \times 10^{-5}$ and $K_2 = 9 \times 10^{-3}$, both in units of $l\ mol^{-1}$ at 25°C. Experimentally, the same equilibrium constants have been estimated as:

$$K_1 = (2 \text{ to } 3) \times 10^{-7}\ l\ mol^{-1}$$

$$K_2 = 0.2 \pm 0.05 \qquad l\ mol^{-1}$$

Recently, Schmid and Krenmayr(32) have reviewed and theoretically calculated the same equilibrium constants to be numerically:

$$K_1 = 4 \times 10^{-7} \quad 1\ mol^{-1} \text{ at } 25^\circ C$$

$$K_2 = 0.16 \quad 1\ mol^{-1} \text{ at } 20^\circ C$$

Turney and Wright(8) have made a rough estimate of the equilibrium constant for the formation of dinitrogen tetroxide from molecular nitrous acid, based on a study by Longstaff and Singer. Their estimation gave:

$$K_{calc.} = 4 \times 10^{-5}$$

$$K_{exp.} = 3 \times 10^{-3}$$

both in units of 1 mol^{-1} at 25°C. There is some uncertainty due to lack of knowledge of the extent of the equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2$$

in aqueous solutions, but investigations based on simple observations indicated that it is rapidly achieved.

A general type of mechanism for rate equations, of monobasic anions, is formulated in the review of Edwards(29).

$$\text{Rate} = k[AO_m^-][B^x][H^+]$$

where AO_m^- represents an oxyanion and B^x is the electron donor.

A possible mechanism obeying this type of rate law would be:

$$AO_m^- + H^+ \rightleftharpoons HAO_m \qquad \text{(fast)}$$

$$HAO_m + H^+ \rightleftharpoons H_2AO_m^+ \qquad \text{(fast)}$$

$$H_2AO_m^+ + B^x \longrightarrow BAO_{m-1}^{x+1} + H_2O \qquad \text{(rate determining)}$$

$$BAO_{m-1}^{x+1} \longrightarrow \text{products} \qquad \text{(fast)}$$

The article deals with reactions of oxyanions with bases i.e. with species having a lone pair of electrons and starts with the premise that the intermediate commonly assumed ($H_2AO_m^+$) is an electron acceptor formed by reaction of an oxyanion with protons. Now strictly this probably does not apply to the current situation because NO_2^- is protonated and reacts with halate oxyanion under conditions of pH where the oxyanion must be virtually exclusively in anionic form, i.e. it is the overall electron pair donor which is protonated.

As a specific example Edwards quotes:

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3 \qquad \text{(fast)}$$

$$H^+ + HBrO_3 \rightleftharpoons H_2BrO_3^+ \qquad \text{(fast)}$$

$$I^- + H_2BrO_3^+ \longrightarrow IBrO_2 + H_2O \qquad \text{(rate determining)}$$

$$IBrO_2 \longrightarrow \text{products} \qquad \text{(fast)}$$

However it is clear from this formulation that the activated state $[H_2BrIO_3]$ for the rate determining step is postulated to be in overall equilibrium with H^+, BrO_3^- and I^- and hence its mechanism of formation is immaterial, the details of its formation might equally have involved HI and BrO_3 or H_2I^+ and BrO_3^- coming together, and a more protracted investigation would be needed to distinguish between these. This means that the rate laws are to some extent uninfluenced by whether one calls the oxyanion the oxidant or the reductant. More detail on this will be considered later.

Turney(33), suggested two general patterns for all the reactions of nitrous acid.

(I) At high acidity

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

Substrate + N_2O_3 ⟶ products which would be consistent with:

$$\text{Rate} = k[\text{substrate}][HNO_2]^2$$

(II) At low acidity

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+$$

Substrate + $H_2NO_2^+$ ⟶ products leading to:

$$\text{Rate} = k'[\text{substrate}][H^+][HNO_2]$$

Although there was, at that time, no direct evidence for acceptor intermediates, the second-order dependence on hydrogen ion concentration (noted later) is support for their existence as a kinetic intermediate. Some recent ^{15}N nuclear magnetic resonance work has for the first time supplied good evidence for the existence of $H_2NO_2^+$ as not only an intermediate, but as existing in solution in quite appreciable concentrations(34).

More information about the rate determining step may sometimes be obtained by the use of D_2O as solvent in place of water. One expects to observe a faster reaction rate if some necessary protonation (or deuteration) takes place before the rate determining step. On the other hand, if protonation is occurring in the transition state, the rate should be slower in D_2O than in H_2O. Heavy water too, may show whether the reaction is an example of general or specific acid catalysis; any increase in rate, when D_2O is used, suggesting specific hydrogen ion catalysis because of the setting up of more favourable pre-equilibrium conditions(26).

However, the use of D_2O is not a simple panacea - in a reaction involving several equilibria before the rate determining step, the effects of D_2O would often be expected to be in opposite senses as far as affecting the rate is concerned. For example whilst the establishment of protonation equilibria would probably enhance the concentration of $D_2NO_2^+$ relative to $[H_2NO_2^+]$, the rate of elimination of D_2O from a complex might well be slower than the corresponding loss of H_2O. Thus unless the mechanism is relatively simple the use of D_2O may not provide definite answers.

SECTION II

GENERAL CONSIDERATIONS

The Establishment of a Method for Following the Reactions

It is apparent from the introduction that two analytical techniques have, in the past, been used to follow the kinetics of the reactions between halates and nitrous acid; the titrimetric method adopted by Kurtenacker and the gravimetric technique used by Lowe and Brown.

These methods, however, are not very suitable for following the change of nitrite concentration in its reaction with halate, or for following the change of halate concentration, because the accuracy is poor. This might be, partly, because nitrous acid is volatile and unstable and partly because the recommended procedures involve interference in one way or another from other species in the reaction mixture(35). Moreover, to remove these species, drastic treatments like boiling and adding highly acidic reagents are needed. Further, it takes a long time to analyse one sample from a run by the above methods.

For reacting or reactive systems, physical methods of analysis can be more reliable than chemical methods. Therefore a spectrophotometric method was sought. No convenient method (titrimetric or spectrophotometric) was, however, found for the determination of halates in the reaction mixture, without complications arising from side effects.

The method selected measures the concentration of nitrite ions during the course of reaction, using the Shinn method as modified by Kershaw and Chamberline(36).

As adapted, the method consists of pipetting small samples from the reaction mixture at known times into about 80 ml water contained in 100 ml standard flasks adding from a burette, 2 ml of 0.5% p-aminobenzene-sulphonamide in 1:1 HCl, shaking, adding 1 ml of 0.1% N-(1-naphthyl)-

ethylenediamine dihydrochloride, and making the whole up to 100 ml with distilled water. Nitrite reacts quantitatively to produce the dye, whose pink colour is fully developed in 10 minutes and remains, under the conditions used here, constant in intensity for more than 1 hour, in solutions containing nitrite only; and for 40 minutes in solutions containing nitrite and halate ions.

The method has certain advantages. First, the dilution with water, not only helps the analysis, but virtually quenches the reaction while the analysis is carried out. The addition of the reagents removes free nitrite ion thereby finally quenching the reaction. Thirdly, the quenching and diazotisation processes are carried out rapidly so that quite fast reactions can be studied and any decomposition of nitrous acid, a side reaction, is minimised. Fourthly, as will be seen, the additives are quite inert in the reaction mixture during the analysis and do not lead to side effects.

From a solution of nitrite, standardised according to the method described by Furman(37), samples were taken, treated as above and the resulting solutions examined spectrophotometrically using a Pye Unicam SP.800 instrument. The optical density at 18,600 cm^{-1} (537.6 nm) was found to be a direct measure of the nitrite ion concentration. This was repeated with fresh standard nitrite solutions to establish a reliable standardisation graph on each spectrophotometer used (Table 1). It can be seen from Fig. 1 that the Lambert-Beer law holds throughout the useful range around 10^{-5} M nitrite ion concentration, and the extinction coefficient of the dye is 5.00×10^{4} l $mole^{-1}$ cm^{-1}.

Furthermore, it was found that the absorption at 537.6 nm was uninfluenced by the addition of other materials used in the kinetic experiments. If a kinetic run is to be analysed this way, it would be convenient to have the nitrite rather dilute in the reaction mixture. This, in turn, means that the halate needs to be fairly concentrated in order to be able to observe conveniently measurable rates.

Table 1

(A)*		(B)*	
[NaNO$_2$]10^5 M	O.D.	[NaNO$_2$]10^5 M	O.D.
0.5838	0.29	0.203	0.102
1.168	0.57	0.406	0.204
1.751	0.88	0.609	0.302
2.335	1.195	0.812	0.405
2.919	1.47	1.015	0.501
3.503	1.68	1.421	0.695
		1.827	0.880

(C)*		(D)*	
[NaNO$_2$]10^5 M	O.D.	[NaNO$_2$]10^5 M	O.D.
0.5838	0.29	0.9075	0.45
1.168	0.58	1.815	0.90
2.335	1.17	2.722	1.36
3.503	1.72	3.630	1.78

(A) SP.800

(B) SP.124

(C) and (D) SP.500

* 1 cm cells were used for all measurements.

The SP.124 with digital onput can be repeatedly read to virtually one further factor of 10 in accuracy, and this instrument was used for most of the work to be described, using 1 cm cells, unless otherwise stated.

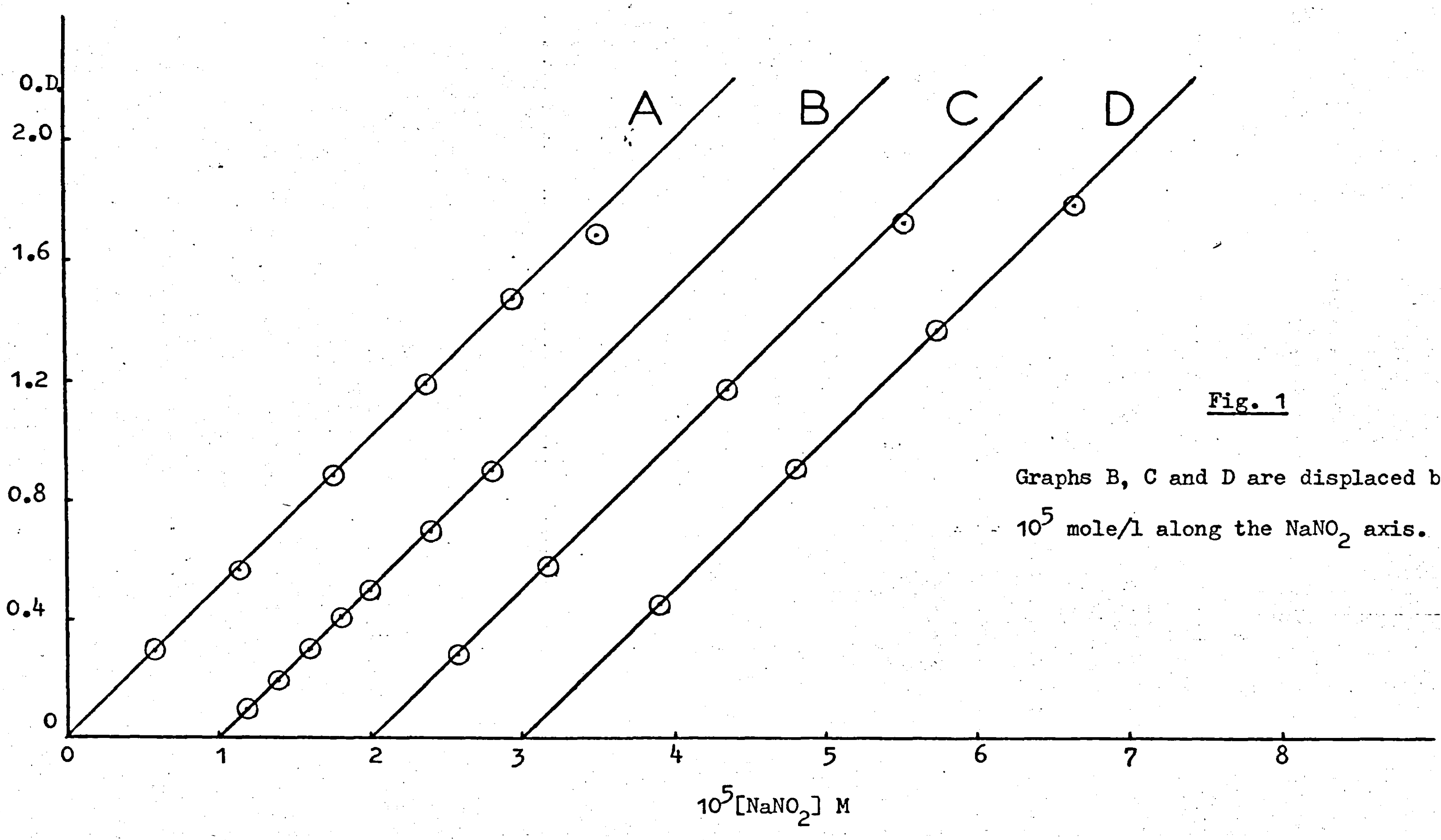


Fig. 1

Graphs B, C and D are displaced by 10^5 mole/l along the $NaNO_2$ axis.

The Acid Catalysed Decomposition of Nitrous Acid

It is well recognised that nitrous acid is itself liable to decomposition. This process would therefore be occurring as a parallel reaction to the reaction of "nitrite" with halate. It was therefore necessary to establish the significance of loss of N(III) via decomposition of nitrous acid relative to loss via the reaction under study.

The rate law for the decomposition of nitrous acid has been considered in the literature but since it was established under conditions different from these used in the present HNO_2/XO_3^- reactions, it was decided to examine the rate of decomposition under conditions close to those required for reaction of N(III) with the halates, in particular where any nitric oxide is free to react further or to escape.

If nitric oxide is generated by decomposition of nitrous acid in water saturated with oxygen, it will form (18,19,40):

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_2 + H^+ + NO_3^-$$

There is adequate oxygen to carry out this reaction. Typically in this section of the work about 10^{-4} mole l^{-1} is the fall in concentration of nitrous acid over up to 5 hours, whereas there is about $10^{-3.5}$ mole l^{-1} of oxygen in air saturated solution at any instant at 25°C.

A series of experiments was performed in which the H^+ and HNO_2 concentrations were similar to those required in the halate/N(III) studies.

Nitrite solution and water, equal to a typical amount of halate solution were placed in a 500 ml stoppered conical flask. Acid was placed in another flask and both were allowed to attain thermal equilibrium in the thermostat at 25°C. The decomposition was started by pouring the contents of one flask into the other, and thorough mixing was ensured by transferring the mixture from one vessel to the other several times. Samples were withdrawn at intervals, quenched, diazotised and examined spectrophotometrically according to the method described.

The spectrophotometric observations give values for total [N(III)]. In fact N(III) is mainly present as NO_2^- and HNO_2 which are in very rapidly established protonation equilibrium, but presumably only HNO_2 decomposes. Hence $[HNO_2]$ is a constant fraction of the total [N(III)] at constant pH, temperature and ionic strength but if any of these three variables is changed then $[HNO_2] \neq K[N(III)]$.

So the rate was measured as:

$$-\frac{d([NO_2^-] + [HNO_2])}{dt}$$

and at constant pH this becomes:

$$-\frac{d[HNO_2](1 + x)}{dt} \qquad \text{where } [NO_2^-] = x[HNO_2]$$

$$\text{or} \quad -\frac{d[NO_2^-](1 + y)}{dt} \qquad \text{where } [HNO_2] = y[NO_2^-] \text{ and } xy = 1$$

The values of x are known (ref. 24).

Initial rates were deduced from the observations by plotting log O.D. versus time, and putting the best straight line through the points.

Initially we do not, of course, know the order of the reaction. The rate of decomposition was slow so that, for example at pH 1.96 and 25°C some 2 hours were required for "[HNO_2]" to change from 10^{-3}M to 0.8×10^{-3}M. These reactions were normally followed over only the first 10 - 20% of reaction. Over such extents of completion rate equations of almost any order will fit (inexact) individual experimental results. Fitting the data by means of a first order relationship was chosen because it was felt that this choice was a middling one - not one likely to be too far from a true order, but not implying that the true order is unity.

These apparent first order constants k' then enabled averaged values of initial rates to be calculated so that by comparing rates from separate experiments the true kinetic form could be deduced.

So the rate is expressed as:

$$k'.[\text{total N(III)}]_o$$

or

$$k'.([HNO_2](1 + x))_o$$

The results for the decomposition of nitrous acid, (0.4 to 13.49×10^{-4}M), while pH varies from 1 to 3.2 at 25°C, were fitted reasonably well to the rate law:

$$\text{Rate} = k_1[HNO_2] + k_2[HNO_2]^2$$

This pH range will later be seen to be significant for the reactions with chlorate and bromate.

When rate/[HNO_2] was plotted against [HNO_2] a straight line was obtained. From the slope, $k_2 = 1.82\ M^{-1}\ min^{-1}$ and from the intercept, $k_1 = 2.75 \times 10^{-4}\ min^{-1}$.

Typical individual runs are shown in Table 2 and Graph 2; the graph of initial rate/$[HNO_2]_o$ versus $[HNO_2]_o$ is given in Fig. 3, where <u>no</u>

experimental result is ignored, and all the runs are collected in Table 3.

The independence of the rates upon pH may immediately be seen by, for example, comparing lines 1 and 12 in the table where similar rates attend similar $[HNO_2]$ values whilst the $[H^+]$ values differ by a factor of 75.

But at high acidity (1.5 - 2.5 M.HCl), the region relevant to studies of the reaction with iodate, the rate of decomposition of nitrous acid is partially $[H^+]$ dependent e.g.

$$\text{Rate} = (k_3 + k_4 [H^+])\, f\, (HNO_2),$$

This is deduced from another series of experiments performed at high acidities in which the concentration of H^+ was changed, all other factors being kept constant and with nitrous acid $\approx$ 8 x 10^{-4} M.

The results are shown in Table 4 and the graph of initial rate versus $[H^+]$ is given in Fig. 4. Values of k_3 and k_4 deduced from Fig. 4 would, of course, refer only to this particular concentration for $[HNO_2]$; but it is clear that below $[H^+] = 0.1$ mol l^{-1}, i.e. the range of pH used for the chlorate and bromate reactions, the rate of decomposition of HNO_2 is independent of $[H^+]$. Even at 2 M hydrogen ion concentration, the decomposition rate is only double that found as $[H^+] \longrightarrow 0$.

Table 2

The reactant conditions for these runs are detailed in Table 3. These runs were all analysed for N(III) as described earlier, using 1 - 5 ml samples as shown over each set of data. Optical densities were measured using 1 cm cells.

(6) (1 ml samples)		(4) (2 ml samples)	
Time (min)	O.D.	Time (min)	O.D.
2	.463	2	.468
10	.450	10	.465
20	.445	20	.460
30	.434	30	.452
45	.424	45	.446
60	.417	60	.438
90	.392	90	.428
120	.373	120	.414
Initial Rate = 1.65×10^{-6} M min^{-1}		Initial Rate = 0.490×10^{-6} M min^{-1}	

(7) (1 ml samples)		(14) (2 ml samples)	
Time (min)	O.D.	Time (min)	O.D.
15	.639	2	.674
30	.624	30	.664
45	.601	60	.647
60	.578	90	.639
90	.543	120	.621
120	.515	180	.604
150	.487	240	.580
180	.464	300	.561
Initial Rate = 2.671×10^{-6} M min^{-1}		Initial Rate = 0.416×10^{-6} M min^{-1}	

Table 2 (continued)

(27) (5 ml samples) Time (min)	O.D.	(I) (1 ml samples) Time (min)	O.D.
2	0.483	2	.397
10	0.479	10	.384
20	0.474	20	.373
30	0.473	30	.360
45	0.466	40	.349
60	0.465	60	.325
90	0.458	90	.304
120	0.447	120	.286
180	0.430		
Initial Rate = 0.121 x 10^{-6}M min^{-1}		Initial Rate = 1.817 x 10^{-6}M min^{-1}	

(VIII) (1 ml samples) Time (min)	O.D.
2	0.402
11	0.390
20	0.380
40	0.362
60	0.345
90	0.320
120	0.301
Initial Rate = 2.423 x 10^{-6}M min^{-1}	

Fig. 2

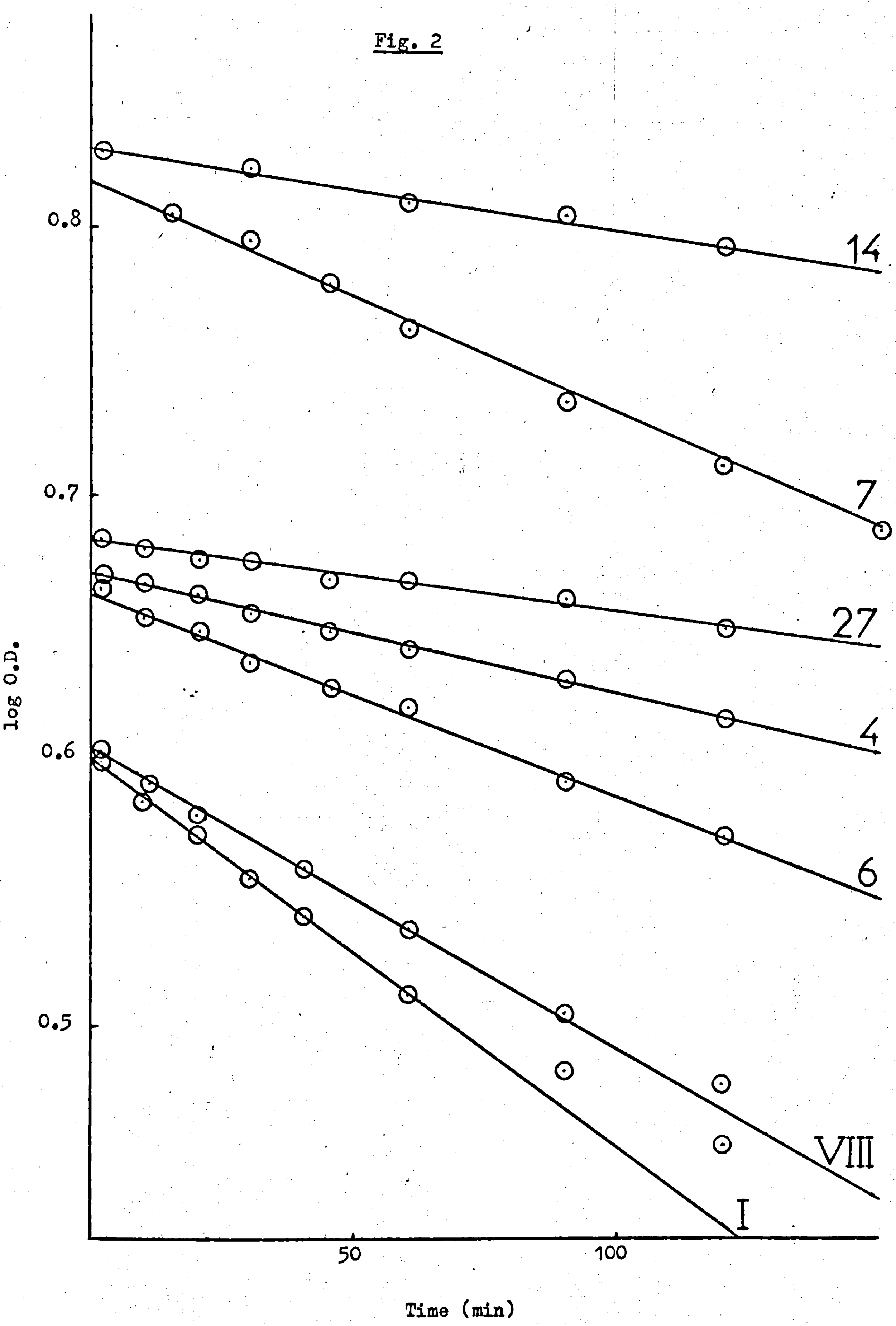


Table 3

$10^3[H^+]M$	$10^4[HNO_2]M$	1 + x	μ	10^6Init. rate ($M\ min^{-1}$)	10^4 Init. rate/$[HNO_2]$ (min^{-1})
154.4	9.209	1.0077	0.1775	1.817	19.73
82.34	10.24	1.0139	0.1113	2.223	21.71
68.33	9.133	1.0161	0.0804	1.778	19.47
29.74	4.581	1.0358	0.0608	0.490	10.69
29.61	8.919	1.0359	0.0612	1.672	18.75
10.55	8.635	1.0990	0.0518	1.650	19.11
4.502	11.21	1.2035	0.0147	2.671	23.84
4.248	11.10	1.2156	0.0146	2.423	21.84
4.248	11.10	1.2156	0.0146	2.400	21.63
2.147	4.744	1.4218	0.0129	0.557	11.74
2.147	4.744	1.4218	0.0129	0.566	11.93
1.956	9.079	1.4649	0.0134	1.914	21.08
1.412	4.112	1.6400	0.0125	0.429	10.42
1.412	4.112	1.6400	0.0125	0.416	10.12
1.408	0.412	1.6390	0.0119	0.013	3.08
1.408	0.412	1.6390	0.0119	0.015	3.63
1.232	7.770	1.7360	0.0131	1.433	18.44
0.808	0.639	2.1119	0.0117	0.027	4.21
0.808	0.639	2.1119	0.0117	0.027	4.25
0.775	3.117	2.1636	0.0122	0.280	8.97
0.775	3.117	2.1636	0.0122	0.264	8.46
0.709	0.645	2.2788	0.0129	0.025	3.93
0.709	0.645	2.2788	0.0129	0.022	3.46
65.61	6.885	1.0167	0.0788	1.059	15.38
29.54	6.757	1.0360	0.0610	1.005	14.88
10.64	6.375	1.0981	0.0516	0.917	14.39
48.12	1.902	1.0225	0.0698	0.121	6.38

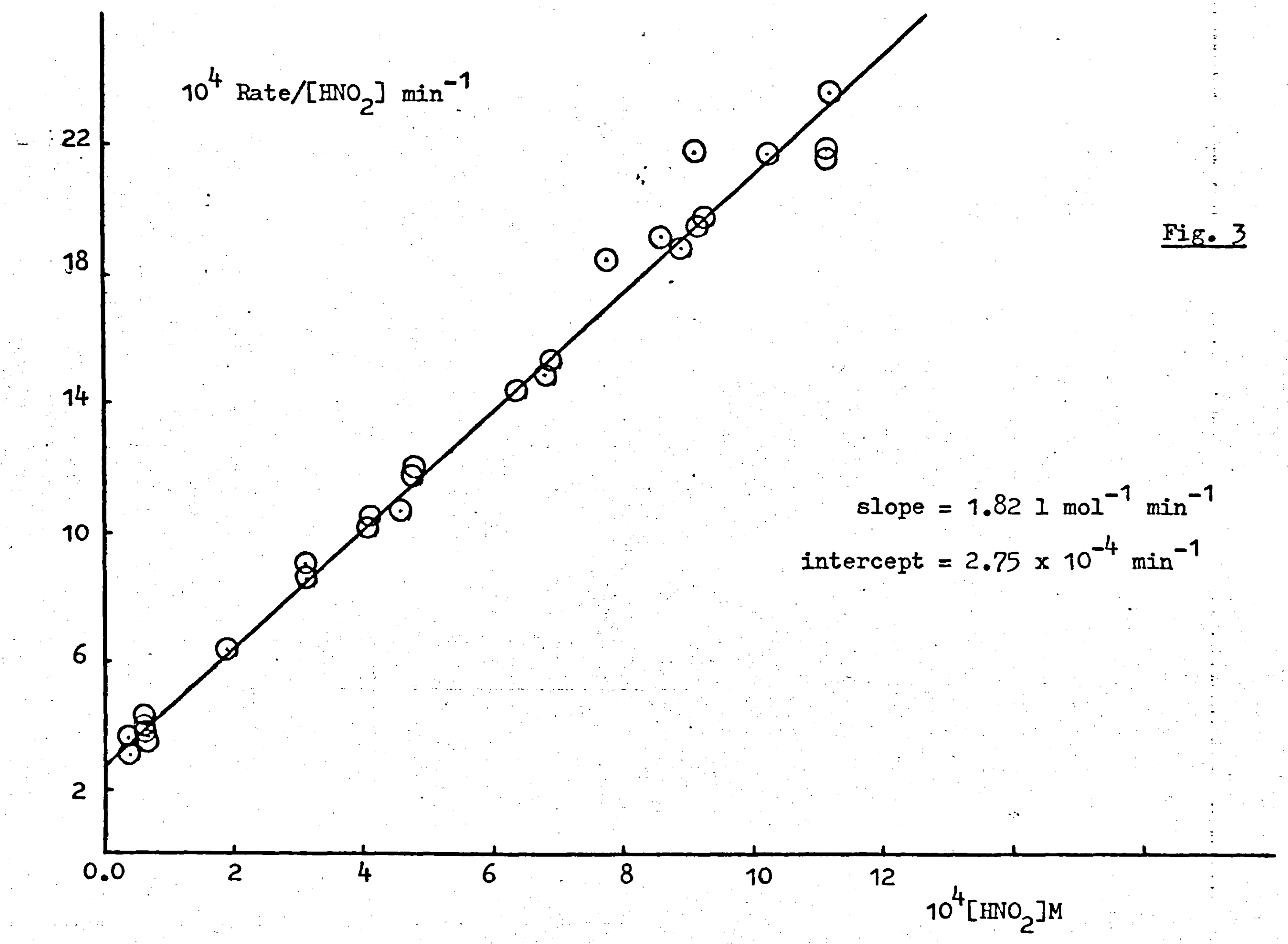

10^4 Rate/[HNO$_2$] min^{-1}
22
18
14
10
6
2
0.0
2
4
6
8
10
12
10^4[HNO$_2$]M
slope = 1.82 l mol^{-1} min^{-1}
intercept = 2.75 x 10^{-4} min^{-1}

Fig. 3

Table 4

All $[HNO_2] \approx 0.0008$ M

	$[H^+]$ M	10^6 Initial rate M min^{-1}
I	2.262	2.69
II	2.088	2.43
III	1.940	2.38
IV	1.520	2.25
V	1.520	2.00
VI	1.520	2.25
VII	1.520	2.22
VIII	1.400	2.12
IX	0.0007 to 0.15	1.39 (from Fig. 2)

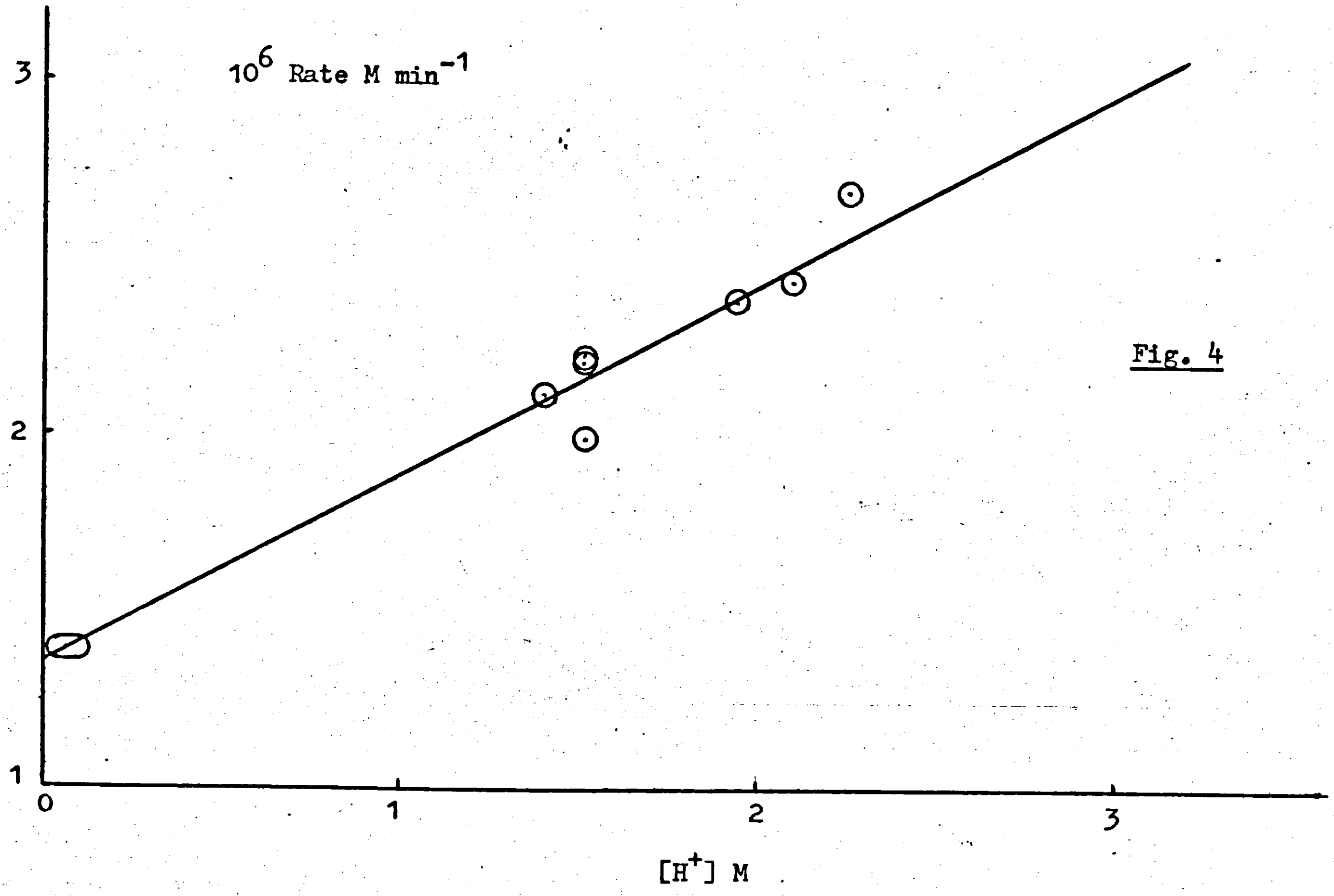


Fig. 4

SECTION III

THE REACTION BETWEEN N(III) AND CHLORATE IONS

EXPERIMENTAL RESULTS

General Technique Adopted

Equal volumes of 2.335×10^{-3} M nitrite and 0.0200 M chlorate solutions were mixed and allowed to stand at room temperature. The pH of the mixture was 5.58. At known times samples were withdrawn, quenched, diazotised and examined spectrophotometrically. No change in the nitrite concentration occurred for several hours under these conditions. Even when the concentrations were raised to 4.67×10^{-3} M nitrite and 0.0400 M chlorate, no reaction could be observed within a reasonable time at this pH.

When the acidity was increased sufficiently reaction took place. It was found that suitable conditions for observing this reaction at 25°C were, $[H^+] \approx 10^{-1}$ to 10^{-2} M, $[NO_2^-] = 10^{-3}$ M and $[ClO_3^-] = 10^{-2}$ M. Separate experiments indicated the necessary amount of buffer (potassium acetate and hydrochloric acid) required to maintain near constancy of pH throughout an experiment(42).

Once preliminary exploratory work was over, all kinetic experiments were carried out in a thermostat controlled to ± 0.02°C. "Analar" grade chemicals were used when available without further purification.

Sodium nitrite, together with potassium chlorate and any other solutions, apart from the buffer, were measured into a 500 ml stoppered conical flask (A) by means of pipettes. The buffer was measured into a second, 250 ml flask (B). The stoppered vessels were then placed into the thermostat and allowed to reach thermal equilibrium. The reaction was started by mixing the reactants, pouring the contents of (B) into (A), then back into (B) and back again into (A), thus ensuring complete mixing. Zero time was taken when the buffer was added to the reagents. Samples were withdrawn, after certain intervals of time, and treated as previously described on page 27. The time for each analysis was taken as that when the pipette had half emptied. Experience with the half-flow-time of each pipette used, enabled samples to be taken at simple times by starting the pipette flow a pre-determined time before the recorded times.

The observations were made over about 80% of nitrite exhaustion and initial rates for the disappearance of nitrite were calculated from graphs of log O.D. vs. time. These were linear over 70% of reaction in most cases when the concentration of chlorate was large compared with that of nitrite.

The optical density readings in a typical experiment are shown in Table 5.

Table 5

$[NaNO_2] = 0.001012$ M $[KClO_3] = 0.0200$ M

pH = 2.255 Temp = 25.0 ± 0.02°C

Time (min)	O.D.
0	(0.506)
2	0.487
5	0.466
10	0.432
20	0.368
40	0.276
60.5	0.199
90	0.126
110	0.091

Perhaps it is worth noting immediately that this records one of the slowest rates observed in the chlorate work and that the initial rate is about 2×10^{-5} mol l^{-1} min^{-1}. Reference to Table 3 shows that under similar conditions HNO_2 decomposes at about 1.6×10^{-6} mol l^{-1} min^{-1}.

Stoichiometry of the Reaction

The overall reaction between nitrite and chlorate, in acid solution, has been represented by the following stoichiometric equation:

$$ClO_3^- + 3HNO_2 \rightleftharpoons Cl^- + 3NO_3^- + 3H^+$$

Perhaps this equation seemed self-evident to Lowe and Brown.

No recent experimental evidence is available for this except a potentiometric titration study by Gyani and Prasad. Their work is carried out with $[H^+]$ varying over the range 0.1 to 3 M. Under these conditions chlorate and nitrite react quite rapidly. The curves, they produced, are unconvincing but are claimed to support a 3:1 ratio. This accords with a fast NO_2^-/ClO_3^- reaction and slow or negligible subsequent reaction of ClO_3^-/Cl^-.

It was decided to check whether the reactants were consumed in the molar ratios suggested.

Reaction mixtures of constant volume and constant buffer concentration were made up and analysed for the excess chlorate as follows:

Preliminary work such as that given in Table 5 indicates the rough rate of reaction.

After a time when the reaction was presumed to have gone to completion, no more nitrite should have been available. 10 ml portions of the solution were placed in a quickfit conical flask to which 1 gm KBr (excess) and 20 ml concentrated HCl were added. The flask was stoppered shaken well and allowed to stand in the dark for 5 - 10 minutes. 100 ml of 1% KI solution was added and the liberated iodine was titrated against standard thiosulphate solution. Table 6 details the results of these determinations of the excess chlorate remaining after exhaustion of nitrite.

Table 6

$[NO_2^-]$ M put in	$[ClO_3^-]$ M put in	ml of 0.02019 M $S_2O_3^{2-}$	$\frac{NO_2^- \text{ put in}}{ClO_3^- \text{ put in}}$	$\frac{NO_2^- \text{ used}}{ClO_3^- \text{ used}}$
0.00325	0.0160	44.2	0.203	2.90
0.00650	0.0160	41.0	0.406	2.95
0.00976	0.0160	38.0	0.610	3.04
0.01301	0.0160	35.1	0.813	3.10
0.01626	0.0160	32.1	1.016	3.13
0.01626	0.0128	23.3	1.270	3.28

The results show that the chlorate consumes three moles of nitrite under the conditions investigated. The trend above this figure is a reflection of the greater extent of decomposition of nitrous acid in experiments containing relatively more nitrous acid. Mixtures used kinetically always contained considerable excess of chlorate.

Determination of the Products of Reaction

The overall products of the reaction between chlorate and nitrite ion, in acid medium, have been reported as chloride and nitrate.

No recent published experimental evidence is available to confirm this and it was decided to identify the products as far as possible.

(i) To investigate the spectral changes during reaction

Let us consider absorption in the region of 47000 - 48000 cm^{-1}. Chlorate, chlorite, hypochlorite and chloride are transparent or weakly absorbing at this wavenumber. Nitrite ion and nitrate ion both have absorption maxima in this region. Figures 5 and 6 illustrate these conclusions and also show that acidification of nitrite (producing nitrous acid) shifts this peak of absorption to higher wavenumbers, but that similar acidification of nitrate is virtually without influence upon the spectrum.

20 ml of 0.0200 M $KClO_3$ and 20 ml of 0.00213 M $NaNO_2$ were added to 50 ml of water in a conical flask. 5 ml of buffer of pH about 1.4 (0.1 M potassium acetate and 0.72 M HCl), were mixed with the reactants and a clock started. Some reaction mixture was transferred to a 5 mm silica cell in the cell compartment of a Pye Unicam SP.800 recording spectrophotometer. Buffer solution of equivalent concentration was used in the reference beam.

The spectrum of the reacting mixture (Fig. 7) was scanned rapidly between 40,000 and 50,000 cm^{-1}, at timed intervals.
Comparison with Figures 5, 6 and 7 indicates that nitrous acid is being oxidised to nitrate ion.

(ii) Qualitative test for nitrate

Common methods available for the detection of nitrate are not useful in the present work, because of the interference of other anions in the system.

But when nitrate is reduced to nitrite with zinc and acetic acid, the nitrite can be readily detected by means of sulphanilamide solution, (see page 27).

A reaction mixture deficient in nitrite was allowed to react to completion (checked by testing a sample for nitrite). When no NO_2^- could be detected, a sample was withdrawn and neutralised with $NaHCO_3$. The solution was reacidified with acetic acid and zinc dust was added.

Tests for nitrite now gave strong positive results.

(iii) Gravimetric analysis for chloride

Two reaction mixtures were prepared. (A) consisted of 0.2145 gm of $KClO_3$ and 0.4312 gm $NaNO_2$ (small excess of nitrite) which were dissolved in 300 ml water. The pH of the solution was adjusted to 1.5 with dilute nitric acid and the reaction allowed to go to completion at room temperature. A slight excess of silver nitrate was added, the solution was heated to boiling and kept in subdued light(42).

The second acidified reaction mixture (B) consisted of 0.1563 gm of $KClO_3$ and 0.3788 gm of $NaNO_2$. This was treated similarly except that after addition of silver nitrate the solution was heated only to 45°.

The solutions containing precipitate were allowed to cool, and the bluish white precipitate was filtered off, dried at 130°C and weighed to constant weight. Table 7 shows the correspondence between chlorate put in and (assumed) chloride found. Silver chlorate, chlorite and hypochlorite would, of course not be precipitated under these conditions.

Table 7

Expt.	Wt. AgCl	Mole ClO_3^-	Mole Cl^-
A	0.2505 gm	0.001750	0.001746
B	0.1799 gm	0.001275	0.001254

Fig. 5

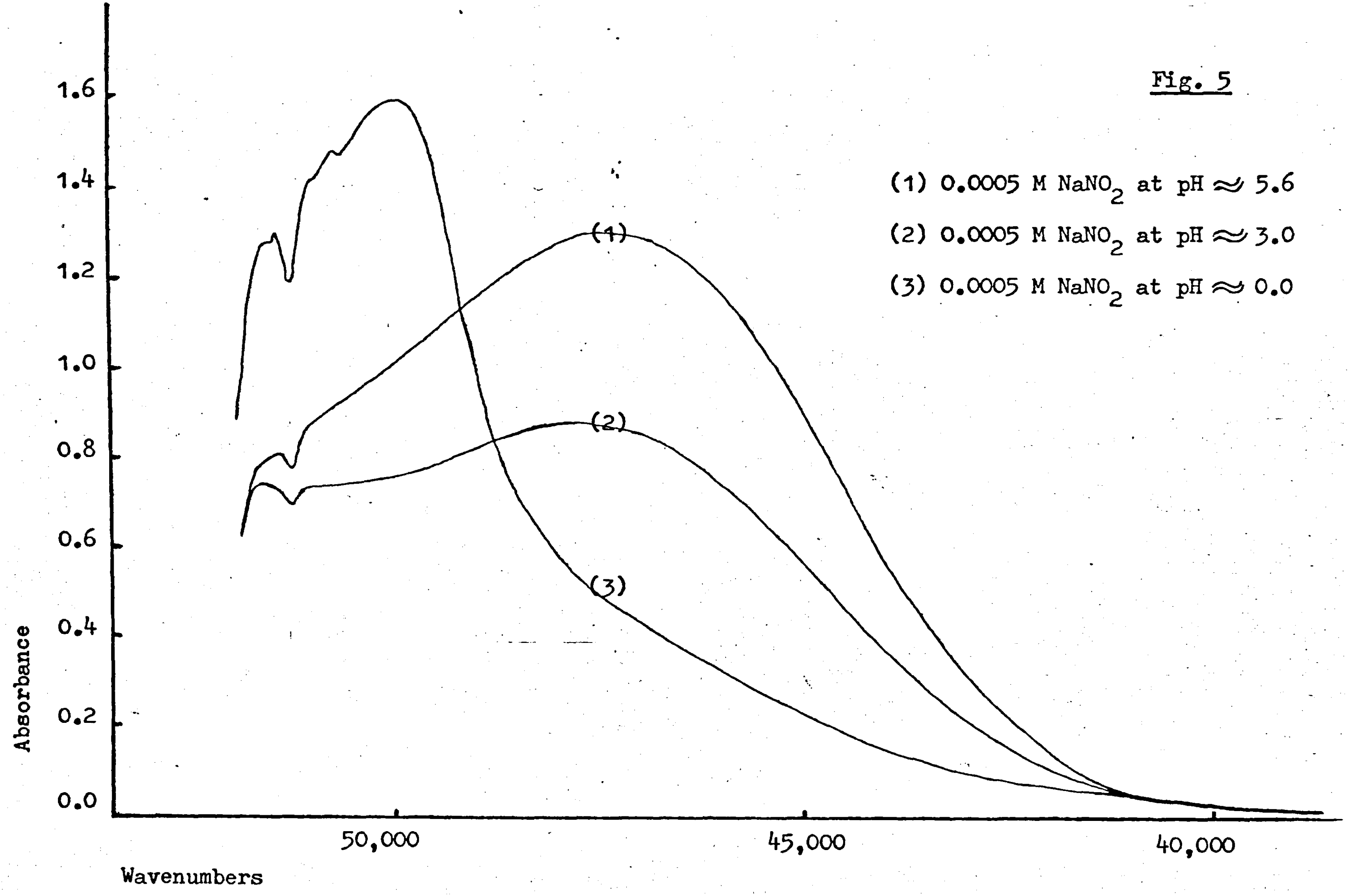

(1) 0.0005 M $NaNO_2$ at pH ≈ 5.6
(2) 0.0005 M $NaNO_2$ at pH ≈ 3.0
(3) 0.0005 M $NaNO_2$ at pH ≈ 0.0
(1)
(2)
(3)
Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Wavenumbers
50,000
45,000
40,000

Fig. 6

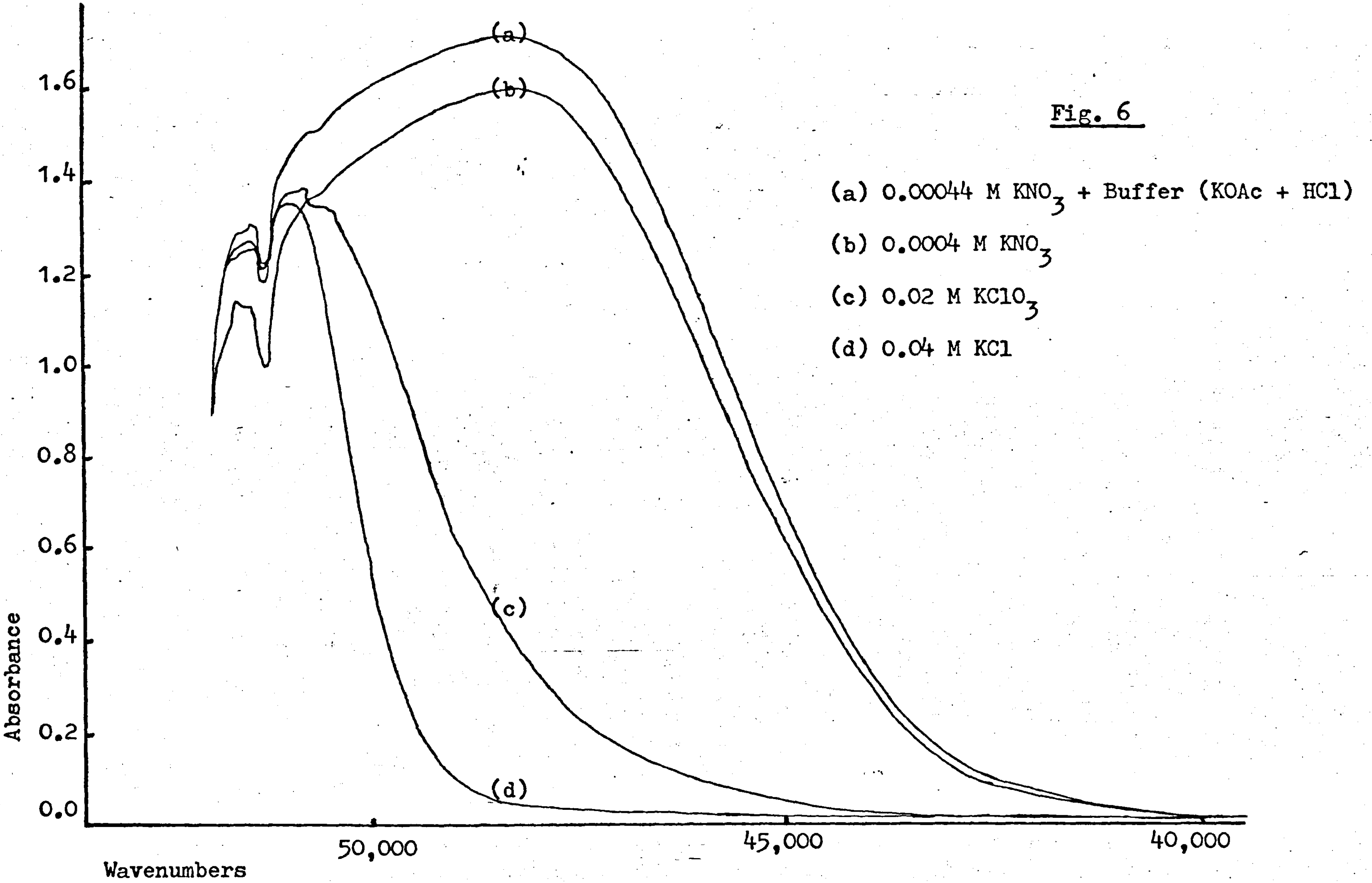
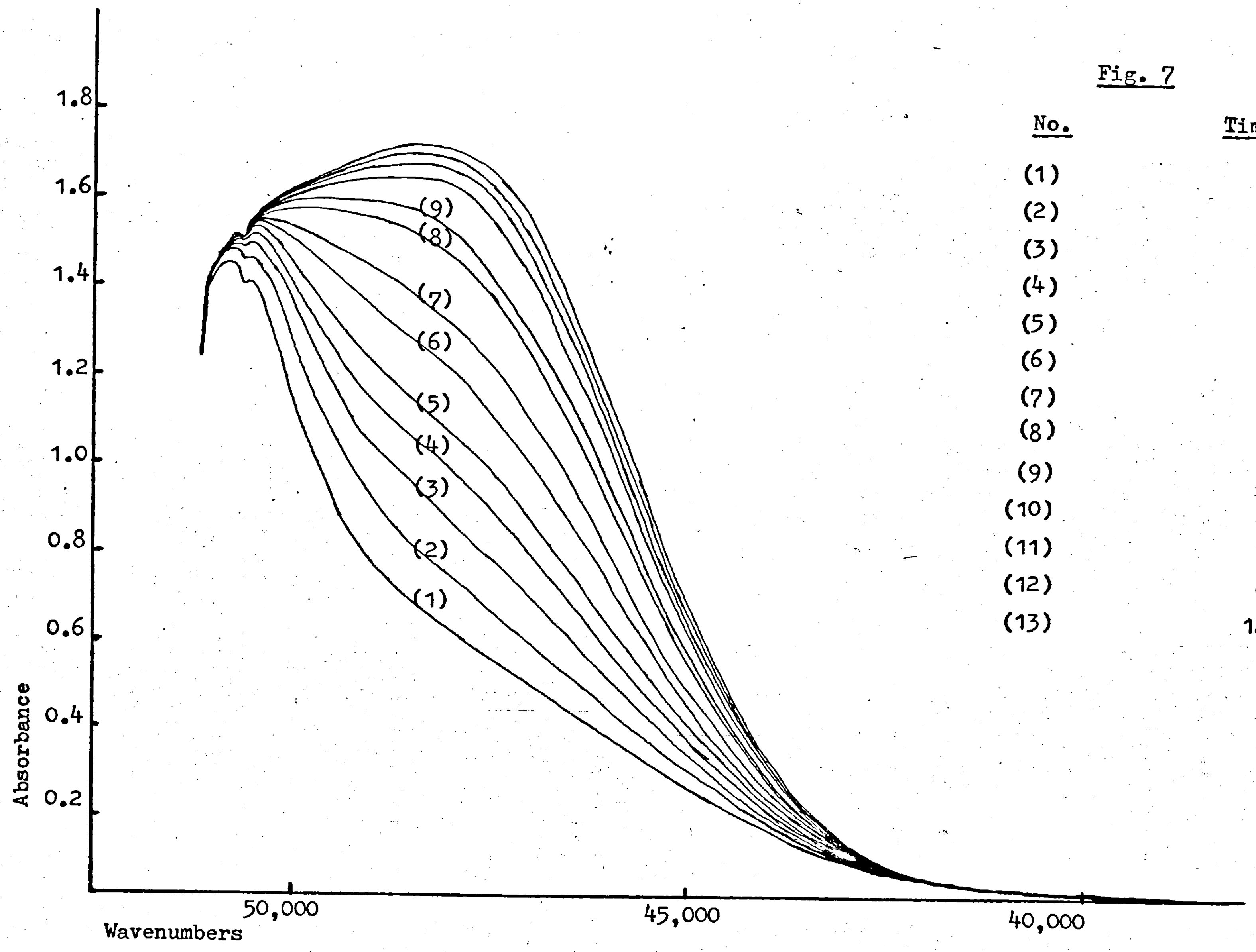

(a) 0.00044 M KNO_3 + Buffer (KOAc + HCl)
(b) 0.0004 M KNO_3
(c) 0.02 M $KClO_3$
(d) 0.04 M KCl
(a)
(b)
(c)
(d)
Absorbance
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Wavenumbers
50,000
45,000
40,000

Fig. 7



No.	Time (min)
(1)	3
(2)	6
(3)	9
(4)	12
(5)	15
(6)	20
(7)	25
(8)	35
(9)	40
(10)	55
(11)	70
(12)	85
(13)	120

Conclusion

The results of the gravimetric analysis show a virtual 1:1 correspondence between reactant chlorate and product chloride.

The qualitative test proved that the reduction of a nitrogen containing product passes via nitrite. The only reasonable assignment is that the product is nitrate.

Commenting on the spectra, the position and the absorbance of the early stages of the reacting mixtures (Fig. 7), show that they contain a mixture of nitrite and acid (Fig. 5). The later spectra (Fig. 7) show that they duplicate the spectrum of nitrate (Fig. 6(b)) or a mixture of nitrate and buffer (which has chloride (Fig. 6(a)).

Moreover, since the maximum absorbance in the spectrum (Fig. 6(a)) corresponding to a concentration of 0.00044 M nitrate, and the maximum absorbance of the finally reacted mixture, which starts from a concentration of 0.00044 M nitrite are both 1.71 at 48,300 cm^{-1} it is clear that nitrous acid is quantitatively converted to nitrate. In fact this is not only shown by the position of maximum absorption, the whole curves for acid nitrate and fully reacted mixture are superimposable between 40,000 and 50,000 wavenumbers.

Taking the analyses together with stoichiometry makes the assumption

$$ClO_3^- + 3HNO_2 \longrightarrow Cl^- + 3NO_3^- + 3H^+$$

the only tenable one.

Reproducibility of Rate Measurements and the Effect of Physical Conditions

It was considered advisable initially to test whether variation in ordinary physical conditions has any effect upon the rate of the chlorate/nitrite reaction. For this purpose, as well as to test the reproducibility of measurements, five kinetic runs were carried out. The first, A, was under normal laboratory conditions. In B, the reaction vessel was wrapped in metal foil to exclude light. The reaction vessel, in C, was packed with short lengths of glass tubing so as to increase the area of glass surface exposed to the solution four-fold. In order to examine the effect of dissolved gases on reaction rate, an experiment labelled D, was carried out in which air was bubbled through water first, then through the reactant solution for half an hour before starting the run, and the air flow was continued during the kinetic run. To test the purity of the reagents used or the sensitivity of the rate towards trace metal ion contaminants, a reaction labelled E was carried out in which 0.05 gm of Na_2EDTA had been added.

Chemical conditions were the same for all five experiments.

The results of these experiments are summarised in Table 8.

Table 8

$[NaNO_2]$ = 0.001674 M $[KClO_3]$ = 0.0160 M

pH = 1.42 Temp = 25.0°C

Table of O.D. as Function of Time

Time (min)	A	B	C	D	E
0	(0.837)	(0.837)	(0.837)	(0.837)	(0.837)
2	0.529	0.522	0.534	0.527	0.532
4	0.333	0.335	0.329	0.325	0.329
6	0.205	0.210	0.211	0.202	0.204
8	0.130	0.134	0.133	0.130	0.128
11	0.062	0.064	0.065	0.060	0.059
15	0.025	0.025	0.026	0.022	0.021

The results are in good agreement with one another, and any discrepancy between the optical densities does not exceed the normal experimental error. The rate of reaction was therefore found to be quite reproducible and independent of the physical effects of light, surface and atmospheric air. There was no change in rate upon addition of a small amount of EDTA.

Therefore it was decided to carry out the experimental kinetics under normal physical conditions.

The General Features of the Reaction Curves

Two reaction mixtures at different pH and chlorate ion concentration were mixed, keeping the concentration of nitrite constant.

The optical density-time data of one of these (B) has already been given in Table 5, the other (A) is now listed in Table 9.

The general features of the plotted results are shown in Fig. 8.

Table 9

$[NaNO_2]$ = 0.001012 M   Temp. = 25.0 ± 0.02°C

$[KClO_3^-]$ = 0.00200 M

[KOAc] = 0.020 M

$[Cl^-]$ = 0.160

pH = 0.940

Time (min)	O.D.
2	0.474
4	0.444
6	0.419
8	0.395
10	0.368
12	0.352
15	0.322
20	0.278
30	0.210
45	0.139
70	0.070

These plots are typical of the forms normally observed, although in most of the work the excess of ClO_3^- was usually larger than in the experiments depicted.

The log plot demonstrates the fact that with chlorate present in excess, the reaction shows closely first order behaviour in nitrous acid (or in some species whose concentration is directly proportional to HNO_2). It is satisfactory to note that both log plots extrapolate back to the same point shown as corresponding to zero time. This point is calculated from the known concentration, and the extinction coefficient (5.00×10^4 l mole^{-1} cm^{-1}) of the diazotised product.

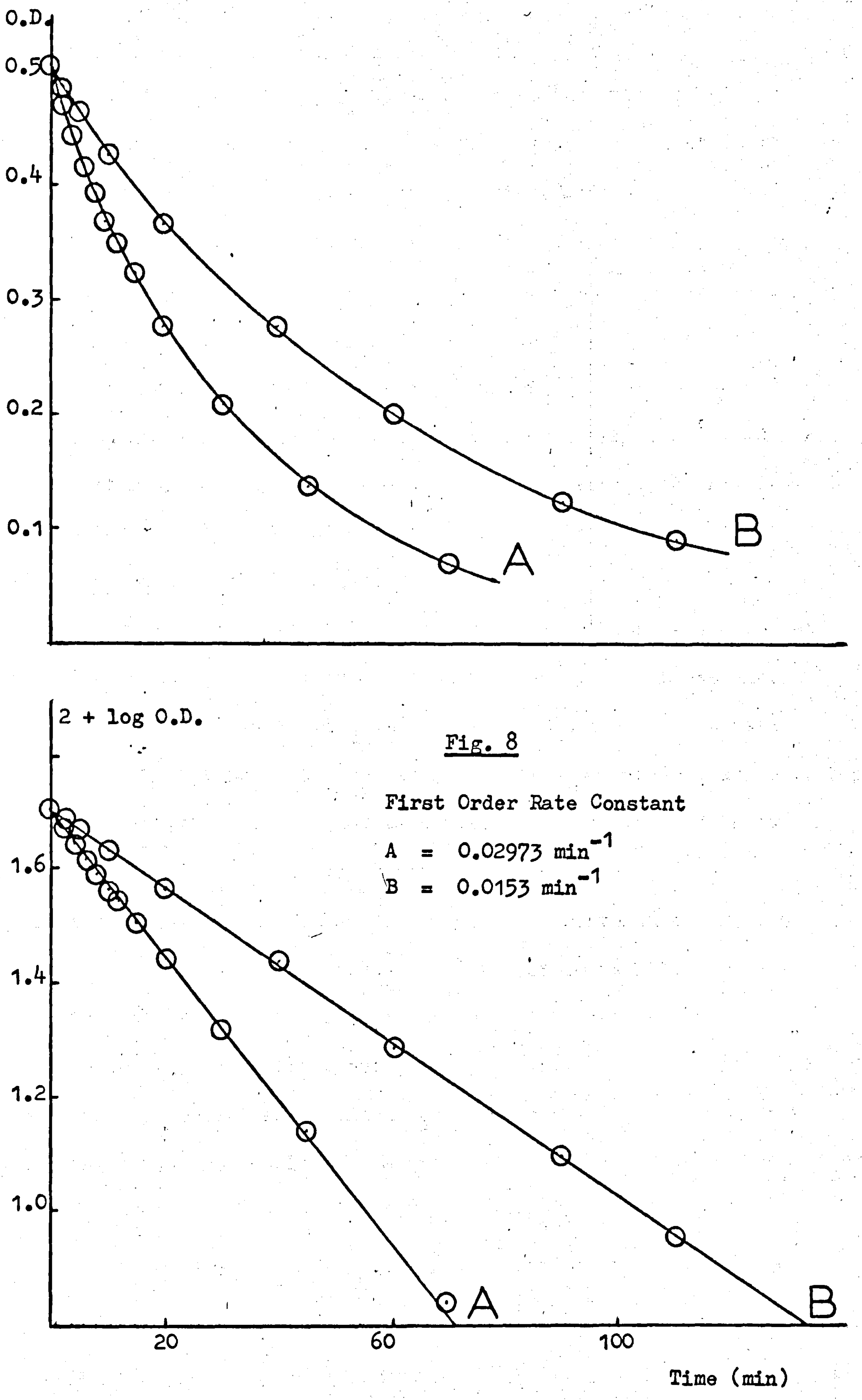


Fig. 8

First Order Rate Constant

A = 0.02973 min^{-1}

B = 0.0153 min^{-1}

The Effect of Added Salts on the Rate of Reaction

The effects of addition of neutral salts to the reaction mixture can be divided in general, into two; those arising from ionic strength changes and those due to specific effects of anions and cations.

Due to association between oppositely charged ions, ion pairs or complexes may be formed. These could affect the reaction in two ways. Firstly the concentrations of some ions present would be altered and therefore the ionic strength of the system would in general be lowered. Secondly ion pairs may involve potential reactants and the ion-paired reactants may react at a different rate (faster or slower) than non-complexed species. Ion pairs may assist the formation of the transition state and hence the phenomenon may catalyse the reaction.

Generally speaking, a reaction between univalent ions will proceed without serious anomalies, so long as no multivalent ions are associated with them. In such reactions, it would be expected that ion association would be minimal in the salts of the alkali metals with singly charged anions, though a minor exception to this has been reported, the oxy-acids show significant ion-pairing, though it is not extensive(43).

Since nitrous acid and chlorate in acid medium are involved, ion association has to be taken into account. In order to be able to use only A.R. reagents, both sodium and potassium ions have to be present in the system. Experiments were carried out in which reaction mixtures contained equal amounts of different added anions or cations. All other parameters were held constant. The results are summarised in Tables 10 and 11.

Table 10

$[NO_2^-]$ = 0.000822 M

$[ClO_3^-]$ = 0.00200 M

pH = 0.86

μ = 0.374 (includes added ions)

$[K^+]$ = 0.207 M

$[Na^+]$ = 0.000822 M

$[OAc^-]$ = 0.0050 M

$[Cl^-]$ = 0.1800 M

Temperature = 25.0°C

Addition of 0.2 M Cl^-		Addition of 0.2 M NO_3^-	
Time (min)	O.D.	Time (min)	O.D.
0	(0.411)	0	(0.411)
2.5	0.383	2	0.393
5	0.353	5	0.355
10	0.304	10	0.306
20	0.222	20	0.227
37	0.135	30	0.166
60	0.067	45	0.106
		62	0.064
Rate constant = 0.0303 min^{-1}		Rate constant = 0.0303 min^{-1}	

Table 11

$[NO_2^-]$ = 0.000853 M

$[ClO_3^-]$ = 0.00800 M

pH = 1.30

μ = 0.284 (includes added ions)

$[Na^+]$ = 0.000853 M

$[K^+]$ = 0.018 M

$[OAc^-]$ = 0.010 M

$[Cl^-]$ = 0.272 M

Temperature = 25.0°C

Addition of 0.2 M Li^+

Time (min)	O.D.
0	(0.426)
2	0.383
5.5	0.321
10	0.258
15	0.199
20.5	0.150
30	0.093
40	0.056

Rate constant = 0.0510 min^{-1}

Addition of 0.2 M Na^+

Time (min)	O.D.
0	(0.426)
2	0.386
5	0.327
10	0.259
15	0.201
20	0.156
30	0.095
40	0.058

Rate constant = 0.0503 min^{-1}

Addition of 0.2 M K^+

Time (min)	O.D.
0	(0.426)
2	0.379
5	0.323
10	0.250
15.5	0.188
20	0.147
30	0.087
40	0.052

Rate constant = 0.0519 min^{-1}

Addition of 0.2 M Cs^+

Time (min)	O.D.
0	(0.426)
2	0.380
5	0.327
10	0.255
15	0.198
20	0.152
30	0.091
40	0.054

Rate constant = 0.0516 min^{-1}

In these reactions and in most of those described in this thesis, [N(III)] is much lower than the concentration of the other reactants and therefore pseudo first order rate constants following loss of [N(III)] from a near-constant medium have normally been calculated in the first instance.

The difference between the average rate constant and any rate constant in the same table, does not exceed 2% from the average.

Therefore it is clear that the reaction rate is independent of the nature of the monovalent anion or cation present or produced in the reaction mixture.

There are no appreciable specific ion effects caused by Cl^-, NO_3^-, Li^+, Na^+, K^+ or Cs^+.

Determination of the Order with Respect to Reactants

To find the order of reaction with respect to each reactant, series of experiments were carried out in which the concentration of one component was increased while holding the other concentrations and conditions virtually constant. For this restricted type of reaction, the rate expression is likely to be :

$$-\frac{dc}{dt} = k[C]^n \quad \text{or} \quad k'[C]^n + k''[C]^m + \text{--------} .$$

where k etc., is the rate constant of the pseudo nth order reactions.

Initial rates were calculated by multiplying each initial concentration of N(III) by (minus) the slope of the corresponding graph of $\log_e$ O.D./time.

The order was determined by plotting log initial rate against log initial concentration. Hydrogen ion was supplied by buffers of potassium acetate and hydrochloric acid(42). The ionic strength was maintained by potassium chloride.

Order with Respect to N(III)

Table 12

$[KClO_3]$ = 0.008889 M

$[KOAc]$ = 0.02777 M

$[H^+]$ = 0.08298 M

$[Cl^-]$ = 0.1111 M

μ = 0.1202

Temp. = 25 ± 0.02°C

$10^4[NO_2^-]$ M	10^2 k min^{-1}
1.032	7.836
2.592	7.860
5.260	7.990
7.999	7.876
9.400	7.807
10.38	7.821

The enumerated values of the pseudo first order constant indicate a first order reaction with respect to nitrite ion, but there is no evidence that the nitrite in acid solution reacts as such..

Each of the above experiments involves the same concentration of H^+. Thus any species in 1:1 equilibrium with nitrite through protonation e.g. HNO_2 or $H_2NO_2^+$ might just as well be implied as a participator in the transition state as NO_2^- itself by this order dependence on N(III).

For example, using the method of calculation given in the appendix, values of [nitrous acid] and the corresponding initial reaction rates are shown in Table 13.

A plot of log rate against log $[HNO_2]$ is shown in Fig. 9.

Table 13

10^6 Initial rate M min^{-1}	10^4[HNO$_2$] M
8.087	1.018
20.37	2.556
42.03	5.188
63.00	7.889
73.39	9.271
81.17	10.24

Figure 9 shows that a plot of log initial rate vs. log[HNO$_2$] is linear and the slope is 1.001. The order with respect to nitrous acid is one. Further evidence on this, however, is found when the order with respect to H$^+$ is investigated.

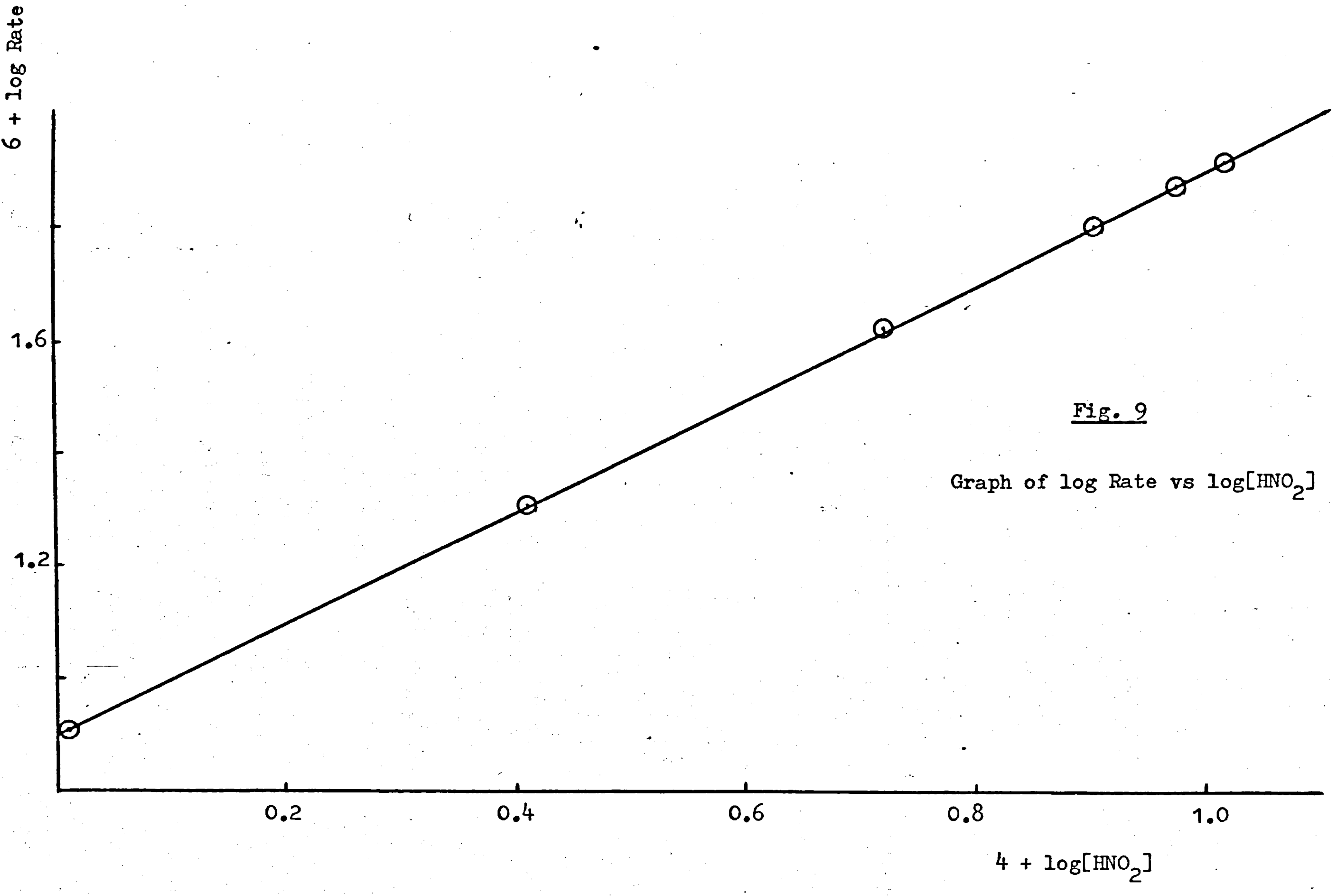


Fig. 9

Graph of log Rate vs log[HNO$_2$]

Order With Respect to Hydrogen Ion Concentration

Table 14

$[NaNO_2]$ = 0.000950 M μ = 0.1438

$[KClO_3]$ = 0.00800 M Temp. = 25.0°C

$10^3[H^+]$ (M)	$10^3[HNO_2]$ (M)	10^6 Initial rate (M min^{-1})	10^3 Initial rate/$[HNO_2]$ (min^{-1})
21.21	.8628	14.82	17.18
29.58	.8787	21.32	24.26
50.70	.9017	37.94	42.08
71.12	.9121	54.55	59.80
92.75	.9205	71.81	78.01
111.6	.9298	87.69	94.31
132.6	.9321	106.3	114.1

It can be seen from Table 14 that $[H^+]$ and initial rate are not directly proportional whereas $[H^+]$ and initial rate divided by $[HNO_2]$ are more closely proportional to one another. These experiments are performed in the pH range where HNO_2 and NO_2^- are both present in equilibrium in significant concentrations. The conclusion from Table 14 and from other similar sets of experiments is that the reaction is first order in both HNO_2 and H^+. When hydrogen ion concentration is high, most of the N(III) in the solution is present as nitrous acid and dividing the rate by nitrous acid concentration will not alter the result dramatically.

A plot of log initial rate/$[HNO_2]$ vs log $[H^+]$ is a straight line with a slope of 1.035 (see Fig. 10.).

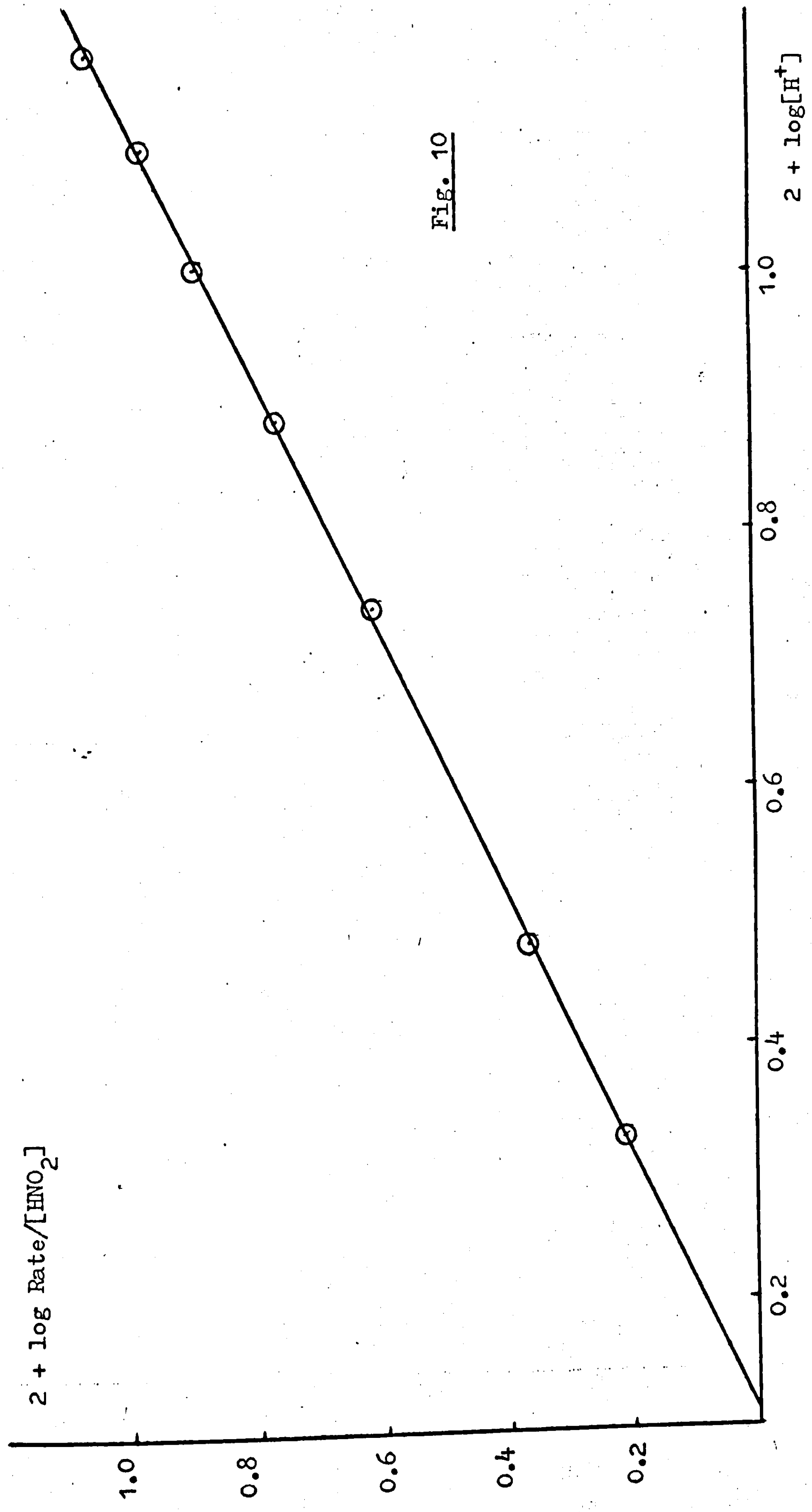


Fig. 10

Order With Respect to Chlorate

Table 15

$[NaNO_2]$ = 0.0010378 M

$[H^+]$ = 0.08298 M

μ = 0.1202

[KOAc] = 0.02777 M

$[Cl^-]$ = 0.111 M

Temp. = 25.0°C

10^5 Initial rate (M min^{-1})	$10^3[ClO_3^-]$ (M)
2.768	3.111
3.994	4.444
4.852	5.333
6.152	6.666
7.341	8.000
8.117	8.888

A plot of log initial rate vs log $[ClO_3^-]$ shows a straight line of slope 1.03 (see Fig. 11). The order with respect to chlorate ion is one.

For each of the three reactants investigated an extrapolation of the initial rate to that appropriate to [reactant] $\doteq$ 0 yields rate = 0, showing that there are insignificant parallel reactions removing N(III).

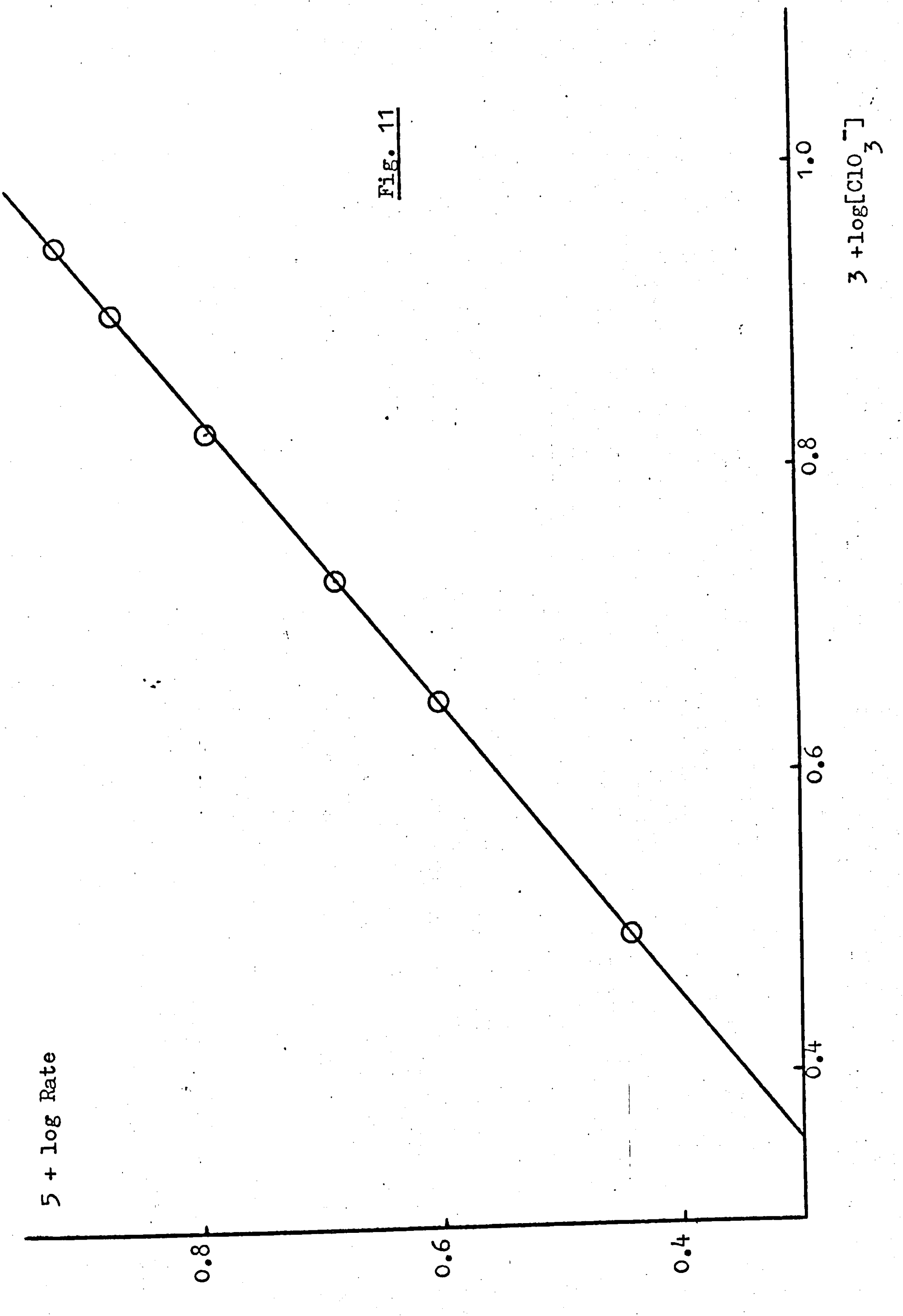


Fig. 11

The Effect of Ionic Strength on Reaction Rate

It has already been shown that simple ions have no specific effects upon reaction rate. It remains, however, necessary to consider the general effect of ionic strength.

The Debye-Hückel theory has been of great value in interpreting the properties of dilute solutions of electrolytes. The behaviour of real solutions containing ions deviates from ideality even at quite low concentrations. Consider a reaction

$$A^{Z_A} + B^{Z_B} \rightleftharpoons AB^{*(Z_A + Z_B)} \rightleftharpoons \text{products}$$

where Z is the charge on an ion and AB^* is the activated complex (transition state).

Assuming that the activated complex is in virtual equilibrium with the reactants, the rate constant can be deduced, according to the Brønsted-Bjerrum theory, as

$$k = k_o \frac{f_A f_B}{f_{AB^*}} \qquad \ldots\ldots (1)$$

where f is an ionic activity coefficient and k_o is the rate constant when the activity coefficient function is unity.

For aqueous solutions at 25°C, the activity coefficient of a Z-valent ion may be represented by the equation:

$$-\log_{10} f = 0.509\, Z^2 . F(\mu) \qquad \ldots\ldots (2)$$

where $F(\mu)$ is some function of ionic strength (μ).

Combining equations (1) and (2) and taking logarithms we obtain:

$$\log_{10}k = \log_{10}k_o - 0.509\, [Z_A^2 + Z_B^2 - (Z_A + Z_B)^2] . F(\mu)$$

$$= \log_{10}k_o + 1.018\, Z_A . Z_B . F(\mu)$$

According to this equation, a plot of log k versus $F(\mu)$ should be linear, the slope depending upon the charge of the ions in the reaction step. If there is no other species participating in the rate law, and if the Debye-Hückel theory applies, the results can be interpreted to give three predictions:

(1) The rate of a reaction between ions of the same sign increases with increasing ionic strength.

(2) The rate of a reaction between ions of opposite sign decreases with increasing ionic strength.

(3) If at least one Z-term is equal to zero, then the ionic strength has no effect on the rate of reaction.

However, in many reactions the actual "reaction step" does not take place between the materials in the form in which they were put into the reaction mixture, because perhaps a number of pre-equilibria are set up. Clearly the present system comes into this category in that $NaNO_2$ is one of the materials whose concentration is actually measured and known at the start of reaction, yet we have evidence that HNO_2 is a part of the activated complex. In order to apply the quantitative idea above, the actual concentrations of the two species in the reaction step are required, so that k can be found. This introduces the complication that either all the pre-equilibrium steps must be guessed (or established) and their pre-equilibrium constants known as functions of the ionic strength; or the transition state can be regarded as in equilibrium with the materials from which the mixture was made up. In the latter case the simplicity of the above compilation is lost because, for example, in the present case one needs to consider an overall equilibrium such as

$$2H^+ + NO_2^- + ClO_3^- \rightleftharpoons H_2NClO_5$$

or perhaps the simpler one of

$$H^+ + HNO_2 + ClO_3^- \rightleftharpoons H_2NClO_5$$

or even one involving elimination of water, but in general an equilibrium involving several species whose activity coefficients and even activities are ionic strength dependent.

Experiments were carried out in which the ionic strength was varied between 0.057 and 0.128 M units by the addition of potassium chloride, the ions of which have already been shown to have no specific effects. The results are summarised in Table 16. Calculations of ion pair concentrations and of the true values of ionic strength are also given in Table 17. For the method of calculation see the appendix.

Apparent first order constants were calculated from graphs of log optical density vs time, and since the rate has been established as equal to

$$-\frac{d[N(III)]}{dt} = k_r\ [HNO_2][H^+][ClO_3^-]$$

where k_r is the true rate constant, Tables 16 and 17 also list calculated values for k_r.

Table 16

$[NaNO_2]$ = 0.00101 M $[OAc^-]$ = 0.0100 M

$[ClO_3^-]$ = 0.0100 M pH = 1.547

Temperature = 25.0°C

$10^2[Cl^-]$ *	$10^2[M^+]$ *	$10^3[HNO_2]$ *	$10^2\ \mu$	$10^2\ k$ (min^{-1})	10^6 I. Rate ($M\ min^{-1}$)	k_r ($M^{-2}\ min^{-1}$)	F (μ) **
4.80	2.10	0.980	5.64	4.34	43.8	128	0.178
5.80	3.10	0.980	6.68	4.22	42.6	123	0.189
6.80	4.10	0.980	7.71	4.07	41.1	117	0.198
8.80	6.10	0.980	9.78	3.91	39.5	110	0.214
9.80	7.10	0.980	10.80	3.81	38.5	107	0.220
10.8	8.10	0.980	11.83	3.75	37.9	105	0.226
11.8	9.10	0.979	12.86	3.67	37.1	102	0.232

* mol l^{-1}

** $F(\mu) = [(\sqrt{\mu}/1 + \sqrt{\mu}) - 0.25\ \mu]$ calculated from initial reactant concentrations.

Table 17

* $10^3[H^+]$	* K_{MClO_3}	* $10^4[MClO_3]$	* $10^3[ClO_3^-]_T$	* K_{MNO_2}	* $10^5[MNO_2]$	* $10^4[HNO_2]_T$	* $10^2[M^+]_T$	$10^2\ \mu_T$	k_r $(M^{-2}\ min^{-1})$	** $F\ (\mu)_T$
35.0	0.60	1.262	9.87	0.41	0.94	9.77	2.09	5.62	130	0.178
35.5	0.58	1.769	9.82	0.40	1.41	9.67	3.08	6.66	127	0.189
35.8	0.57	2.255	9.77	0.40	1.62	9.64	4.08	7.69	122	0.198
36.5	0.55	3.567	9.64	0.38	2.30	9.61	6.06	9.74	117	0.214
36.8	0.54	3.717	9.63	0.38	2.53	9.55	7.06	10.8	114	0.220
37.0	0.54	4.166	9.58	0.37	2.96	9.51	8.06	11.8	112	0.226
37.2	0.53	4.569	9.54	0.37	3.13	9.49	9.05	12.8	110	0.232

* mol l^{-1} units

** $F\ (\mu)_T = [(\sqrt{\mu}\ /1 + \sqrt{\mu}\ ) - 0.25\ \mu]$ calculated from "true" ionic strength.

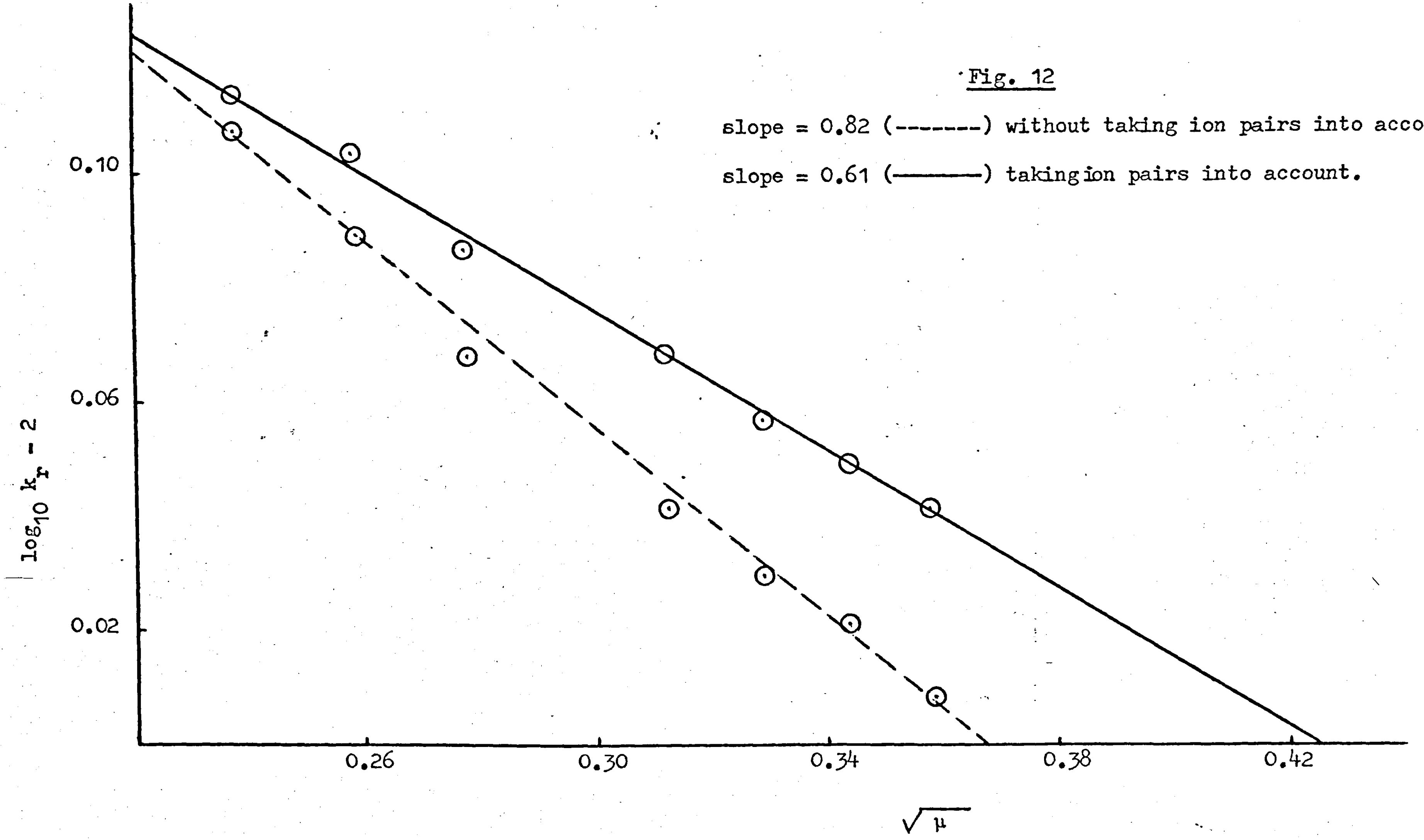
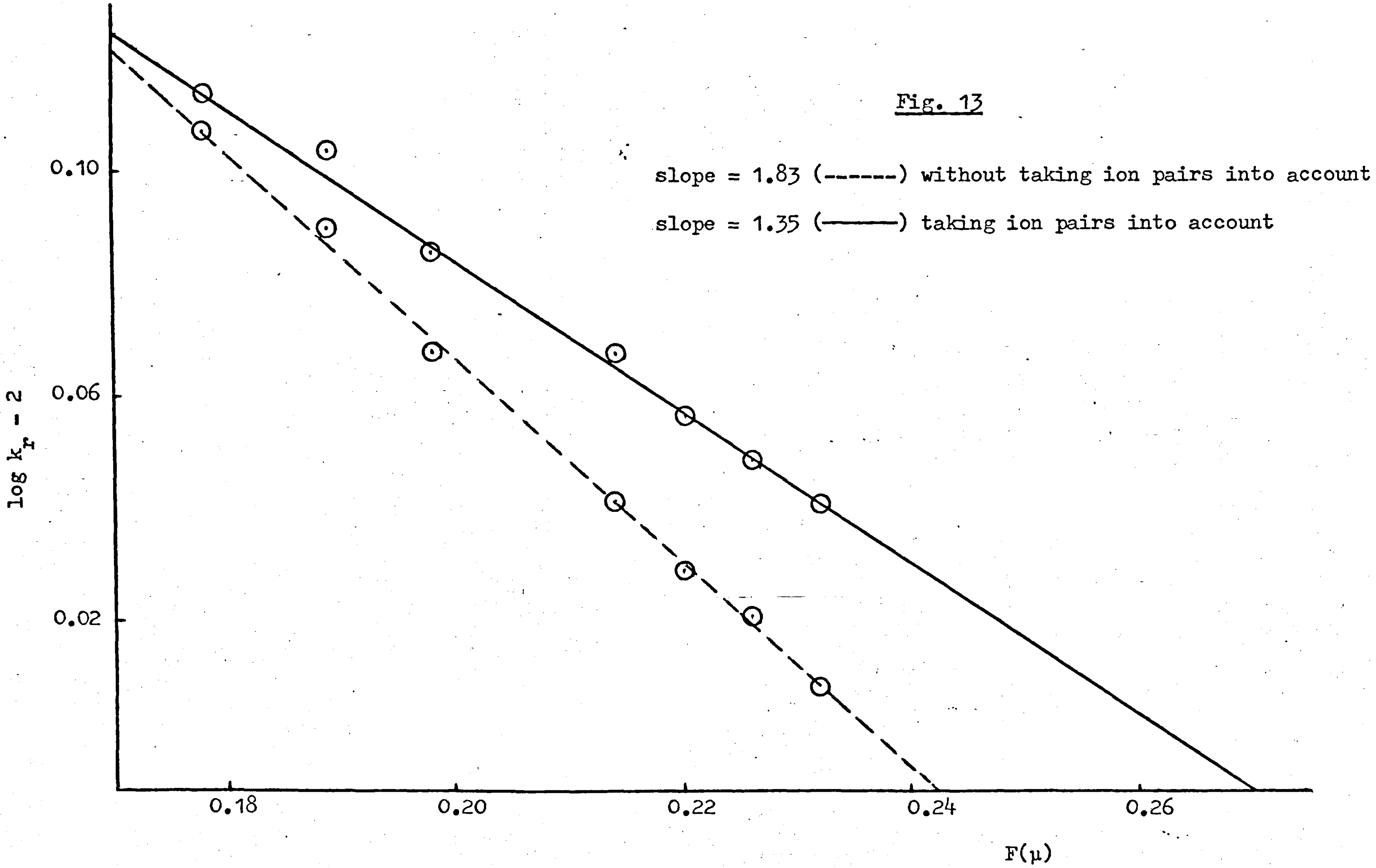


Fig. 12

slope = 0.82 (-------) without taking ion pairs into account.

slope = 0.61 (———) takingion pairs into account.

Fig. 13



slope = 1.83 (------) without taking ion pairs into account

slope = 1.35 (———) taking ion pairs into account

Tables 16, 17 and Figures 12, 13

Comments

In considering what function $F(\mu)$ should be, there is considerable latitude. Graphs of log k_r versus two commonly used functions ($\mu^{\frac{1}{2}}$ and $\left\{\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.25\ \mu\right\}$), are shown in Figs. 12 and 13.

Commenting on Tables 16 and 17, the range of variation of ionic strength is within the limits of dilution of Debye-Hückel theory, but is not enough to decide anything very firmly.

Perhaps all that can firmly be deduced is that increase in ionic strength leads to a fall in rate constant.

To investigate the matter further, results from experiments of different reactant concentrations and different ionic strength are collected in Table 18, and a plot of log k_r against $F(\mu)$ is shown in Fig. 14.

Although the points are scattered along the both sides of the line the slope is again close to - 1.3.

Extrapolation of k_r to zero $F(\mu)$ shows that the rate law at zero ionic strength is

$$\text{Rate} = 220[H^+][HNO_2][ClO_3^-]\ \text{mol l}^{-1}\ \text{at}\ 25^{\circ}C$$

when referred to rate of loss of N(III).

Table 18

$10^3[ClO_3^-]_T$ (M)	$10^2[H^+]_T$ (M)	$10^4[HNO_2]_T$	$10^2\mu_T$	10^6 I.R. ($M\ min^{-1}$)	k_r $M^{-2}min^{-1}$	$F(\mu)_T$
8.71	8.28	10.1	12.0	81.2	111	0.227
8.82	13.1	10.6	13.7	129	105	0.236
8.84	13.8	10.6	14.4	140	108	0.239
8.73	9.24	10.5	12.2	92.6	109	0.228
8.61	3.40	10.2	9.63	35.3	118	0.212
8.78	11.2	10.5	13.4	111	108	0.234
8.67	6.28	10.4	11.0	64.6	114	0.221
8.71	7.62	10.5	11.5	78.4	112	0.225
7.94	13.3	9.32	14.7	106	108	0.241
7.87	11.2	9.30	14.7	87.7	107	0.240
7.80	9.27	9.21	14.5	71.8	108	0.239
7.72	7.11	9.12	14.3	54.5	109	0.239
7.65	5.07	9.02	14.2	37.9	108	0.238
7.57	2.96	8.79	14.2	21.3	108	0.238
7.54	2.12	8.63	14.2	14.8	107	0.238
9.87	3.50	9.77	5.62	43.8	130	0.178
9.82	3.54	9.67	6.66	42.6	127	0.189
9.77	3.58	9.64	7.69	41.1	122	0.198
9.64	3.65	9.61	9.74	39.5	117	0.214
9.63	3.68	9.55	10.8	38.5	114	0.220
9.58	3.70	9.51	11.8	37.9	112	0.226
9.54	3.72	9.49	12.8	37.1	110	0.232
1.98	14.8	9.84	16.9	29.7	103	0.249
1.99	18.5	9.90	18.7	37.9	104	0.255
1.98	10.9	8.34	12.9	20.0	111	0.232
9.81	72.4	8.24	10.9	67.5	115	0.221
19.0	60.7	7.96	17.0	97.9	107	0.250
1.83	19.2	7.61	39.1	24.9	93.0	0.287
1.83	19.8	7.61	39.1	26.3	95.0	0.287
1.83	19.2	7.61	39.1	25.0	93.0	0.287
1.83	19.8	7.61	39.1	25.8	94.0	0.287

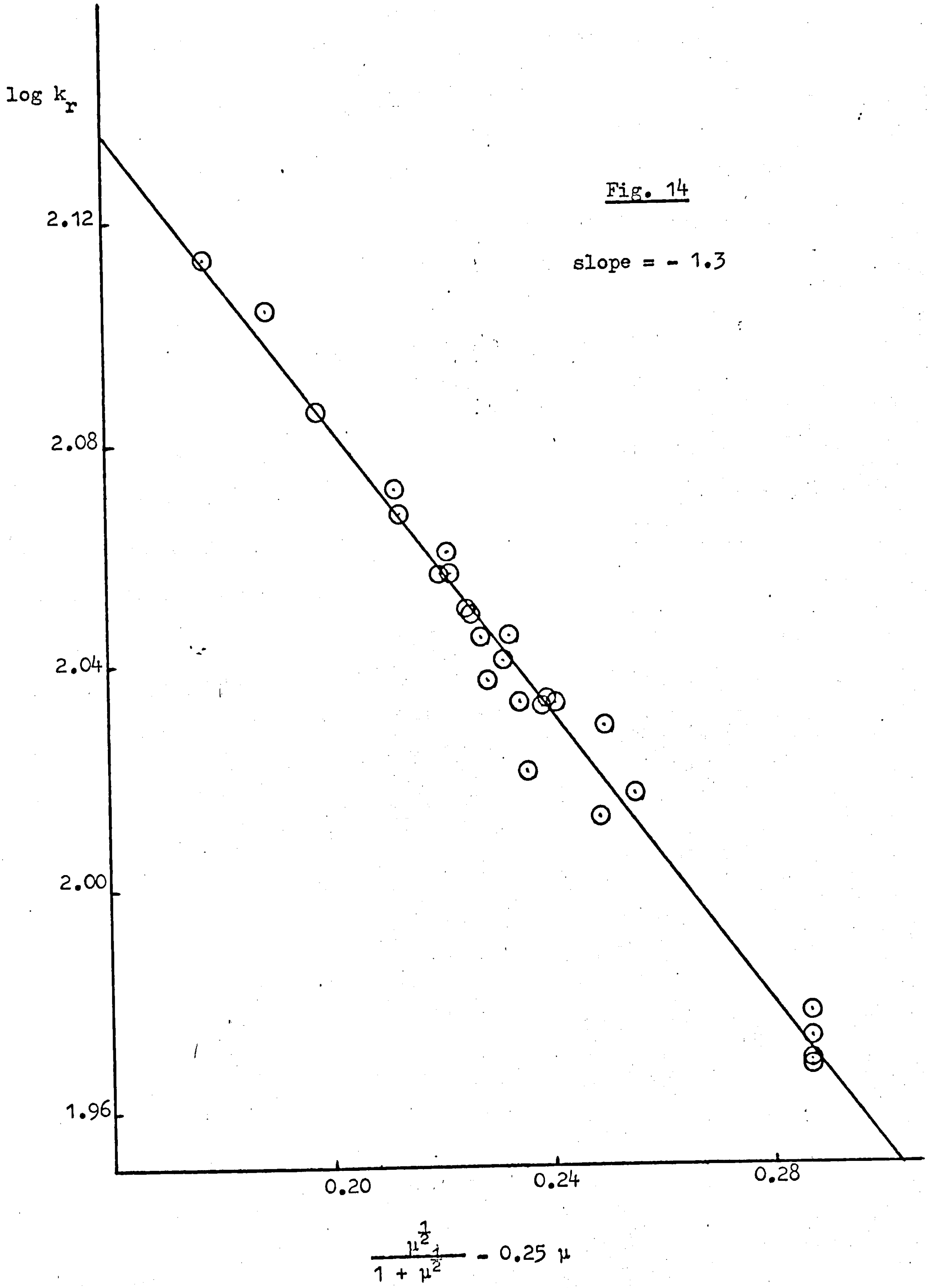

log k_r
2.12
2.08
2.04
2.00
1.96
0.20
0.24
0.28
$\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.25\,\mu$
slope = - 1.3

Fig. 14

The Effect of Temperature on Reaction Rate

The relationship which connects the rate constant of a reaction with the temperature was expressed by Arrhenius in the form:

$$k = A\ e^{-E/RT}$$

where A and E are constants specific to a particular reaction. The value of the activation energy (E), can be calculated graphically from the slope of log rate constant versus 1/T, thus,

$$\log k_r = \frac{-E}{2.303\ R} \cdot \frac{1}{T} + \log A$$

Experiments were carried out, in which the nominal conditions of concentration were identical (i.e. concentrations were identical except that no allowance was made for expansion with rise in temperature) and the temperature was varied between 10.0 and 35.0 $\pm$ 0.02°C.

The results are summarised in Table 19. A graph of log k_r versus 1/T is given in Fig. 15.

Table 19

$[NO_2^-] = 0.000962$ M $[ClO_3^-] = 0.00889$ M $[Na^+] = 0.000962$ M $[OAc^-] = 0.002222$ M

$K_{MNO_2} = 0.381$ M^{-1} $K_{MClO_3} = 0.551$ M^{-1} $[K^+] = 0.01111$ M $[Cl^-] = 0.00889$ M

$[NO_2^-]_T = 0.000958$ M $[ClO_3^-]_T = 0.00883$ M $[M^+] = 0.0120$ M $[H^+]_T = 0.0872$ M

$\mu = 0.0985$

t°C	10^3 I/T	$10^3 K_{HNO_2}$ (M)	$10^3[HNO_2]$ (M)	$10^2 k$ (min^{-1})	10^6 Initial Rate (M min^{-1})	k_r (M^{-2} min^{-1})	log k_r
10.0	3.532	0.824	0.949	2.13	20.5	28.0	1.447
15.0	3.471	0.929	0.948	3.59	34.6	47.4	1.676
20.0	3.412	1.052	0.947	5.57	53.6	73.6	1.867
25.0	3.355	1.127	0.946	8.77	84.4	115	2.064
30.0	3.299	1.172	0.945	13.9	134	184	2.264
35.0	3.246	1.197	0.945	21.7	209	287	2.457

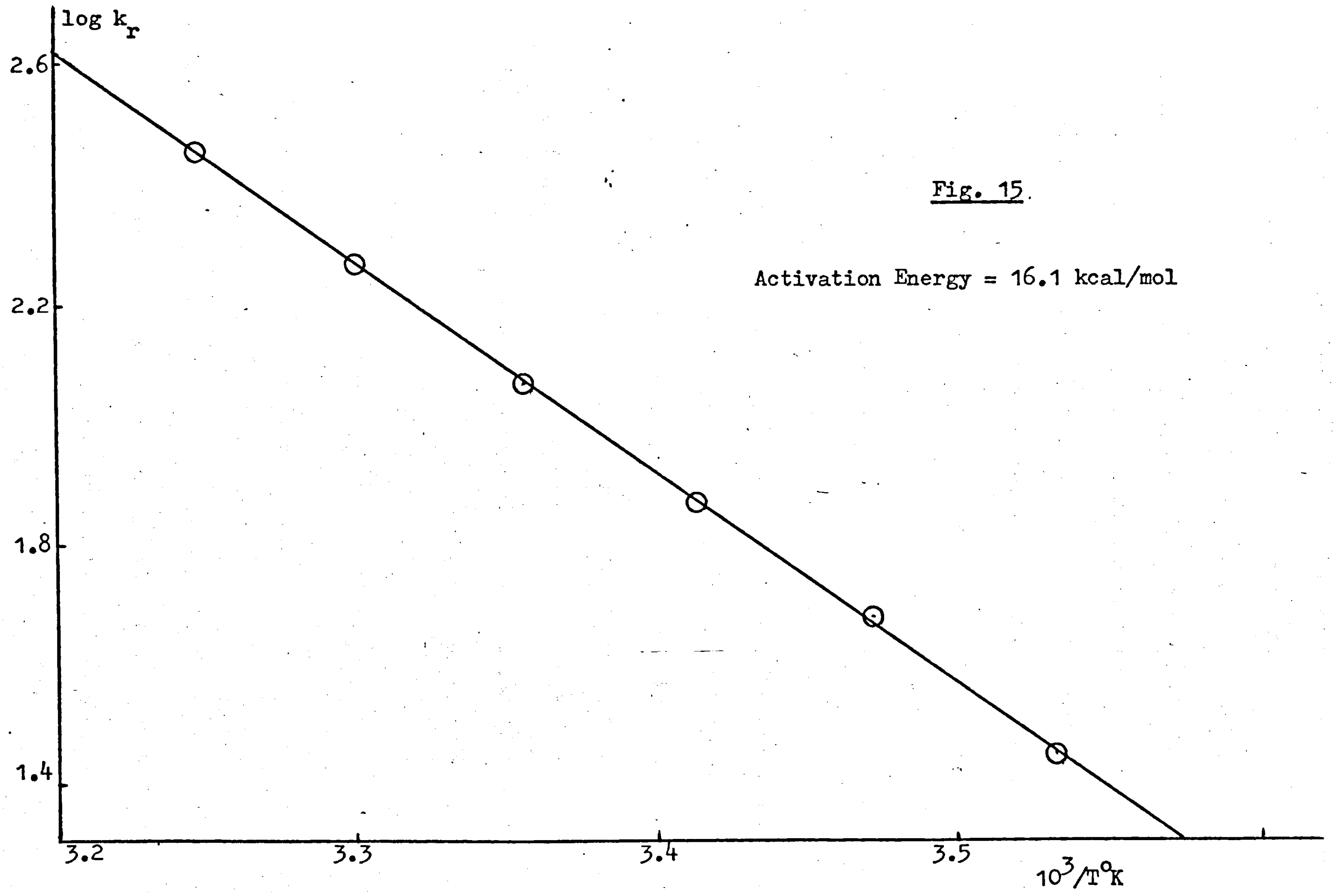


Fig. 15.

Activation Energy = 16.1 kcal/mol

E is found to be 16.1 kcal mol^{-1} from this work. Some comments may be made upon these results. k_r has been calculated assuming H^+, HNO_2 and ClO_3^- are the reactants. Thus the temperature variations of the equilibria set up between NO_2^- and H^+, NO_2^- and M^+, and ClO_3^- and M^+ have all been taken into account, using published figures directly or by extrapolation. The figure of 16.1 kcal mol^{-1} therefore is still a composite quantity - it includes a normally understood minimum energy requirement as two entities come together to form the activated state, together with two other terms. The combination of the three species H^+, HNO_2 and ClO_3^- into activated complex may well involve two steps. The second of these is the one just referred to; but the first would also involve a ΔH term and would be included in the Arrhenius calculation. Another small recognised term arises from the effect of temperature upon activity coefficients. Finally, of course, there is up to ½ % error on rate constant measurements between the extremes of 10°C and 35°C arising from the expansion of water mentioned earlier.

No attempt has been made to correct the activation energy figure quoted, however, because it corresponds to the figures normally given for reactions.

The Reaction Between Cl(III), Cl(I) and N(III)

Rate of oxidation of nitrite by hypochlorite has been reported to be very fast in acid solution(44). Around pH 1, the reaction was found to be complete within ten seconds(33), with almost complete transfer of hypohalite oxygen to the nitrite. In the present work, reaction mixtures were prepared using sodium hypochlorite solution instead of chlorate. For example, on mixing equal volumes of sodium nitrite ($\approx$ 0.002 M) and sodium hypochlorite (nominal concentration 0.002 M) at pH $\approx$ 2 and at pH $\approx$ 3, no nitrite could be detected after the reaction had been quenched 10 to 15 seconds after mixing the reagents. This confirms the Russian reports and shows that the reaction between N(III) and Cl(I) is at least 500 times as fast as the corresponding reaction using Cl(V), but no quantitative results have been obtained.

No published results have been found on the rate of reaction between chlorite and N(III). No analar chlorite is obtainable, so that technical grade was used in an exploratory study.

When mixtures containing nominally equal concentrations (0.002 M) of chlorite and nitrite were prepared at pH 2, as with the hypochlorite reactions, the nitrite was undetectable after the shortest time (10 sec) when analysis was attempted. Even when nitrite was initially 0.00171 M and chlorite 0.000768 M, reaction was effectively instantaneous at this pH (the higher part of the pH range at which the chlorate reaction was examined), and the ratio of consumption of nitrite to chlorite was calculated to be about 2:1.

When the pH of the reaction was raised to about 3, the reaction proceeded at a measurable rate. An example is shown in Table 20. By plotting 1/O.D. vs. time, a straight line for over 85% reaction, was obtained (see Fig. 16).

Table 20

$[NaNO_2]$ = 0.001706 M $[NaClO_2]$ = 0.000768 M

Temp. = 25°C   pH = 3.0

Time (min)	O.D.
0	(0.853)
2	0.428
4	0.273
6	0.198
8	0.158
10	0.136
12	0.121
15	0.107
20	0.092
30	0.085
60	0.081

Note theoretical final O.D. = 0.085 without making allowance for the decomposition of nitrous acid or for the impurity of the sodium chlorite, but accepting the 2:1 ratio of the stoichiometry. The experiment is consistent with these considerations.

The second order constant under these conditions is 335 $l\ mol^{-1}\ min^{-1}$.

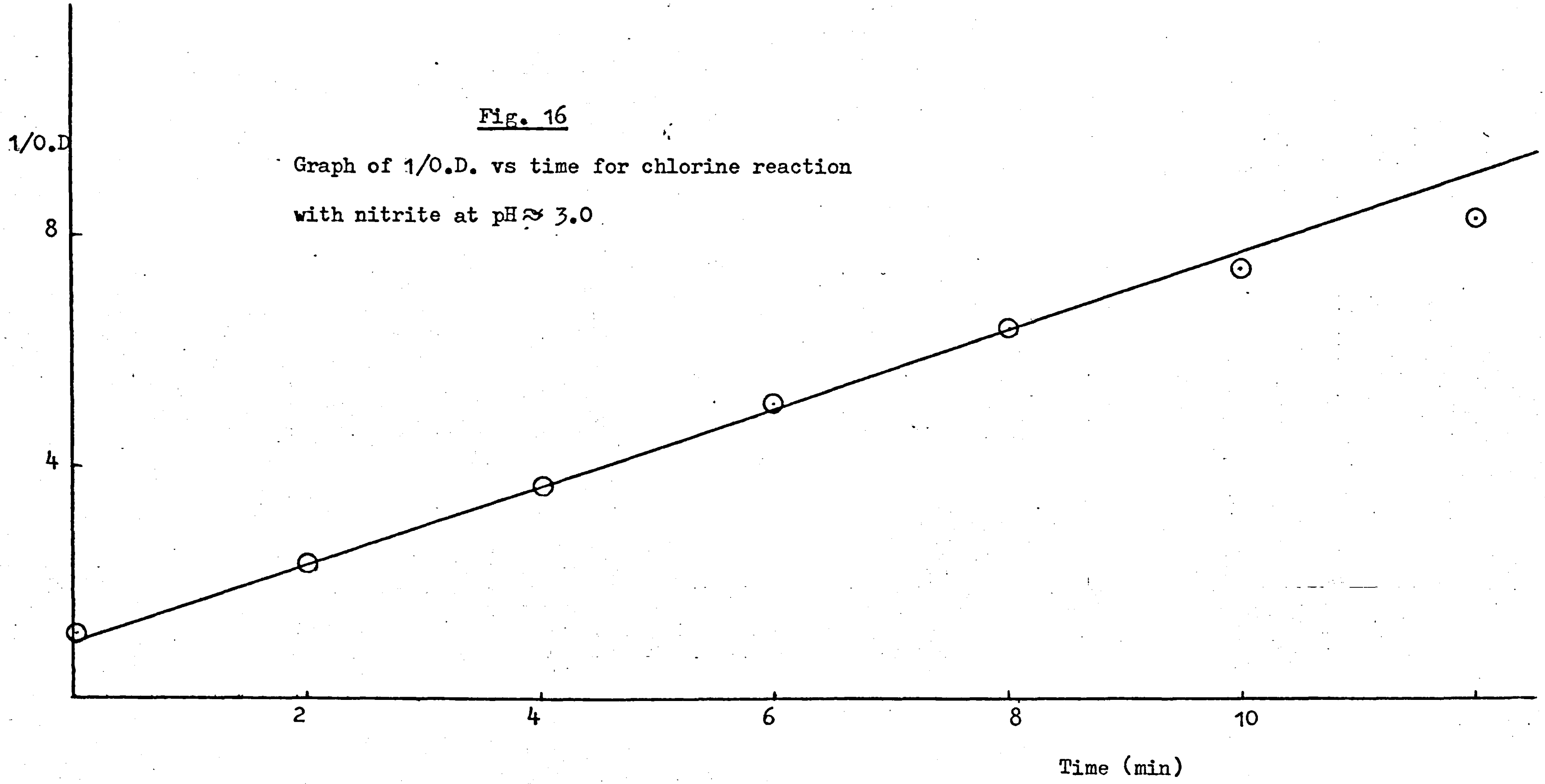


Fig. 16

Graph of 1/O.D. vs time for chlorine reaction with nitrite at pH $\approx$ 3.0

SECTION IV

THE REACTION BETWEEN N(III) AND BROMATE IONS

EXPERIMENTAL RESULTS

General Technique Adopted

All kinetic experiments were carried out in a thermostat controlled to ± 0.02°C. A series of experiments was carried out with mixtures of standard solutions of nitrite and bromate to ascertain the most suitable conditions for studying the reaction between these substances. Analar grade chemicals were used without further purification. When solutions of the two reagents (approximate concentration 10^{-2} M each) were mixed at room temperature, no change in nitrite concentration occurred for several hours, but on acidification reaction took place. It was found that good conditions for observing the rate of this reaction were at pH values between 2.4 and 3.2, [N(III)] around 10^{-3} M and $[BrO_3^-]$ around 10^{-2} M at 25°C. For the pH range mentioned, buffers of potassium hydrogen phthalate and hydrochloric acid were found to be suitable; separate experiments indicating the necessary amount required to maintain near constancy of pH throughout an experiment.

Analysis for [N(III)] was even easier than for the reaction with the chlorate because it was found that the spectral absorption of samples from different mixtures, analysed according to the method mentioned on page 27, remained constant for some hours.

Solutions of sodium nitrite and potassium bromate were mixed in a 500 ml stoppered conical flask and thermostated separately from the required amount of buffer for half an hour. Zero time was taken when the acid buffer was added to the reagents. After ensuring complete mixing, the vessels were replaced in the thermostat and samples were withdrawn, quenched at definite times and analysed for nitrite. As in the chlorate reaction the observations were made over 80% of reaction and the initial rate for the disappearance of nitrite were calculated from graphs of log O.D. vs. time. These graphs were normally linear over 70% of reaction, provided the bromate was present in large excess over the nitrite.

Reproducibility of Measurements and the Effect of Physical Conditions

As with the chlorate reaction it was decided to test whether the reaction was affected by any physical conditions, as well as to test the reproducibility of measurements.

Five kinetic runs were carried out. The experiment, labelled A was under normal laboratory conditions. The flask in run B, was packed with short lengths of glass tubing so as to increase the area of the glass surface exposed to the solution more than four-fold. In C the reaction vessel was wrapped in metal foil to exclude light. In order to examine the effect of dissolved gases, an experiment labelled D, was carried out where atmospheric air was bubbled first through water, then through the reactant solution for half an hour before starting the run and continued during the kinetic run. To test the sensitivity of the reaction to metal ion catalysis, a reaction, labelled E, was carried out in which 0.05 gm of Na_2EDTA had been added.

The results of these experiments are summarised in Table 21.

Table 21

$[NaNO_2]$ = 0.001642 M　　　$[KBrO_3]$ = 0.0100 M

pH = 2.3　　　Temp = 25.0°C

Time (min)	Table of O.D. as a function of time				
	A	B	C	D	E
0	(0.821)	(0.821)	(0.821)	(0.821)	(0.821)
2	0.537	0.540	0.545	0.539	0.543
4	0.321	0.321	0.332	0.315	0.318
6	0.180	0.184	0.189	0.176	0.180
8	0.096	0.099	0.106	0.092	0.091
10	0.048	0.051	0.056	0.048	0.044

The similarity of these results led to all future runs being carried out under normal laboratory conditions.

The General Features of the Reaction Curves

Three identical reaction mixtures were made and the reaction was followed to check general features of the reaction curves.

The optical density- time data are shown in Table 22.

The general appearance of the reaction curve is shown as graphs of the optical density (averaged out for the three runs) and log O.D. against time (Fig. 17).

Table 22

$[NaNO_2]$ = 0.0006766 M

$[KBrO_3]$ = 0.003333 M

[K.H.Phthalate] = 0.008333 M

$[Cl^-]$ = 0.008333 M

$[H^+]$ = 1.424 M

μ = 0.0148

Temperature = 25.0°C

Time (min)	O.D.(1)	O.D.(2)	O.D.(3)
0	(0.338)	(0.338)	(0.338)
2	0.314	0.314	0.315
5	0.284	0.283	0.285
10	0.235	0.234	0.232
15	0.193	0.193	0.191
20	0.157	0.159	0.155
25	0.130	0.127	0.128
35	0.083	0.084	0.085
55	0.036	0.038	0.036

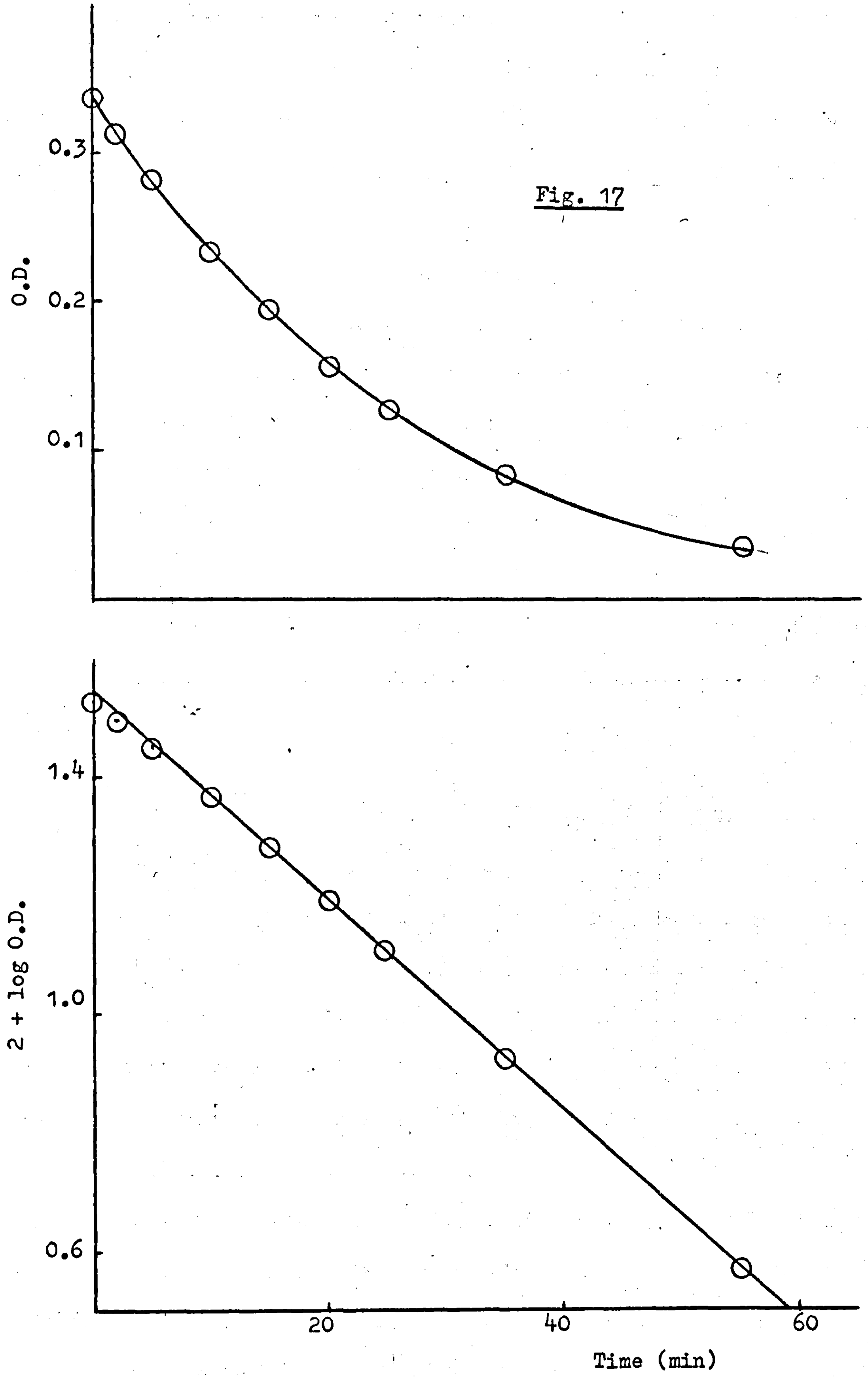


Fig. 17

These three runs are consistent in showing a slight apparent induction period. Thus the log O.D./time graphs extrapolates to an optical density of 0.348 rather than 0.338 at zero time. Alternatively they indicate that the reaction appears to start (with O.D. = 0.338) from time 1.4 min. This feature, while not extensively investigated, was confirmed with other reaction mixtures.

However, apart from this minor kinetic anomaly (taking the first 5% or so of the time to reach half reaction), the log O.D./time graphs are linear for more than two half-lives, and all subsequent runs were treated in this way to extract the information.

Stoichiometry of the Reaction

The overall reaction between nitrite and bromate, in acid solution, is generally assumed to be represented by the following stoichiometric equation:

$$BrO_3^- + 3HNO_2 \rightleftharpoons Br^- + 3NO_3^- + 3H^+$$

Again, no modern experimental evidence is available for this except the potentiometric titration studies by Gyani and Prasad. Their titrations used pH values of 0 to 1. Under these conditions BrO_3^- and N(III) react rapidly. Whilst NO_2^- and BrO_3^- might be expected to react in a 3:1 ratio at higher pH values bromate would also be expected to react with Br^- as the acidity increases(42). The potentiometric results are hence of little use.

It had already been established that the lowest pH value likely to be useful in kinetic studies would be about 2.4. To examine the stoichiometry, solutions 0.00412 M in $NaNO_2$ and 0.0250 M in $KBrO_3$ were used, buffered to pH 2.

Reaction mixtures of constant volume and constant buffer concentration were made up and analysed for excess bromate as previously described for chlorate. The results are summarised in Table 23.

Table 23

Molar ratio $NaNO_2/KBrO_3$ put in	Molar ratio NO_2^-/BrO_3^- used
0.1648	2.996
0.3296	3.031
0.5493	3.024
0.8240	3.037
1.648	3.049
2.747	3.096

The results show that 1 mole of bromate reacts with three moles of nitrite under the conditions investigated (the tendency for the ratio to rise slightly as $[NO_2^-]$ rises may again be due to decomposition of HNO_2)in runs which had to be left longer for completion.

Since the acidity is higher than any used kinetically it seems safe to assume the 3:1 stoichiometry in the slightly less acid conditions used from now on.

As with chlorate, there is sufficient thermodynamic driving force in all the steps from Br(V) to Br(-I) to oxidise N(III) to N(V) and hence the reducing potentials are consistent with the stoichiometry found for both reactions.

Identification of Products of Reaction

Like the chlorate reaction, the fact that the products of the reaction between bromate and nitrite ions, in acid medium, are bromide and nitrate has long been taken for granted, there is no modern literature evidence.

Unlike the situation found in the chlorate/nitrite reaction it was not found possible to use the absorption spectrum to demonstrate the change from N(III) to N(V). This is because bromate has a high extinction coefficient (about 2000 $l\ mol^{-1}\ cm^{-1}$) at $50{,}000\ cm^{-1}$, in the region where nitrate absorbs. On diluting the bromate to lower its absorption it was not found possible to prepare a reaction mixture for both observing a spectrum and having a convenient rate of reaction.

(i) Qualitative Test for Nitrate

As in the case of the chlorate reaction with nitrite, nitrate was identified in mixtures in which [N(III)] had become undetectable following reduction back to nitrite by metallic zinc in acetic acid solution, the nitrite being detected colorimetrically.

(ii) Gravimetric Analysis for Bromide

A reaction mixture was prepared by dissolving 0.2920 gm $KBrO_3$ and 0.4317 gm $NaNO_2$ in 300 ml water. The pH of the solution was adjusted to about 2.0 with 2 M nitric acid. The reaction was left to go to completion at room temperature. Determination of bromide was carried out as that for chloride except that precipitation was carried out in the dark. Starting from this reactant ratio of 3.5:1; the weight of AgBr produced was 0.3280 gm.

Result:

$$0.001748 \text{ mole } BrO_3^- \longrightarrow 0.001747 \text{ mole } Br^- (99.9\%)$$

The excess (less than 0.001 mole) of nitrite is not likely to interfere with the gravimetric analysis and hence the result shows that bromide is produced mole for mole from bromate.

Although the detection of nitrate is not quantitative, arguments presented earlier show that the qualitative test really leaves no alternative when the stoichiometry is coupled with the analysis for bromide. It is accepted that the equation generally written for this reaction is correct.

The Effect of Added Salts on the Rate of Reaction

To study these effects on the bromate/nitrite reaction three experiments were carried out. The essential reactant concentrations were identical in all three, but runs A, B and C contained respectively the additions of 0.2333 M NaCl, KCl and KNO_3.

The results are summarised in Table 24.

Table 24

$[NaNO_2]$ = 0.0006766 M $[KBrO_3]$ = 0.003333 M

[K.H.Phthalate] = 0.0125 M $[Cl^-]$ = 0.0075 M

pH = 3.055 μ = 0.251

Temperature = 25 ± 0.02°C

Time (min)	O.D.(A)	O.D.(B)	O.D.(C)
0	(0.338)	(0.338)	(0.338)
2	0.318	0.321	0.320
5	0.299	0.301	0.300
10	0.266	0.267	0.269
15	0.235	0.234	0.238
20	0.209	0.209	0.210
25	0.185	0.185	0.186
35	0.143	0.143	0.146
55	0.087	0.087	0.090
10^6 Initial rate = ($M\ min^{-1}$)	16.6	16.6	16.4

The differences between these rates are within likely experimental errors and hence it can be concluded that the reaction rate is independent of the nature of the monovalent anions or cations investigated here. The ones examined are, of course, those relevant to the present study - either being added to the mixture or being produced by reaction.

Determination with the Order with Respect to Reactants

Essentially the same technique was used here as for the Cl(V)/N(III) reaction.

For each reactant studied, the reaction mixture was constant except for the concentration of that reactant.

Each run was plotted as $\log_{10}$ O.D. versus time (because nitrite was always present in small amount) and multiplication of the slope of each run by 2.303 times the initial concentration of nitrite gave the initial rate of reaction.

By examining the variation of initial rate with concentration of each reactant in term the relevant order with respect to each reactant was determined.

Hydrogen ion was supplied by buffers of potassium hydrogen phthalate and hydrochloric acid. The ionic strength was maintained by potassium chloride.

Order with Respect to N(III)

Table 25

$[KBrO_3]$ = 0.008889 M
$[H^+]$ = 0.002382 M
μ = 0.02547
[K.H.Phthalate] = 0.01235 M
$[Cl^-]$ = 0.009877 M
Temperature = 25 ± 0.02°C

$10^4 NO_2^-$ M	10^2 k min^{-1}
1.266	21.1
3.165	20.9
4.432	21.1
6.331	20.5
6.331	20.5
9.496	21.1
12.66	20.6
12.66	20.8

The order with respect to N(III) is one, the variation of rate within each run, giving the same result as variation between different initial concentration ions. This, however, does not distinguish between such possible reactants as NO_2^- and HNO_2 because at constant $[H^+]$, μ and T, each N(III) species is present at a constant fraction of the total [N(III)].

However, since the working pH range is near the pK of nitrous acid the interdependence of $[H^+]$ and $[NO_2^-]$ and $[HNO_2]$ should easily allow a deduction about the effective N(III) reactant to be made from the variation of rate with $[H^+]$.

Order with Respect to Hydrogen Ion

Table 26

$[NaNO_2]$ = 0.0002595 M $\qquad$ μ = 0.02014

$[KBrO_3]$ = 0.004444 M $\qquad$ Temperature = 25 ± 0.02°C

$10^3[H^+]$ (M)	$10^3[HNO_2]$ (M)	10^6 Initial rate (M min^{-1})	10^3 Initial rate/ $[HNO_2]$ (min^{-1})
0.526	0.0928	3.04	32.7
0.743	0.1143	5.26	46.0
0.893	0.1262	6.87	54.4
1.205	0.1455	10.81	74.3
1.606	0.1635	16.06	98.2

In these experiments $[H^+] \approx 10^{-3}$ M and the dissociation constant of $HNO_2 \approx 10^3$ M so that on varying $[H^+]$, although the nominal reaction mixture is otherwise constant, the relative concentrations of HNO_2 and NO_2^- are changing.

Firstly, we could consider that HNO_2 and NO_2^- might be equally reactive and hence no account need be taken of the relative amounts of the two. If this were so then merely by plotting log $[H^+]$ versus log initial rate, the order with respect to H^+ would be found.

In fact this plot is curved and the average slope indicates an order of about 1.5 (see Fig. 18). Although this might be interpreted as a mixture of reaction paths of order 1 and 2 in H^+, a more satisfying result is found by considering the change in $[HNO_2]$ consequent upon change in $[H^+]$.

(The effect of considering NO_2^- and H^+ has been tried but again there is no definite result).

When log (initial rate/[HNO_2]) is plotted against log [H^+] a straight line is obtained with a slope of 0.985 (see Fig. 19).

Thus rate is first order in HNO_2 and in H^+. To clear up the point of whether the acid-catalysis is general or specific, more experiments were carried out using either acetic acid or $NaHSO_4$ + NaOH as the source of hydrogen ion. The results are shown in Tables 27 and 28.

The plots of log (initial rate/[HNO_2]) versus log [H^+] are straight lines of slope 1.02 for acetic acid and 0.98 for $NaHSO_4$ + NaOH (see Figs. 20 and 21).

Therefore it is the order with respect to hydrogen ion which is one, that is the reaction is catalysed specifically by hydrogen ion and it is not subject to general acid catalysis.

More important than the individual slopes of near-unity obtained from the phthalate, acetate and hydrogen-sulphate experiments is the fact that the rates of reaction are essentially the same under comparable conditions whether [H^+] is derived from acetic acid or sulphuric acid. Thus, apart from a change in ionic strength from 0.01 to 0.02 M, reactant conditions are the same for the acetate and hydrogen sulphate series. Therefore (initial rate/[H^+][HNO_2]) should be virtually the same if acetic acid and sulphuric acid or hydrogen sulphate ion are unable to react directly in place of hydrogen ion.

The average value of this ratio is 1.24 M^{-1} min^{-1} for the acetic acid experiments, and 1.22 M^{-1} min^{-1} for the hydrogen sulphate experiments.

The specific hydrogen ion catalysis is clear.

Table 27

The acid used is acetic acid.

$[NaNO_2]$ = 0.0009067 M μ = 0.0106

$[KBrO_3]$ = 0.008889 M Temp. = 25.0 ± 0.02°C

$10^3[H^+]$ (M)	$10^3[HNO_2]$ (M)	10^6 Initial rate ($M\ min^{-1}$)	10^3 Initial rate/ $[HNO_2]$ (min^{-1})
1.263	0.5315	83.6	157
1.248	0.5290	81.1	153
1.204	0.5239	79.6	152
1.112	0.5034	69.2	137

Table 28

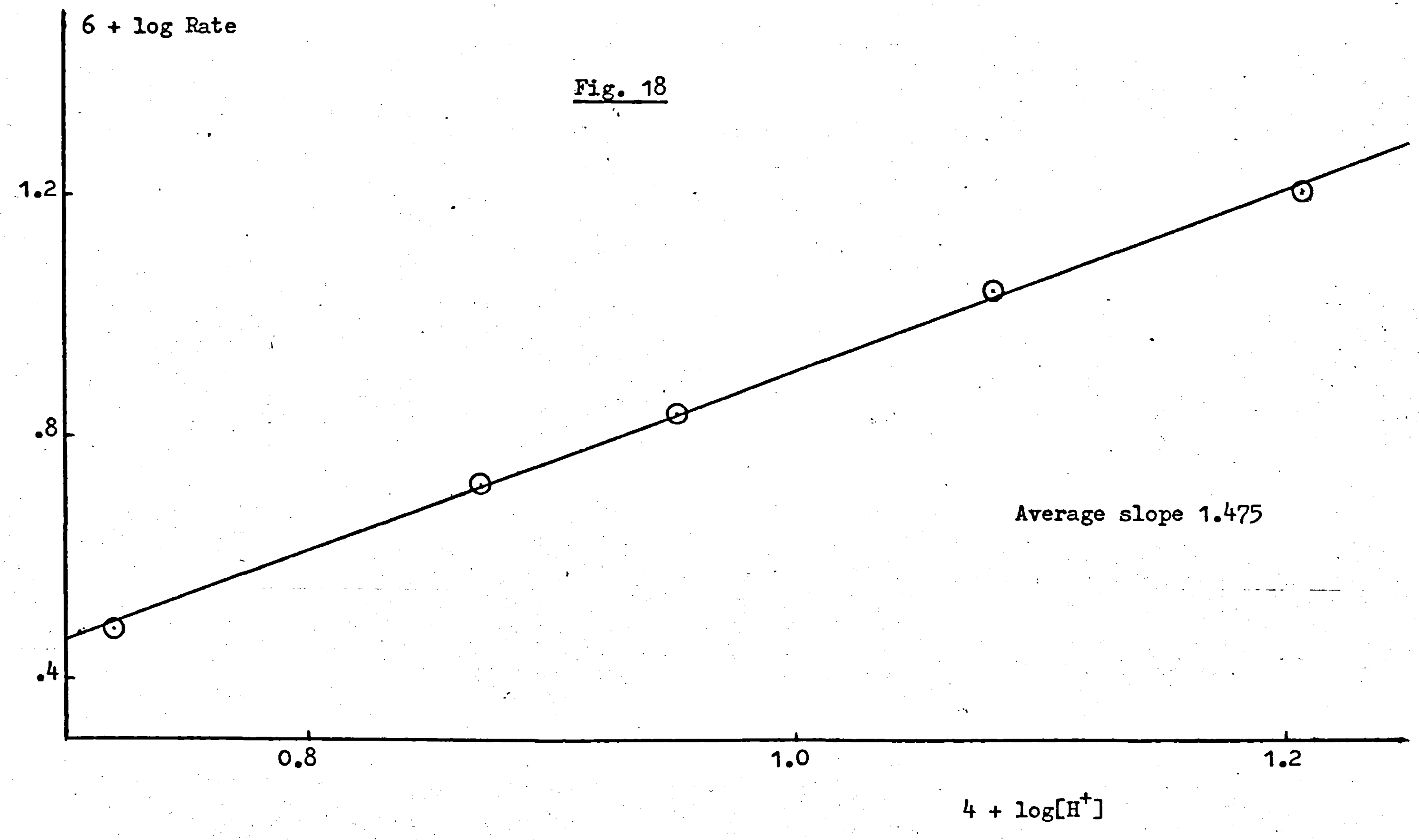
The buffer used is $NaHSO_4 + NaOH$

$[NaNO_2]$ = 0.0009067 M μ = 0.020

$[KBrO_3]$ = 0.008889 M Temp. = 25.0 ± 0.02°C

$10^3[H^+]$ (M)	$10^3[HNO_2]$ (M)	10^6 Initial rate ($M\ min^{-1}$)	10^3 Initial rate/ $[HNO_2]$ (min^{-1})
0.9543	0.4561	52.8	116
0.9765	0.4613	55.9	121
3.829	0.7265	339	466

Fig. 18



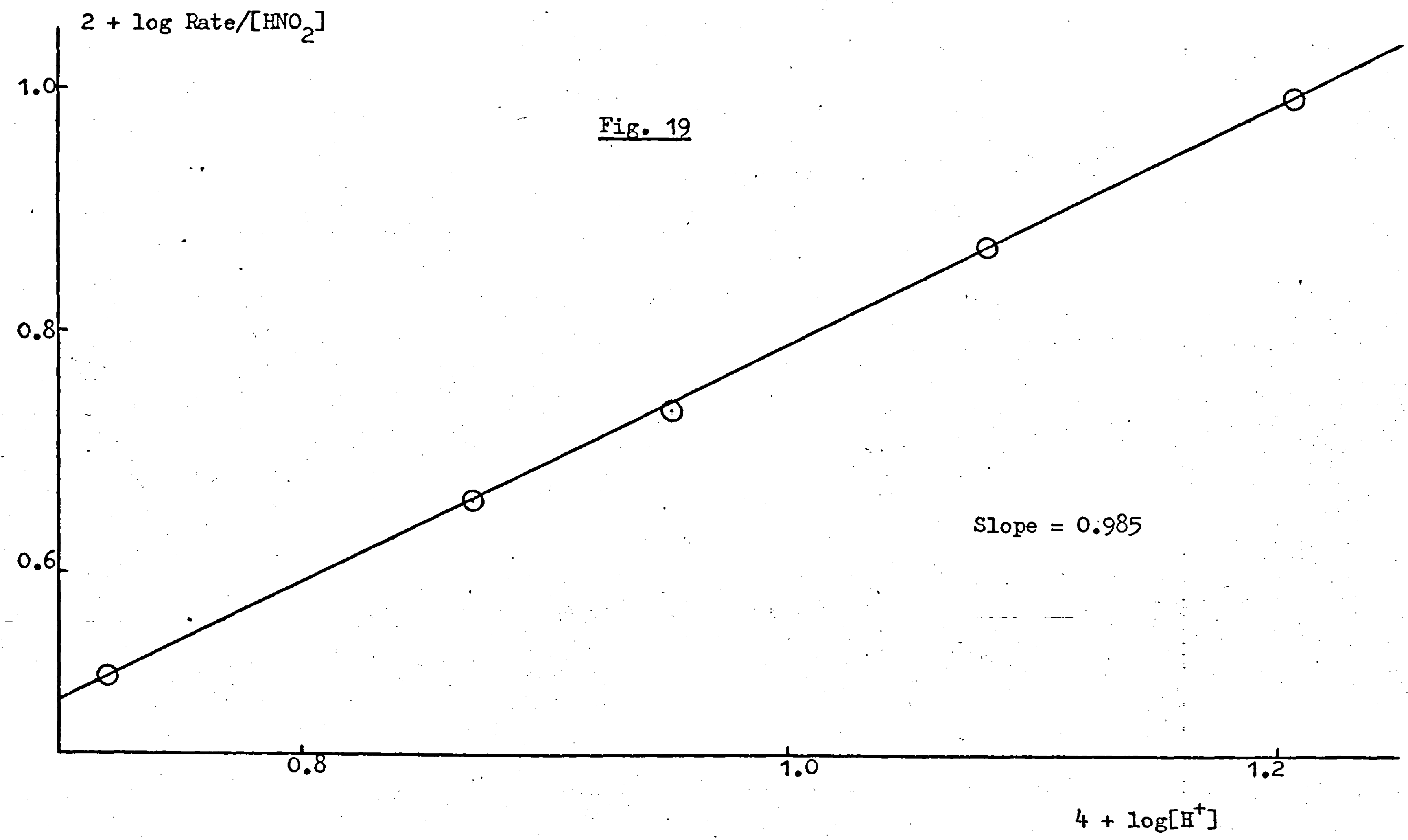


Fig. 19

Slope = 0.985

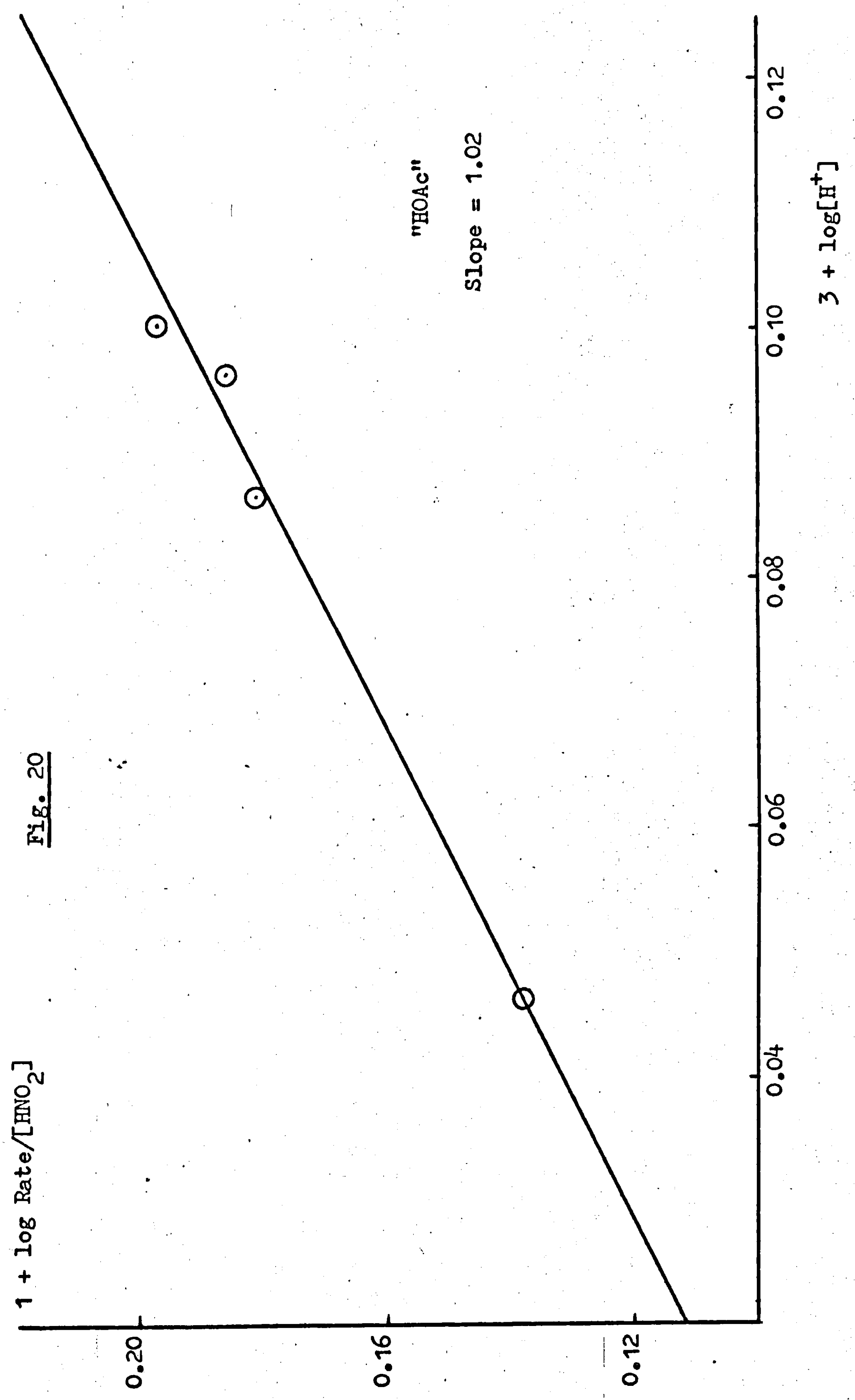
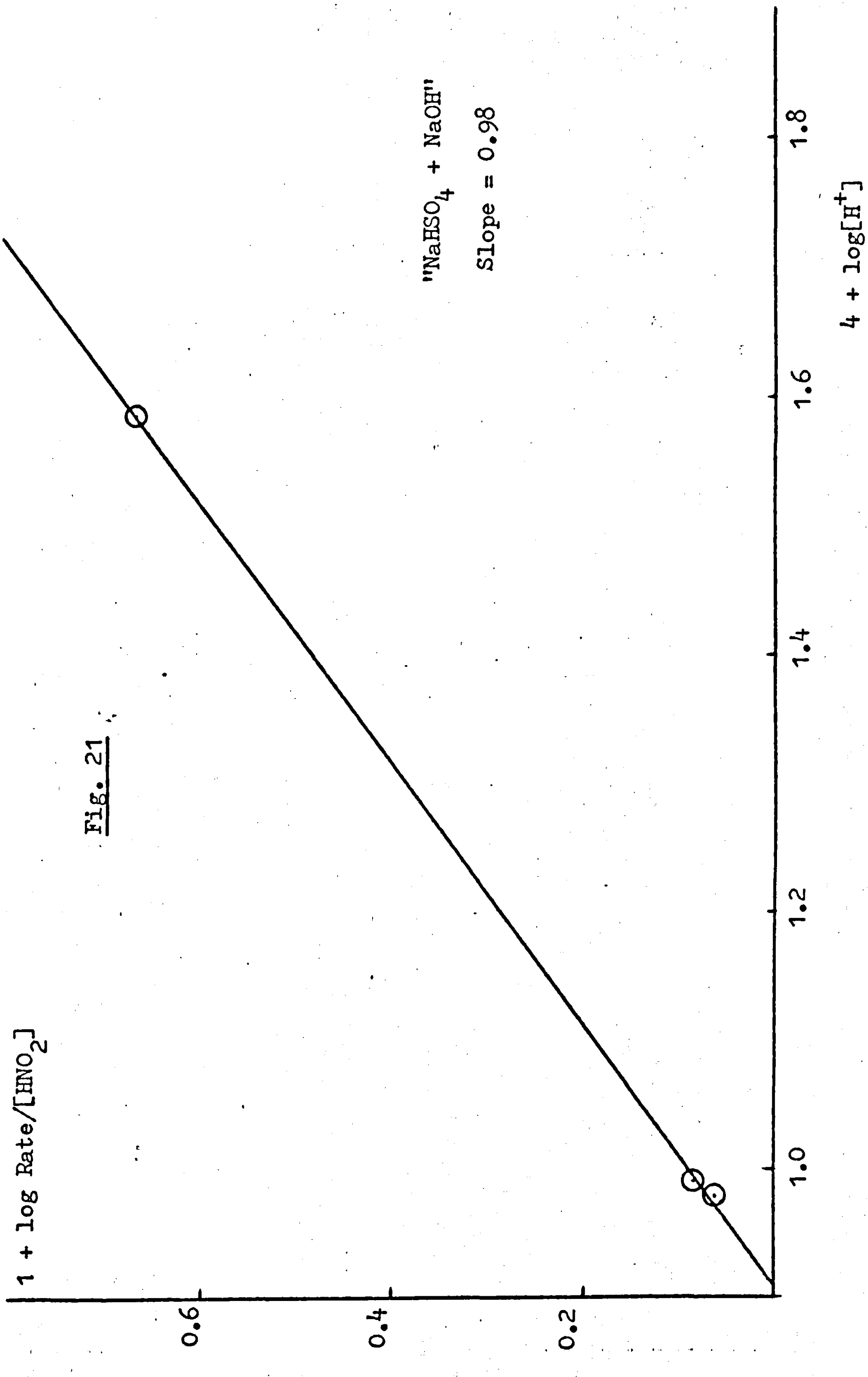

1 + log Rate/[HNO$_2$]
0.20
0.16
0.12
3 + log[H$^+$]
0.04
0.06
0.08
0.10
0.12
"HOAc"
Slope = 1.02

Fig. 20



1 + log Rate/[HNO$_2$]
0.6
0.4
0.2
1.0
1.2
1.4
1.6
1.8
4 + log[H$^+$]
"NaHSO$_4$ + NaOH"
Slope = 0.98

Fig. 21

Order with Respect to Bromate

Table 29

$[NaNO_2]$ = 0.0009973 M   [K.H.Phthalate] = 0.01587 M

$[H^+]$ = 0.000853 M $[Cl^-]$ = 0.00635 M

μ = 0.02001   Temp. = 25.0 ± 0.02°C

10^6 Initial rate (M min^{-1})	$10^3[BrO_3^-]$ M
0.620	1.111
1.239	2.222
1.830	3.333
2.490	4.444
4.970	8.889

A plot of log initial rate versus log $[BrO_3^-]$ shows a straight line of slope 1.00, the order with respect to bromate ion is therefore one. (See Fig. 22).

It should be added that not only do the log rate/log [reactant] graphs have slope one for H^+, HNO_2 and BrO_3^- but all rate/[reactant] graphs would extrapolate to zero rate at zero [reactant]. As with the chlorate reaction there are no detectable parallel side reactions of different order.

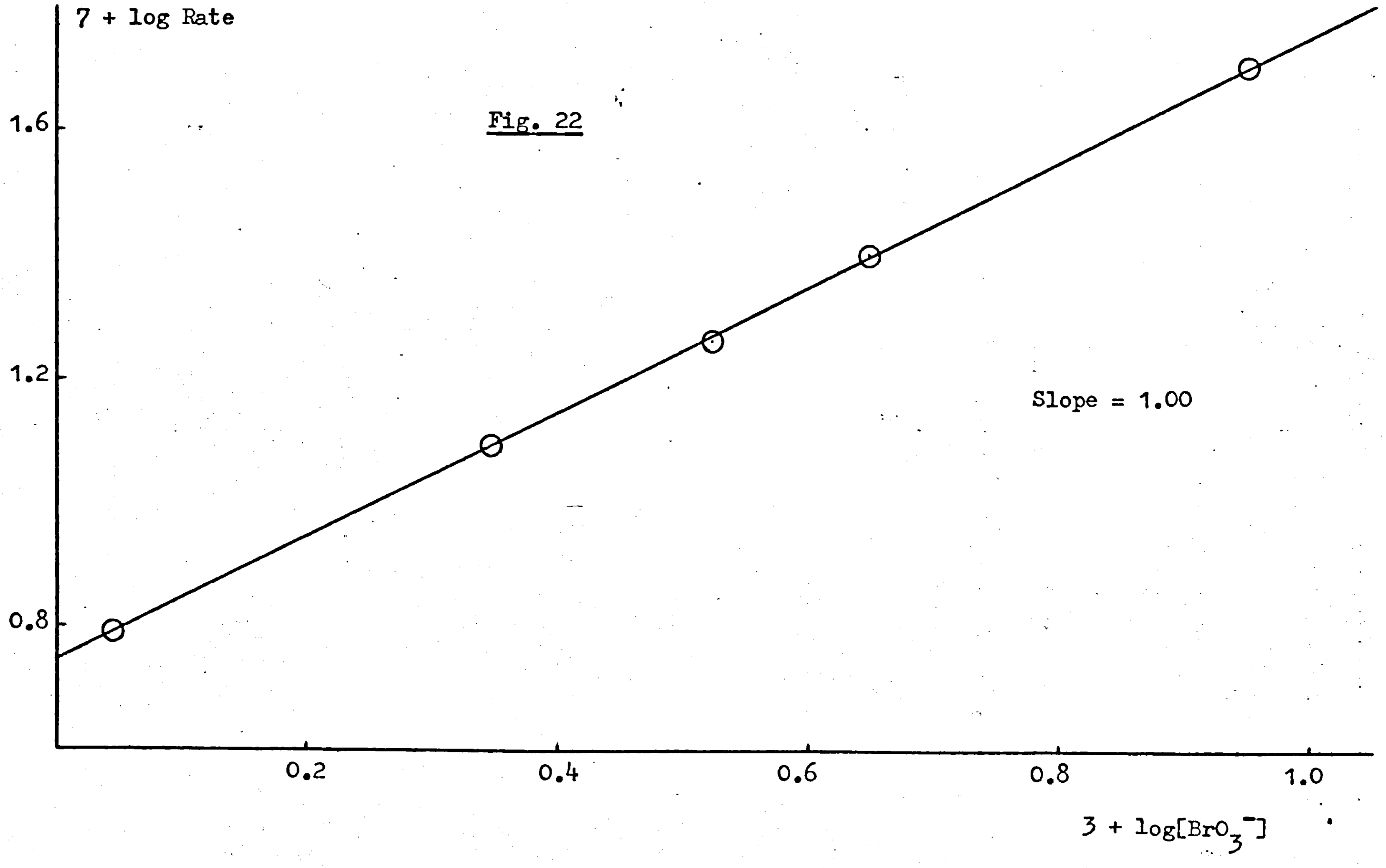


Fig. 22

The Effect of Ionic Strength on Reaction Rate

In order to study the effect of ionic strength on the bromate-nitrite reaction, experiments were carried out in which the ionic strength was varied with NaCl, KCl and KNO_3. Calculations of ion pair concentrations and of true free ion concentrations were made (the method is described in the appendix).

The apparent first order k values were obtained from plots of log O.D. versus time and the rate constants were calculated as:

$$-\frac{d[NO_2^-]}{dt} = k_r[HNO_2][H^+][BrO_3^-]$$

where k_r is the rate constant.

The results are summarised in Tables 30 and 31.

Table 30

$[NO_2^-]$ = 0.0006766 M $[BrO_3^-]$ = 0.003333 M

[H.Phthalate$^-$] = 0.006 M Temperature = 25.0 ± 0.02°C

$10^3[Na^+]$ M	$10^3[K^+]$ M	$10^3[Cl^-]$ M	$10^3[NO_3^-]$ M	pH	$10^3[HNO_2]$ M	10^2 μ	10^2k slope min^{-1}	10^6 Rate M min^{-1}	10^{-2} k_r M^{-2} min^{-1}
0.6766	15.83	7.500	-	3.013	.3677	1.741	2.77	18.8	138
58.98	15.83	65.80	-	3.027	.3518	7.574	2.71	18.3	132
117.3	15.83	124.1	-	3.034	.3457	13.41	2.70	18.3	130
234.0	15.83	240.8	-	3.035	.3403	25.08	2.68	18.1	126
0.6766	15.83	7.500	-	3.013	.3677	1.741	2.79	18.9	139
0.6766	74.17	65.80	-	3.027	.3518	7.574	2.68	18.1	131
0.6766	132.5	124.1	-	3.034	.3457	13.41	2.64	17.9	127
0.6766	247.0	240.8	-	3.035	.3403	25.08	2.65	18.0	125
0.6766	15.83	7.500	-	3.013	.3677	1.741	2.75	18.6	137
0.6766	27.50	7.500	11.66	3.020	.3610	2.908	2.73	18.5	137
0.6766	74.17	7.500	58.30	3.027	.3518	7.574	2.76	18.7	135
0.6766	132.5	7.500	116.6	3.040	.3430	13.41	2.57	17.4	127

Table 31

K_{MBrO_3}*	$10^5[MBrO_3]$*	$10^3[BrO_3^-]_T$*	K_{MNO_2}*	$10^6[MNO_2]$*	$10^3[H^+]$*	$10^4[HNO_2]_T$*	$10^2[M^+]_T$*	$10^2\ \mu_T$	$10^{-2}(k_r)_T$ (M^{-2} min^{-1})
0.19	1.10	3.322	0.48	5.81	1.107	3.645	1.649	1.74	140
0.16	4.30	3.290	0.40	19.58	1.182	3.416	7.475	7.57	138
0.14	7.30	3.260	0.36	30.95	1.220	3.299	13.30	13.40	139
0.13	10.80	3.225	0.33	52.32	1.268	3.140	24.97	25.1	141
0.19	1.10	3.322	0.48	5.81	1.107	3.645	1.649	1.737	141
0.16	4.30	3.290	0.40	19.58	1.182	3.416	7.475	7.57	137
0.14	7.30	3.260	0.36	30.95	1.220	3.299	13.30	13.40	136
0.13	10.80	3.225	0.33	52.32	1.268	3.140	24.97	25.1	140
0.19	1.10	3.322	0.48	5.81	1.107	3.645	1.649	1.737	140
0.18	2.30	3.310	0.46	9.60	1.124	3.546	2.814	2.90	139
0.16	4.30	3.290	0.40	19.58	1.182	3.416	7.475	7.57	141
0.14	7.30	3.260	0.36	30.95	1.201	3.273	13.30	13.40	136

* mol l^{-1} units

It can be seen that ion-pairing of the salts of the oxy-acids is consistent with the comment of Davies(43) that it is general though not very extensive. It is apparent from Table 31 that the rate of reaction is independent both of the nature and of the amount of the monovalent ions present. There is no general effect of ionic strength upon the rate constant.

The deviation of any rate constant in the table from the mean of all of them, does not exceed 2%. Thus, the mean rate constant (13900 M^{-2} min^{-1}) gives the rate of loss of N(III) at 25°C at any ionic strength:

$$-\frac{d[NO_2^-]}{dt} = 13900[H^+][HNO_2][BrO_3^-] \quad M\ min^{-1}$$

Values of observed rates at 25°C for reactions with different concentrations of reactants and with different ionic strengths are compared with the predicted values in Table 32. Ion pairing has been taken into account in calculating the true concentrations.

Table 32

$10^3[BrO_3^-]_T$	$10^3[H^+]$	$10^4[HNO_2]$	$10^2\ \mu_T$	10^2 (k)	10^6 Initial rate M min^{-1}	
(M)	(M)	(M)		min^{-1}	observed	predicted
3.311	1.387	3.987	2.109	3.83	25.9	25.4
3.311	1.387	3.987	2.109	3.74	25.3	25.4
3.250	1.277	3.369	13.98	2.87	19.4	19.4
3.260	1.121	3.162	13.39	2.39	16.2	16.1
8.847	1.306	0.5914	2.445	9.28	9.63	9.49
8.847	1.337	5.971	2.445	9.47	98.3	98.1
8.853	0.826	4.726	2.533	4.69	48.6	48.0
8.853	1.016	5.255	2.533	6.31	65.5	65.7
8.847	1.037	0.5329	2.445	6.67	6.93	6.80
8.847	1.086	0.5447	2.445	7.07	7.34	7.27
8.847	0.497	0.3498	2.445	2.05	2.13	2.13
8.847	0.497	0.3498	2.445	2.04	2.12	2.13
8.847	0.336	0.2659	2.445	1.068	1.11	1.10
8.847	0.544	0.3713	2.445	2.36	2.45	2.48
3.315	1.460	3.885	4.609	3.96	26.8	26.1
3.315	1.411	3.830	4.609	3.70	25.1	24.9
3.325	1.329	3.970	1.484	3.65	24.7	24.4
3.325	1.424	4.081	1.484	4.04	27.3	26.9
3.325	1.392	4.045	1.484	3.92	26.5	26.0
3.325	0.698	2.899	1.484	1.374	9.30	9.34
3.280	1.536	3.841	7.734	3.97	26.8	26.9
3.280	1.292	3.562	7.734	3.12	21.1	21.0
8.847	0.769	0.3969	2.446	4.22	3.81	3.75
8.847	0.570	0.3325	2.446	2.65	2.39	2.33
8.847	0.863	4.271	2.446	4.99	45.0	45.3
8.855	4.24	7.315	2.583	42.7	387.	382
8.853	0.687	4.261	2.533	3.46	35.9	36.0
8.853	1.180	0.564	2.533	7.71	8.01	8.19

The Effect of Temperature on Reaction Rate

A series of experiments was followed at a variety of temperatures, all other conditions being kept constant. The energy of activation was calculated from the Arrhenius relationship:

$$k = A\, e^{-E/RT}$$

a plot of log k versus 1/T giving a slope of E/2.303R. Ion pairing has been taken into account in calculating the true concentrations. The results are summarised in Table 33, and plot of the results is given in Fig. 23.

The activation energy (determined in the conventional way) is 15.5(kcal mol^{-1}).

Table 33

$[NO_2^-] = 0.0008826$ M $[BrO_3^-] = 0.008696$ M $[Na^+] = 0.0008826$ M $[H.Phthalate^-] = 0.009$ M

$K_{MNO_2} = 0.4583\ M^{-1}$ $K_{MBrO_3} = 0.18\ M^{-1}$ $[K^+] = 0.02733$ M $[Cl^-] = 0.00745$ M

$[BrO_3^-]_T = 0.008651$ M $[M^+]_T = 0.02817$ M $[H^+] = 0.001201$ M $\mu = 0.02744$

t^oC	10^3 I/T	$10^3\ K_{HNO_2}$ (M)	$10^4[HNO_2]$ (M)	10^2 k min^{-1}	10^6 Initial Rate M min^{-1}	k_r $M^{-2}\ min^{-1}$	log k_r
10.0	3.5323	0.7115	5.473	2.22	19.6	3440	3.537
15.0	3.4710	0.8032	5.223	3.44	30.7	5600	3.748
20.0	3.4118	0.9095	4.960	5.28	46.6	9050	3.957
25.0	3.3545	0.9745	4.811	7.86	69.4	13900	4.142
30.0	3.2992	1.0135	4.727	11.8	105	21300	4.328
35.0	3.2457	1.035	4.682	17.4	154	31600	4.500

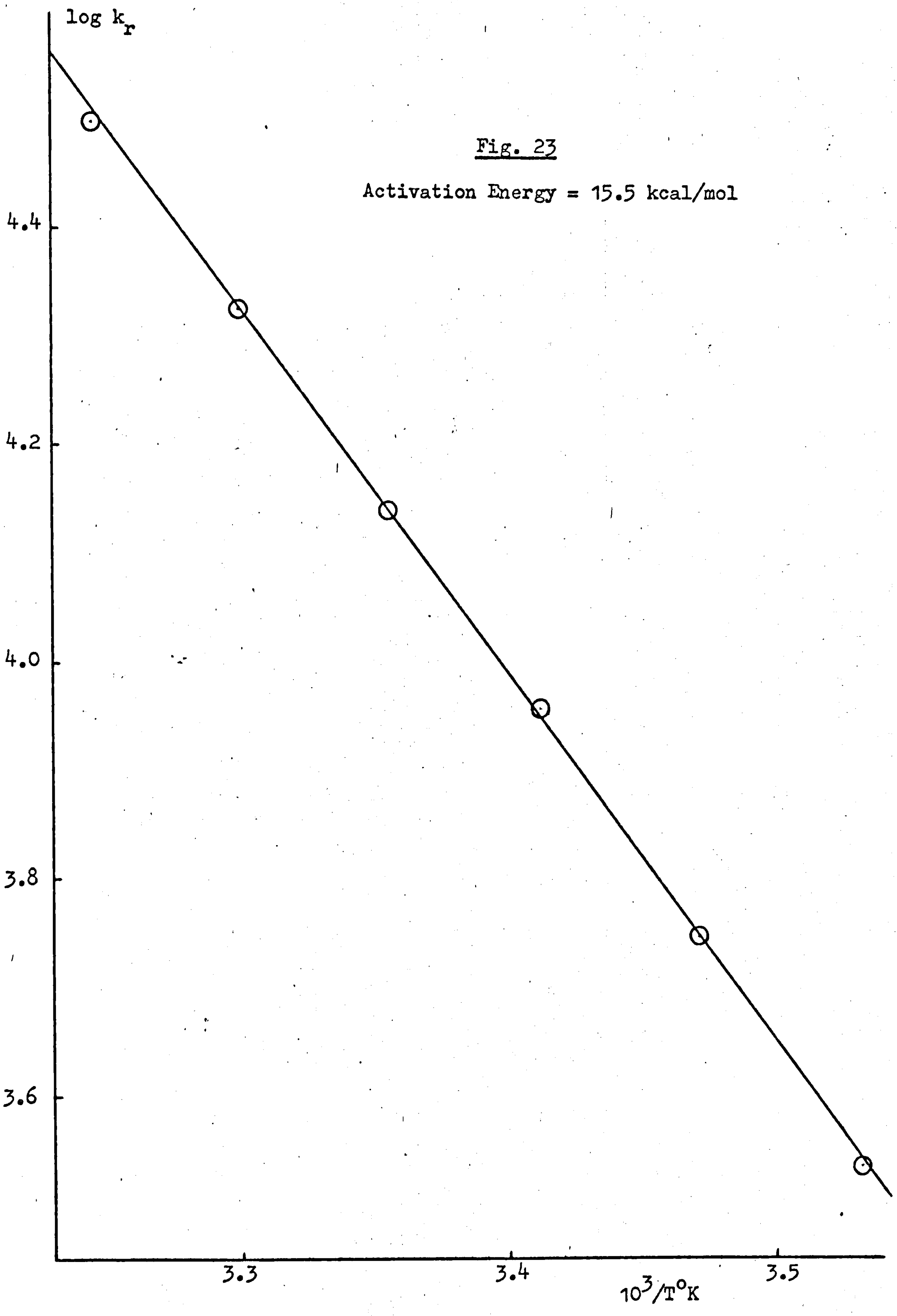


Fig. 23

Activation Energy = 15.5 kcal/mol

SECTION V

THE REACTION BETWEEN N(III) AND IODATE IONS

EXPERIMENTAL RESULTS

General Technique Adopted

Six mixtures containing equal volumes of 0.002075 M $NaNO_2$ and 0.0200 M KIO_3 were mixed in a conical flask and allowed to stand at room temperature. The pH values of the mixtures were 4.02, 3.37, 3.27, 3.00, 2.82 and 1.43. At known times samples were withdrawn, quenched, diazotised and examined spectrophotometrically. No change in nitrite concentration occurred for several hours under any of these conditions. Even when the concentrations of reactants were doubled, no reaction could be observed within a reasonable time using acidity within the range of the pH - meter scale.

It was found that suitable conditions for a reaction to take place at 25°C were $[H^+] \approx 1.4$ to 2.26 M, $[NO_2^-] = 10^{-3}$ M and $[IO_3^-] = 10^{-2}$ M.

All kinetic experiments were carried out in a thermostat controlled to ± 0.02°C. "Analar" grade chemicals were used when available without further purification.

The necessary amount of acid required for an experiment, (Analar hydrochloric acid) was standardised against anhydrous sodium carbonate.

Sodium nitrite, together with potassium iodate and any other solutions, (75 ml) apart from acid, were measured into a stoppered conical flask (A) by means of pipettes. Into a second flask (B) was measured the acid (50 ml). The stoppered vessels were then placed into the thermostat and allowed to reach thermal equilibrium. The reaction was started by mixing the reactants, pouring (B) into (A). After ensuring complete mixing, samples were withdrawn, after measured intervals of time and treated as described on page 27.

It was found that the absorbance of the dye solution was stable for only forty minutes, and after that a deep red colour was developed, due to interference of the iodate in the sample. Because of this and also to minimise the complication due to decomposition of nitrous acid, relatively fast reactions were carried out throughout this part of the work.

Reproducibility of Measurements and the Effect of Physical Conditions

To find out whether any physical conditions have an effect on the reaction rate, four experiments were prepared. The first, A, was under normal laboratory conditions. In B, the reaction vessel was wrapped in metal foil to exclude light. The vessel in C, was packed with short lengths of glass tubing so as to treble the area of glass surface exposed to the solution.

The effect of dissolved gases on reaction rate was studied in the experiment D. Atmospheric air was bubbled first through water, then through the reactant solution for half an hour before starting the run and was continued during the kinetic run.

The results of these experiments are summarised in Table 34.

Table 34

$[NaNO_2]$ = 0.000980 M $[KIO_3]$ = 0.007407 M

$[H^+]$ = 2.444 M Temp. = 25 ± 0.02°C

Time (min)	Table of optical density as function of time A	B	C	D
0	(0.490)	(0.490)	(0.490)	(0.490)
2	0.360	0.355	0.362	0.356
4	0.250	0.246	0.248	0.249
6	0.164	0.158	0.164	0.160
8	0.096	0.093	0.097	0.095
10	0.045	0.042	0.046	0.049

The results show that ordinary laboratory conditions are adequate for obtaining reproducible results.

Stoichiometry of the Reaction

Potentiometric titration measurements on the nitrite/iodate reaction were carried out by Gyani and Prasad(27) at pH 0 ± 1 in sulphuric acid; and near pH 1 in HCl. Under most of these conditions the iodate/nitrite reaction is slow so that nitrous acid decomposition becomes important, especially since the authors state that more than 1 hour wait was usually needed before each stable measurement could be made. Gyani and Prasad put the NO_2^-/IO_3^- ratio as 4.5:1 to 5:1. Other authors(5c) appear to have assumed that the stoichiometry is $2\frac{1}{2}$:1.

It was decided therefore to find out the stoichiometric ratio.

Reaction mixtures were prepared having the same volume and the same hydrogen ion concentration. When the reaction was shown to have exhausted the N(III), portions of the solution were pipetted into 15 ml of $NaHCO_3$ (1 M). When no more effervescence occurred, 1 gm of KI was added and the liberated iodine (from ICl) was titrated against sodium thiosulphate using starch as indicator. When the liquid became colourless, hydrochloric acid was added and the liberated iodine (which is equivalent to the iodate content of the solution) was again titrated against thiosulphate solution.

The results are shown in Table 35.

Table 35

$\frac{\text{moles } NaNO_2 \text{ put in}}{\text{moles } KIO_3 \text{ put in}}$	$\frac{\text{moles } NaNO_2 \text{ used}}{\text{moles } KIO_3 \text{ used}}$
1.660	2.773
1.328	2.619
0.830	2.413
0.694	2.326
0.347	2.162
0.332	2.168
0.174	2.084
0.166	2.076
0.087	2.032

The experiments detailed above were normally quenched after about 5 min.

The apparent conclusion from the results is that stoichiometry is variable - with a low N(III)/I(V) ratio, as in the kinetic experiments to be described, the stoichiometry is calculated to be approaching 2:1; but as the reactant ratio rises the stoichiometry appears to rise towards 3:1. Referring back to the studies on HNO_2 alone, it seems likely that under conditions of very high acidity, the decomposition rate of HNO_2 is approaching the rate of loss of N(III) by reaction with I(V) and the higher [N(III)] is the more competitive the decomposition becomes. A plot of the reactant molar ratio put in against ratio used is shown in Fig. 24.

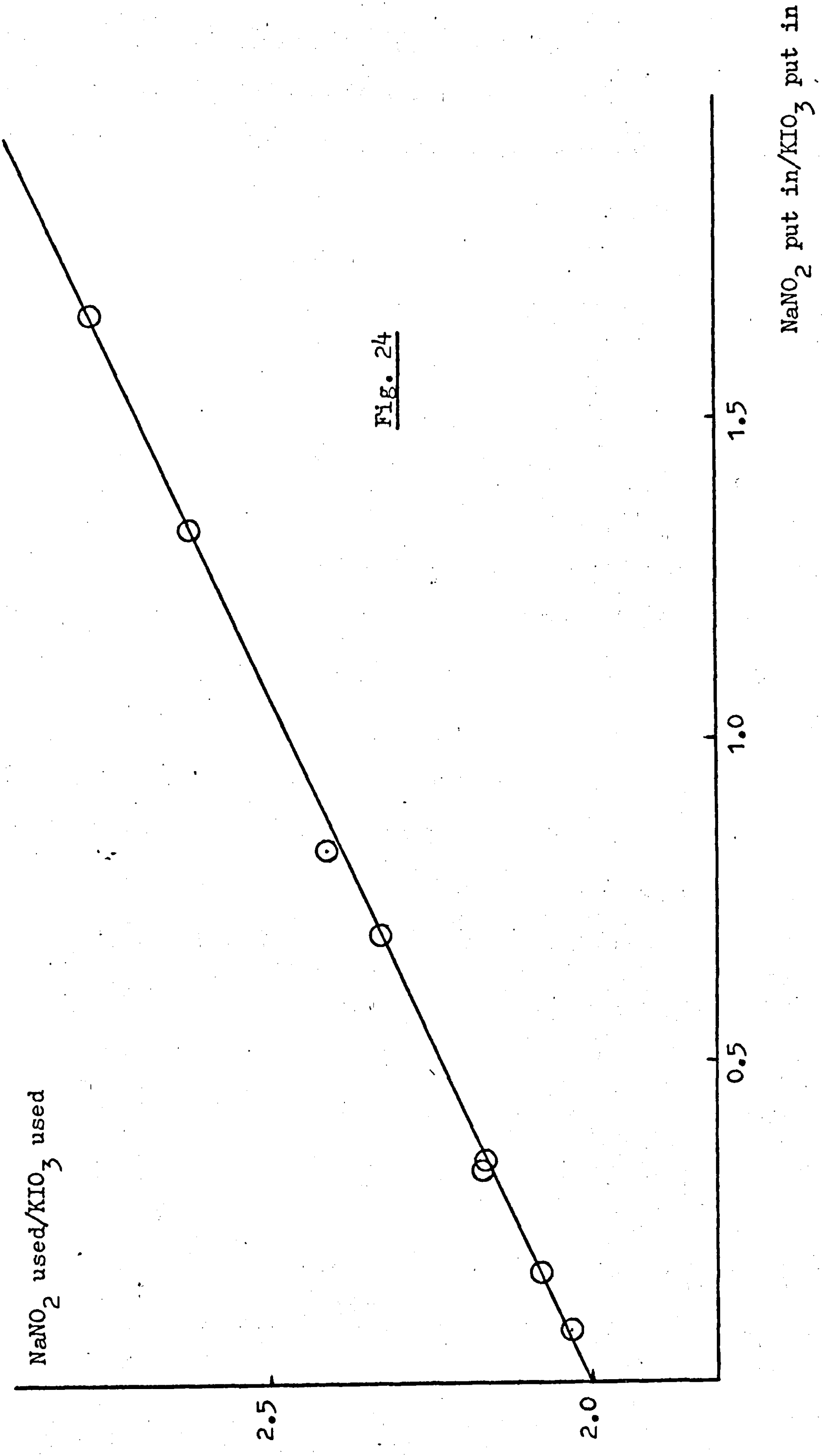


Fig. 24

Determination of the Products of the Reaction

The overall products of the reaction between iodate and nitrite, in acid medium, have been reported, by Kurtenacker and Gyani and Prasad, to be iodine and nitrate, in spite of the last authors having carried out some of their work in hydrochloric acid.

No other literature evidence was found and it was decided to attempt to determine the nature of the products.

(i) To investigate the spectral changes during reaction.

When kinetically suitable mixtures of iodate and nitrous acid were scanned over the visible and ultra-violet regions, the only measurable absorbance was between 25,000 and 32,500 wavenumbers. These solutions contained hydrochloric acid and the only known material that could be present, which absorbs at about 29,100 cm^{-1} (max ε =273) is iodine monochloride(41) (probably largely present as ICl_2^-).

25 ml of 0.0405 M $NaNO_2$ and 50 ml of 0.015 M KIO_3 were mixed in a conical flask. 50 ml of 5.6075 M HCl were added to the reactants, this instant being taken as the start of reaction.

The mixture was transferred to a 10 mm silica cell, which was placed in the cell compartment of a Pye Unicam SP.800 recording spectrophotometer. An acid solution of equivalent concentration was used in the reference beam. The spectrum of the reacting mixture was scanned rapidly between 25,000 and 35,000 cm^{-1} at timed intervals. For comparison the spectrum of commercial, chemical reagent, iodine monochloride diluted with hydrochloric acid was recorded on the same chart (see Fig. 25).

(ii) Mass spectrometric analysis of non-polar extract after the addition of cyclohexene to a completed reaction mixture.

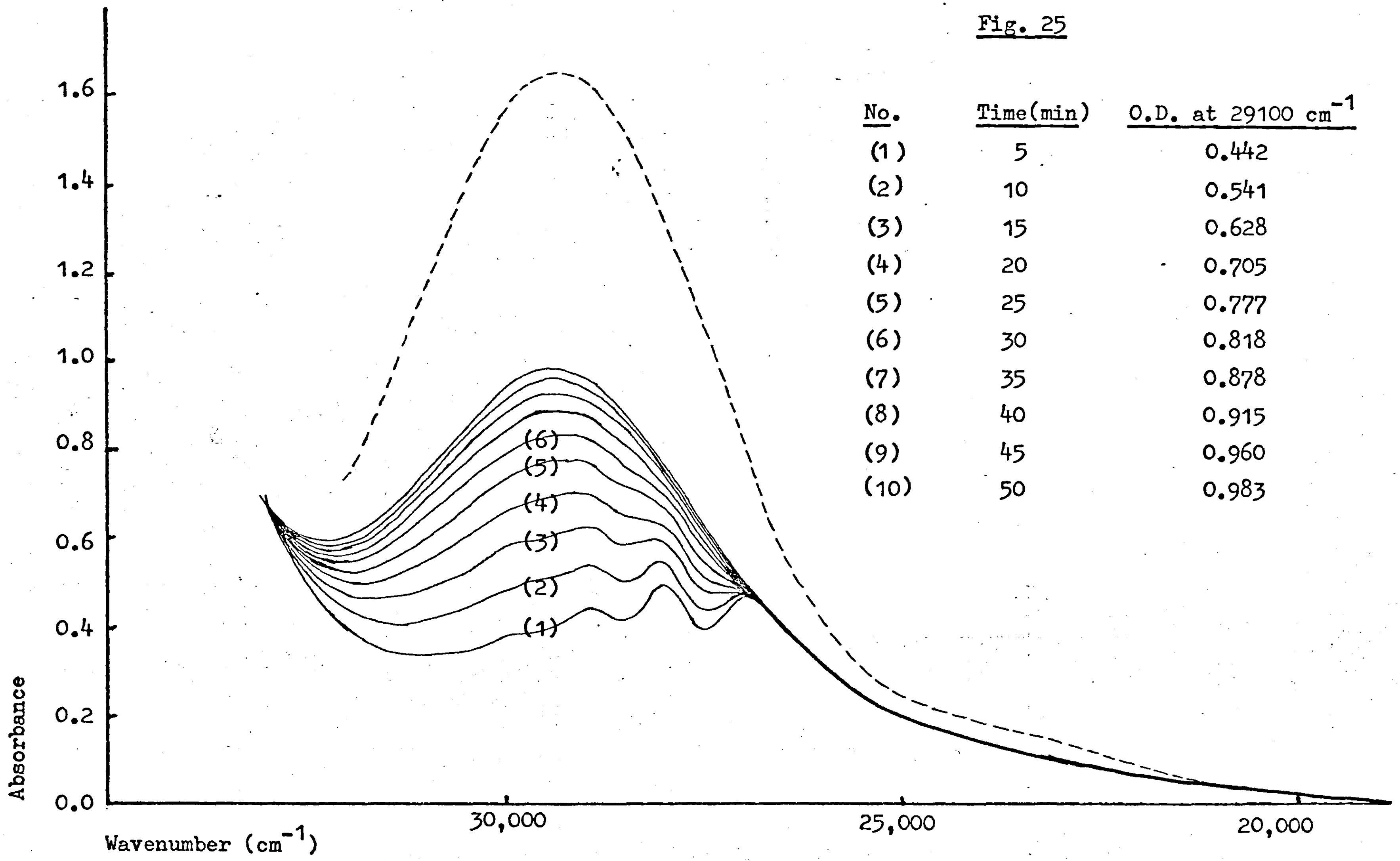
It was decided to attempt to extract iodine monochloride from the reaction products, if it was present, by exploiting an addition reaction with an olefin such as cyclohexene. 5 ml of cyclohexene were added to a reaction mixture after it had been allowed to go to completion at room temperature. On addition of the cyclohexene the colour of the solution changed immediately from yellow to colourless. Using a magnetic stirrer, agitation was carried out for half an hour. The organic layer was separated and combined with four other similar extracts. The extracts were washed with water, dried and distilled under reduced pressure to remove unchanged cyclohexene. The residue, a brown yellowish liquid, was examined using a Micromass 12 spectrometer. (See spectrum 26b). Commercial iodine monochloride was diluted with hydrochloric acid and treated as above (see spectrum 26a). The two mass spectra are shown together on page 123.

(iii) Qualitative test for nitrate

The same technique as was used with the other reactions (see page 48) was successful in demonstrating qualitatively that nitrate results from the iodate oxidation of nitrite.

(iv) The spectrum of reacting and exhausted mixtures showed no significant absorption near 21000 cm^{-1} (see Fig. 25) which would be characteristic of iodine in aqueous solution, nor was there ever any deposition of iodine from reactant mixtures containing hydrochloric acid.

Fig. 25



No.	Time(min)	O.D. at 29100 cm^{-1}
(1)	5	0.442
(2)	10	0.541
(3)	15	0.628
(4)	20	0.705
(5)	25	0.777
(6)	30	0.818
(7)	35	0.878
(8)	40	0.915
(9)	45	0.960
(10)	50	0.983

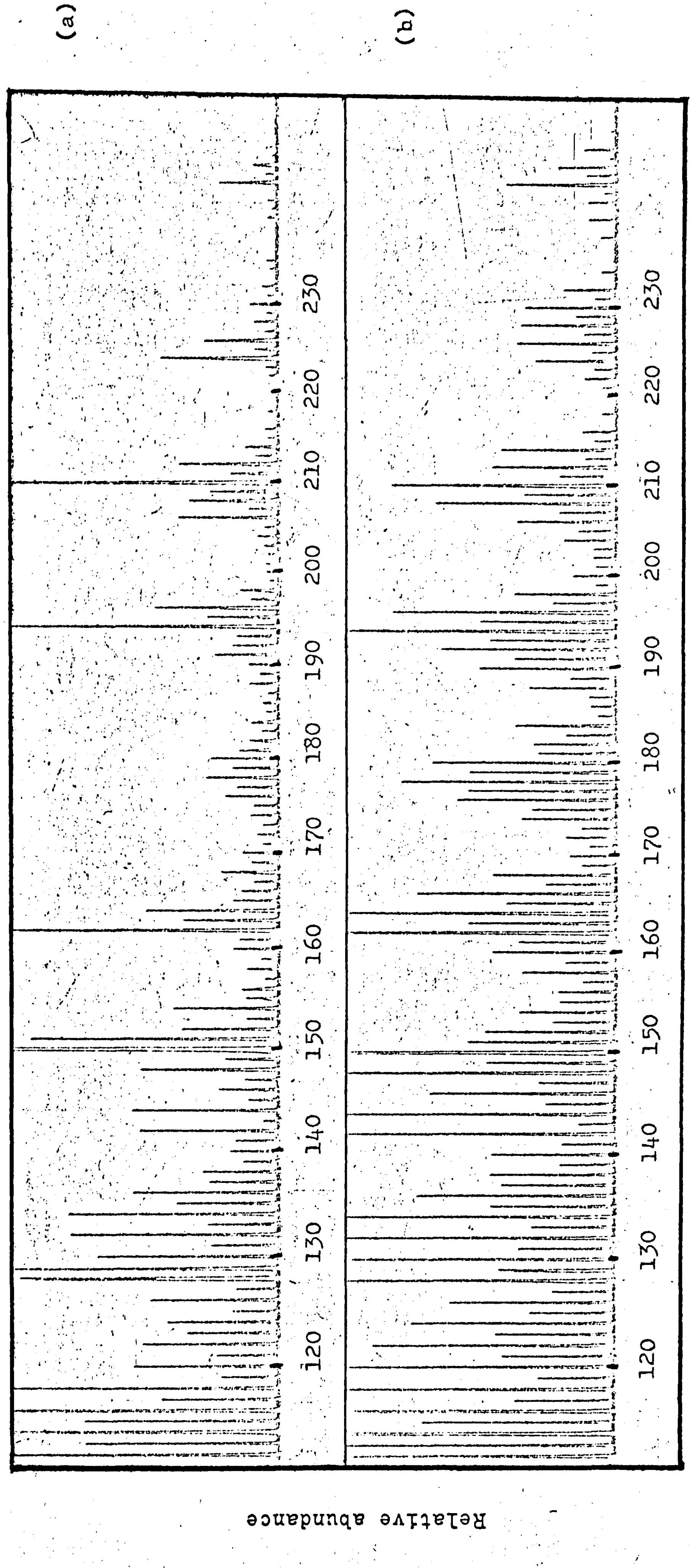

(a)
(b)
120
130
140
150
160
170
180
190
200
210
220
230
m/e
Relative abundance

Fig. 26

It is immediately apparent from the absorption spectra (Fig. 25) that the spectrum of authentic iodine monochloride in hydrochloric acid (dotted curve) exhibits similar spectral position and shape to the spectra of the reacting mixture. One can infer that the developing product is probably iodine monochloride, which in the presence of considerable [Cl^-] is largely converted to ICl_2^-.

More evidence about the identity of this product comes from the mass spectra. (Fig. 26).

A comparison of the peaks in the mass spectra shows many identifiable similarities.

Perhaps the most important feature is the general similarity of the two mass spectra. Although the cyclohexene may have had some impurities or the instrument may not have been clean, the use of the same stock of cyclohexene and the consequent production of two mass spectra neither of which exhibits any significant peak which is absent from the other, and where the patterns are closely similar argues strongly that authentic ICl (a) is matched by the product ICl in (b).

The spectra were indexed from the N_2 and O_2 mass peaks at 28 and 32 respectively. The lower mass numbers of course may correspond to spectra produced from the cyclohexane skeleton and are of little interest.

The molecular ion region (highest recorded m/e values) shows that there are two prominent peaks at 244 and 246, having a peak height ratio of 2 or 3 to 1. It seems likely that this feature corresponds to $C_6H_{10}I^{35}Cl$ and $C_6H_{10}I^{37}Cl$ (244 and 246 respectively).

The prominent pair of peaks at m = 162 and 164 have a similar abundance ratio and can be identified with ICl, and the peaks around 209 may include $C_6H_{10}I$.

Having confirmed that iodine monochloride is a product further consideration of the absorption spectra reveals much valuable information.

The maximum of the absorption spectrum, of the reacting mixture, has an optical density of 0.983.

Let us assume (1) that the O.D. is approaching 1.0 for complete reaction, (2) that decomposition of nitrous acid can be neglected and (3) that 1 mole of iodate produces 1 mole of ICl.

Since all the reactants and medium have negligible absorbance at, 29,100 cm^{-1} the O.D. is a direct measure of the iodine chloride whence from the known extinction coefficient, [ICl] produced = 0.0037 M. The initial concentration of nitrogen(III) was 0.0081 M. This is all consumed by the excess iodate. Coupling this result with the measured 2:1 stoichiometry we see that assumption (3) above is approximately realised, and hence iodate appears to produce ICl quantitatively within the limits of error of this calculation.

Nitrate of course is the other product.

The General Features of the Reaction Curves

Three identical reaction mixtures were made up and in each the reaction was followed to observe its general features and its repeatability.

The optical density - time data are shown in Table 36.

Table 36

$[NaNO_2]$ = 0.000752 M $[KIO_3]$ = 0.00600 M

$[H^+]$ = 2.243 M Temp. = 25.0°C

Time (min)	A	B	C
0	(0.376)	(0.376)	(0.376)
2	.314	.317	.316
4	.256	.255	.255
6	.205	.205	.206
8	.159	.160	.160
10	.120	.120	.122
12	.086	.087	.086
15	.045	.046	.047

Fig. 27

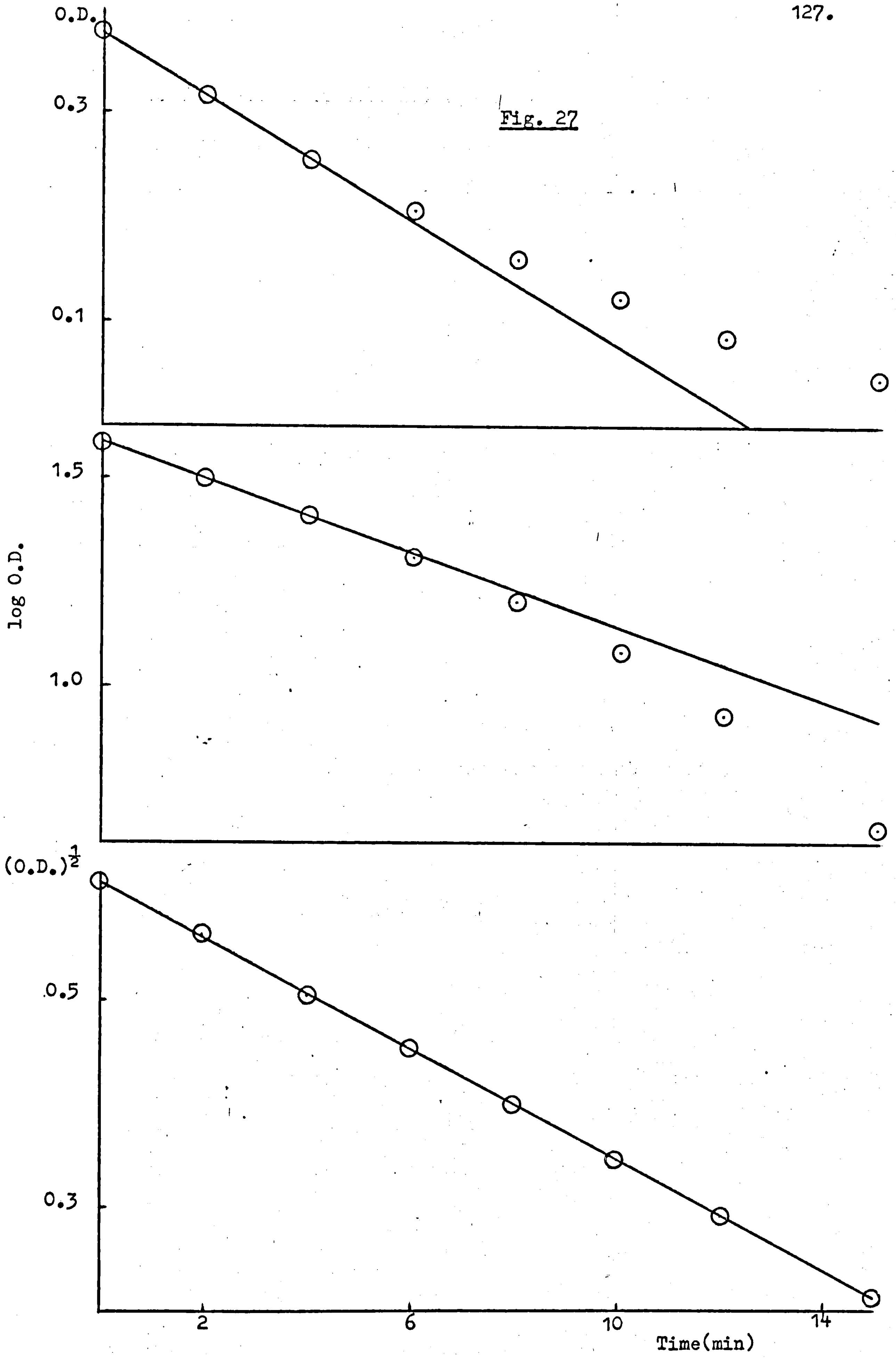


Fig. 27 analyses the behaviour of the system. A graph of the average optical density from the three runs of Table 36 against time shows that the rate of reaction falls off more rapidly than would correspond to a reaction of zero order in N(III). The order with respect to N(III) is therefore greater than 0. The plot of log O.D. against time shows that the rate does not fall off as rapidly as would be required for a process of the first order; hence the order in N(III) is less than 1.

When $(\mathrm{O.D.})^{\frac{1}{2}}$ is plotted versus time, a good straight line is obtained to about 90% reaction. The inference is strongly that the order with respect to N(III) is 0.5.

For a pseudo half order reaction

$$-\frac{d[N(III)]}{dt} = k(N(III))^{\frac{1}{2}}$$

or in integrated form $kt = -2\,[N(III)]^{\frac{1}{2}} + \text{constant}$.

Hence if $2[N(III)]^{\frac{1}{2}}$ were plotted against t, the gradient of the graph would be -k.

The Effect of H_2EDTA^{2-} on the Rate of Reaction

To test whether impurity of the chemicals caused by the presence of transition metal ions has any effect on the rate of reaction, three experiments were carried out in which the concentration of H_2EDTA^{2-} was varied over a ten-fold range and compared with a run in the absence of a complexing agent. The ion was added as the disodium salt.

The optical density - time data are shown in Table 36A.

Table 36A

$[NaNO_2]$ = 0.000814 M $[H^+]$ = 1.5200 M

$[KIO_3]$ = 0.00600 M $[Cl^-]$ 1.5200 M

Temp. = 25.0 ± 0.02 C°

	Molarity of EDTA as indicated above each column		
Time (min)	0	2×10^{-4} M	2×10^{-3} M
0	(0.407)	(0.407)	(0.407)
2	0.377	0.375	0.380
5	0.356	0.355	0.358
8	0.338	0.334	0.336
11	0.314	0.310	0.317
15	0.287	0.284	0.290
20	0.252	0.248	0.255
30	0.189	0.188	0.190

It can be seen that the addition of small quantities of EDTA produces no effect on the rate of reaction, whence no catalytic effects are being caused by the presence of traces of metal ions, and no further precautions need be taken to exclude such trace contaminants.

Determination of the Order of Reaction with Respect to Reactants

The order of reaction with respect to each reactant was investigated by carrying out sets of experiments in which the concentration of one reactant was changed, all other concentrations and conditions being kept constant.

Concentrations of N(III) were measured as optical densities, and results were plotted as $(O.D.)^{\frac{1}{2}}$ versus time.

The reason for this general treatment becomes apparent once the results for order with respect to N(III) (which were indicated in the preliminary studies) are confirmed.

The order was found by plotting log initial rate (obtained from $(N(III))_o^{\frac{1}{2}}$ x 0.08945 x slope of the graph of log $(O.D.)^{\frac{1}{2}}$ /time, for reactions in which the observations are made on 1 ml samples diluted to 100 ml) against log concentration.

The numerical factor 0.08945 arises because initial rate is equal to $kc_o^{\frac{1}{2}}$; and k, when found from a graph of $c^{\frac{1}{2}}$ versus t is equal to -2 x gradient. But $(O.D.)^{\frac{1}{2}}$ was plotted, i.e. using 1 cm cells after 100-fold dilution, $(10^{-2}\ \varepsilon c)^{\frac{1}{2}}$ was plotted versus t. Hence measured slope needs to be multiplied by $(500)^{-\frac{1}{2}} = 0.04472$. Including the number 2 in this factor we obtain 0.08945.

Working in high acidities, ($[H^+] \approx 1.4$ to 2.2 M), all N(III) put in (about 10^{-3} M $NaNO_2$) can be considered as nitrous acid without further calculation.

Order with Respect to N(III)

Table 37

$[KIO_3]$ = 0.00600 M $[HCl]$ = 2.243 M

Temp. = 25.0 ± 0.02°C

$10^4[HNO_2]$ M	$10^2[HNO_2]^{\frac{1}{2}}$ $M^{\frac{1}{2}}$	10^5 I.R. M min^{-1}	10^3 $k_{\frac{1}{2}}$ $M^{\frac{1}{2}}$ min^{-1}
(1) 3.10	1.76	4.31	2.45
(2) 4.58	2.14	5.21	2.43
(3) 6.34	2.52	5.97	2.37
(4) 7.52	2.74	6.55	2.39
(5) 8.68	2.95	7.04	2.39
(6) 9.74	3.12	7.41	2.38
(7) 11.90	3.45	8.21	2.38
(8) 14.88	3.86	9.08	2.35
(9) 17.98	4.24	10.09	2.38

The order with respect to nitrous acid is 0.5. Figure 28 further emphasises this point.

The above result gives the order as determined from initial rates in different experiments. In all runs [N(III)] was much smaller than the other reactant concentrations and the order with respect to HNO_2 can also be investigated directly throughout any individual run. Figure 29 shows the effect of plotting $(O.D.)^{\frac{1}{2}}$ versus time for the runs whose initial rates are listed above. The linearity of each graph and the parallel nature of all the lines shows that the reaction is of order 0.5 in HNO_2 throughout its course. Individual reactions were followed for more than 70% completion, the average slope of these graphs is -0.0265, whence the mean 0.5 order rate constant over the course of these runs is 0.00237 $M^{\frac{1}{2}}$ min^{-1}.

Clearly the order of the reaction is maintained throughout its course.

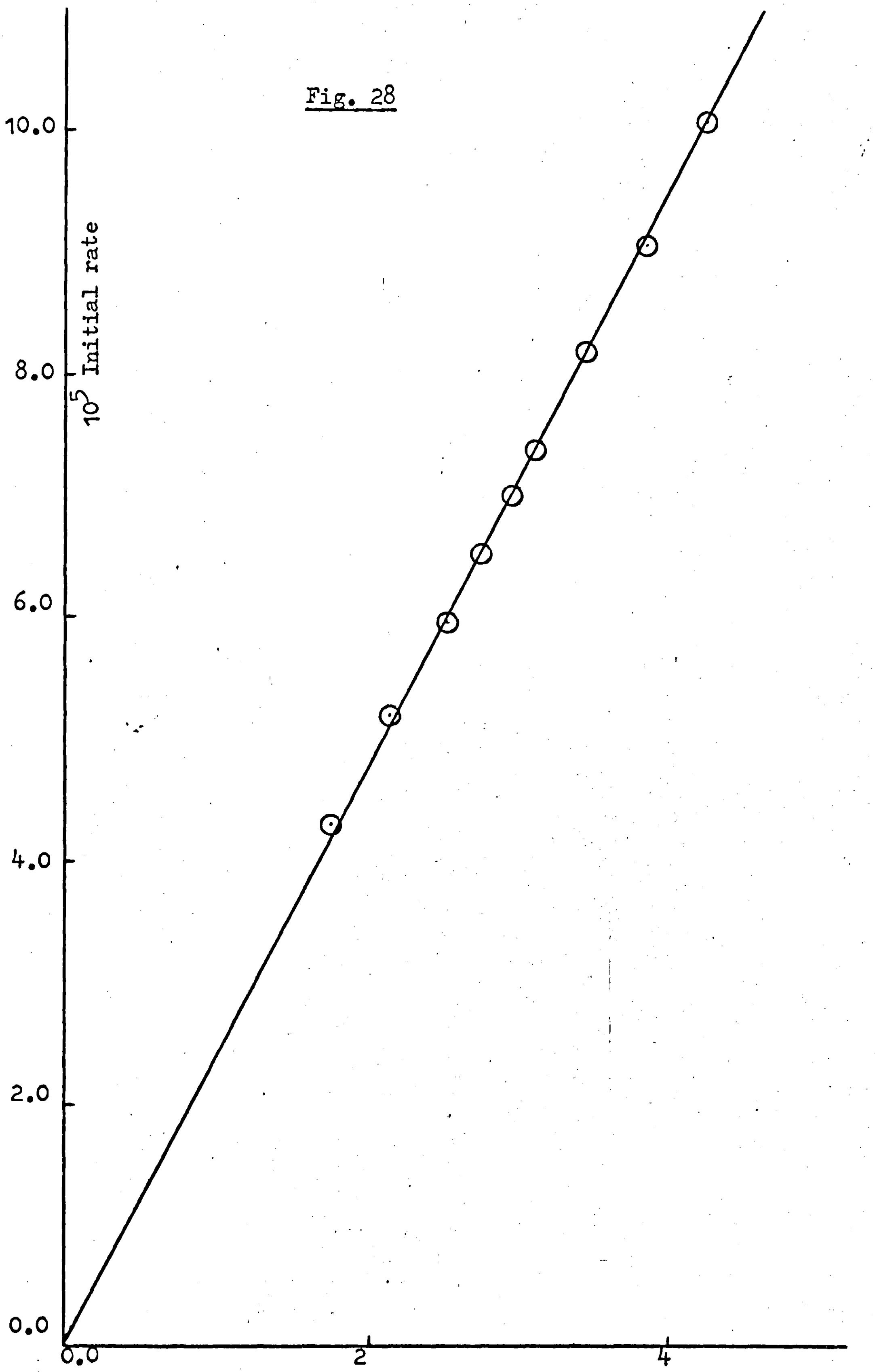


Fig. 28
10.0
8.0
6.0
4.0
2.0
0.0
10^5 Initial rate
0.0
2
4
$10^2[HNO_2]^{\frac{1}{2}}$ $M^{\frac{1}{2}}$

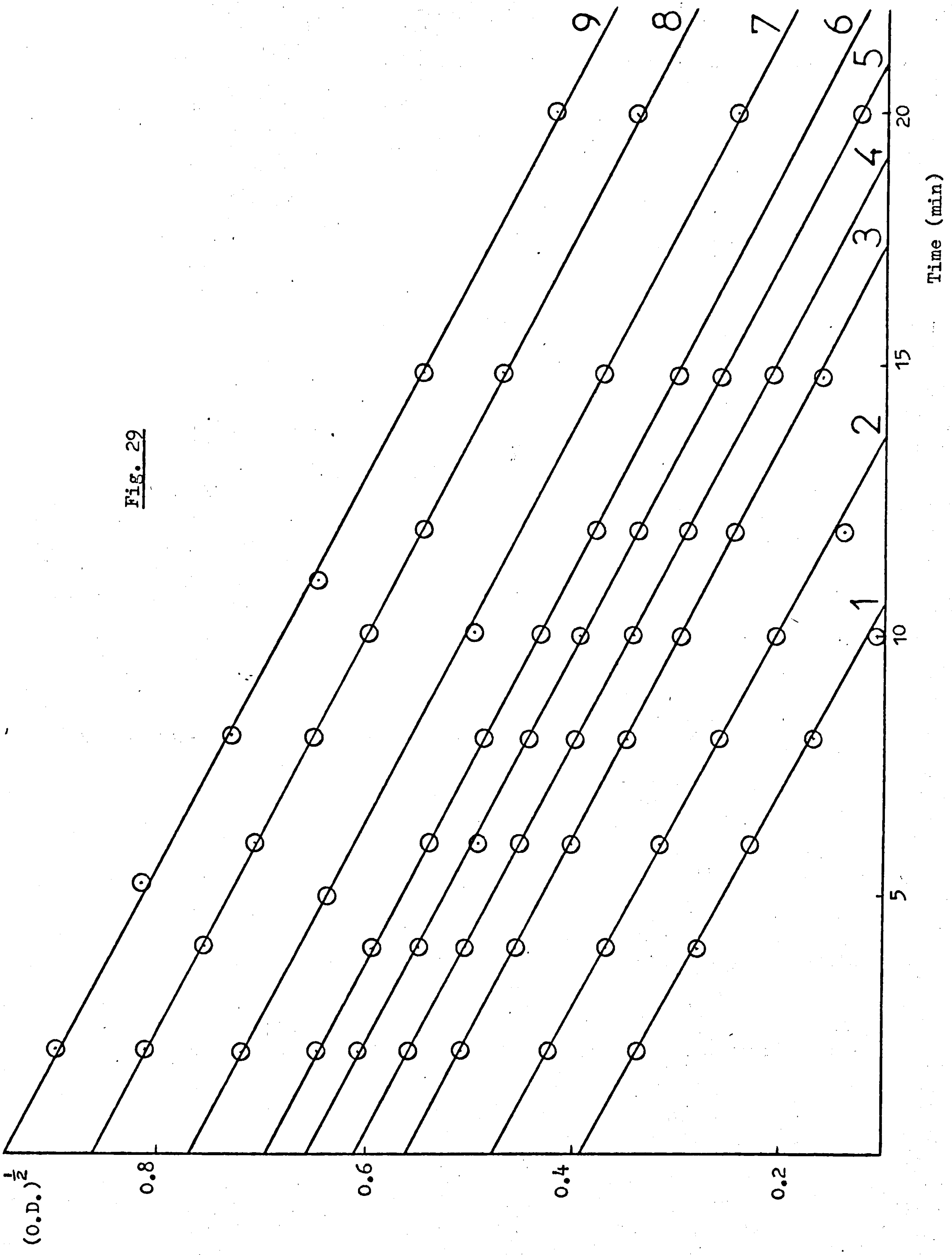


Fig. 29

Order with Respect to Hydrogen Ion

The ionic strength in the following set of experiments was made up with NaCl.

Table 38

$[HNO_2]$ = 0.000794 M

$[KIO_3]$ = 0.00800 M

$[Cl^-]$ = 2.262 M

Temp. = 25.0 ± 0.02°C

$[Na^+]$ (M)	$[H^+]$ (M)	H_o	10^5 Initial rate ($M\ min^{-1}$)	10^5 I.R./$[h_o]$ (min^{-1})
0.0008	2.262	- 0.78	8.37	1.39
0.1750	2.088	- 0.72	7.33	1.40
0.3230	1.940	- 0.66	6.42	1.40
0.4790	1.784	- 0.61	5.65	1.39
0.6550	1.608	- 0.53	4.71	1.39
0.8390	1.424	- 0.44	3.85	1.40

(H_o was taken from tables given by Paul and Long(45).

A graph of log initial rate/log$[H^+]$ is a straight line of slope 1.7.

When log initial rate is plotted against the acidity function, H_o, a straight line of slope 0.99 was obtained, Fig. 30. Perhaps even more significant is Fig. 31 which shows that initial rate versus h_o extrapolates through the origin.

Dividing initial rate by h_o (where $H_o = -\log h_o$), a good constant was obtained, Table 38.

Therefore, the order with respect to the acidity function, h_o is one.

Another important conclusion can be drawn from Table 38; namely that increase in $[Na^+]$ has no effect on the reaction rate. It is particularly noticeable that the reduction of $[Na^+]$ to a very low level in the first recorded run has no detectable effect upon the kinetics.

It is perhaps relevant, at this point, again to draw attention to the relative rates of the redox and decomposition reactions involving HNO_2.

Table 36 for instance illustrates reactions observed at the lower end of the $[H^+]$ range used. These reactions are, however, still fast compared with the rate of decomposition under similar conditions. No correction has been applied to allow for the decomposition, the only measure taken being to concentrate on observing relatively fast reactions between I(V) and N(III).

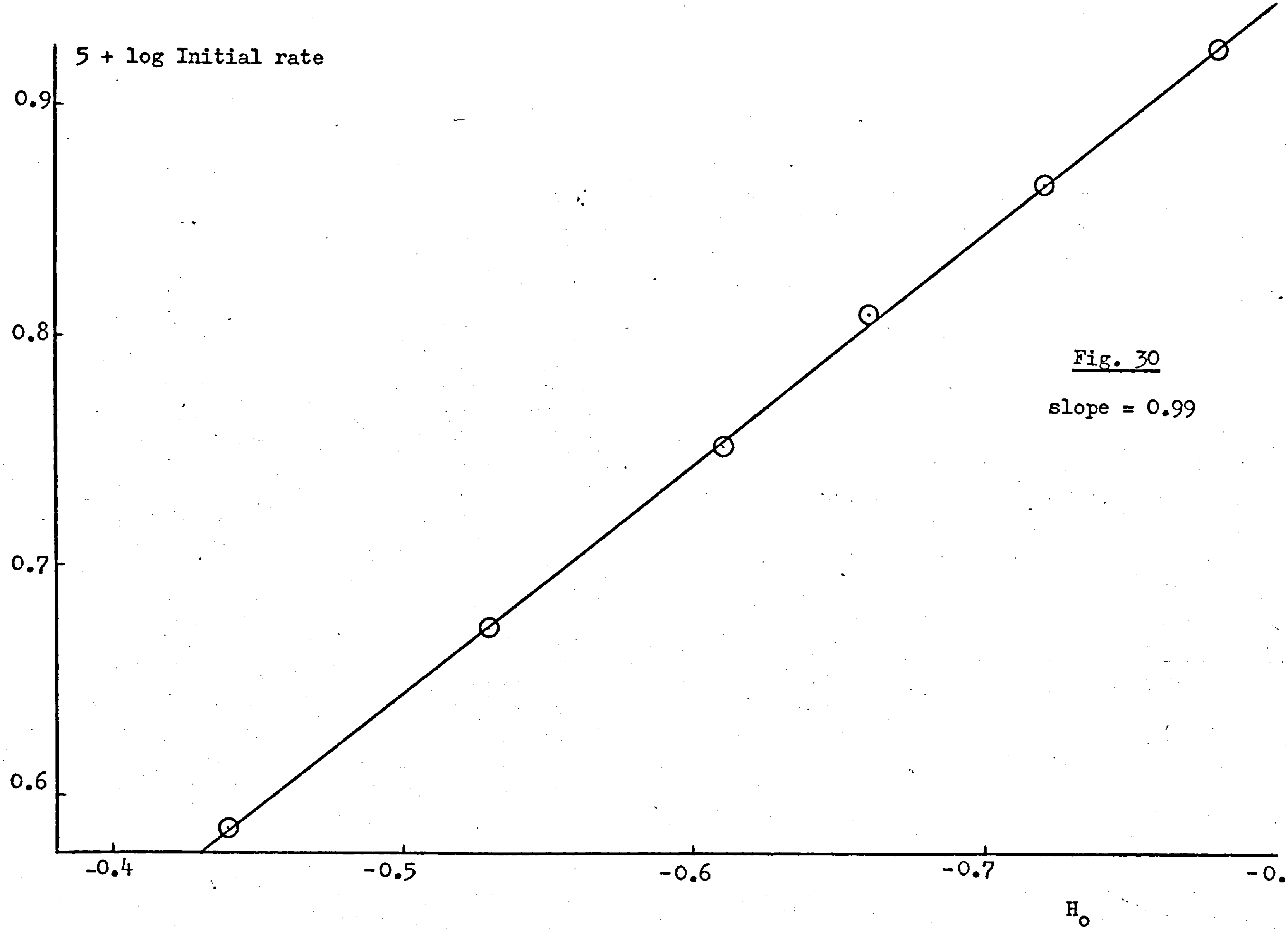


Fig. 30

slope = 0.99

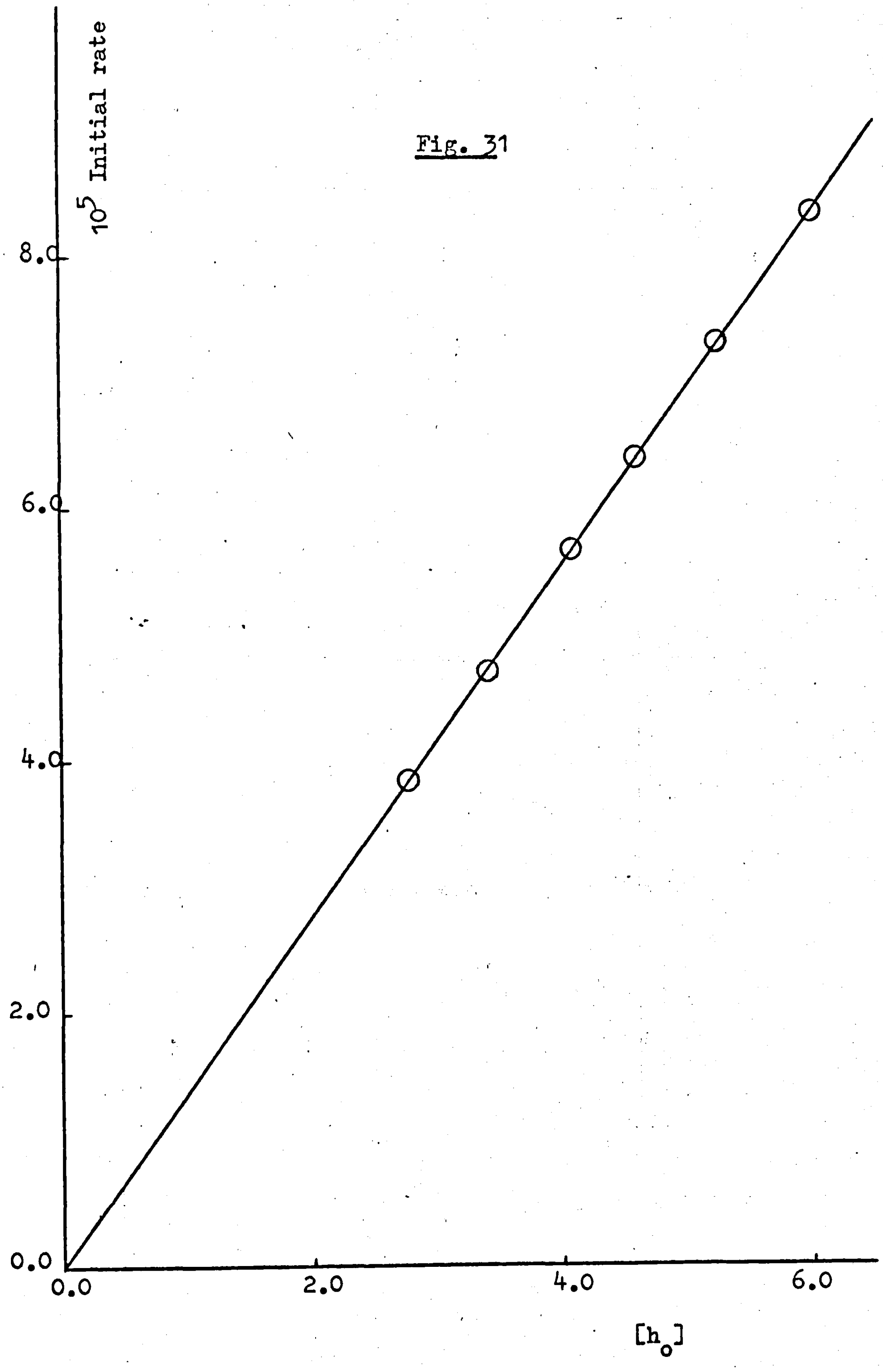


Fig. 31

Order with Respect to Iodate

Table 39

$[NaNO_2]$ = 0.000784 M $[HCl]$ = 2.186 M

Temp. = 25.0 ± 0.02°C

10^3 $[KIO_3]$ M	10^5 Initial rate (M min^{-1})
0.32	0.95
1.00	2.19
2.00	3.51
3.00	4.52
4.00	5.49
6.00	6.99
8.00	8.12
10.00	8.92

A plot of log initial rate versus log $[IO_3^-]$ is not a straight line, and the slope of the best line through the points is about 0.6 (see Fig. 32).

However, at lower iodate concentrations, the slope tends to rise towards one, and at higher concentrations the slope tends downwards.

Another set of experiments was carried out, in which 0.478 M NaCl was present in the reaction mixture.

The results are shown in Table 40.

Table 40

$[HNO_2] = 0.000812$ M $[Na^+] = 0.478$ M

$[H^+] = 1.834$ M $[Cl^-] = 2.312$ M

Temp. = 25.0 ± 0.02°C

$10^3[KIO_3]$M	10^5 Initial rate (M min^{-1})
0.48	0.96
1.00	1.79
1.60	2.58
2.40	3.40
3.20	4.15
4.80	5.42
6.00	6.12

These results are also included in Fig. 32.

Although the conditions are distinct in the two sets of experiments, the conclusion about the order with respect to iodate are very similar.

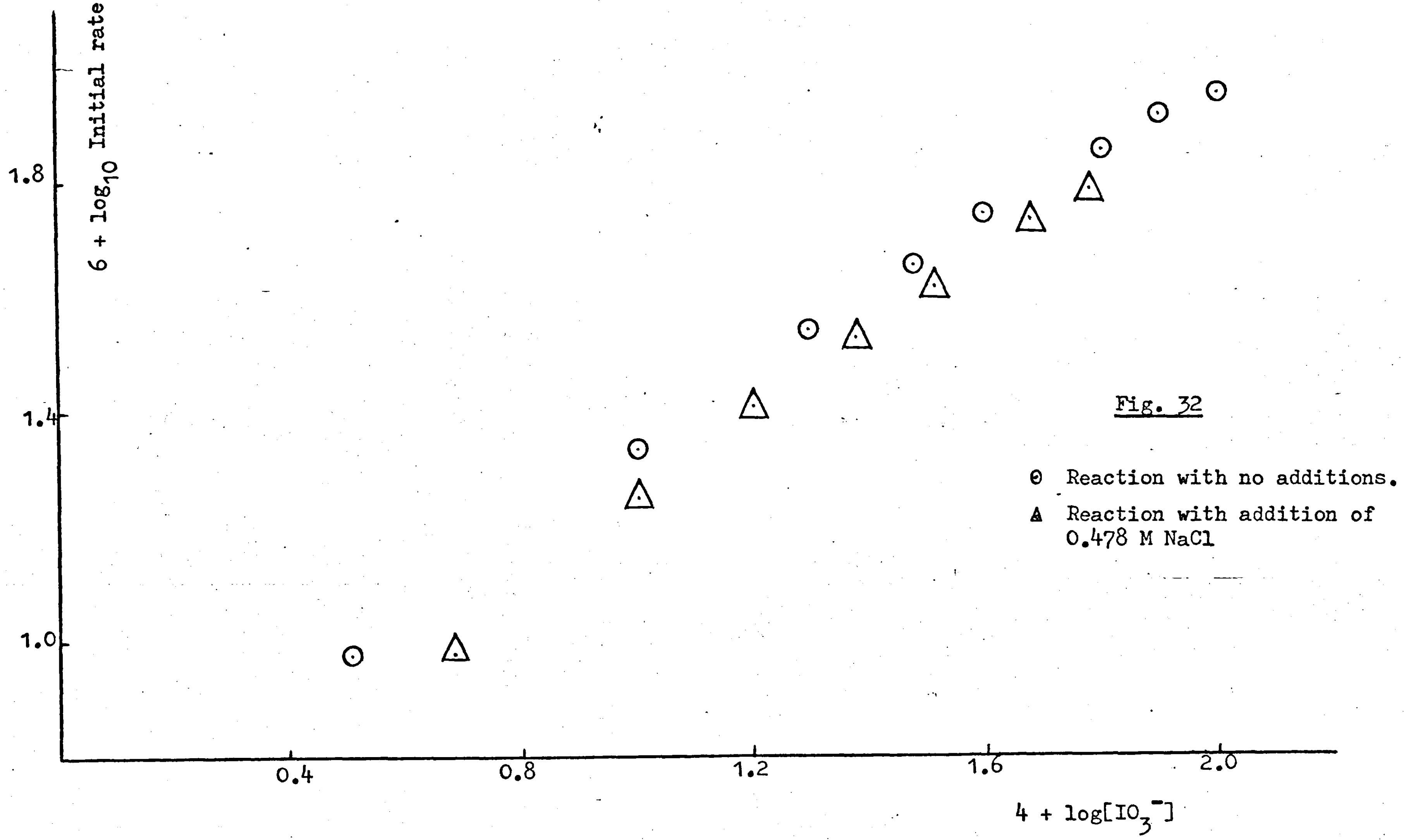


Fig. 32

6 + $\log_{10}$ Initial rate
1.8
1.4
1.0
0.4
0.8
1.2
1.6
2.0
4 + $\log[IO_3^-]$
⊙ Reaction with no additions.
△ Reaction with addition of 0.478 M NaCl

Order with Respect to Chloride Ion

Table 41

$[HNO_2]$ = 0.000848 M $[KIO_3]$ = 0.00400 M

$[H^+]$ = 1.792 M Temp. = 25.0 ± 0.02°C

$10^2[Na^+]$ M	$[Cl^-]$ M	10^5 Initial rate ($M\ min^{-1}$)	$[Cl^-]^3$ M^3
0.09	1.792	1.73	5.75
7.70	1.868	2.18	6.52
17.50	1.966	2.50	7.60
32.30	2.114	3.18	9.45
47.90	2.270	4.01	11.70
65.50	2.446	4.75	14.63

A plot of log initial rate versus log $[Cl^-]$ is a straight line of slope 3.15 (see Fig. 33).

The apparent order with respect to chloride ion is three.

In order to increase $[Cl^-]$, $[Na^+]$ has also necessarily been increased. However, we have already seen (Table 38) that Na^+ has no effect upon the kinetics, therefore the variations in these experiments are all attributable to Cl^-. Fig. 34 shows that when $[Cl^-]^3$ is plotted against rate, the line can reasonably be extrapolated to pass through the origin.

No account of changes in ionic strength have been taken here, but μ is so high that the variation from 1.8 to 2.5 would not be expected to have any drastic effect upon the experimental conditions.

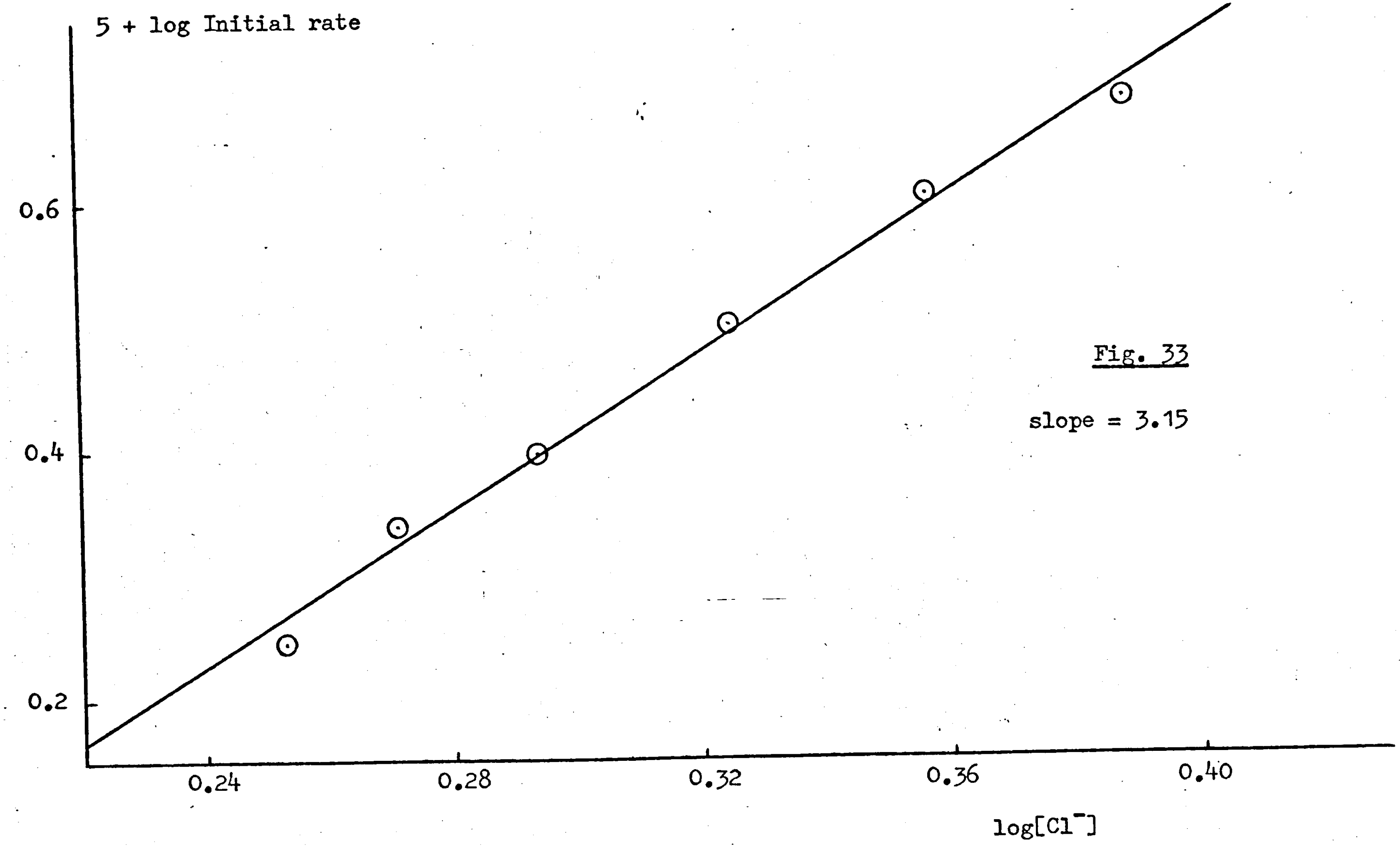


Fig. 33

slope = 3.15

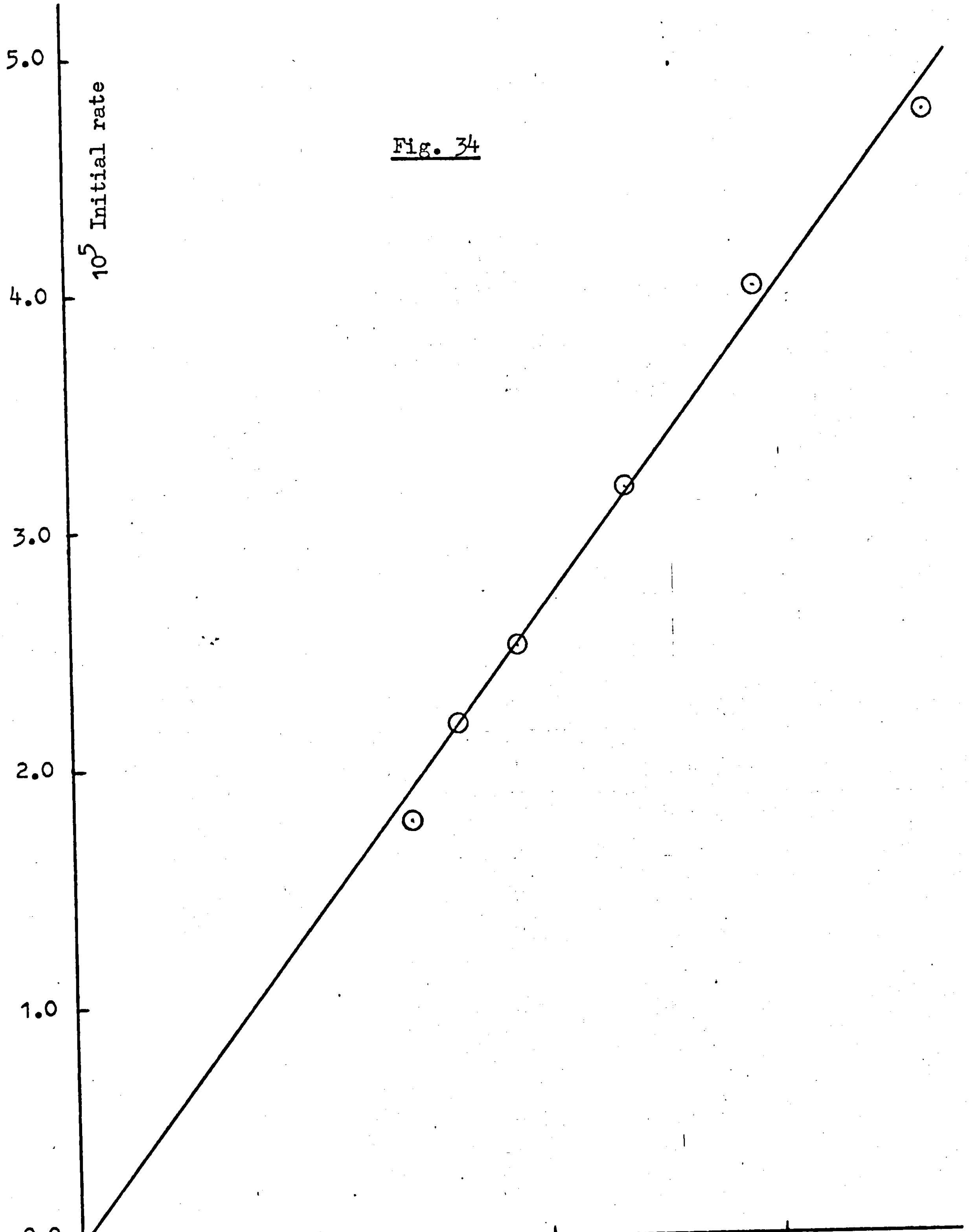


Fig. 34
5.0
4.0
3.0
2.0
1.0
0.0
0.0
4.0
8.0
12.0
10^5 Initial rate
[Cl⁻]^3 M^3

The Effect of Added Salts on the Rate of Reaction

(i) The effect of added cations

It can be seen from Table 38, that changing the sodium ion concentration, almost 1000 fold while keeping the ionic strength constant, has no effect on the reaction rate.

The lack of effect of general ionic strength has been mentioned in the previous section.

In order to check the effect of other monovalent cations on the rate of reaction, two sets of experiments were carried out. Four runs, in each set, employed identical reactant mixtures namely A, B. C and D and contained respectively the additions of 0.478 M LiCl, NaCl, KCl and CsCl. The first set (Table 42) has an additional similar fifth experiment E, with no additives.

The results are summarised in Tables 42 and 43.

Table 42

$[NaNO_2]$ = 0.000812 M

$[KIO_3]$ = 0.00400 M

Temp. = 25.0 ± 0.02°C

$[H^+]$ = 1.834 M

$[Cl^-]$ = 2.312 M (in A, B, C and D)

$[Cl^-]$ = 1.834 M (in E)

Time (min)	E	A(Li^+)	B(Na^+)	C(K^+)	D(Cs^+)
0	(0.406)	(0.406)	(0.406)	(0.406)	(0.406)
2	0.380	0.353	0.359	0.369	0.365
5	0.346	0.285	0.293	0.311	0.306
8	-	0.230	0.233	0.263	0.252
10	0.292	-	-	-	-
11	-	0.176	0.182	0.216	0.208
15	0.244	0.118	0.124	0.162	0.156
20	0.200	0.060	0.066	0.108	0.099
25	0.157	-	0.025	0.060	-
30	-	-	-	-	0.022
35	0.085	-	-	-	-
10^5 I.R. = ($M\ min^{-1}$)	2.42	4.91	4.87	3.98	4.10
$\frac{10^6 \text{ I.R.}}{[Cl^-]^3}$ =	3.92	3.97	3.94	3.22	3.32

Table 43

$[NaNO_2]$ = 0.000848 M $[H^+]$ = 1.792 M

$[KIO_3]$ = 0.00400 M $[Cl^-]$ = 2.270 M

Temp. = 25.0 ± 0.02°C

Time (min)	$A(Li^+)$	$B(Na^+)$	$C(K^+)$	$D(Cs^+)$
0	(0.424)	(0.424)	(0.424)	(0.424)
2	0.381	0.386	0.395	0.389
5	0.326	0.329	0.346	0.342
8	0.276	0.278	0.303	0.298
11	0.230	0.230	0.266	0.257
15	0.175	0.177	0.219	0.207
20	0.117	0.114	0.167	0.153
25	0.070	-	0.121	0.105
10^5 I.R. = $(M\ min^{-1})$	4.02	4.01	3.15	3.33
$\frac{10^6\ I.R.}{[Cl^-]^3}$ =	3.44	3.43	2.69	2.85

It can be seen from Tables 42 and 43 that, when the initial rate is divided by $[Cl^-]^3$, Li^+ and Na^+ have no significant effect upon the reaction rate. Hence $[Na^+]$ and $[Li^+]$ cannot enter into any major term of the rate expression.

Replacement of Li^+ or Na^+ by K^+ or Cs^+ does produce a small retardation in rate. The retarding effect of K^+ slightly exceeds that of Cs^+; and that this result is observed in both sets.

All experiments carried out between I(V) and N(III) have required the presence of a small concentration of K^+, hence the effect of K^+ upon reaction rate has been investigated more fully than with the other cations - see Table 44.

Table 44

$[NaNO_2]$ = 0.000812 M $[H^+]$ = 1.834 M

$[IO_3^-]$ = 0.00400 M Temp. = 25.0 ± 0.02°C

$[K^+]$ M	$[Cl^-]$ M	10^5 I.R (M min^{-1})	10^6 I.R/$[Cl^-]^3$
0.0040	1.834	2.42	3.92
0.0518	1.881	2.56	3.85
0.1474	1.977	2.87	3.71
0.2430	2.073	3.19	3.58
0.3864	2.216	3.64	3.34
0.4820	2.312	3.98	3.22

It is confirmed from Table 44 that the retarding effect of K^+ is relatively small; when $[K^+]$ varies by 120 fold the rates decrease by about 18%.

This indicates that $[K^+]$ is not present as such in the denominator of the rate expression. The effect of K^+ must be a secondary retarding one, for example, it seems possible that K^+ acts by weakly forming ion pairs with a potential reactant e.g. IO_3^- and hence slightly lowering $[IO_3^-]$.

However, extrapolating initial rate/($[Cl^-]^3[h_o][HNO_2]^{\frac{1}{2}}[IO_3^-]^{0.6}$) to zero $[K^+]$ should give the theoretical rate constant at zero $[K^+]$.

The calculations are summarised in Table 45, and the plot is given in Fig. 35.

The rate constant at zero $[K^+]$ is 8.66 x 10^{-4} in mole l^{-1} min^{-1} units. To a good approximation this value applies throughout most of this work because $[K^+]$ was quite low in most experiments.

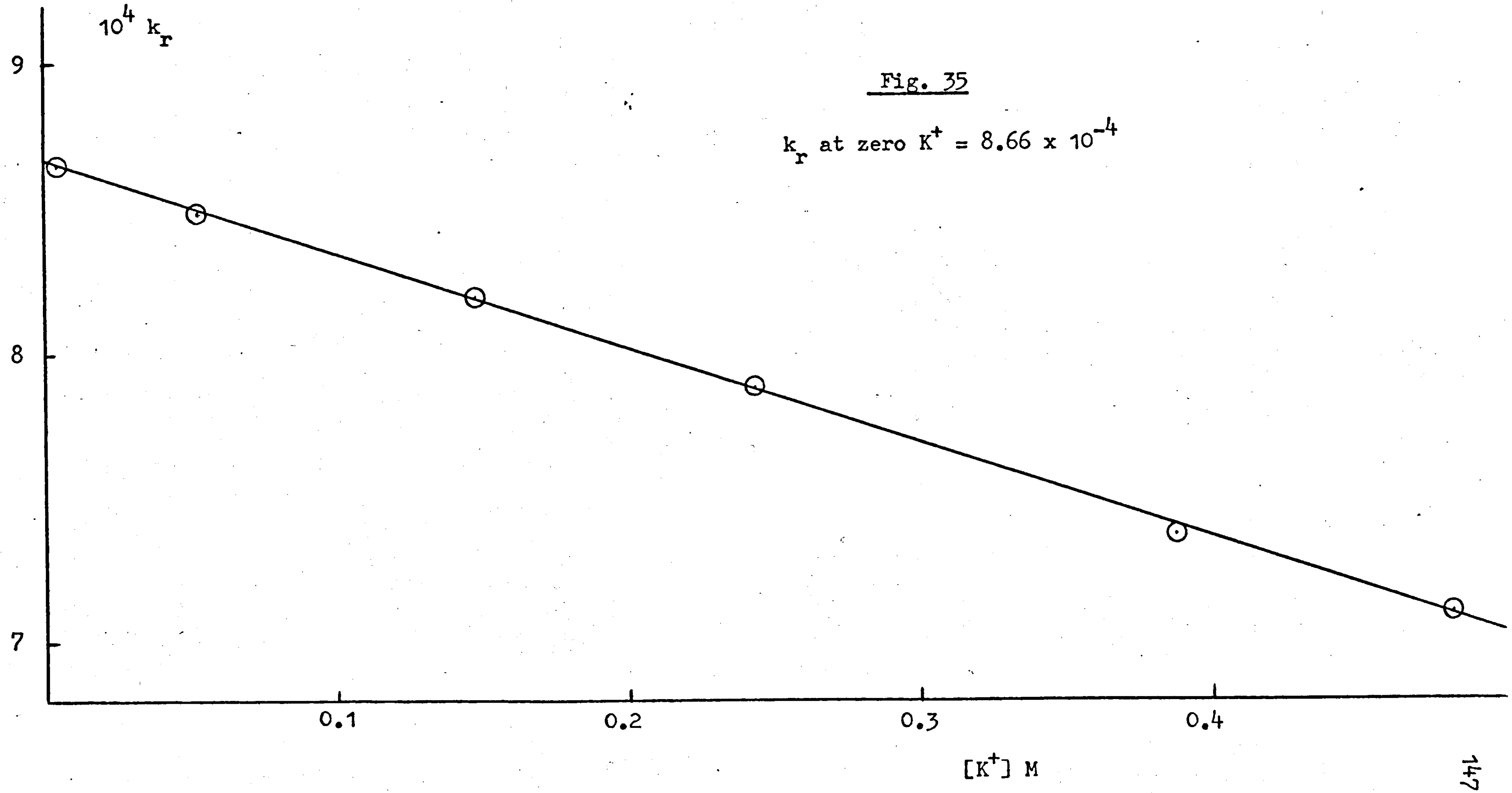


Fig. 35

k_r at zero K^+ = 8.66×10^{-4}

Table 45

10^4 Initial rate/($[Cl^-]^3[h_o][HNO_2]^{\frac{1}{2}}[IO_3^-]^{0.6}$)	$[K^+]$ M
8.65	0.0040
8.48	0.0518
8.19	0.1474
7.88	0.2430
7.37	0.3864
7.10	0.4820

(ii) The effect of added anions.

It has already been established that Cl^- has a very marked effect upon the rate of reaction - so much so that it clearly has a direct participating effect in helping to produce the activated state. The question arises - is the Cl^- effect a general one shown by anions?

It has been shown that sodium ion has no signifiant effect on the reaction rate even at concentrations as high as 0.8 M. In order to investigate the effect of added anions on the rate of the reaction, sodium salts were therefore used.

Two mixtures, A and B were prepared at constant conditions and initial concentration of reactants, except that B contained an addition of 0.400 M $NaNO_3$. The optical density/time results are summarised in Table 46.

Table 46

[$NaNO_2$] = 0.000820 M [H^+] = 1.816 M

[KIO_3] = 0.00500 M [Cl^-] = 1.816 M

Temp. = 25.0 ± 0.02°C

Time (min)	(A)	(B)
0	(0.410)	(0.410)
2	0.387	0.385
5	0.344	0.342
8	-	0.306
10	0.285	-
11	-	0.269
15	0.228	0.223
20	0.180	0.171
25	0.133	0.124
35	0.060	0.049
10^5 Initial rate =	2.89 M min^{-1}	2.92 M min^{-1}

Another set of experiments in which small concentrations of acetate and of phosphate were present showed that these additives also produced no effect upon the rate.

Cl^- thus produces a specific effect, other anions investigated having no influence on the rate.

The Effect of Temperature on the Rate of Reaction

The rate of reaction was measured at a variety of temperatures under two sets of conditions. In one set, the mixture contained only HCl, KIO_3 and $NaNO_2$ in water. In the other set, NaCl was added.

The nominal energy of activation for the reaction was calculated using effectively the Arrhenius equation:

$$k = A\,e^{-E/RT}$$

as Initial rate = $A\,e^{-E/RT}$ x Constant function of concentration terms.

A plot of $\log_{10}$ initial rate versus 1/T giving a slope of -E/2.303R.

The results are shown in Tables 47 and 48 and the plots are shown in Figs. 36 and 37.

Table 47

$[NaNO_2]$ = 0.000820 M　　$[H^+]$ = 1.816 M

$[KIO_3]$ = 0.00500 M　　$[Cl^-]$ = 1.816 M

T^oC	$10^3/T^oK$	10^5 Initial rate (M min^{-1})	6 + log I.R.
10.0	3.532	0.69	0.8388
15.0	3.471	1.08	1.0334
20.0	3.412	1.73	1.2381
25.0	3.355	2.89	1.4609
30.0	3.299	4.48	1.6513
35.0	3.246	6.71	1.8267

Table 48

$[NaNO_2]$ = 0.000820 M
$[KIO_3]$ = 0.00500 M
$[Na^+]$ = 0.400 M
$[H^+]$ = 1.816 M
$[Cl^-]$ = 2.216 M

T^oC	$10^3/T^oK$	10^5 Initial rate (M min^{-1})	5 + log I.R.
10.0	3.532	1.24	0.0934
15.0	3.471	1.97	0.2945
20.0	3.412	3.13	0.4955
25.0	3.355	4.77	0.6785
30.0	3.299	7.59	0.8802

The reaction mixture containing the greater $[Cl^-]$ (and of course $[Na^+]$) has, according to these experiments, a lower energy requirement by some 1 kcal/mol. This may be experimental error, but appears to be consistent, not only as an averaged effect calculated from the graphical slopes, but also, as found by comparing individual results, e.g. the ratios of rates at 10°C and 30°C are respectively 6.50 and 6.12 whilst the ratios at 15°C and 25°C are correspondingly 2.68 and 2.42. Both ways of examining the results indicate the higher energy requirement in the solution containing a lower concentration of chloride.

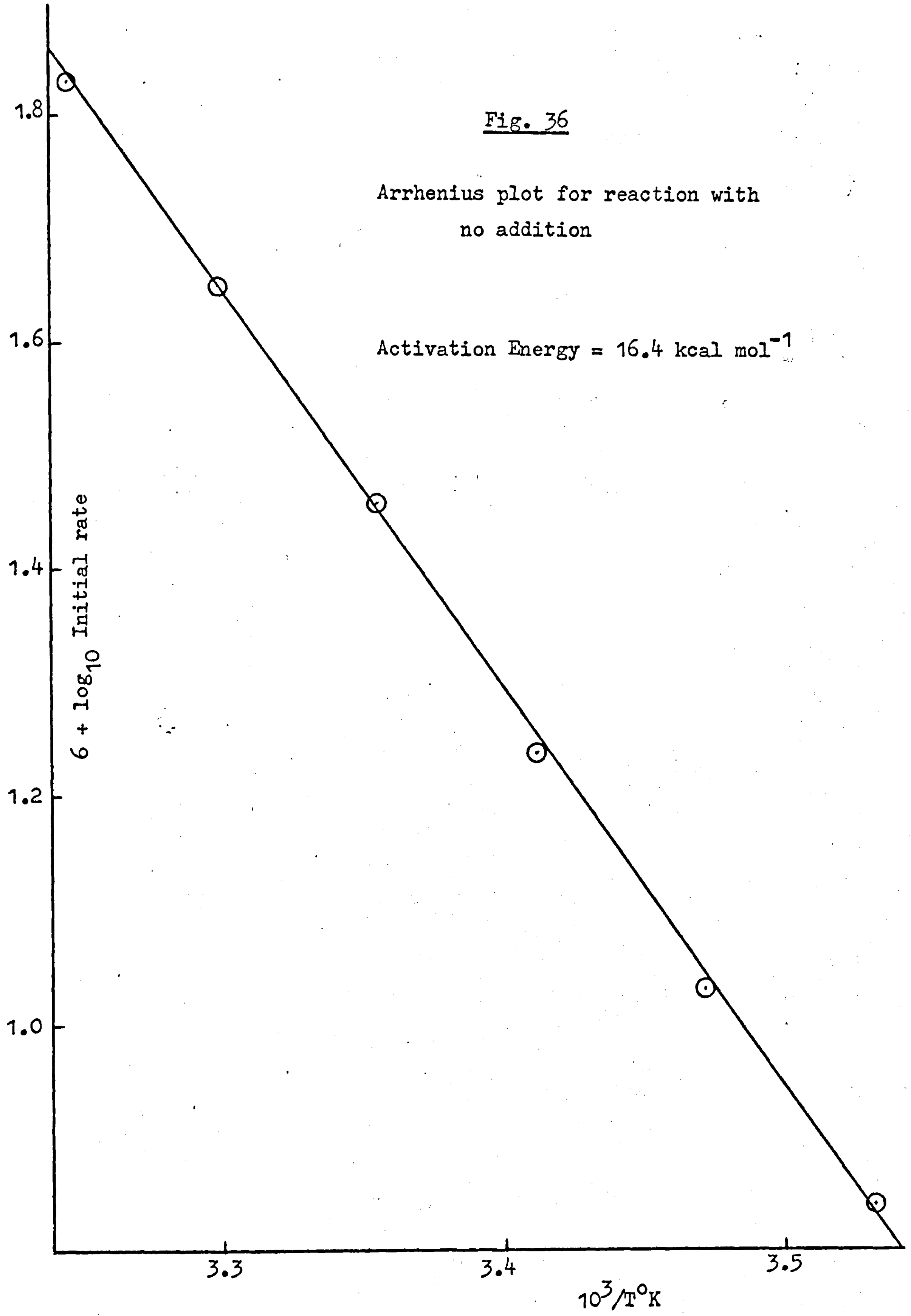


Fig. 36
Arrhenius plot for reaction with no addition
Activation Energy = 16.4 kcal mol^{-1}
6 + log$_{10}$ Initial rate
1.8
1.6
1.4
1.2
1.0
3.3
3.4
3.5
10^3/T°K

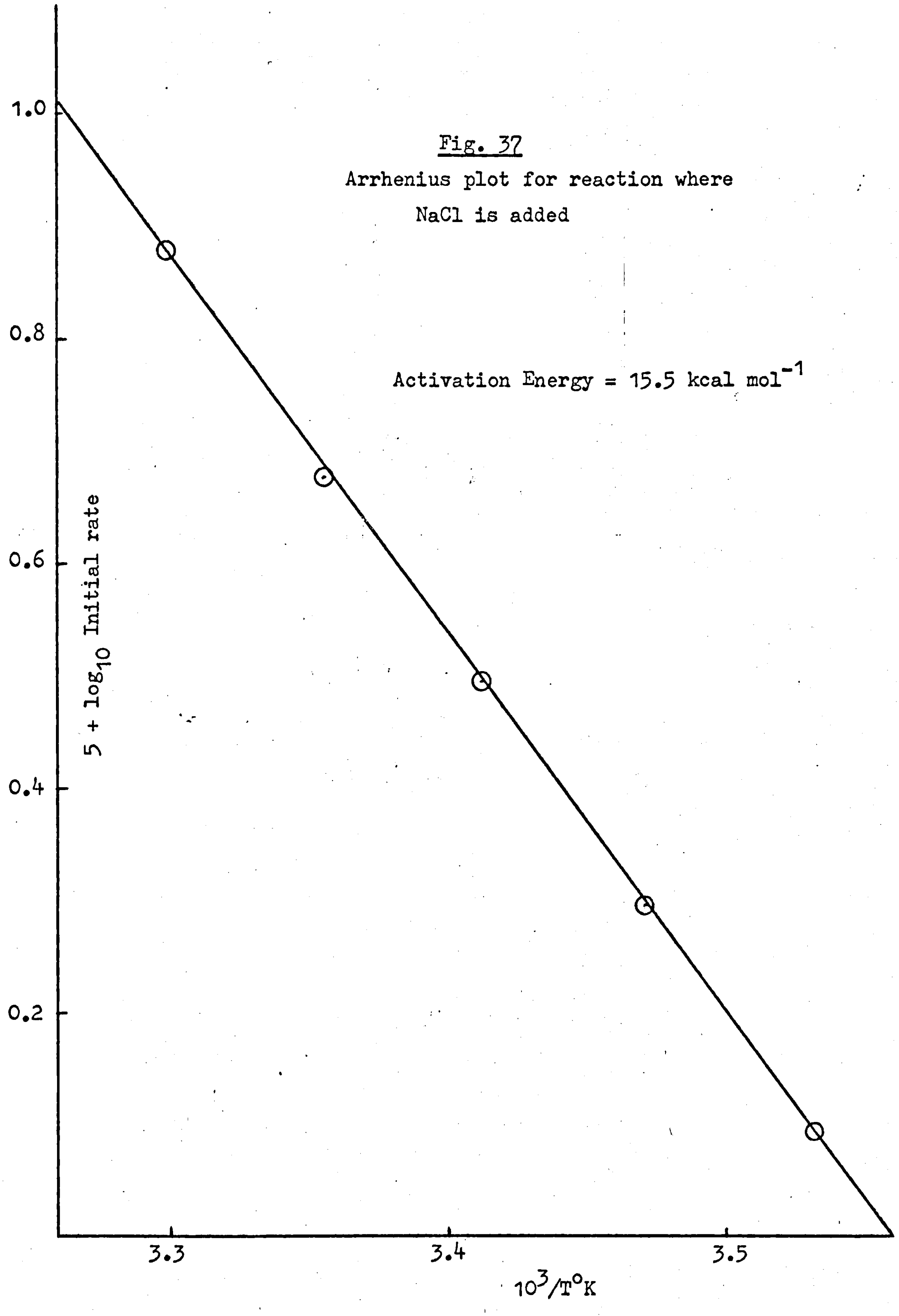


Fig. 37

Arrhenius plot for reaction where NaCl is added

SECTION VI

GENERAL DISCUSSION

General Discussion of Possible Mechanistic Types

As pointed out in the introduction, Edwards discusses redox processes in terms of oxyanion-base reactions. He makes the point that rates of these reactions are often acid-dependent. He goes on to deduce that presumably the role of the protons is to labilise the oxygen by converting it from an oxide ion in an oxyanion to water. The addition of protons to an oxyanion should make it easier to break a bond between oxygen and the central atom, because, for example, the electronic rearrangement necessarily converts partial double bonds into single bonds, and delocalisation effects are reduced.

In the present work, this could refer to

$$HNO_2 + H^+ \longrightarrow NO^+ + H_2O$$

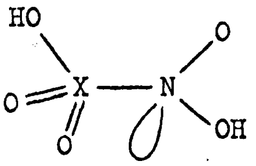
but in a redox process in which HNO_2 becomes HNO_3 or NO_3^-, the N-centre is not losing an oxygen by breaking an N-O bond, it is gaining an extra N-O bond. It seems odd to first break an N-O link and then form two more under the same conditions.

Hence if any labilisation is occurring it seems more likely to concern the halogen-O links, either present in an HXO_3 species or in an X(V) - N(III) complex.

It may be that protonation of NO_2^- occurs preferentially because NO_2^- is a much stronger base than XO_3^-, then XO_3^- or the X(V) - N(III) complex is the next most likely material to be protonated rather than HNO_2.

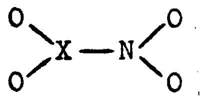
Two of Edwards' examples concern HNO_2 as the oxyanion which reacts with the electron donors ClO_3^- and BrO_3^-. The implication of electron donor must not refer to the overall reaction but to the formation of an activated complex.

His formulation would presumably imply that it is the X lone pair which forms a bond to one of the atoms of HNO_2 e.g. to give:

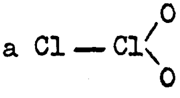


leaving a lone pair on the nitrogen.

However, there are some criticisms one can level at such a formulation; X - N bonds are not particularly strong and hence may not be particularly likely to form; considerable reorganisation would be needed in both fragments if electrons were passed across the X - N bond which then parted again. If further, the rate determining step eliminated water, as Edwards proposes, then

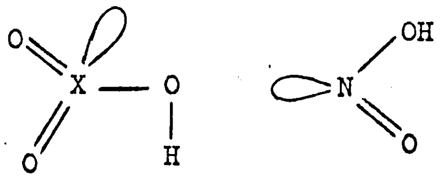


is a possible configuration of the product, which would then seem to require attack by water to go on towards products and this sequence seems surprising.

However, in the example of the BrO_3^-/I^- reaction quoted in the introduction, Edwards clearly envisages an I - Br bond in the intermediate, and Dodgen and Taube$^{(53)}$ formulate a  $Cl-Cl\begin{smallmatrix}O\\ O\end{smallmatrix}$ intermediate in the Cl(V) - Cl(-I) reaction.

There seems no greater intrinsic likelihood of such a transition state than for one involving the nitrogen using its lone pair to bond to bromine.

It is known from ^{18}O studies (54) that the oxidation of SO_3^{2-} by ClO_3^- proceeds via a Cl---O---S entity. Similarly the hypochlorite/nitrite work$^{(33)}$ seems to imply the existence of an oxygen bridge between Cl(I) and N(III) centres in the activated complex. Therefore, one should certainly consider such a transition state which might overcome some of the difficulties just mentioned.



If an electron switch occurs with the X - OH electrons going entirely to X, the lone pair on N being used to form a new O - N link, then one has products which can alter smoothly into the products of this step without requiring much (if any) further energy. Any similar formulation in terms of X acting as the donor of the lone pair leads again to theoretically awkward products. Thus, HNO_2 looks more likely to be the donor than HXO_3, both in the overall reaction sense and in the formulation of this step.

One further feature of such a mechanism which is consistent with general observation - the reaction centre does carry the extra hydrogen atom - providing a valid reason why the extra hydrogen is needed to alter the electronic environment of an oxygen from one originally carrying a partial formal negative charge (which might repel the lone pair) to a more reactive centre.

If the mechanisms for ClO_3^- and BrO_3^- with NO_2^- and ClO_3^- and BrO_3^- with SO_3^{2-} are similar then one might expect some other similarities, e.g. not too diverse activation energies or non-exponential terms or kinetic forms.

It may be noted, however, that Edwards lists SO_3^{2-} as the donor in its reaction with IO_3^-.

The N(III)-Chlorate Reaction

The major results may be summarised as follows.

(a) The reaction is of the first order with respect to nitrous acid, chlorate and hydrogen ion.

(b) The rate of reaction is unaffected by the presence of a number of added monovalent anions or cations.

(c) The rate of reaction is decreased with increasing ionic strength. The slope of log rate constant vs $F(\mu)$ is about -1.

(d) The reacting molar ratio $N(III)/ClO_3^-$ is 3:1.

(e) The overall products of the reaction are chloride and nitrate ions (plus hydrogen ion).

(f) Ordinary physical conditions have no effect upon the rate of the reaction and the general features of the reaction curves show that under the conditions applied, the reaction has no apparent anomalies.

(g) The activation energy is 16.1 kcal mol^{-1}.

(h) The rates of oxidation of nitrous acid by Cl(III) and Cl(I), under conditions similar to those used for N(III)/Cl(V), are fast and extremely fast respectively. The stoichiometry for N(III)/Cl(III) was found to be about 2:1

(i) The overall rate law of the reaction is

$$\text{Rate} = k_r[H^+][HNO_2][ClO_3^-]$$

At 25°C, the rate constant, k_r extrapolated to zero ionic strength, is 220 M^{-2} min^{-1}.

(j) No e.s.r. signals could be detected when rapidly reacting systems using concentrated reagents were passed through the cavity cell of a Varian E-4 S.P.

(k) The rate of decomposition of nitrous acid in a reaction mixture is normally less than 2% of the rate of the oxidation.

Concerning item (k) above, the rate of the decomposition has been neglected in all calculations because very slow oxidation runs were deliberately avoided.

Rate is directly proportional to $[H^+]$, $[HNO_2]$ and $[ClO_3^-]$. Hence the rate determining step either involves participation of one of each of these species or involves species whose concentrations are directly proportional to the entities above. For example, the following schemes would be consistent with the observations:

1) $H^+ + HNO_2 + ClO_3^- \rightleftharpoons H_2NClO_5 \xrightarrow{\text{r.d. step}}$

2) $H^+ + HNClO_4^- \rightleftharpoons H_2NClO_5 \xrightarrow{\text{r.d. step}}$

3) $H_2NO_2^+ + ClO_3^- \rightleftharpoons H_2NClO_5 \xrightarrow{\text{r.d. step}}$

4) $HNO_2 + HClO_3 \rightleftharpoons H_2NClO_5 \xrightarrow{\text{r.d. step}}$

As mechanistic steps the last two are more attractive than the first because 2-body collisions are more likely than 3-body, and definite concentrations of $H_2NO_2^+$ or $HClO_3$ could be maintained, proportional to HNO_2 and ClO_3^- respectively at constant pH by very rapid protonation equilibria

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+$$

and $$H^+ + ClO_3^- \rightleftharpoons HClO_3$$

established before the rate determining step.

For reasons given in the general considerations let us neglect formation of the transition state via elimination of water. Whatever is involved, the three species will come together and this will involve more than one step, but an overall equilibrium could be postulated after the pre-equilibria establishing HNO_2 giving the complex H_2NClO_5 (step 1 above).

Aside from the shape of such a complex, such a theoretical equilibrium ought to account for the effect of ionic strength upon the rate constant - namely that when rate is referred to calculated concentrations of ClO_3^-, H^+ and HNO_2, log k versus a function of ionic strength, $F(\mu)$, shows a negative slope of 1.

For the postulated equilibrium

$$K_{therm} = a(H_2NClO_5)/a(ClO_3^-).a(H^+).a(HNO_2)$$

and assuming that for uncharged species a = concentration.

$$\text{Rate} = k'[H_2NClO_5] = k'K_{therm}[ClO_3^-][H^+][HNO_2]\ f_{ClO_3^-}.f_{H^+}$$

dividing by concentrations and setting $k'K_{therm} = k_o$

$$k = k_o\ f_{ClO_3^-}.f_{H^+}$$

$$\log k = \text{constant} + \log f_{ClO_3^-} + \log f_{H^+}$$

For aqueous solutions at 25°C:

$$\log k \approx -0.5.Z^2.F(\mu)$$

hence log k = constant - $F(\mu)$ as observed.

The species H_2NClO_5 is an attractive one for understanding how the reaction step occurs.

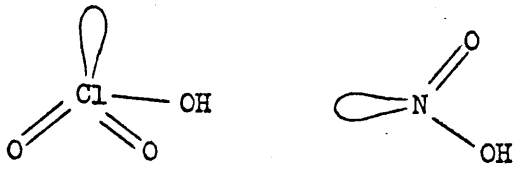
It is not possible to decide whether the proton adds last to the Cl-N complex, or whether $HClO_3$ and HNO_2, or ClO_3^- and $H_2NO_2^+$ come together - the kinetic and salt effect analyses cannot distinguish between the possibilties.

pK for chloric acid has been reported as $\leqslant 0$. Since pK for nitrous acid is about 3.14 and equivalent protons in multi-ionising acids involve successive proton dissociation constants differing by factors of 10^4 to 10^5, hence pK for the dissociation of $H_2NO_2^+$ would be expected to be in the same region as that for $HClO_3$.

So either or both of the species, $H_2NO_2^+$ or $HClO_3$ could be one of the two species going into the rate determining step.

However, the slow rate of the reaction could be partly due to the very small concentration of $HClO_3$ (or $H_2NO_2^+$). If $[HClO_3]$ is always low its concentration is linearly related to ClO_3^- and to H^+. This is observed in the kinetics.

Now considering how HNO_2 and $HClO_3$ might come together. We have:

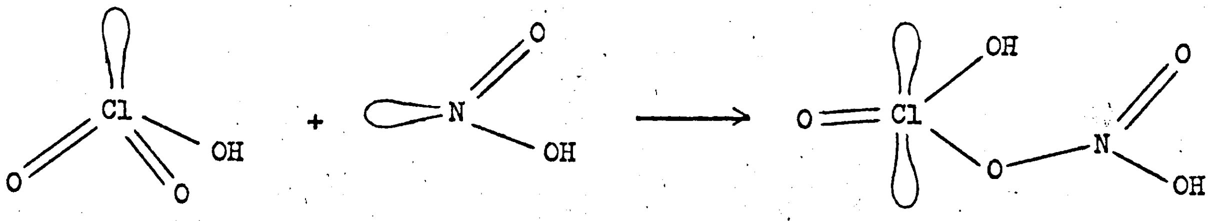


There might be some hydrogen bonding assistance in coming together, although this would have to compete with hydrogen bonding with the solvent.

Whilst the N is ready with a pair of electrons to form a new bond to O, the O atom has no orbitals available to accommodate electrons.

However, if two electrons of the Cl-O bond are withdrawn to Cl and a new bond is simultaneously formed with the electrons from nitrogen, N-O bond formation has led to the activated state, and Cl-O rupture produces the known NO_3 configuration of one product.

Should the extra proton remain associated with the chlorine part of the complex, the formation could be pictured:



Again Cl-O fission could lead to N(V) and Cl(III).

This kind of activated state (sometimes with hydrogen attached to the O atom being transferred) is a demonstrable one if the reaction can be carried out in a neutral or mildly basic solution, because labelled ^{18}O can be incorporated in the original oxidant and detected in the oxidised product under conditions where the redox reaction is faster than exchange of O atoms between the oxyanion and the solvent. The type of mechanism is therefore well known. It is not so easy to test the mechanism taking place in acid solution because the rates of isotopic oxygen exchange with the solvent are much faster in such media than under near neutral conditions.

The final complex could fall apart in various ways, to $H_2NO_3^+$ and ClO_2^- or to HNO_3 and $HClO_2$. These are likely to be virtually irreversible ($E^{\ominus}\ NO_3^-/NO_2^- = 0.94$ V, $E^{\ominus}\ ClO_3^-/ClO_2^- = 1.21$ V).

This model leads directly to one observed product and to ClO_2^- or $HClO_2$ which is the normal form of Cl(III) under acid conditions and which has been shown to react further with N(III) more rapidly than Cl(V) does.

Now let us consider the possibility that it is not ClO_3^- or $HClO_3$ which is involved in the rate determining step, but (for example) ClO^-. This would mean that there are some fast steps involving ClO_3^- or $HClO_3$ with HNO_2 or $H_2NO_2^+$ which can be written noncommittally.

$$\mathrm{Cl(V)} + \mathrm{N(III)} \longrightarrow \mathrm{Cl(III)} + \mathrm{N(V)}$$

$$\mathrm{Cl(III)} + \mathrm{N(III)} \longrightarrow \mathrm{Cl(I)} + \mathrm{N(V)}$$

The Cl(I) may or may not need to rearrange but suppose it rapidly becomes ClO^- or HClO which then is involved in the slow rate determining step,

$$HClO + HNO_2 \longrightarrow Cl^- + NO_3^- + 2H^+$$

This would mean that 2/3 of the N(III) would be oxidised very rapidly, then once HClO is formed the reaction would proceed slowly. This is not what we observe. The other possibility, that it is ClO_2^- or $HClO_2$ which is involved in the rate determining step, can be rejected on the same basis.

As a matter of consistency the formulations given above involve no species with unpaired electrons and no e.s.r. signals were observed while reaction took place. Two-electron transfer is the clue to this observation.

Therefore, if one of the complexes specified earlier is involved in the rate determining step it must undergo some spontaneous change which will be primarily responsible for reaction, and subsequent reactions are fast involving well known intermediates of Cl(III) and Cl(I).

One such possibility is formally

$$H^+ + HNO_2 + ClO_3^- \overset{fast}{\rightleftharpoons} H_2NClO_5$$

$$H_2NClO_5 \xrightarrow{slow} N(V) + Cl(III)$$

$$Cl(III) + HNO_2 \xrightarrow{fast} N(V) + Cl(I)$$

$$Cl(I) + HNO_2 \xrightarrow{fast} N(V) + Cl(-I)$$

with the coordination spheres around the central atoms rearranging and protonating or deprotonating much faster than the rate determining step.

The production of H^+ because of

$$HNO_2 \xrightarrow{oxidation} NO_3^- + H^+$$

is not enough to change the ratio of the buffer in the reaction mixture significantly.

The overall stoichiometric equation required by the mechanism is

$$3HNO_2 + ClO_3^- (+ H^+) \longrightarrow 3NO_3^- + Cl^- + 3H^+ (+ H^+)$$

and this is observed.

The N(III)-Bromate Reaction

The experimental results may be summarised thus:

(a) The reaction shows first order behaviour in hydrogen ion, bromate and nitrous acid.

(b) Added Na^+, K^+, Cl^-, NO_3^- and HSO_4^- ions do not have specific effects upon the reaction rate, and also the rate is invariant as ionic strength is altered.

(c) Three mols of N(III) are oxidised by 1 mol of BrO_3^- to give NO_3^- and Br^-.

(d) The rate is uninfluenced by change of simple physical conditions.

(e) No free radicals could be detected when fast reacting mixtures were examined for e.s.r. signals.

(f) The activation energy is 15.5 kcal mol^{-1}.

(g) Rates of decomposition of HNO_2 are up to about 2% of the observed total rate of loss of N(III).

(h) The rate law for the reaction is:

$$\text{Rate} = k_r [H^+][HNO_2][BrO_3^-]$$

and $k_r = 13900\ M^{-2}\ min^{-1}$ at 25° irrespective of ionic strength.

The kinetic and stoichiometric evidence concerning the N(III)/BrO_3^- reaction is similar to that obtained in the chlorate reaction, except that the reaction in the case of bromate involves a pH range in which N(III) is present both as reactive HNO_2 and as the ineffective NO_2^- in significant amounts; and in this reaction no variation of rate constant with ionic strength is found.

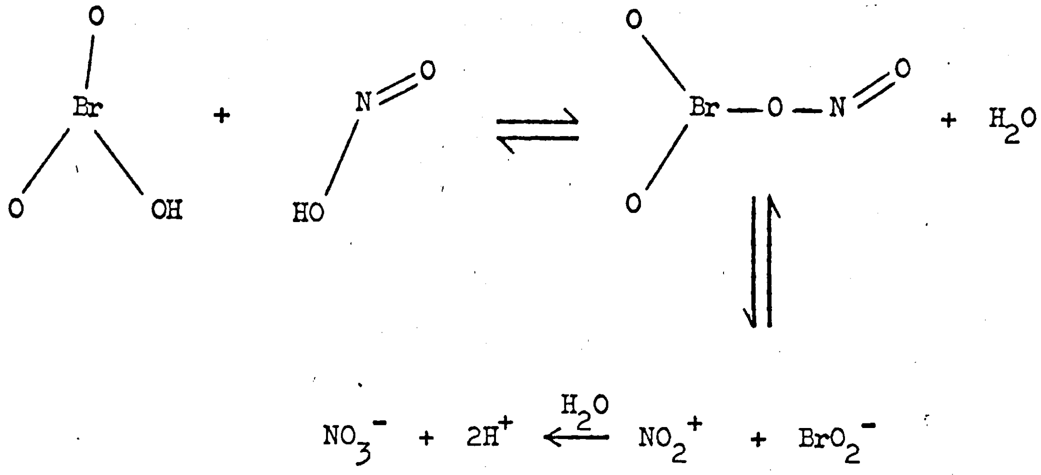
The similarity of the general kinetics, and of the activation energy would at first sight suggest that both chlorate and bromate react with N(III) through corresponding mechanisms.

The effect of ionic strength, however, seems to point to a considerable difference in reaction details. The complete lack of effect of ionic strength implies that the activity terms in the rate equation cancel to unity, and in turn this means that the equilibrium establishing the transition state involves similar ionic types as "reactant" and "products".

The species producing the activated state are established as one non-ionic substance and two singly charged entities. The only way of balancing these charged entities (remembering that charge squared will enter their effects) is the existence of two single charged species amongst the "products" of the equilibrium setting up the transition state.

There does not seem to be any simple modification of the Cl(V) - N(III) complex leading to this situation, e.g. elimination of water from an uncharged H_2NBrO_5 entity introduces no ionic species; protonation equilibria involving H_2NBrO_5 can introduce the correct ionic strength dependence but an incorrect order of reaction with respect to H^+. Loss of NO_3^- in a reversible step before the rate determining step would account for the kinetics and the ionic strength effect but would imply that NO_3^- retards the reaction, which is contrary to observation.

The following postulate accounts for the observations so far: $HBrO_3$ and HNO_2 set up an equilibrium eliminating water. The product is also in equilibrium with dissociation products BrO_2^- and NO_2^+, which are thereby assigned a large possibility of reacting together again to reform $NBrO_4$. One of the dissociation products, NO_2^+ for preference because of its known reactivity with water, may also take part in the rate determining step by reaction with the medium.



$$NO_3^- + 2H^+ \xleftarrow{H_2O} NO_2^+ + BrO_2^-$$

One H^+ would be taken up by the basic anions (e.g. BrO_2^-) produced, and the Br(III) produced could rapidly react with further N(III) species.

Rate is therefore proportional to $[NO_2^+]$, neglecting the concentration of water.

Effectively $[NO_2^+]$ is controlled by

$$H^+ + BrO_3^- + HNO_2 \rightleftharpoons NO_2^+ + BrO_2^- + H_2O$$

whence $$[NO_2^+] \propto \frac{[H^+][BrO_3^-][HNO_2]}{[BrO_2^-]} \quad \frac{f_{H^+} f_{BrO_3^-}}{f_{BrO_2^-} f_{NO_2^+}}$$

which accounts for the lack of ionic strength effect and yields the correct kinetics, but leaves as unconfirmed the inhibition of the reaction by Br(III). So far no way of testing this hypothesis has been devised. Nor has it seemed profitable to attempt the reaction in very concentrated acid where NO_2^+ could be stabilised, because any real mechanism of course represents merely the fastest way of accomplishing the chemical change.

No doubt other real routes would be explored by this thermodynamically favoured reaction if the normal route were artificially hampered. However the above theoretical interpretation of the course of reaction might lend itself to investigation in different media where the reactivities of NO_2^+ and/or water had been modified, though it seems quite possible that other important species present in the above scheme might alter with the medium and hence cloud any conclusions.

Thus whereas in both chlorate and bromate reactions the evidence leads one to reject N-X bond formation in the activated state, elimination of water does seem to play a role in the bromate reaction but not in the chlorate reaction. Essentially the same skeleton X(V) - O - N(III) is, however, formed, but the dehydrated (bromate) form reacts in a different way from the other (chlorate) form.

Ideally, a detailed comparison of the present study with that of Kurtenacker would show whether or not the present results and interpretation is superior. It is not easy to make such a comparison, however, partly because of the differences in reaction conditions and partly because there is some doubt over the method of reporting Kurtenacker's experiments.

However, considering the first experiment on BrO_3^-/NO_2^- reported by Kurtenacker; the reaction mixture appears to contain: 15×10^{-3} M N(III), 5×10^{-3} M BrO_3^- and 2M CH_3COOH, at 21°C. From this one may calculate the ionic strength and hence find that $[H^+] = 5.9 \times 10^{-3}$ M and $[HNO_2] = 13.5 \times 10^{-3}$ M. Correcting the presently found rate constant to 21°C, and neglecting ion pairing, Kurtenacker's result would be consistent with the present one if initial rate:

$$= 9500 \times 13.5 \times 10^{-3} \times 5.9 \times 10^{-3} \times 5 \times 10^{-3} \text{ M min}^{-1}$$
$$= 3.8 \times 10^{-3} \text{ M min}^{-1}$$

The observed value in Kurtenacker's run is about 3.2×10^{-3} M min^{-1}. After a lapse of 60 years the agreement is reasonable, and obviously it is the same reaction which is being studied.

However, this experiment is one of few in which Kurtenacker used equivalent reacting concentrations of Br(V) and N(III). When excess Br(V) was used he reports that the order with respect to N(III) fell from one to virtually zero. Under these conditions Kurtenacker's results are difficult to accept because a reactant is more likely to display a true (high) order when it is present in low concentration, whereas Kurtenacker observes just the reverse.

When we come to consider comparison with Kurtenacker's ClO_3^-/NO_2^- results it is notable amongst other differences, that in the earlier work N(III) is maintained in excess.

In a typical run at 20°C, Kurtenacker used 0.01 M $KClO_3$, 0.0681 M $NaNO_2$ and 0.85 M $KHSO_4$. This leads to an ionic strength of approximately 1 and approximate reactant concentrations of 0.01 M ClO_3^-, 0.065 M HNO_2 and 0.15 M H^+.

To be consistent with the present work this should lead to:

$$\text{initial rate} = 83 \times 0.01 \times 0.065 \times 0.15 \text{ M min}^{-1}$$
$$\approx 8 \times 10^{-3} \text{ M min}^{-1}$$

Kurtenacker's result is 7.0×10^{-3} M min^{-1} in reasonable agreement considering the long extrapolation of our rate constant to $\mu = 1$, and the calculation of a rate 10 or 100 times faster than those observed in the present work.

Variation of conditions in the earlier work, however, led, in the absence of the ionic strength concept to misinterpretation of the results, the formulation of a rate law involving a term uncatalysed by H^+ and some questionable arguments as to why this is not observed when chlorate and nitrite are mixed in neutral solution.

The N(III)-Iodate Reaction

The present kinetic analysis of the N(III)/I(V) reaction in an aqueous HCl medium, can be summarised as follows:

(a) The order with respect to N(III) is 0.5.

(b) The order with respect to iodate is about 0.6.

(c) The order with respect to the acidity measure, h_o, is one.

(d) The order with respect to chloride ion is three.

(e) The cations Na^+ and Li^+ produce no effect on the reaction rate, whilst K^+ and Cs^+ do produce relatively small retardation.

(f) Anions investigated NO_3^-, HPO_4^{--} and OAc^- (excluding Cl^-), produce no influence on the rate.

(g) No signals from paramagnetic substances could be observed using an e.s.r. instrument.

(h) Change of ordinary physical conditions has no effect on the rate of reaction.

(i) The apparent stoichiometric ratio of the reaction is variable - with a ratio as in the kinetic experiments, N(III)/I(V) the stoichiometry is 2:1.

(j) NO_3^- and ICl have been identified as products.

(k) The activation energy of the reaction is about 16.4 kcal mol^{-1}. A lower energy, 15.5 kcal mol^{-1}, was needed when $[Cl^-]$ was increased in the reaction mixture.

(l) There is no evidence for more than one rate term. The following one was found to fit the results reasonably (remembering that the order with respect to iodate is slightly variable):

$$\text{Rate} = k_r[HNO_2]^{\frac{1}{2}}[h_o][IO_3^-]^{0.6}[Cl^-]^3 \quad M\ min^{-1}$$

where $k_r \approx 8 \times 10^{-4}\ M^{-4.1}\ min^{-1}$ at 25°C. The k_r values of 43 experiments were calculated, using this rate law. The results are summarised in Table 49.

Table 49

10^2 $[HNO_2]^{\frac{1}{2}}$ $(M^{\frac{1}{2}})$	$[h_o]$ (M)	10^2 $[IO_3^-]^{0.6}$ $(M^{0.6})$	$[Cl^-]^3$ (M^3)	10^3 $[K^+]$ (M)	10^5 I.R. $(M\ min^{-1})$	10^4 k_r $(M^{-4.1}\ min^{-1})$
2.74	6.17	4.64	11.29	6.00	6.55	7.40
3.45	6.17	4.64	11.29	6.00	8.21	7.37
2.70	6.17	4.64	11.29	6.00	6.47	7.41
3.12	6.17	4.64	11.29	6.00	7.41	7.35
2.95	6.17	4.64	11.29	6.00	7.04	7.38
4.24	6.17	4.64	11.29	6.00	10.09	7.36
3.86	6.17	4.64	11.29	6.00	9.08	7.28
2.52	6.17	4.64	11.29	6.00	5.97	7.33
1.76	6.17	4.64	11.29	6.00	4.31	7.58
2.14	6.17	4.64	11.29	6.00	5.21	7.53
2.80	5.90	6.31	10.45	10.00	8.92	8.19
2.80	5.90	3.64	10.45	4.00	5.49	8.74
2.80	5.90	4.64	10.45	6.00	6.99	8.73
2.80	5.90	5.52	10.45	8.00	8.12	8.52
2.80	5.90	2.40	10.45	2.00	3.51	8.47
2.80	5.90	1.59	10.45	1.00	2.19	8.00
2.80	5.90	3.06	10.45	3.00	4.52	8.56
2.80	5.90	0.80	10.45	0.32	0.95	6.88
2.82	6.03	5.52	11.57	8.00	8.37	7.71
2.82	4.08	5.52	11.57	8.00	5.65	7.69
2.82	5.25	5.52	11.57	8.00	7.33	7.75
2.82	4.57	5.52	11.57	8.00	6.42	7.80
2.82	3.39	5.52	11.57	8.00	4.71	7.71
2.82	2.75	5.52	11.57	8.00	3.85	7.77

Table 49 (continued)

10^2 $[HNO_2]^{\frac{1}{2}}$ $(M^{\frac{1}{2}})$	$[h_o]$ (M)	10^2 $[IO_3^-]^{0.6}$ $(M^{0.6})$	$[Cl^-]^3$ (M^3)	10^3 $[K^+]$ (M)	10^5 I.R. (M min^{-1})	10^4 k_r ($M^{-4.1}$ min^{-1})
2.91	4.17	3.64	14.63	4.00	4.75	7.35
2.91	4.17	3.64	5.75	4.00	1.82	7.17
2.91	4.17	3.64	9.45	4.00	3.18	7.62
2.91	4.17	3.64	11.70	4.00	4.01	7.76
2.91	4.17	3.64	7.60	4.00	2.50	7.45
2.91	4.17	3.64	6.52	4.00	2.18	7.57
2.85	4.37	3.64	12.36	4.82	3.98	7.10
2.85	4.37	3.64	6.17	4.00	2.42	8.65
2.85	4.37	3.64	6.66	51.8	2.56	8.48
2.85	4.37	3.64	8.91	243	3.19	7.90
2.85	4.37	3.64	10.88	386	3.64	7.38
2.85	4.37	3.64	7.73	147	2.87	7.93
2.85	4.37	3.19	12.36	3.20	4.15	8.45
2.85	4.37	2.68	12.36	2.40	3.40	8.24
2.85	4.37	4.06	12.36	4.80	5.42	8.67
2.85	4.37	1.00	12.36	0.48	0.96	6.24
2.85	4.37	2.10	12.36	1.60	2.58	7.98
2.85	4.37	4.64	12.36	6.00	6.12	8.57
2.85	4.37	1.59	12.36	1.00	1.79	7.31

The average of $k_r = 7.8 \times 10^{-4}\ M^{-4.1}\ \text{min}^{-1}$ while h_o has been varied over a factor of 2.5, $[HNO_2]$ over a factor of 6, $[IO_3^-]$ over a factor of 30, and $[Cl^-]$ over the range 1.8 to 2.45 M.

The kinetics are obviously more complex than for the other reactions studied, and the details are largely new.

The present investigation cannot effectively be compared with the previous work of Kurtenacker, partly because Kurtenacker's study was effectively of a different reaction. Acidity, in the 1914 work, was invariably supplied by sulphuric acid, although the accelerating effect of Cl^- was noted. The iodine-containing product was iodine itself. Further the main reactant conditions were different; and surprisingly although Kurtenacker recognised that nitrous acid suffered decomposition, he chose to run all experiments with N(III) in large excess over iodate, and deliberately made the N(III) solution acid half an hour before adding the iodate!

All Kurtenacker's experiments showed the characteristics of autocatalysis, rate rising and then falling again. It is not easy to see why this should be, but the production of H^+ because of

$$HNO_2 \xrightarrow{\text{oxidation}} NO_3^- + H^+$$

is not enough to account for the apparent autocatalysis, and clearly Kurtenacker's own interpretation is wrong. He ascribed the effect to the occurrence of a two stage reaction, iodate reacting with nitrite to give iodite in a relatively slow step, followed by a faster reaction of iodite with nitrite. This does not bear analysis because iodite would be formed mole for mole from iodate. The iodite cannot both react faster than iodate, and build up in the system to give an increased rate. Either iodite reacts more readily than iodate with nitrite, and hence its rate of reaction is undetectable kinetically; or it reacts more slowly in which case the whole reaction gradually slows down and the order appears to fall throughout reaction progress.

All that can be compared are the facts that reaction occurs only in regions of fairly high acidity, and that the rate is strongly dependent upon chloride ion concentration.

On the basis of the present observations it is not possible to decide upon a unique mechanism for the reaction. However, the field of alternatives can be narrowed down.

Consider first the order of 0.5 with respect to N(III), which is definitely indicated by the experiments, rather than for example a fortuitous combination of parallel processes involving a zero order term and a first order term.

The only seemingly likely explanation for this kinetic feature is:

$$2\text{N(III)} \rightleftharpoons (\text{N(III)})_2$$

with the monomer being the effective reductant, the most obvious candidates being perhaps:

$$2\text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}$$

or possibly higher protonated forms of these essential species.

Bunton and Stedman(46) interpreted the u.v. absorption spectra of solutions of nitrite in perchloric acid as showing that HNO_2 is both protonated and dehydrated at high acidities. Their conclusions are a little tentative but the value of the equilibrium constant deduced is between 0.1 and 1. If this is correct then under the present kinetic conditions, the major fraction of N(III) is present as the "monomeric" species, not the "dimer". The situation is suitable for explaining a second order dependence on N(III) if N_2O_3 were the effective reactant or one of first order if it is HNO_2; but does not support a reaction of 0.5 order in N(III).

Longstaff and Singer⁽⁴⁷⁾ also concluded after consideration of much evidence that the bulk of "analytical" nitrous acid is present as molecular nitrous acid.

Apart from associated condensation equilibria such as:

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

$$2NO^+ + H_2O \rightleftharpoons N_2O_3 + 2H^+$$

it is difficult to think of suitable equilibria employing only simple N(III) species; and the question arises as to whether other oxidation states or (say) chlorine substituted species are involved.

Under some conditions (e.g. presence of large quantities of NO_3^-), it may be that the following equilibria are relevant:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$N_2O_3 \rightleftharpoons NO + NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4$$

The existence of these reactions does not detract from the conclusion that N(III) in moderately concentrated aqueous acid solution is present mainly as HNO_2 - a point substantiated by the great similarity of the u.v. spectra (due to molecular HNO_2) in the region of 28000 cm^{-1} observed in 4M H_2SO_4, 4M $HClO_4$, 0.05 - 4 M HNO_3 and 0.05 M HCl, all with max $\varepsilon \approx 60$.

Under the present conditions NO is free to escape or react in other ways so that two limiting conditions need to be recognised, (a) no other removal of NO, (b) complete loss of NO.

From:

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \rightleftharpoons NO + \tfrac{1}{2}N_2O_4 + H_2O$$

$$[NO_2] \propto \frac{[HNO_2]^2}{[NO]} \qquad \text{and } [N_2O_4] \propto [NO_2]^2$$

so that if a definite amount of NO remains, a reaction whose rate depended upon $[NO_2]$ or $[N_2O_4]$ would have an order of over 1 in HNO_2, and since this the major N(III) species, an order of over 1 in N(III). This remains true unless e.g. in the presence of much HNO_3 a further overall reaction:

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O$$

effectively converts the "made up" N(III) into N_2O_4 so that the latter's minor depolymerisation product, NO_2 can, as a reactant, imply a first order process with respect to NO_2, hence an 0.5 order process with respect to N_2O_4 and hence to N(III).

The discussion shows that although something equivalent to:

$$2N(III) \rightleftharpoons (N(III))_2$$

is required, the identification cannot be done with any degree of certainty.

If:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

with HNO_2 being involved in furthering the reaction with iodate is the explanation, then (apart from the hydrogen concerned in producing HNO_2, which has already been taken account of) the N(III) argument does not include any aspect of the order with respect to protons.

However, if some reaction such as:

$$HNO_2 + H_2NO_2^+ \rightleftharpoons HNO_2O_3^+ + H_2O$$

provides the small concentration of "monomeric" N(III), then this carries some implication of order with respect to H^+, to which may be added the complication that either HNO_2 or $H_2NO_2^+$ might be the N(III) species going on to be oxidised.

Thus if:

$$[HN_2O_3^+] \approx \text{total } [N(III)]$$

$$[HNO_2] = a_1 \left(\frac{[N(III)]}{[H^+]}\right)^{\frac{1}{2}}$$

whence, remembering

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+$$

$$[H_2NO_2^+] = a_2 ([N(III)][H^+])^{\frac{1}{2}}$$

Each combination of N(III) equilibria carries its own hydrogen ion dependence for the rate.

Coming to the observed variation of rate with $[H^+]$, the apparent order with respect to $[H^+]$ is about 1.7. However, in the region of hydrogen ion molarity about 2, the proton transfer power of the medium is not accurately measured by $[H^+]$. This arises because of the protons are not in the state of dilution which could allow them unrestricted powers of attracting and orienting solvent molecules. As $[H^+]$ rises there is increasing competition amongst the protons for solvation sheaths and (neglecting any similar effect from the anions) the protons are effectively squeezed into being more available.

It is well known that acidity functions such as H_o have been devised to give better measures of the proton-donating power of the medium than the nominal $[H^+]$; and that in strongly acid conditions rates of reactions involving hydrogen ion are often simpler functions of h_o than of $[H^+]$(48).

In the present case rate is directly proportional to h_o and this seems unlikely to be coincidental, and can be interpreted to mean that 1 H^+ (in addition to that in HNO_2) is required to reach the configuration of the transition state.

Considering the variable order with respect to IO_3^-, let us call the nitrogen species going into the activated complex N, and the iodate species I, then, disregarding the Cl^-:

$$N + I \rightleftharpoons NI \xrightarrow{\text{rate det. step}}$$

$$[NI] = K[N][I]$$

where [N] and [I] here refer to the concentrations (or better activities) in equilibrium with the activated complex. Under many circumstances the concentration of NI is thought to be low relative to [N] and [I] so that, in considering setting up the equilibrium at the start of the reaction, there is normally no need to take notice of any depletion from initial concentrations of N and I (say $[N]_o$ and $[I]_o$); and [N] can be regarded as $[N]_o$ etc., in which case the rate, which is proportional to [NI] and therefore to [N][I] will appear to be proportional to $[N]_o[I]_o$ - obvious first order behaviour in each reagent.

But if, as in the present case, $[I]_o \gg [N]_o$ and if K is large - not an impossible situation because we find a fair rate even though the product $[N]_o[I]_o$ is probably below 10^{-6} M^2 - then the situation is somewhat different.

Sample calculations make this more obvious.

Suppose we use mol l^{-1} units and K is 100. Then consider three mixtures:

	$10^2[I]_o$	$10^4[N]_o$	$10^4[NI]$calc.
(A)	1.0	1.0	0.50
(B)	1.0	0.5	0.25
(C)	2.0	1.0	0.67

The order with respect to N will be one under conditions where the order with respect to I is much lower than one (and this latter order will be variable). What has been assumed is that a significant fraction of N is present as the activated complex (which may still have to reorganise its energy to react), so that increase in [I] cannot bring about a proportionate increase in [NI].

(Note that the order with respect to N of unity will still imply an overall order with respect to total N(III) of 0.5 from earlier considerations).

In conclusion, the excess of iodate compared with the very small effective [N(III)] leads to the observation of a lower and slightly variable (in the correct sense) order, rather than the true order. Hence true order may well be one.

The pK for HIO_3 is about 0.8. It is a weaker acid than $HClO_3$ or $HBrO_3$ and hence an appreciable concentration of the molecular acid is present in the solution. This might be the source of the order with respect to $[H^+]$, but if the true order with respect to hydrogen ion is one, and the observed order with respect to I(V) is about 0.6, this seems to imply that the reactive I(V) species is IO_3^- and hence that $[H^+]$ reacts in some other way - e.g. by attacking an I-N complex.

The apparent high order of the reaction with respect to chloride introduces a number of possibilities.

It is obviously necessary to consider for example, whether nitrosyl chloride is involved in the mechanism. Bayliss and Watts(55) report that the spectra of HNO_2 in concentrated hydrochloric acid correspond to almost total conversion of N(III) into NOCl. All the nitrosyl halides are reactive though they are normally powerful oxidising agents. This later generalisation may merely reflect reactions which have been investigated, but if a real generalisation would be leading N(III) in the wrong direction as far as change of oxidation state is concerned. Further, treatment of NOCl with water is normally stated to give HNO_3, HNO_2, NO and HCl. It seems (a) that NOCl is not likely to form in appreciable amount in 2M HCl, (b) it is hard to see how this could lead to the observed order of reaction.

However, nitrous acid alone in HCl does not increase its rate of decomposition rapidly as $[Cl^-]$ is increased. This might lead one to decide that the Cl^- effect is more likely to be associated with IO_3^-.

Possible support for this contention comes from considering halate/halide reactions generally - the rates of these are often found to involve second order dependence of halide, first order dependence on halate and first or second order in hydrogen ion.

Remembering that the iodate/ nitrous acid reaction seems faster in HCl than in HNO_3, and that it gives different products from the reaction in H_2SO_4, it becomes attractive to consider whether the controlling feature is the reaction between IO_3^- and Cl^- at high acidity.

It has been reported(49) that this reaction is ninth order:

$$\text{Rate} = k[IO_3^-][Cl^-]^4[H^+]^4$$

The evidence is insufficient for deciding how the chloride is necessary for the above reaction. The kind of explanation favoured by Edwards:

$IO_3^- + H^+ \rightleftharpoons HIO_3$ (fast)

$HIO_3 + H^+ \rightleftharpoons H_2IO_3^+$ (fast)

$H_2IO_3^+ + X^- \rightleftharpoons XIO_2 + H_2O$ (fast)

$H^+ + X.IO_2 + N^- \rightleftharpoons NX + HIO_2$ (rate-determining I)

$HIO_2 + X^- \rightleftharpoons XIO + OH^-$ (fast)

$XIO + X^- \rightleftharpoons X_2 + OI^-$ (rate-determining II)

$OI^- + H^+ \rightleftharpoons HOI$ (fast)

$H^+ + HOI + X^- \rightleftharpoons IX + H_2O$ (fast)

(where X^- is a halide ion, and N^- is a nucleophilic ion), is not immediately applicable since it begins with a requirement for the formation of $H_2IO_3^+$ which subsequently loses water. The present kinetic analysis seems to require elimination of water from N(III) species and, in any case, the hydrogen ion dependence of the rate shows that there are not enough protonated species to allow the formation of both $H_2IO_3^+$ and HNO_2 before the transition state.

Although the experimental order (nine) and the mechanistic detail cannot now be accepted without question, the general features cannot be forgotten.

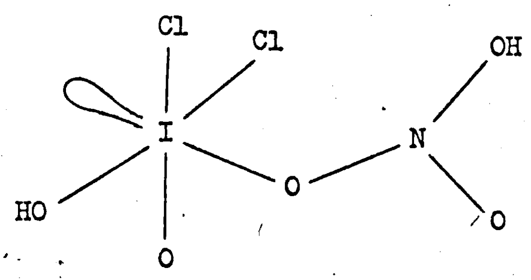
If chlorine were produced by such a reaction, then we have the statement by Vaksberg(50) that the oxidation of nitrite by chlorine is practically instantaneous at pH values below 6.

Further, other workers(16), state that iodate reacts with chloride to produce chlorine and iodine chlorides.

Now ICl is an observed product, but if it arose because of IO_3^- reacting with Cl^- then the yield of ICl would correspond to the IO_3^- put in and would probably be independent of the presence of HNO_2. This is contrary to our experimental findings, and further, on deliberately mixing just IO_3^- with 2 M HCl, the spectrum shows no absorption due to ICl in times far greater than used kinetically.

The comments upon order with respect to H^+, however, raise a point about that with respect to Cl^-. In 2M HCl the chloride ions, although less hydrated than the hydrogen ions, do have a degree of hydration and hence enter into competition for the solvent. As with H^+ this could therefore lead to a rapidly rising availability of Cl^- as concentration rises and hence to an apparent order in Cl^- higher than the true value. If this argument has substance the rate certainly depends upon $[Cl^-]$, but the number of chloride ions necessary to form the transition state might be 2 or 3.

An alternative idea on the use of Cl^- would be if the coordination number of the iodine needed to be expanded by the addition of Cl^- to produce the best transition complex, one of several possibilities being:



One of Edwards' arguments for assuming Cl^- catalysis to occur by stepwise reaction with a succession of intermediates is that several reactions between mixed oxidation states of the halogens show this particular kinetic feature, and the same kind of mechanistic explanation can be put forward for all. This analogy, however, is a somewhat restricted one. Reactions involving Tl(I), Sn(II) and Sb(III) centres are known where the order with respect to Cl^- is again high, see, for example, (reference 51 and 52). In these cases it seems very likely that multiple coordination of Cl^- to the reacting centre is involved. The same may well apply to the I(V) centre in the present reaction.

The many uncertainties in the foregoing section show that it is probably unprofitable to speculate upon the mechanistic details.

APPENDIX

Appendix

Methods of Calculation

pH Measurements and calculations of hydrogen ion concentrations

In kinetic experiments results are usually expressed initially in terms of concentrations of reactants. In this work the relevant measurement for hydrogen ion was pH.

pH measurements were carried out using a Pye Dynacap pH meter in conjunction with an Ingold glass and calomel electrode. The instrument was calibrated by means of 0.05M potassium hydrogen phthalate solution, and was checked at other points in the pH scale.

The interpretation of the pH scale has been discussed by Gold(38). The modern definition of pH is neither a theoretical concept nor a quantity which has a simple physical meaning. It is based on the experimentally measured difference of e.m.f.s of a cell containing a standard solution in one instance and the solution under test in the other. Since the residual liquid-junction potential is small, the difference in e.m.f. is assumed to be proportional to the difference between the logarithms of the hydrogen ion activities of the two solutions. Thus each pH value has been interpreted as:

$$\mathrm{pH} = -\log_{10}\left\{f^{\pm}_{(1:1)}[\mathrm{H}^+]\right\}$$

where $f^{\pm}_{(1:1)}$ is the mean activity coefficient for a typical 1:1 electrolyte.

It has been found(38) that, in the restricted range of dilute aqueous solutions, the logarithms of the mean activity coefficients of all 1:1 electrolytes can be represented by a modified expression derived by Debye and Hückel.

A limitation on the significance of pH arises from the residual liquid junction potential which will be more important the more dissimilar the standard and test solutions are. For dilute solutions in the pH range (3-9), the value of this term is very small and the resulting uncertainty in the meaning of pH does not exceed 0.01 unit. Outside this pH range the resulting error is significant. Therefore, at lower pH readings (1-2), a comparison of the pH value of the unknown solution with a standard solution of a similar pH value was also made.

As far as the calculation of $[H^+]$, from the pH is concerned:

$$[H^+] = \log_{10}^{-1} (0.51F_{(\mu)} - pH)$$

Calculation of ion pair concentrations

Negatively charged ion(s) and positively charged ion(s) may sometimes be held together by electrostatic forces in aqueous solution as an ion pair. The extent of ion-pair formation, in dilute aqueous solutions, depends on ionic charges, temperature and partly upon the specific ions concerned. As a result of ion pairing, true reactant concentrations may be much less than that put in. Even if an ion-paired reactant is equally as reactive as the free species, ion association must be considered when calculating the true ionic strength of the medium, and the charges on reacting species. It is expected that ion pairing would be low but perhaps not insignificant between alkali metal ions and univalent anions, and this is generally true.

It can be concluded that, in the present work, where the nominal reactants are salts of oxy-acids, the ion pairs which reach a significant concentration will be MXO_3 and MNO_2, where M^+ is Na^+ or K^+. In general,

$$L^- + M^+ \rightleftharpoons ML$$

where L^- is a univalent 'ligand'.

If x represents the concentration of ML at equilibrium, and a and b represent the respective initial concentrations of M^+ and L^-,

$$K = \frac{x}{(a-x)(b-x)}$$

where the equilibrium association constant K, for a real system at 25°C is given by:

$$\log K = \log K_o + 1.02\, Z_a Z_b .\, F_{(\mu)}$$

where $Z_a = +1$, $Z_b = -1$ and

$$F_{(\mu)} = \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.25\,\mu$$

Hence,

$$Kx^2 - (aK + bK + 1)\,x + Kab = 0$$

This quadratic equation may be solved for x (one of the routes being physically inadmissible) to give a definite value if K is known or can be estimated under the equilibrium conditions of ionic strength.

The association constants for potassium halates in aqueous solution at 25°C, corrected to zero ionic strength have been reported as(39):

$K^+ClO_3^-$: $K_o = 0.91$

$K^+BrO_3^-$: $K_o = 0.25$

$K^+IO_3^-$: $K_o = 0.56$

These are clearly not infinitesimally low.

The association constant for $Na^+NO_2^-$ is not reported in the literature, and the equilibrium constant of the nitrate at 25°C has been taken as the one for the nitrite ; $K_o = 0.63$(39). The justification for this last assumption rests on analogy. Firstly none of the four constants given here for 1:1 alkali-oxysalt pairs is very different from the others, and secondly the reported constants for KNO_3 and KNO_2 are very similar.

Calculation of nitrous acid concentration

In the real system N(III) is mainly present as NO_2^- + HNO_2. These two species are in very rapidly established protonation equilibrium

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

for which the equilibrium constant is known as a function of ionic strength(23,24).

$$K_o = \frac{[H^+][NO_2^-]}{[HNO_2]} \qquad \frac{f_{H^+} . f_{NO_2^-}}{f_{HNO_2}}$$

On setting the activity coefficients of non-ionic species equal to unity, the ionisation constant for the nitrous acid can be derived as outlined in the introduction (page 13).

Hence:

$$K_\mu = \frac{[H^+]\ ([N(III)] - [HNO_2])}{[HNO_2]}$$

$$[HNO_2] = \frac{[H^+][N(III)]}{[H^+] + K_\mu}$$

BIBLIOGRAPHY

1 Feit, W., and Kubierschky, K., Chem. Ztg., 1891, 15, 351

2 Schwicker, A. Chem. Ztg., 1891, 15, 845

3 Scholtz, M., Chem. Ztg., 1905, 11, 570

4 Busvold, N., Chem. Ztg., 1914, 38, 28

5(a) Kurtenacker, A., Monatsh, 1914, 35, 407

(b) Kurtenacker, A. Monatsh., 1914, 35, 925

(c) Kurtenacker, A., Monatsh., 1920, 41, 91

6 Lowe, W.G., and Brown, D.J., Z. Anorg. Chem., 1934, 221, 173

7 Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume VIII, Supplement II, Nitrogen (Part II), London, 1967, Longmans

8 Turney, T.A., and Wright, G.A. Chem. Rev., 1959, 59, 497

9 Waldorf, D.M. and Babb, A.L. J. Chem. Phys., 1964, 40, 1165;
Wayne, L.G., and Yost, D.M., J. Chem. Phys., 1951, 19, 41

10 Pascal, P., Rev. Gen. Sci., 1923, 34, 388 (C.A. 17, 3447)

11(a) Jones, L.H., Badger, R.M. and Moore, G.E., J. Chem. Phys., 1951, 19, 1599

(b) D'Or, L., and Tarte, P., J. Chem. Phys., 1951, 19, 1064

(c) McGraw, G.E., Bernitt, D.L. and Hisatsune, I.C., J. Chem. Phys., 1966, 45, 1392

12(a) Porter, G., J. Chem. Phys., 1951, 19, 1278

(b) Singer, K., and Vamplew, P.A., J.C.S., 1956, 3971

13 Palm, A., J. Chem. Phys., 1957, 26, 855

14 Cox, A.P. and Kuczkowski, R.L., J. Amer. Chem. Soc., 1966, 88, 5071

15(a) Cox, A.P., Brittain, A.H., and Finnigan, D.J., Trans. Faraday Soc., 1969, 65, 1963

(b) Cox, A.P. Brittain, A.H., and Finnigan, D.J., ibid., 1971, 67, 2179

(c) Cox, A.P., Brittain, A.H., Finnigan, D.J., and Smith, J.G., J.C.S., Faraday Trans. II, 1972, 68, 548

16 Comprehensive Inorganic Chemistry, Bailar Jr., and others, Pergamon, 1973, Volume 2

17 Altshuller, A.P., J. Phys. Chem., 1957, 61, 251

18 Abel, E., and Schmid, H., Z. Phys. Chem., 1928, 136, 430

19 Abel, E, Schmid, H., and Romer, E., Z. Phys. Chem. 1930, A, 148, 337

20 Sanderson, R., Chemical Bonds and Bond Energy, Academic Press, New York, 1971, page 81

21 Latimer, W., The Oxidation States of the Elements and their Potentials in Aqueous Solutions, Prentice-Hall, Inc., N.J., 1961

22 Bunton, C., Llewellyn, D., and Stedman, G., Chem. Soc. Special Publication, 1957, No.10, page 113

23 Lumme, P., and Tummavuori, J. Acta, Chem., Scand. 1965, 19(3), 617

24 Lumme, P., and Tummavuori, J., ibid., 1968, 22(6), 2003

25 Johnson, G.K., Smith, P.N., Appelman, E.H., and Hubbard, W.N., Inorg. Chem., 1970, 9, 119

26 Chaffee, E., and Edwards, J.O., Progress in Inorganic Chemistry, Volume 13, Interscience, 1970, page 217

27 Gyani, B.P. and Prasad, R.K., J. Indian C.S., 1964, 41(6), 449

28 Higginson, W.C.E., and Marshall, J.W., J.C.S., 1957, 447

29 Edwards, J.O. Chem., Rev., 1952, 50, 455

30 Turney, T.A., and Wright, C.A., J.C.S., 1958, 2415

31 Turney, T.A., J.C.S., 1960, 4263

32 Schmid, H., and Krenmayr, P., Monatsh., 1967, 98(2), 417, 430

33 Turney, T.A. Oxidation Mechanisms, Butterworths, London, 1965

34 Bonnett, R., Holleyhead, R., Johnson, B.L. and Randall, E.W., Queen Mary College, unpublished work.

35 Kolthoff, I.M., and Elving, P.J., Treatise on Analytical Chemistry, Interscience, 1961, Part II, Volume 5, 275

36(a) Shinn, M.B., Ind. Eng. Chem., (Anal. Ed.)., 1941, 13, 33

(b) Kershaw, N.F., and Chamberlin, N.S., Ind. Eng. Chem., 1942, 14(4), 312

37 Furman, N.H., Scott's Standard Methods of Chemical Analysis, Sixth Edition, Volume I, Van Nostrand Co., 1962, p.746

38 Gold, V., pH Measurements, Methuen, London, 1956

39 Stability Constants, Special Publication, No. 17, The Chemical Society, London 1964

40 Bodenstein, M., Z. Phys. Chem., 1922, 100, 68, (C.A. 16, 1896)

41 Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Supplement II, (Part I), London, 1956, Longmans

42 Vogel, A.I., A Text Book of Quantitative Inorganic Analysis, 3rd Edition, Longmans, 1961

43 Davies, C.W., Ion Association, Butterworths, London, 1962

44 Shilov, E.A., J. Appl. Chem., (U.S.S.R.). 1944, 17, 354, (C.A. 39, 2705)

45 Paul, M.A., and Long, F.A., Chem. Rev., 1957, 57, 1

46 Bunton, C.A., and Stedman, G., J.C.S., 1958, 2440

47 Longstaff, J.V.L., and Singer, K., J.C.S., 1954, 2604

48 Howlett, K.E., Sci. Progr., 1965, 53, 297

49 Hirade, J., Bull.Chem. Soc., Japan, 1935, 10, 97 (C.A. 29, 5001)

50 Vaksberg, N.M., J. Appl. Chem. (U.S.S.R.), 1940, 13, 1504 (C.A. 35, 3919)

51 Bonner, N.A., J. Amer. Chem. Soc., 1949, 71, 3909

52 Amphlett, C.E., Quart, Rev., 1954, 8, 219

53 Dodgen, H., and Taube, H., J.A.C.S., 1949, 71, 3330

54 Halperin, J., and Taube, H., J.A.C.S., 1950, 72, 3319

55 Bayliss, N.S., and Watts, D.W., Australian J. Chem., 1956, 9, 319 (C.A. 50, 16380)