A MECHANISTIC STUDY
OF SOME REDOX REACTIONS
OF NITROGEN(III)

By

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To NADIA, my wife

whose faith and inspiration
made this work possible,

and

to my children.

Abstract

Oxidation of nitrogen(III) by chlorite, periodate and chlorate is reported in this work.

The introduction reviews the reported, assumed and proposed reactivities of non-metallic oxyanions in aqueous acid solutions in general and the reactants studied in the present investigation in particular.

Mechanistic studies of the reactions, N(III)/Cl(III) and N(III)/I(VII) are reported for the first time.

Nitrite and chlorite react under mildly acid conditions ($pH \sim 4$) in the molar ratio of 2:1. The rate equation is represented by,

$$\text{Rate} = [NO_2^-]^{1.5}[ClO_2^-]^{0.5}[H^+]^{1.5}(k + k'[Cl^-])$$

The reaction between nitrite and periodate has been studied in aqueous hydrochloric acid solution ($pH \sim 0$). Its rate equation is represented by,

$$\text{Rate} = k[HNO_2]^{0.5}[H_5IO_6][H^+][Cl^-][Br^-]$$

The rate of reaction is particularly catalysed by traces of Br^-. This observation may nominate the reaction as the simplest method that may be used for the quantitative estimation of traces of Br^- present in chlorides.

In a rather differently oriented study, the reaction between N(III)/Cl(V) has been studied in water/dioxan solutions. The specific rate constant for the reaction increases as the dielectric constant of the medium decreases, a result which agrees with the mechanism suggested by other workers. The ionization constants of nitrous acid in similar water-dioxan mixtures are also reported.

Acknowledgements

It is my pleasure to take this opportunity of thanking all the members of the Department of Chemistry who by their help and friendship made the conditions in which this research was done so pleasant. It is not easy to select particular people, but the following deserve special attention.

Dr. K. E. Howlett, my supervisor, for his unfailing help and patience and the way in which he taught, by example as well as by discussion, the research method.

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Contents

Page No.

List of Tables

1. Introduction

Redox Reactions of Oxyacids

The non-metallic oxyanions have been the subject of several review articles.

Abel(1) has reviewed some of the oxyacid redox reactions in aqueous solutions. He concluded that, when such oxyacids are reduced or oxidized, the overall change of valency is not accompanied by a change in charge, and electrons do not appear to take any part. The overall result is simply a loss or addition of oxygen atoms which turn into oxygen ions or come from oxygen ions. However, there does not seem to be any doubt that this is not the normal, actual path of the reaction.

Abel continues his discussion of the actual path of the reaction and concludes that for oxyanion reduction, acceptance of an electron by the anion of the oxyacid seems to be out of the question. So there must be a cation present whose charge is decreased by electron transfer. This cation can only be the result of an extremely slight dissociation of the oxyacid anion according to

$$XO_m^{n-} \rightleftharpoons XO_{m-p}^{2p-n} + {}_pO^{2-} \; ; \; 2p > n$$

and Abel illustrates this assumption with a mechanism of the reaction between hydrogen peroxide and iodous acid anion for which m = 2, n = 1 and the simplest case of p = 1, so that for the reduction of IO_2^- by H_2O_2 the equilibrium

$$IO_2^- \rightleftharpoons IO^+ + O^{2-}$$

is established, followed by the bimolecular rate determining step involving electron transfer

$$IO^+ + HO_2^- \xrightarrow{r.d.s.} I + HO_2 \longrightarrow I^- + H^+ + O_2$$

$$(HO_2^- \text{ is formed by } H_2O_2 \rightleftharpoons HO_2^- + H^+)$$

then,

$$IO^- \rightleftharpoons I^+ + O^{2-}$$

$$I^+ + HO_2^- \longrightarrow I + HO_2 \longrightarrow I^- + H^+ + O_2$$

The overall reaction is

$$IO_2^- + 2H_2O_2 \longrightarrow I^- + 2H_2O + 2O_2$$

For the oxidation of IO_2^- by H_2O_2, the rate determining step might involve electron transfer

$$IO_2^- + H_2O_2 \xrightarrow{r.d.s.} IO_2 + OH^- + OH \longrightarrow IO_2^+ + 2OH$$

followed by the reversible step

$$IO_2^+ + O_2^- \rightleftharpoons IO_3^-$$

the overall reaction is after adding $2H^+$ on both sides

$$IO_2^- + H_2O_2 \longrightarrow IO_3^- + H_2O$$

Thus, Abel suggests that oxyacids show some basic character (i.e. oxyacids are amphoteric).

The amphoteric character of HNO_2 could be represented by

$$NO^+ + OH^- \rightleftharpoons HNO_2 \rightleftharpoons H^+ + NO_2^-$$

Kinetic evidence for the production of NO^+ and OH^- has been reported by Franck and Spence$^{(2)}$.

Abel$^{(1)}$ has also discussed the function of hydrogen ions in the reactions of oxyacids and commented that, the function of hydrogen ions that appear in the rate expression of redox reactions of oxyacids, (and which might be taken to imply the polymolecularity of the reaction) is not one of appearing as distinct species in the rate determining step, they are only involved in the equilibrium

$$XO_m^{n-} + 2pH^+ \rightleftharpoons XO_{m-p}^{2p-n} + {}_pH_2O \;;\; 2p > n$$

which means that polymolecularity turns into bimolecularity. One of the examples he gives is the reaction between nitrous acid and Fe(II)aq.

$$\text{Rate} = k[Fe^{2+}][HNO_2][H^+]$$

for which his postulated rate determining step is

$$Fe^{2+} + NO^+ \longrightarrow Fe^{3+} + NO$$

hence,

$$\text{Rate} = k'[Fe^{2+}][NO^+]$$

where $[NO^+] \alpha [HNO_2][H^+]$.

Thus, the third order reaction which might have been trimolecular in fact involves only bimolecular steps.

Abel's arguments are perhaps somewhat old-fashioned. and the concept of rather unreactive O^{2-} ions present in aqueous solution conflicts with more modern evidence on the likelihood of the hydrolysis

$$O^{2-} + H_2O \longrightarrow 2OH^-$$

Much of the detail in Abel's review must therefore be discounted, but his analysis makes several useful points.

The redox reactions of oxyacids are also discussed by Edwards(3,4) who interprets these reactions in terms of acid-base concepts. The role of hydrogen ions is postulated by Edwards, to convert the oxyanion to less stable forms (becoming an electron acceptor, i.e. acids of the Lewis kind) which can then react with other chemical entities (bases of the Lewis kind).

Edwards formulated three general types of rate laws and their corresponding mechanisms to describe the features of the redox reactions of oxyacids.

In the first type, for an oxyanion whose charge is (n-), the catalysis by hydrogen ion is of n th order and the rate law would be

$$\text{Rate} = k_1[XO_m^{n-}][B^x][H^+]^n$$

where XO_m^{n-} refers to the oxyanion and B^x is the electron donor. A possible mechanism for such reactions would be,

$$XO_m^{n-} + nH^+ \rightleftharpoons H_nXO_m \qquad \text{(fast)}$$

$$H_nXO_m \rightleftharpoons XO_{m-1}H_{n-2} + H_2O \qquad \text{(fast)}$$

$$XO_{m-1}H_{n-2} + B^x \longrightarrow BXO_{m-1}H^x_{n-2} \qquad \text{(rate determining)}$$

$$BXO_{m-1}H^x_{n-2} \longrightarrow \text{Products} \qquad \text{(fast)}$$

In the second type distinguished by Edwards, $(n+1)H^+$ terms appear in the rate equation for reaction of an XO_m^{n-} species. For example taking the commom case of n=1

$$R = k_2[XO_m^-][B^x][H^+]^2$$

and this would be understood in terms of the following mechanism:-

$$XO_m^- + H^+ \rightleftharpoons HXO_m \qquad \text{(fast)}$$

$$HXO_m + H^+ \rightleftharpoons H_2XO_m^+ \qquad \text{(fast)}$$

$$H_2XO_m^+ + B^x \longrightarrow BXO_{m-1}^{x+1} + H_2O \qquad \text{(rate determining)}$$

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

The third general type of rate law is

$$\text{Rate} = k_3[XO_m^{n-}][B^x][H^+]^{n+1}[N^-]$$

in which N^- is a nucleophilic ion or particle. The rate determining step after the pre-equilibria given in the second type is given by

$$BH_{n-2}XO_{m-1}^{x+1} + N^- \longrightarrow NB^{x+1} + XO_{m-1}H_{n-2}^-$$

Elimination of water is involved in the three types of mechanisms given by Edwards. However, Chaffe and Edwards$^{(4)}$ stated that, it is difficult to postulate any reasonable mechanism that does not involve replacement in the oxyanion coordination sphere as an essential part. They are presumably referring to substitution by B^x (thereby taking up some empty coordination sites vacated by the elements of water) in the rate determining steps of the first two mechanisms, and in a pre-equilibrium step in the third type.

Two of Edwards' examples consider HNO_2 as the oxyanion reacting with the 'electron donors' ClO_3^-. However, Abdul-Jawad$^{(5)}$ has criticized the formulation postulated by Edwards for the reaction between HNO_2 and ClO_3^-.

The redox reactions of N(III) have been the subject of a review article by Beck et. al.$^{(6)}$. A table that lists most of the redox reactions of the oxyanion NO_2^- and the oxyacid HNO_2 that are reported up to the end of 1973 is given.

The reactions of N(III) show that$^{(6)}$, the order of reaction in the second reactant may be zero, between zero and one, or one. Beck et. al. have given a general scheme to explain the three types of reactions in which the first step is a reversible interaction between nitrite ion (nitrous acid) and another reactant, X leading to the formation of a more reactive species which is then oxidized or reduced by a reagent, R

$$N(III) + X \underset{k-1}{\overset{k_1}{\rightleftharpoons}} N(III)Z + Y$$

$$N(III)Z + R \xrightarrow{k_2} \text{Products}$$

Based on the stationary state of N(III)Z, the general rate would be given by the equation,

$$\text{Rate} = \frac{k\,[N(III)][X][R]}{k-1[Y] + k_2[R]}$$

and depending on the relative value of the two terms in the denominator, the order of reaction in the other reagent (whether oxidizing or reducing) will be

zero if $k_2[R] \gg k-1[Y]$

one if $k_2[R] \ll k-1[Y]$

zero to one if the two terms are comparable.

The reactivities of N(III) species have been considered by several authors.

The 'standard reduction potentials' of N(III) in aqueous acidic and basic solutions are described$^{(7)}$ by the following equations:-

In basic media,

	$E^\ominus$(298 K)
$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^-$	0.01 V
$NO_2^- + H_2O + e^- = NO + 2OH^-$	-0.46 V
$2NO_2^- + 3H_2O + 4e^- + N_2O + 6OH^-$	0.15 V

In acidic media,

$2HNO_2 + 4H^+ + 4e^- = N_2O + 3H_2O$	1.29 V
$HNO_2 + H^+ + e^- = NO + H_2O$	0.99 V
$NO_3^- + 3H^+ + e^- = HNO_2 + H_2O$	0.94 V

Being a monobasic acid, nitrous acid, $\mathrm{H} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}} - \overset{\cdot\cdot}{\mathrm{N}} = \overset{\cdot\cdot}{\mathrm{O}}:$ shows amphoteric possibilities; as indicated, the unshared pair electron on nitrogen imparts basic and reducing properties to the acid, whereas the N = O double bond imparts acidic and oxidizing properties to the acid(8).

Nitrogen(III) lies in the middle of a range of oxidation states (3- to 5+) which exist for nitrogen. N(III) may act as an oxidizing agent with the formation of N(I) or N(II), or may act as a reducing agent with the formation of N(V) as a stable product.

The relevant equilibria known or believed to exist in aqueous solutions of N(III) are(9a)

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$HNO_2 + H_3O^+ \rightleftharpoons H_2NO_2^+ + H_2O$$

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

$$NO^+ + NO_2 \rightleftharpoons N_2O_3^+$$

$$N_2O_3 \rightleftharpoons NO + NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4$$

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

and when the acid is nitric acid, the following additional equilibria may be assumed(9b)

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

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

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

Furthermore, compounds of the type NOX (X being Cl, Br, NO_3, HSO_4, OAc etc.,) are formed by the reaction,

$$HONO + H^+ + X^- \longrightarrow NOX + H_2O$$

The extent to which these NOX compounds may be formed in dilute aqueous solutions is open to wide variations of interpretation. Some authors, see later, assume their ready formation and use in main reaction sequences at pH 3, but since the species like NOCl are known to react rapidly with water this must be open to question.

It is common knowledge that in basic media N(III) is much more stable than in acidic media, i.e. NO_2^- is less reactive than protonated forms. It is suggested(5) that the stability of nitrite is reduced in acid solution because the proton tends to destroy the symmetry of the ion, and this appears to be a kinetic effect as far as the N(III) - N(V) change is concerned. The polarizing power of the proton is further confirmed by the oxygen exchange between water and nitrous acid, which is much faster than that between water and NO_2^-(10).

Anbar and Taube(11) have formulated the rate law,

$$\text{Rate} = k[NO_2^-][H^+]^2$$

for the exchange of oxygen between N(III) and water in the pH range 4 - 6. At $I = 1.0$ mol dm^{-3} and 25°C, $k = 2.6 \times 10^8$ dm^6 mol^{-2} min^{-1}. They found that the rate is unaffected by phosphate and acetate buffers at concentrations up to 0.1 mol dm^{-3}, but that at higher phosphate buffer concentrations catalysis was observed. They also concluded that Br^- at 0.2 mol dm^{-3} does not catalyse the exchange reaction. They then formulated the following reaction as a rate determining step,

$$H_2NO_2^+ \longrightarrow NO^+ + H_2O$$

but they said that "it must be admitted that isomeric change in $H_2NO_2^+$ fits the data equally well".

One might comment that the assumption of a kinetically significant concentration of $H_2NO_2^+$ at pH 5 - 6 perhaps needs some justification. Crudely, taking pK_2 for $H_2NO_2^+$ as 3 at the experimental ionic strength, $[HNO_2]/[NO_2^-] \approx 10^{-2}$, and if pK_1 were -2, then $[H_2NO_2^+]/[HNO_2] \approx 10^{-7}$, whence $[H_2NO_2^+]$ might be 10^{-9} [total N(III)] at pH 5. Such a concentration would probably require a diffusion controlled rate of a bimolecular step to account for an observable reaction rate.

Bunton et. al.(12a, b, c, d) have extensively studied the oxygen exchange reaction between nitrous acid and water. They postulated two paths through which nitrous acid and water can exchange oxygen atoms in solution, these paths are:-

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

followed by

$$(1) \quad H_2NO_2^+ + H_2O^{18} \rightleftharpoons H_2N\overset{+}{O}O^{18} + H_2O$$

$$(2) \quad H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

Bunton et. al. compared the rate constants for oxygen exchange and diazotization reactions. Although these constants were obtained from experiments under very different concentration of reagents, the agreement between them is good:

$$k_{ex} = 31.2 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

$$k_c = 40 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

at 0°C.

They criticized the postulated mechanism in which NO^+ is formed(11,13) when nitrous acid reacts with H_2O_2 under conditions similar to those under which the exchange reaction is studied in phosphate buffer, commenting that it is equally probable that the reactive intermediate is nitrosylphosphate which then reacts with H_2O_2. At low pH the phosphate anion $H_2PO_4^-$ is the ionic dominant species, so that

$$H_2NO_2^+ + H_2PO_4^- \rightleftharpoons NOH_2PO_4 + H_2O \xrightarrow[\text{(fast)}]{H_2O_2} \text{Products}$$

The effect of added anions (X^-) on the rate of exchange is interpreted(12) as being due to (a), anions possibly having a primary or secondary salt effect, or (b), the fact that they may provide a new path for oxygen exchange such as:-

$$H_2NO_2^+ + X^- \rightleftharpoons NOX + H_2O$$

and added ClO_4^-, NO_3^-, Br^-, Cl^- and CNS^- do increase the rate of exchange. These effects depend upon the nature and concentration of the added salt. The sequence of catalysis is $Br^- > CNS^- \approx Cl^- > ClO_4^- > NO_3^-$. The second mode must play a part whenever the bulk reactivity of the added anions towards nitrous acidium ion is comparable with that of the nitrite ion. So that, in solutions of nitrous acid buffered with phosphate and carboxylate ions, attack of these nucleophilic anions may swamp the uncatalysed attack of NO_2^-, the rate of exchange will be of first order with respect to nitrous acid, and will depend on the nature and concentration of the buffer. Although, with acetate buffer, the rate law is given as:-

$$\text{Rate} = k[HNO_2][OAc^-][H^+]$$

with phosphate buffer, the reaction is however, complicated by the coexistence of mono- and di-basic anions which will have different reactivities towards the nitrous acidium ion.

The equilibrium

$$HONO + H^+ \rightleftharpoons NO^+ + H_2O$$

in aqueous acid solutions has been studied extensively(14,15,16).

The correllation of the spectrophotometrically calculated values for the concentration of NO^+ and HNO_2 with the acidity function Jo, reported by Singer and Vamplew(14) and Turney and Wright(15) is criticized on the basis that this function is inadequate in dealing with small molecules and ions such as HONO and NO^+ (16).

Contrary to their previously reported results, Bayliss et. al.(16), have reported in their latest spectrophotometric study of the spectra of $NaNO_2$ in aqueous solutions of sulphuric and perchloric acids, over the acid concentrations 0 - 100% H_2SO_4 (by wt.) and 0 - 72% $HClO_4$ (by wt.) that the nitrous acidium ion ($H_2NO_2^+$), does not exist in spectrophotometrically determinable amounts. The values they give for the above equilibrium constant at various temperatures in the two acidic media are:

In aq. H_2SO_4		In aq. $HClO_4$	
t°C	K_1	t°C	K_1
4.5	2.6×10^{-5}	3.5	8.7×10^{-7}
19.5	1.7×10^{-5}	15	7.6×10^{-7}

Of course nitrous acid has been of great interest to organic chemists and much information about systems containing HNO_2 is derived from, for example, nitrosation work. The actual or possible carriers in nitrosation, arranged in order of decreasing electrophilic reactivity of the carrier(17) are deduced to be

NO^+, $H_2NO_2^+$, NOX, $NONO_3$, $NONO_2$, NOOAc and HNO_2

(X = halide)

Despite the claimed lack of experimental evidence for the existence of $H_2NO_2^+$ in aqueous acid solutions there seems strong evidence on kinetic grounds that the nitrosonium ion exists substantially in the form of $H_2NO_2^+$. A general rate law$^{(18)}$ for the reactions of nitrous acid,

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

suggests a mechanism:

$$HONO + H^+ \rightleftharpoons H_2NO_2^+$$

$$\text{substrate} + H_2NO_2^+ \rightleftharpoons \text{Products}$$

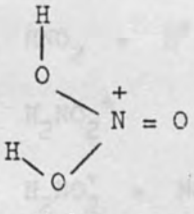
although not disproving the contention that it may virtually all be present as NO^+.

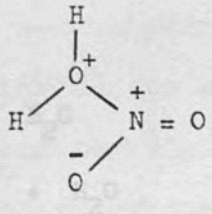
Morrison and Turney$^{(19)}$, suggested that in aqueous perchloric acid, nitrous acid in low concentration may be involved in two concurrent equilibria:

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

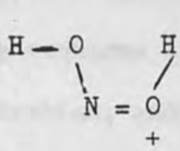
$$\text{and} \quad HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O$$

Lidstone$^{(20)}$ suggested that the nitrous acidium ion is more stable than nitric acidium ion because $H_2NO_2^+$ can exist in more canonical forms. He formulates the resonance structures for $H_2NO_3^+$ as

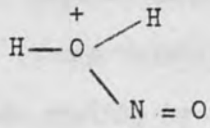

(a)


(b)

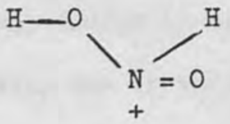
and for $H_2NO_2^+$



(c)



(d)



(e)

commenting that structures (a) and (b) are the only ones for the nitric acidium ion; structures (c) and (d) are the analogous structures for the nitrous acidium ion, and that the different behaviour of the nitrous acidium ion requires that it shall have as its thermodynamically most stable form, the non-analogous structure (e). If this is true, of course, the two hydrogen atoms of $H_2NO_2^+$ are non-equivalent and the estimated pK_1 for $H_2NO_2^+$ given earlier might be seriously in error.

Bunton et. al.(12b,21) have studied the spectra of nitrite in perchloric acid solution. Nitrogen trioxide (N_2O_3) is detected in solutions of nitrous acid (> 0.05 mol dm^{-3}) in perchloric acid (4 - 7 mol dm^{-3}). They concluded that the concentration of N_2O_3 should increase with increasing acidity and be proportional to $[\text{nitrite}]^2$ when $[HNO_2] \approx [\text{nitrite}]$. With further increase in perchloric acid concentration both molecular nitrous acid and dinitrogen trioxide are converted into the nitrosonium and possibly nitrous acidium ion by the reactions:

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

$$\text{and} \quad H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

$$\text{or} \quad H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

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

They also said that there is physical evidence for dinitrogen trioxide in a region where there is no kinetic evidence, and kinetic evidence for it in a region where there is no physical evidence. This is usually so for any reactive intermediate, because kinetic evidence for its existence usually requires it to be formed relatively slowly and/or to be in low concentration, and captured rapidly by a substrate, and in these low concentrations it cannot be detected by the comparatively insensitive physical methods.

The equilibrium constant

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

has been redetermined by Turney(22). Spectrophotometric and distribution methods were used, and the value of K_a is given as 0.2 ± 0.05 at 20°C.

In conclusion it is clear that not only is the actual situation of N(III) in acidic solution complicated, but so also is the interpretation of the evidence for the existence of different species, for the rates at which they are interconverted, and for the equilibrium constants governing the relative amounts of the species.

The Oxidation of Nitrogen(III) by Halogen Oxyanions

Determined rate laws for the redox reactions of the nitrite ion and nitrous acid with halogen oxyanions (XO_m^-) are listed in Table 1. $[H^+]$ always appears in these rate equations.

The table also includes the suggested nitrogen containing species involved in the rate determining step for each reaction.

A comparison of the kinetic parameters for the analogous reactions of hypochlorite and hypobromite(23,24), shows that the rate constants are generally larger, for hypochlorite reactions except for the reaction with nitrite.

The reactions between N(III) and halates (XO_3^-) have been recently studied$^{(5)}$. The kinetic stoichiometric and activation energy parameters for the reactions between N(III) and BrO_3^- and ClO_3^- are very similar (i.e. 3 moles of nitrite react with one mole of BrO_3^- and with one mole of ClO_3^- while E = 65 and 67 kJ mol^{-1} respectively. This does not necessarily mean that the reactions proceed through corresponding mechanisms. The effect of ionic strength (variation of ionic strength does not affect the rate of reaction between N(III) and BrO_3^- whereas it does affect the rate of reaction with ClO_3^-), points to some difference in reaction details. In the case of BrO_3^- being the oxidant,

$$BrO_3^- + HNO_2 + H^+ \rightleftharpoons BrNO_4 + H_2O \rightleftharpoons BrO_2^- + NO_2^+ \xrightarrow{r.d.s.} \text{Products}$$

is postulated and when ClO_3^- is the oxidant,

$$ClO_3^- + HNO_2 + H^+ \rightleftharpoons H_2ClNO_5 \xrightarrow{r.d.s.} \text{Products}$$

However, in the reactions listed in the table, the electron transfer is accomplished by the transfer of an oxygen atom,

$$NO_2^-\,(HNO_2) \xrightarrow{oxid.} NO_3^- + (H^+)$$

The reactions between N(III) and the oxidising agents ClO_2^- and IO_4^- are reported for the first time.

Periodate reactions in organic chemistry are well known$^{(26,27)}$. However, kinetic work on the oxidation by periodate of inorganic materials is still scanty.

Crouthamel et. al.$^{(28)}$ made an extensive study of the ultraviolet absorption spectra of aqueous periodate solutions, and they outlined important conclusions from the results they obtained. Periodic acid was designated as the hydrated species, H_5IO_6 because the ionization of three

Table 1

Reactions of N(III) with XO_m^-

Reactant (XO_m^-)	Rate laws	Important nitrogen containing species	Ref.
ClO^-	$k[HOCl][NO_2^-]$	NO_2^-	23
BrO^-	$\frac{k[BrO^-][NO_2^-]}{[OH^-]} + 3k'[BrO^-]^2$	NO_2^-	24
ClO_2^-	$k_1[NO_2^-]^{1.5}[ClO_2^-]^{0.5}[H^+]^{1.5}$ $+ k_2[NO_2^-]^{1.5}[ClO_2^-]^{0.5}[H^+]^{1.5}[Cl^-]$	$OONO^-$	XXX
ClO_3^-	$k[HNO_2][ClO_3^-][H^+]$	H_2NClO_5	XXX
	$(k_1 + k_2[H^+])[ClO_3^-][HNO_2]$	H_2NClO_5	5
	$k[HNO_2][ClO_3^-][H^+]$	NO^+	6
	$k[HNO_2][ClO_3^-][H^+]$	H_2NClO_5	5
BrO_3^-	$(k_1 + k_2[H^+]^2)[BrO_3^-]$	NO	5
	$k[HNO_2][BrO_3^-][H^+]$	NO^+	6
	$k[HNO_2][BrO_3^-][H^+]$	NO_2^+	5
IO_3^-	$(k_1 + k_2[IO^-][H^+][IO_3^-][HNO_2]$	?	25
	$k[HNO_2]^{0.5}[IO_3^-]^{0.6}[Cl^-]^3.h_o$	?	5
IO_4^-	$k[HNO_2]^{0.5}[H_5IO_6][Cl^-][Br^-][H^+]$	NOBr, ($H_2NO_2^+$, N_2O_3)	XXX

XXX Results of the present work.

hydrogen ions was observed. The species, H_5IO_6, $H_4IO_6^-$, IO_4^- and $H_3IO_6^{3-}$ and their inter-equilibria were adequate to explain completely the spectrophotometric and potentiometric data on periodate in the pH range 0 - 7 and the temperature range 0 - 70°C.

Based on the equilibria involved in aqueous acid solutions described by

$$H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^- \; ; \; K_1$$

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \; ; \; K_d$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{=} + H^+ \; ; \; K_2$$

the true and apparent constants at 25°C are given$^{(28)}$ as

$$K_1 = \frac{a_{H^+} \cdot a_{H_4IO_6^-}}{a_{H_5IO_6}} = 5.1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_2 = \frac{a_{H^+} \cdot a_{H_3IO_6^{=}}}{a_{H_4IO_6^-}} = 2.0 \times 10^{-7} \text{ mol dm}^{-3}$$

and

$$K_d = \frac{a_{IO_4^-} \cdot a^2_{H_2O}}{a_{H_4IO_6^-}} = 40$$

$$K_1{'} = \frac{a_{H^+}(a_{IO_4^-} + a_{H_4IO_6^-})}{a_{H_5IO_6}} = 2.3 \times 10^{-2} \text{ mol dm}^{-3}$$

$$K_2{'} = \frac{a_{H^+} \cdot a_{H_3IO_6^{=}}}{a_{IO_4^-} + a_{H_4IO_6^-}} = 4.35 \times 10^{-9} \text{ mol dm}^{-3}$$

The conclusion that IO_4^- is the major component in neutral aqueous solution is criticized by Symons et. al.$^{(29,30)}$ who reported that the hydrated ions such as $H_4IO_6^-$ or, possibly $H_2IO_5^-$ are more important than

IO_4^- and that no accurate pK value can be assigned to H_5IO_6, and in fact they suggested the region of +2 to +3 for the pK of the acid. However, later work$^{(31-34)}$ has supported the conclusion that IO_4^- is a major species in neutral aqueous solutions of periodate. The value of Kd is reported to be 28 $\pm$ 1 and the hydration/dehydration equlibrium represented by

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O$$

is not catalysed by hydrogen ion, and is among the most rapid reactions of its kind, where the rate constant for dehydration = $(5.6 \pm 0.6) \times 10^3\ sec^{-1}$, and the rate constant for hydration = $(1.9 \pm 0.2) \times 10^2\ sec^{-1}$ at 20° and ionic strength, 0.1 mol dm^{-3} in the pH range 3.4 - 5.0.

There is no evidence$^{(30)}$ for the formation of the cation IO_3^+ when I(VII) compounds are dissolved in concentrated sulphuric acid, but protonated periodic acid $H_6IO_6^+$ and iodine heptoxide, I_2O_7 are thought to be formed under some conditions.

It has also been reported that the cation IO_3^+ is excluded as a species derived from periodate$^{(35)}$.

The rate of oxygen exchange between periodate and water in non-buffered solutions is fast, which is probably due to the existence of a variety of polyhydrated and polymeric species in rapidly established equilibrium$^{(36)}$.

2. The Reaction Between N(III) and Cl(III)

2.1 The establishment of a method for following the reaction

Conventional chemical methods of analysis, besides being time consuming are not satisfactory for precise determinations at low levels of concentrations. For reacting systems, physical methods such as spectrophotometric methods can be more reliable than chemical methods.

A spectrophotometric method for following the rate at which nitrite is consumed in its reactions with halates which has successfully been used(5) is the Shinn method as modified by Kershaw and Chamberline(37). In this method an excess of 0.5% sulfanilamide in 1:1 HCl to diazotize the nitrite is added, followed by the addition of a suitable amount (again excess) of 0.1% N(-1-Naphthyl)-ethylenediamine dihydrochloride as a coupling agent forming an azo dye cation(38) for which the pink colour develops completely in 10 minutes and remains constant in intensity for about an hour.

The absorption peak of the dye is reported to be at

550 nm with molar absorption coefficient of 40000(38) $m^2\ mol^{-1}$

537.6 nm with molar absorption coefficient of 50000(5) $m^2\ mol^{-1}$

and 543 nm, reported by Bendschneider and Robinson(39) who ten years after Kershaw and Chamberline rediscovered the same method.

Accordingly, the wavelength at which the dye shows a maximum absorption has been reinvestigated. 2cm^3 samples taken from a solution of exactly known concentration (about 0.001 mol dm^{-3} $NaNO_2$ containing about trace of NaOH) were run into a 100 cm^3 volumetric flask containing 80 cm^3 water and 2 cm^3 of 0.5% sulfanilamide; 1 cm^3 of 0.1% of the coupling agent was added and the whole was made up to the mark. After 10 minutes, the absorbance of the dye was measured at the various wavelengths shown,

λ(nm) =	535	536	537	538	539	540	542	543
Absorbance =	1.001	1.002	1.004	1.006	1.004	1.004	1.002	1.000

Thus a standardized wavelength in the region 540-538 nm gives similar sensitivity. The wavelength 538 nm was chosen and used throughout the experimental work. This clearly agrees with λmax found earlier$^{(5)}$, and the technique provides a good method for the determination of nitrite alone in solution.

However, when the above method was used to follow the concentration of N(III) in its reaction with Cl(III), the [N(III)] determined in the reaction mixture after a reaction time of one minute had only about one third of the expected value. Thus a modification was sought, so that the method could be used under the reaction conditions. Presumably the rate of diazotization was unable to compete with the N(III)/Cl(III) reaction at this acidity.

Several experimental conditions were studied; e.g. variation of the ratio of HCl:H_2O in which the sulfanilamide is dissolved; variation of the concentration of the sulfanilamide, of the time intervals between addition of each reagent and of the order at which each reagent is added. The most satisfactory results are obtained using the following procedure:

(1) The sample containing N(III) (and Cl(III)) is added to 2 cm^3 of 1.5% sulfanilamide in 0.1 mol dm^{-3} HCl plus $\sim$ 80 cm^3 H_2O contained in 100 cm^3 volumetric flask.

(2) After 5 minutes, 2cm^3 of $\sim$ 3 mol dm^{-3} HCl are added to ensure completion of the diazotization reaction.

(3) The coupling agent is added 2 minutes after the additon of HCl. The pink colour develops in 10 minutes and is stable for about 60 minutes.

This method quenches the reaction however fast it is, because addition of the sample to be analysed to 80 cm^3 H_2O containing the sulfanilamide slows down the reaction due to dilution, and the unreacted nitrite is then consumed by the diazotization reaction which still takes place rapidly.

Results obtained using this method gave consistent kinetics throughout any one run.

The molar absorption coefficient varies slightly as the concentration of nitrite is varied. In a set of determinations solutions of nitrite were made as used in reaction mixtures and the absorbance of samples treated as just described was measured, the results are:

Table 2

10^6[$NaNO_2$] mol dm^{-3}	A	ε m^2 mol^{-1}
2.696	0.143	53040
4.282	0.226	52780
6.741	0.356	52810
7.213	0.380	52680
13.482	0.693	51400

The average molar absorption coefficient is 52540, but the table shows that for about 5-fold variations in [$NaNO_2$], the value of ε falls as [NO_2^-] rises and deviates by up to 2% from the average. Therefore, in the treatment of the kinetic results the molar absorption coefficient was calculated for each experiment from the results shown in Table 2.

2.2 General technique adopted

Preliminary investigations showed that the reaction between nitrite and chlorite does not proceed at pH 7. A measurable rate was obtained when the pH of the reaction mixture was reduced to about 4.5 at 25°C with $[NO_2^-] = 10^{-4}$ mol dm^{-3} = $[ClO_2^-]$. Solutions were buffered and the necessary amount of the buffer used to maintain near-constancy of pH was determined experimentally.

"Analar" grade chemicals were used when available without further purification. The sodium chlorite used was prepared from a "technical" grade product, containing about 80% $NaClO_2$. It was dissolved in warm, slightly basic aqueous media and crystallised by cooling. The crop of crystals was dried at 120°C for about 2 hours. It was analysed titrimetrically by the use of a standard sodium thiosulphate solution. The salt was found to be 97% pure in $NaClO_2$. Although somewhat unsatisfactory, large losses in the recrystallisation forced the acceptance of this material for the kinetic work. The impurities, likely to be Cl^- or ClO_3^- are far less reactive.

To each of the nitrite and chlorite solutions, prepared in 500 cm^3 volumetric flasks, a drop of $\sim$ 1 mol dm^{-3} NaOH was added so that the solutions were stabilized(40). No one solution was used for longer than a week, although slightly basic solutions of nitrite and chlorite are known to be stable for quite long periods of time.

To start a kinetic run, sodium nitrite and sodium chlorite solutions were measured into 250 cm^3 stoppered conical flasks (A) and (B) respectively, the buffer and any other solutions were measured into a third flask (C) by means of pipettes and the stoppered flasks were then deeply immersed into the thermostat maintained at (say) 25 ± 0.02°C and allowed to reach thermal equilibrium.

The contents of (B) were mixed with those of (A) by pouring (B) into (A), back into (B) then back again into (A). The reaction (and the clock) was started by pouring the contents of (C) into (A) then back to (C) and back again into (A), complete mixing being obtained, and all the reagents being definitely present in the reacting mixture at known concentrations.

At intervals of time, samples were withdrawn and analysed for N(III) as described on page 31 . The time for each analysis was taken as that when the pipette had about half emptied. A fast flowing pipette was used and subsidiary trials showed that it was convenient to start the pipette flow 4 seconds before the recorded time.

2.3 Preliminary experiments

Initially it was thought that since there is no mention in the literature of a mechanistic study of the reaction between N(III) and Cl(III), this might be due to unreported complexities and/or lack of repeatability. To test for this possibility twenty runs were carried out varying [$NaNO_2$], [$NaClO_2$] and [H^+] all at 25°C and an ionic strength of 0.015 mol dm^{-3}. The results are listed in Table 3 which shows the concentrations of reagents present, the calculated values for [HNO_2], the initial rate and the second order rate constant (calculated as indicated later) deduced for each experiment.

The fact that no reaction is observed at pH 7 implies that NO_2^- and ClO_2^- ions are not capable of reacting together. The acid dissociation constant of $HClO_2$ is more than a power of ten greater than that of HNO_2 (about 10^{-2} as against $10^{-3.3}$ mol dm^{-3}) so that at pH 4.5, HNO_2 is a more important species than $HClO_2$. Hence in a first consideration of the results possible involvement of $HClO_2$ is ignored.

Table 3

$[KHC_8H_4O_4] = 0.0143$ mol dm^{-3} I = 0.015 mol dm^{-3}

T = 25°C

$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$10^5[H^+]$ mol dm^{-3}	$10^5[HNO_2]$ mol dm^{-3}	10^6I.R. mol dm^{-3}min^{-1}	k dm^3 mol^{-1} s^{-1}
1.35	2.46	9.58	1.27	1.38	32.6
3.37	2.46	8.98	3.00	6.20	40.1
6.74	2.46	9.25	6.17	15.1	33.1
16.85	2.46	8.15	13.74	47.0	31.0
3.37	0.98	9.15	3.05	4.25	42.5
3.37	4.92	8.94	2.99	7.35	33.8
3.37	12.30	9.39	3.13	13.0	35.3
*4.61	3.11	8.43	3.80	10.4	42.0
*2.76	4.35	8.43	2.28	6.00	44.0
*6.45	1.86	8.43	5.32	14.0	44.1
1.35	2.46	4.43	0.62	0.64	44.5
3.37	2.46	4.19	1.46	1.94	37.0
6.74	2.46	4.18	2.92	4.90	33.0
1.32	2.50	17.43	2.10	3.70	40.5
3.30	2.50	17.43	5.23	15.0	41.8
6.59	2.50	17.43	10.46	38.9	38.3
3.30	1.00	17.43	5.23	10.0	44.1
3.30	5.00	17.43	5.23	18.5	36.5
3.37	0.98	4.38	1.52	1.50	42.6
3.37	4.92	4.30	1.50	2.88	37.2

* I = 0.019 mol dm^{-3}

For calculations of $[H^+]$, $[HNO_2]$ and initial rate (I.R.), see appendix.

A superficial examination of the initial rates in table 3 suggests an apparent order of 1 to 2 in nitrous acid, 0 to 1 in chlorite and 1 to 2 in H^+. For example, considering experiments at constant $[NaClO_2]$ and $[H^+]$, but varied $[HNO_2]$, we have:

$10^5[HNO_2]$ mol dm^{-3}	=	2.1	5.23	10.46
10^6 I.R. mol dm^{-3} min^{-1}	=	3.7	15.0	38.9
10 I.R./$[HNO_2]$ (min^{-1})	=	0.18	0.29	0.37

The ratio, I.R./$[HNO_2]$ would be constant if the reaction were of the first order in HNO_2 and rise proportional to $[HNO_2]$ if second order. The actual result could be understood in various ways:

(I) There might be a single term in the rate equation, i.e.

$$\text{Rate} = k[N(III)]^{1-2}\ [Cl(III)]^{0-1}\ [H^+]^{1-2} \qquad \ldots\ldots \quad (1)$$

and the H^+ involvement might arise only through pre-equilibrium with either N(III) or Cl(III) species, or through a more direct reactant role.

(II) There might be more than one term, e.g.

$$\text{Rate} = k'[N(III)]^2 + k''[N(III)][Cl(III)] \qquad \ldots\ldots \quad (2)$$

with H^+ possibly involved in either term.

As an example of a simple version of I, a rate equation of the form:

$$\text{Rate} = -d[N(III)]/dt = k[HNO_2]^{1.5}[ClO_2^-]^{0.5} \qquad \ldots\ldots \quad (3)$$

was tried and the values of k (table 3) calculated by this rate equation, show a moderate agreement for 10-fold variation in [N(III)] and [Cl(III)] and a 4-fold variation in $[H^+]$.

Perhaps, more important at this stage is the conclusion that there are no obvious complexities in the reaction that might hinder its study spectrophotometrically and the fact that runs are reproducible.

2.4 Effect of physical conditions

It has been found that the reaction between nitrite and chlorite can be studied spectrophotometrically, and the preliminary work showed reproducibility of the results. In order to test whether variation in ordinary physical conditions has any effect upon the rate of the reaction, the following experiments, all under the same chemical conditions were performed.

(a) Under normal laboratory conditions (in duplicate).

(b) The reaction flask was packed with short lengths of glass tubing, so that the area of glass surface exposed to the solution was trebled, the volume of solution being unaltered from (a).

(c) The reaction flask was wrapped in metal foil to exclude light.

(d) 1.43×10^{-3} mol dm^{-3} Na$_2$ EDTA was added to the reaction mixture.

The observations of change in absorbance with time are shown in table 4.

Table 4

$10^4[NaNO_2] = 6.509$ mol dm^{-3} $10^4[NaClO_2] = 2.460$ mol dm^{-3}

$10^2[KHC_8H_4O_4] = 1.43$ mol dm^{-3} T = 25°C

t(min)	Absorbance (A) (a)	(b)	(c)	(d)
0	0.661	0.661	0.661	0.661
1	0.645	0.644	0.645	0.642
4	0.586	0.584	0.590	0.590
8	0.522	0.523	0.522	0.534
12	0.474	0.473	0.475	0.487
16	0.432	0.433	0.433	0.440

The results are in good agreement with one another, although the addition of EDTA does seem to produce a small effect. This point was confirmed by several experiments and it was always shown that EDTA produces a slight retardation of the reaction. Although this effect is hardly significant, all the experiments described in this part of the work were carried out in the presence of EDTA(0.00143 mol dm^{-3}), unless otherwise stated; it is being assumed that the rate in the presence of a low concentration of EDTA is really that uncatalysed reaction between N(III) and Cl(III).

2.5 Effect of reaction products on the rate of reaction

For this purpose, two kinetic runs, (a) and (b) were done, starting with the same initial nitrite, chlorite and buffer concentrations, but in experiment (b), 5 x 10^{-4} mol dm^{-3} of KCl and of KNO_3 were added to the reaction mixture. The results of those experiments are given below:

Table 5

$10^4[NaNO_2] = 4.797$ mol dm^{-3} $10^4[NaClO_2] = 2.137$ mol dm^{-3}

$10^2[KHC_8H_4O_4] = 1.43$ mol dm^{-3} $T = 25^\circ C$

t(min)	Absorbance (a)	Absorbance (b)
0	0.504	0.504
1	0.500	0.500
6	0.477	0.479
12	0.452	0.451
18	0.430	0.430
24	0.409	0.405
30	0.393	0.391

This result shows that the reaction products do not affect the rate of the reaction.

2.6 Stoichiometry of the reaction

The product of the oxidation of nitrite is expected to be nitrate, and the product of the reduction of chlorite by nitrite is most likely to be chloride. An equation which would be compatible with this can be represented by:

$$2NO_2^- + ClO_2^- \xrightarrow{H^+} 2NO_3^- + Cl^-$$

in which two moles of "nitrite" react with one mole of chlorite to produce two moles of nitrate and one mole of chloride in acidic medium.

2.6.1 Estimation of the molar ratio of reactants

A summary of four experiments carried out at pH of about 3.8 is listed in Table 6, and confirms the molar ratio of 2:1 represented by the above equation.

In each experiment, the nitrite to chlorite ratio was always higher than 2. The amount of nitrite remaining unreacted was determined spectrophotometrically. This was obtained by withdrawing samples from the reaction mixture at intervals of time for analysis in the usual way (see page 31) When the absorbance readings were constant for intervals of more than one hour the reaction was presumed to have gone to completion.

Table 6

$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$10^4[NaNO_2]$ mol dm^{-3}	$\frac{[NaNO_2]\text{ reacted}}{[NaClO_2]\text{ reacted}}$
(put in)	(put in)	(remained)	
7.528	2.298	2.940	1.996
7.528	1.532	4.459	2.003
6.022	1.915	2.252	1.969
4.517	1.532	1.477	1.984
		av.	1.988

2.6.2 Quantitative tests for the products of reaction

2.6.2.a Test for nitrate:

In the wavelength region, 47,000 - 48,000 cm^{-1}, chlorite, hypochlorite and chloride are transparent or weakly absorbing. Nitrate and nitrite ions both have absorption maxima in this region (Fig. 1). However, acidification of nitrite solution (mainly present as HNO_2) shifts the peak of absorption to higher wavelengths, but similar acidification of nitrate has no influence upon its spectrum (Fig. 2).

At pH values where N(III) is present mainly as HNO_2 (i.e. $pH < 3$), the reaction between N(III) and Cl(III) is very fast. To avoid the complexities in the spectrum that might arise from the presence of buffer species such as, acetate and phthalate anions, a reaction mixture composed of, 4.167×10^{-4} mol dm^{-3} $NaNO_2$, 5.348×10^{-4} mol dm^{-3} $NaClO_2$ and 4.31×10^{-3} mol dm^{-3} HCl was allowed to react completely (this requires only about 1 minute). The spectrum of a sample of the mixture was recorded in the region 40,000 - 50,000 cm^{-1} (Fig. 3). It is obvious that the maximum absorbance of 1.68 at 46,600 cm^{-1} compares very well with the value 1.66 at the same wavelength obtained for similarly acidified 4.167×10^{-4} mol dm^{-3} $NaNO_3$, and indeed the whole absorption band from 41,000 to 51,000 cm^{-1} is virtually superimposable (compare Figs. 2 and 3). Hence nitrite is quantitatively converted to nitrate.

2.6.2.b Test for chloride:

In a series of experiments the concentration of Cl^- formed in the reaction between chlorite and nitrite (in excess) at $pH \approx 3$, was determined by potentiometric titration (Ag^+) of chloride ion. The results are given in table(7) and show that Cl^- is produced mole for mole from chlorite in its reaction with nitrite.

Table 7

10 $[NaNO_2]$ mol dm^{-3} (initially)	10^2 $[NaClO_2]$ mol dm^{-3} (initially)	10^2 $[Cl^-]$ mol dm^{-3} (determined)
4.403	4.779	4.825
4.403	4.779	4.795
4.403	3.823	3.930

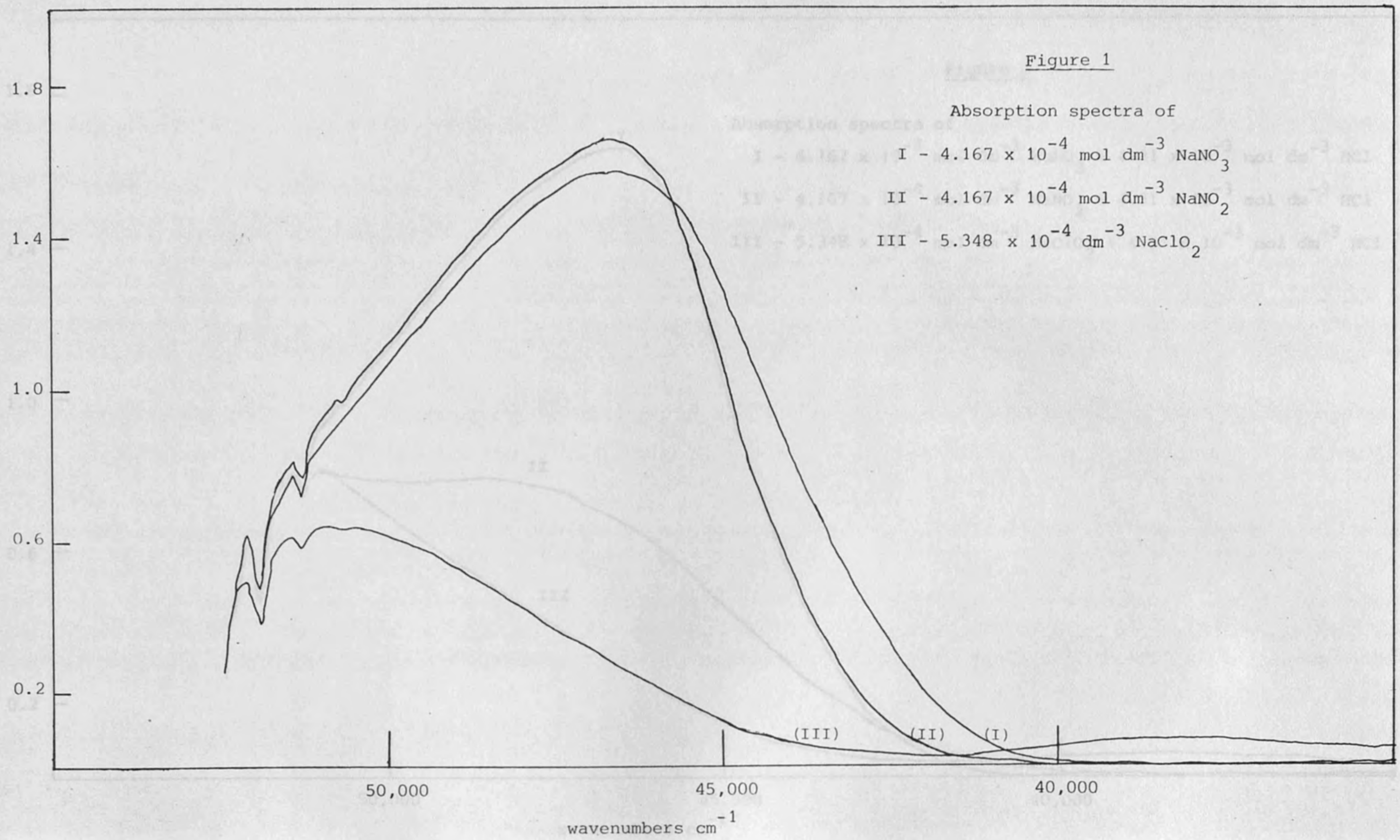


Figure 1

Absorption spectra of

I - 4.167×10^{-4} mol dm^{-3} $NaNO_3$

II - 4.167×10^{-4} mol dm^{-3} $NaNO_2$

III - 5.348×10^{-4} dm^{-3} $NaClO_2$

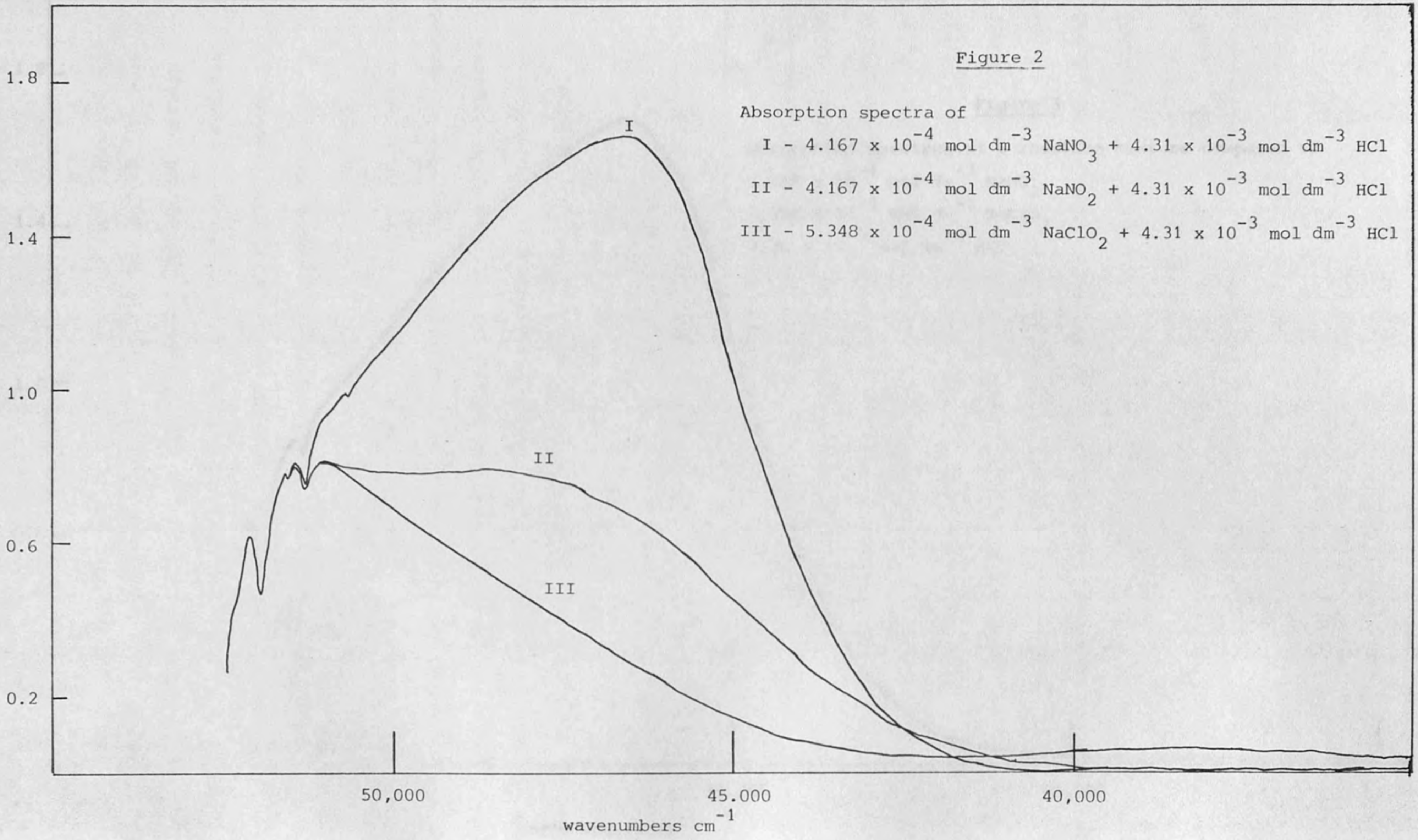


Figure 2

Absorption spectra of

I - 4.167×10^{-4} mol dm^{-3} $NaNO_3$ + 4.31×10^{-3} mol dm^{-3} HCl

II - 4.167×10^{-4} mol dm^{-3} $NaNO_2$ + 4.31×10^{-3} mol dm^{-3} HCl

III - 5.348×10^{-4} mol dm^{-3} $NaClO_2$ + 4.31×10^{-3} mol dm^{-3} HCl

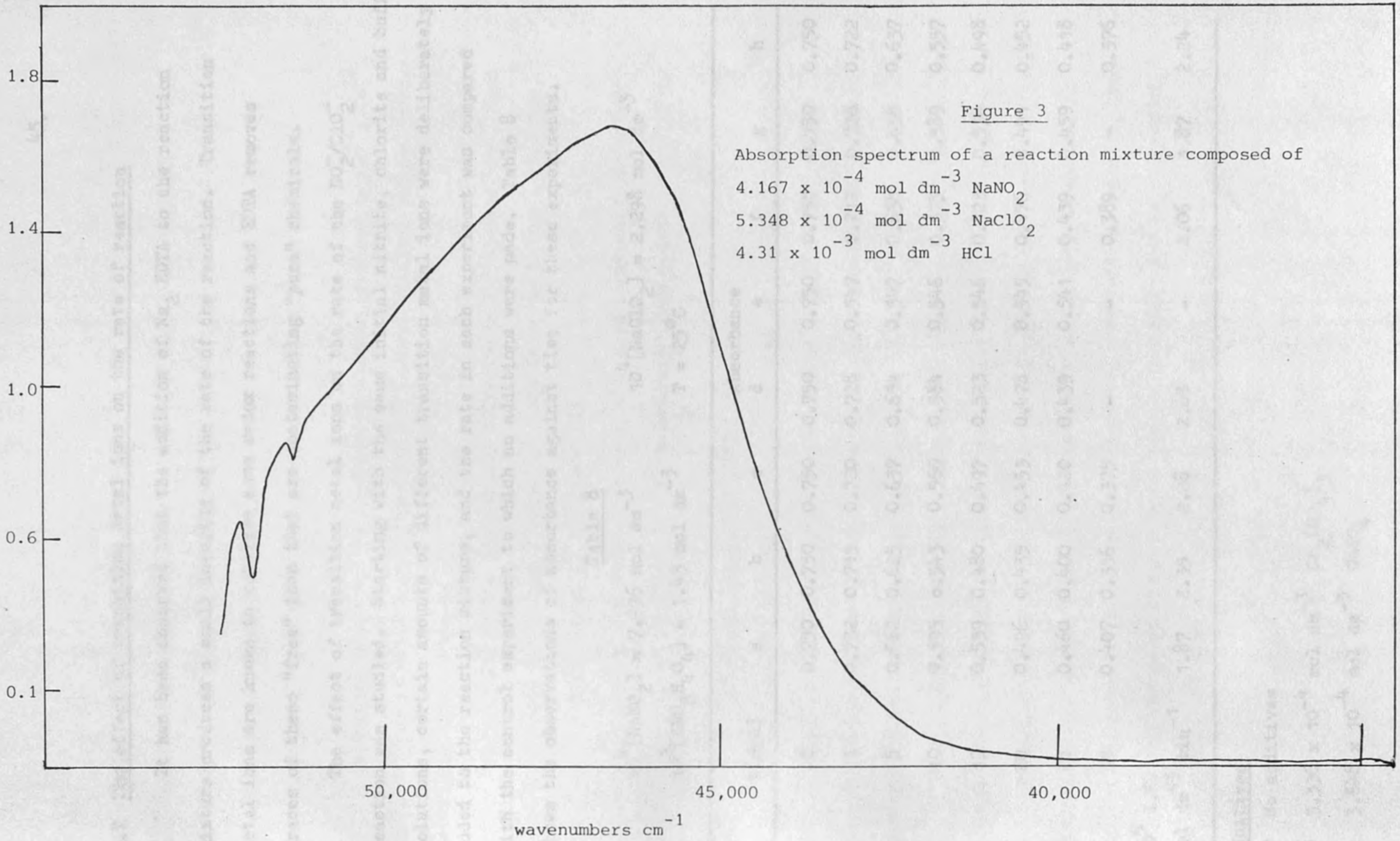


Figure 3

Absorption spectrum of a reaction mixture composed of
4.167×10^{-4} mol dm^{-3} $NaNO_2$
5.348×10^{-4} mol dm^{-3} $NaClO_2$
4.31×10^{-3} mol dm^{-3} HCl

2.7 The effect of transition metal ions on the rate of reaction

It has been observed that the addition of Na_2 EDTA to the reaction mixture produces a small lowering of the rate of the reaction. Transition metal ions are known to catalyse some redox reactions and EDTA removes traces of these "free" ions that are contaminating "pure" chemicals.

The effect of transition metal ions on the rate of the NO_2^-/ClO_2^- reaction was studied. Starting with the same initial nitrite, chlorite and buffer solutions, certain amounts of different transition metal ions were deliberately added to the reaction mixture, and the rate in each experiment was compared with the control experiment to which no additions were made. Table 8 shows the observations of absorbance against time for these experiments.

Table 8

$10^4[NaNO_2] = 7.296$ mol dm^{-3} $10^4[NaClO_2] = 2.298$ mol dm^{-3}
$10^2[KHC_8H_4O_4] = 1.43$ mol dm^{-3} T = 25°C

	Absorbance							
t(min)	a	b	c	d	e	f	g	h
0	0.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
1	0.732	0.715	0.720	0.728	0.547	0.712	0.726	0.722
5	0.662	0.625	0.637	0.654	0.547	0.638	0.658	0.637
10	0.595	0.543	0.560	0.584	0.546	0.575	0.589	0.557
15	0.539	0.480	0.497	0.523	0.546	0.523	0.534	0.498
20	0.496	0.435	0.453	0.478	0.545	0.476	0.491	0.452
25	0.460	0.400	0.420	0.439	0.541	0.439	0.459	0.418
35	0.407	0.356	0.375	-	-	0.389	-	0.376
10^5 I.R. mol dm^{-3} min^{-1}	1.87	2.35	2.28	2.03	-	2.06	1.87	2.24

Additives

(a) No additives

(b) 3.336×10^{-4} mol dm^{-3} $Cr_2(SO_4)_3$

(c) 3.648×10^{-4} mol dm^{-3} $CuSO_4$

(d) 3.724×10^{-4} mol dm^{-3} $Ni(NO_3)_2$

(e) 3.609×10^{-4} mol dm^{-3} $FeSO_4$ (mean of duplicate results)

(f) 3.844×10^{-4} mol dm^{-3} $Co(NO_3)_2$

(g) A piece of Cu metal (~ 2 x 1 inches)

(h) 3.336×10^{-4} mol dm^{-3} $Cr_2(SO_4)_3$ + 1.43×10^{-3} mol dm^{-3} EDTA

In general there are no spectacular effects produced by Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+} or metallic copper but they all (except metallic copper) produce detectable accelerations.

The presence of the potentially effective redox species, Fe^{2+} does completely alter the course of reaction, and it seems probable that the chlorite reacts very rapidly with iron(II).

Comparison of (c) with (h) shows that EDTA does counteract the effect of Cr^{3+}, though not wholly with this relatively large concentration of Cr^{3+}.

2.8 The salt effect on the rate of reaction

It is a general observation that the rates of reactions involving ions in solution are affected by the presence of neutral salts. These effects are due, either to the changes in the ionic strength or to the specific effects of anions and/or cations.

In the solution oppositely charged ions associate. In dilute solutions we need only to consider ion-pairs. According to Davies(41), ion-pairs and complexes could modify the reaction in two ways: in the first, the ionic strength of the medium depends upon the extent of ion-pair formation; in the second, ion-pairs might be involved in the rate determining step, thus altering the charge of the activated complex and hence the ionic type of the reaction, and also modifying the reactivity of the system.

Association between two univalent ions will in general be negligible in dilute solutions, but will be appreciable between higher charges.

Davies(42) also concluded that solutions of oxyanions show significant but not extensive ion-pairing.

It is found here that measurements of rates using reaction mixtures containing KNO_3 and $NaNO_3$, show no specific ion effect due to K^+, Na^+ or NO_3^-; but catalysis due to Cl^- when KCl was added to the reaction mixture was obvious and investigation of this specific ion effect is reported later.

Table 9 shows the absorbance variation with time for two reaction mixtures containing 0.24 mol dm^{-3} $NaNO_3$ in one and 0.24 mol dm^{-3} KNO_3 in the second.

Table 9

$10^4[NaNO_2] = 6.741$ mol dm^{-3} $10^4[NaClO_2] = 2.470$ mol dm^{-3}

$10^2[KHC_8H_4O_4] = 1.430$ mol dm^{-3} T = 25°C

t(min)	$NaNO_2$ (0.24 mol dm^{-3})	KNO_3 (0.24 mol dm^{-3})
0	(0.748)	(0.748)
1	0.713	0.714
4	0.643	0.640
8	0.560	0.561
12	0.502	0.503
16	0.461	0.459
20	0.422	0.425
25	0.391	0.395

On the other hand, the effect of variation of ionic strength on the rate of the reaction was studied by addition of KNO_3 to reaction mixtures where other reactants were kept constant.

The rate constant k of a bimolecular reaction represented by

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_3} C$$

can be deduced from Brønsted-Bjerrum theory as

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_{AB}} \quad \ldots\ldots \quad (4)$$

where k_o is the rate constant when the activity coefficient term (equation 4) can be set equal to unity, and assuming that the transition complex, AB, is in virtual equilibrium with the reactants A and B.

The activity coefficient of the complex, γ_{AB}, is not measurable, but if the charges carried by A and B are z_a, z_b respectively, (and the charges could be either positive or negative), then the charge of the complex is the algebraic sum $(z_a + z_b)$.

For aqueous solution at 25°C, the activity coefficient of a z-valent ion is often assumed to be given by

$$-\log_{10} \gamma = 0.509\ z^2 .\ F(I) \quad \ldots\ldots \quad (5)$$

where F(I) is some function of the ionic strength (I).

Substituting equation (5) into (4) and taking logarithms gives,

$$\log_{10} k = \log_{10} k_o - 0.509\ [z_a^{\ 2} + z_b^{\ 2} - (z_a + z_b)^2] .\ F(I) \ \ldots \quad (6)$$

$$= \log_{10} k_o + 1.018\ z_a\ z_b\ .\ F(I) \quad \ldots\ldots \quad (7)$$

Equation (7) predicts a linear plot of log k versus F(I) with intercept equal to log k_o and a slope determined by the values of z_a and z_b. Furthermore, equation (7) predicts that the rate of a bimolecular reaction increases if z_a and z_b have the same sign, decreases if z_a, z_b have opposite signs and remains unaltered if z_a and/or z_b is zero.

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 established. For example, the reactions that are specifically catalysed by hydrogen ions are thought to consist of at least two steps$^{(43)}$. The first step is a reversible proton transfer between the catalyst and one of the species undergoing reaction. Such a case, involving the protonation of NO_2^- ions put in as $NaNO_2$ in a reversible step to form HNO_2, this molecule then being involved in the actual reaction step leading to products, may well be operating here.

In table (10) the results of experiments in which the ionic strength varied from 0.0167 to 0.257 mol dm^{-3} by addition of KNO_3 are shown. The function F(I) is

$$(I^{\frac{1}{2}}/1 + I^{\frac{1}{2}} - 0.25\ I)$$

Table 10

$10^4[NaNO_2] = 7.296$ mol dm^{-3} $10^4[NaClO_2] = 2.298$ mol dm^{-3}

$10^2[KHC_8H_4O_4] = 1.43$ mol dm^{-3} T = 25°C

$10^2[I]$ mol dm^{-3}	F(I) mol dm^{-3}	$10^5[H^+]$ mol dm^{-3}	$10^{-6}k_r$ dm$^{7.5}$ mol$^{-2.5}$s^{-1}
1.67	0.110	8.622	1.30
3.67	0.152	10.510	1.15
8.81	0.207	12.720	0.97
15.38	0.243	14.615	0.88
18.81	0.256	15.810	0.82
22.24	0.265	16.436	0.78
25.67	0.272	17.274	0.78

A plot of F(I) against log k_r is a straight line with a slope -1.45 as shown in Fig. 4. Extrapolation of the line to F(I) = 0, gives a value of $k_r = 1.97 \times 10^6$ $dm^{7.5}$ $mol^{-2.5}$ s^{-1} (k_r refers to the specific rate constant calculated by Rate = $[NO_2^-]^{1.5}$ $[ClO_2^-]^{0.5}[H^+]^{1.5}$).

Note: Although the amount of buffer added to each reaction mixture was the same, the variation of $[H^+]$ with variation of I has to be taken into account.

In solution

(1) $KHC_6H_4(COO)_2 \longrightarrow K^+ + HC_6H_4(COO)_2^-$

and (2) $HC_6H_4(COO)_2^- \rightleftharpoons H^+ + C_6H_4(COO)_2^{2-}$

Ionization in step (1) may be considered as virtually complete and un-influenced by variation of the ionic strength. The second step (2) can be affected by addition of KNO_3 in two ways; in the first, the increase in ionic strength will preferentially reduce the activity of the divalent anion because the thermodynamic constant K_o of step (2) is given by

$$K_o = \frac{a_{H^+} \, a_{C_6H_4(COO)_2^{2-}}}{a_{HC_6H_4(COO)_2^-}} \qquad \ldots\ldots \quad (8)$$

where (a) denotes the activity of each species, and equation (8) can be written as,

$$K_o = K_c \quad \frac{\gamma_{H^+} \, \gamma_{C_6H_4(COO)_2^{2-}}}{\gamma_{HC_6H_4(COO)_2^-}} \qquad \ldots\ldots \quad (9)$$

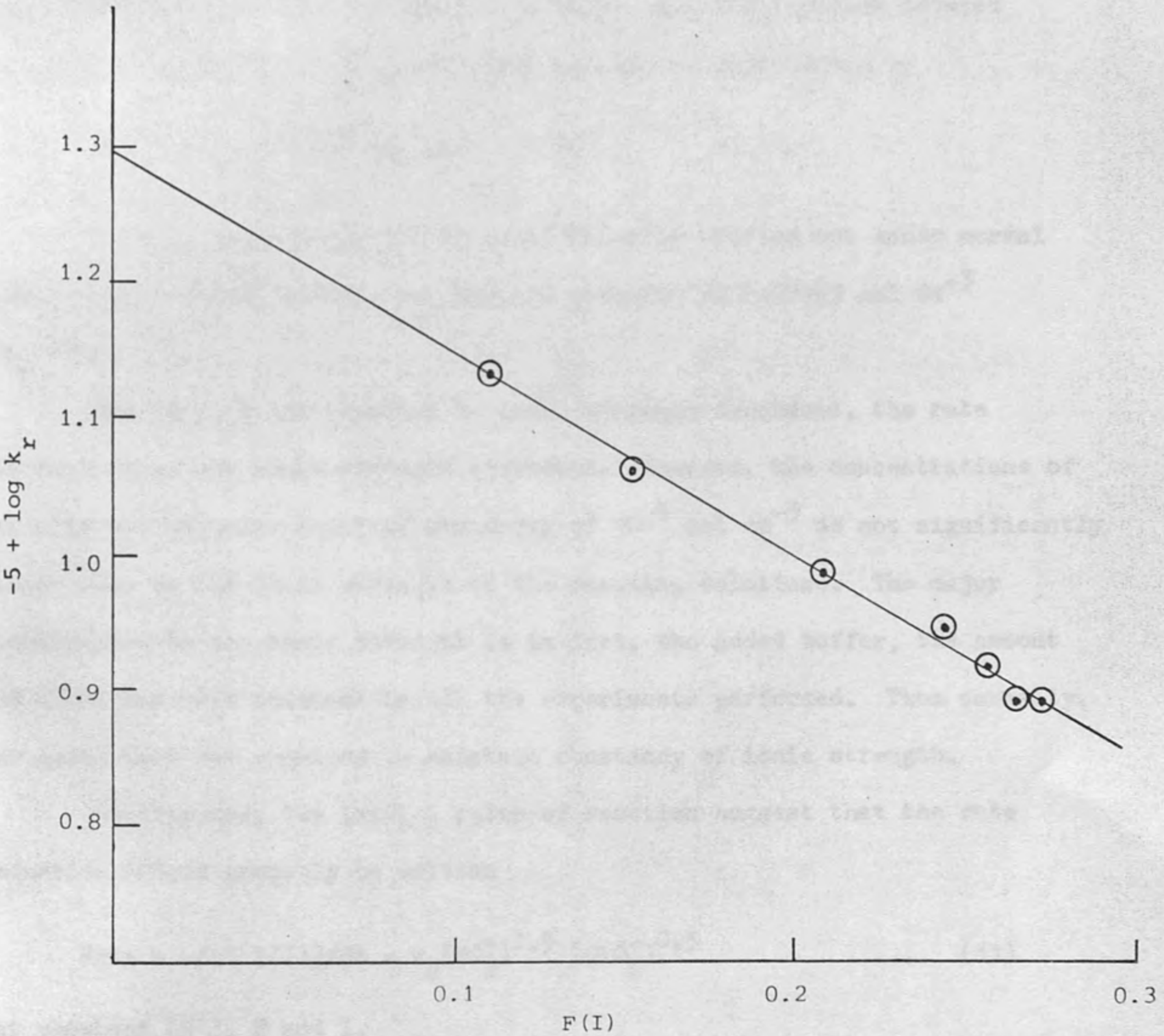
where K_c is the concentration equilibrium constant and γ is the activity coefficient.

The activity coefficients of univalent ions can be assumed equal, thus equation (9) reduces to

$$K_o = K_c \cdot \gamma_{C_6H_4(COO)_2^{2-}} \qquad \ldots\ldots \quad (10)$$

Figure 4

Plot of log k_r versus F(I) for N(III)/Cl(III) reaction



As the ionic strength increases, $\gamma_{C_6H_4(COO)_2^{2-}}$ decreases (equation 5) hence K_c increases and a greater concentration of H^+ is present.

In the second place, addition of KNO_3 will increase the amount of K^+, which will form ion-pairs preferentially with the divalent ion, reducing its concentration, and hence further increasing $[H^+]$.

2.9 The rate equation and the rate constant of reaction

Preliminary investigations have shown that the reaction between nitrite and chlorite is acid dependent and can be represented by

$$2NO_2^- + ClO_2^- \xrightarrow{H^+} 2NO_3^- + Cl^-$$

Kinetic experiments can be satisfactorily carried out under normal laboratory physical conditions, and the addition of 0.00143 mol dm^{-3} Na_2 EDTA.

The rate of the reaction is ionic strength dependent, the rate decreasing as the ionic strength increases. However, the concentrations of nitrite and chlorite being of the order of 10^{-4} mol dm^{-3} do not significantly contribute to the ionic strength of the reacting solutions. The major contributor to the ionic strength is in fact, the added buffer, the amount of which was kept constant in all the experiments performed. Thus normally, no inert salt was required to maintain constancy of ionic strength.

Furthermore, the initial rates of reaction suggest that the rate equation should probably be written

$$\text{Rate} = -d[N(III)]/dt = k_2[NO_2^-]^{1.5}\ [ClO_2^-]^{0.5} \qquad \ldots\ldots \quad (11)$$

at constant $[H^+]$, T and I.

Evaluation of this rate equation can be obtained by integration as follows:

Since

$$\int \frac{dx}{(ax+b)^{n}(cx+d)^{m}} = \frac{1}{(m-1)(bc-ad)}\left[\frac{1}{(ax+b)^{n-1}(cx+d)^{m-1}} - a(m+n-2)\int\frac{dx}{(ax+b)^{n}\ (cx+d)^{m-1}}\right] \qquad \ldots\ldots\ (12)$$

if $m > 1$, $n > 0$ and $bc-ad \neq 0$

To integrate the rate equation let,

$[NaNO_2]_o = a$, $[NaClO_2]_o = b$ and $[NaNO_2]_t = a-x$,

thus, $[NaClO_2]_t = b-x/_2$ where the subscripts o and t indicate values at time zero and t, and x is the concentration of $NaNO_2$ reacted at time t.

Thus, the rate equation can be written as

$$dx/dt = k_2(a-x)^{1.5}(b-x/_2)^{0.5} \qquad \ldots\ldots\ (13)$$

Rearrangement of equation (13) and integration gives,

$$k_2\int dt = \int \frac{dx}{(-\ x/_2+b)^{0.5}(-\ x+a)^{1.5}} \qquad \ldots\ldots\ (14)$$

$$= \frac{1}{-\frac{1}{2}(-b+\frac{a}{2})}\left[\frac{1}{(b-x/_2)^{-0.5}(a-x)^{0.5}} - \left(-\frac{1}{2}(\frac{3}{2}+\frac{1}{2}-2)\right)\left(\int\frac{dx}{(-x/_2+b)^{0.5}(-x+a)^{0.5}}\right)\right] \qquad \ldots\ldots\ (15)$$

so that

$$k_2\int_o^t dt = \frac{1}{-\frac{1}{2}(-b+a/_2)} \cdot \left.\frac{1}{(b-x/_2)^{-0.5}\ (a-x)^{0.5}}\right]_o^x \qquad \ldots\ldots\ (16)$$

and

$$k_2t = \frac{-2}{\frac{[NaNO_2]_o}{2} - [NaClO_2]_o}\left[\sqrt{\frac{[NaClO_2]_t}{[NaNO_2]_t}} - \sqrt{\frac{[NaClO_2]_o}{[NaNO_2]_o}}\right] \qquad \ldots\ldots\ (17)$$

From which a plot of $\sqrt{\frac{[NaClO_2]_t}{[NaNO_2]_t}}$ versus time should give a straight line, the slope of which is related to k_2 the 'second order' rate constant by

$$k_2 = \frac{-2}{\frac{[NaNO_2]_o}{2} - [NaClO_2]_o} \cdot \text{slope} \qquad \ldots\ldots \quad (18)$$

The applicability of the rate equation to the reaction between nitrite and chlorite, was tested by several experiments at various initial nitrite, chlorite and hydrogen ion concentrations at constant ionic strength at 25°C. The rate constant was calculated by plotting $(ClO_2^-/NO_2^-)^{0.5}$ versus time and the value of the second order rate constant k_2 was found by means of equation (18). The specific rate constant k_r was then calculated according to

$$k_r = k_2/[H^+]^{1.5} \qquad \ldots\ldots \quad (19)$$

The value of k_r for the various experiments carried out are given in table (11).

The results of three experiments, shown in tables (12a, 12b, 12c) and their respective plots in Figs. 5a, 5b and 5c are illustrative of the method of calculation and the applicability of the rate equation.

pK of HNO_3 is several units lower than pK for HNO_2, so that the starting reactants consist largely of $(HNO_2 + NO_2^-)$ and ClO_2^- at pH 4.5, whereas the products exist essentially as H^+, NO_3^- and Cl^-,

$$2HNO_2 + ClO_2^- \longrightarrow 2NO_3^- + Cl^- + 2H^+$$

Thus in many runs at 50% completion, 10^{-4} mol dm^{-3} of H^+ has been produced. The concentration of acid phthalate in the buffer used (usually $\sim 1.5 \times 10^{-2}$ mol dm^{-3}) is ample to prevent significant changes in pH due to the product during a kinetic run.

Table 11

$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$10^6[H^+]$ mol dm^{-3}	$10^{-6} k_r$ dm$^{7.5}$mol$^{-2.5}$s^{-1}	F(I)
6.741	2.470	86.51	1.32	.109
3.370	2.470	86.51	1.26	.109
1.348	2.470	86.51	1.42	.109
3.370	4.940	86.51	1.26	.109
3.370	0.988	86.51	1.35	.109
6.741	2.470	171.8	1.36	.109
3.370	2.470	171.8	1.28	.109
1.348	2.470	171.8	1.39	.109
3.370	4.940	171.8	1.36	.109
3.370	0.988	171.8	1.37	.109
6.741	2.470	27.48	1.27	.113
7.296	2.298	86.23	1.34	.110
5.501	3.845	86.19	1.30	.110
3.370	2.470	50.86	1.39	.110
			Av.1.33	

Table 12a

t (min)	absorbance	$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$([NaClO_2]/[NaNO_2])^{0.5}$
0	0.748	7.296	2.298	0.561
1	0.731	7.130	2.215	0.557
5	0.667	6.506	1.903	0.541
10	0.599	5.847	1.573	0.519
15	0.546	5.326	1.313	0.496
20	0.502	4.897	1.098	0.473
25	0.469	4.575	0.937	0.453
35	0.418	4.077	0.688	0.411

$10^5[H^+] = 8.622$ mol dm^{-3} slope = -0.00421 min^{-1}

$k_2 = 1.04$ dm^3 mol^{-1} s^{-1} $k_r = 1.30 \times 10^6$ dm$^{7.5}$ mol$^{2.5}$ s^{-1}

Table 12b

t (min)	absorbance	$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$([NaClO_2]/[NaNO_2])^{0.5}$
0	0.574	5.501	3.845	0.836
1	0.559	5.357	3.773	0.839
3	0.530	5.079	3.634	0.846
5	0.501	4.801	3.495	0.853
10	0.443	4.246	3.217	0.870
15	0.394	3.776	2.982	0.889
20	0.354	3.393	2.791	0.907
30	0.292	2.798	2.494	0.944
45	0.233	2.233	2.216	0.996

$10^5[H^+] = 8.619$ mol dm^{-3} slope = $+0.00342$ min^{-1}

$k_2 = 1.04$ dm^3 mol^{-1}s^{-1} $k_r = 1.3 \times 10^6$ dm$^{7.5}$ mol$^{-2.5}$ s^{-1}

Table 12c

t (min)	Absorbance	10^4[$NaNO_2$] mol dm^{-3}	10^4[$NaClO_2$] mol dm^{-3}	([$NaClO_2$]/[$NaNO_2$])$^{0.5}$
0	0.692	6.741	2.470	0.605
1	0.675	6.575	2.387	0.602
4	0.628	6.118	2.158	0.594
8	0.578	5.631	1.915	0.583
12	0.532	5.182	1.690	0.571
16	0.494	4.812	1.505	0.559
20	0.462	4.50	1.350	0.548

$10^5[H^+]$ = 8.651 mol dm^{-3}

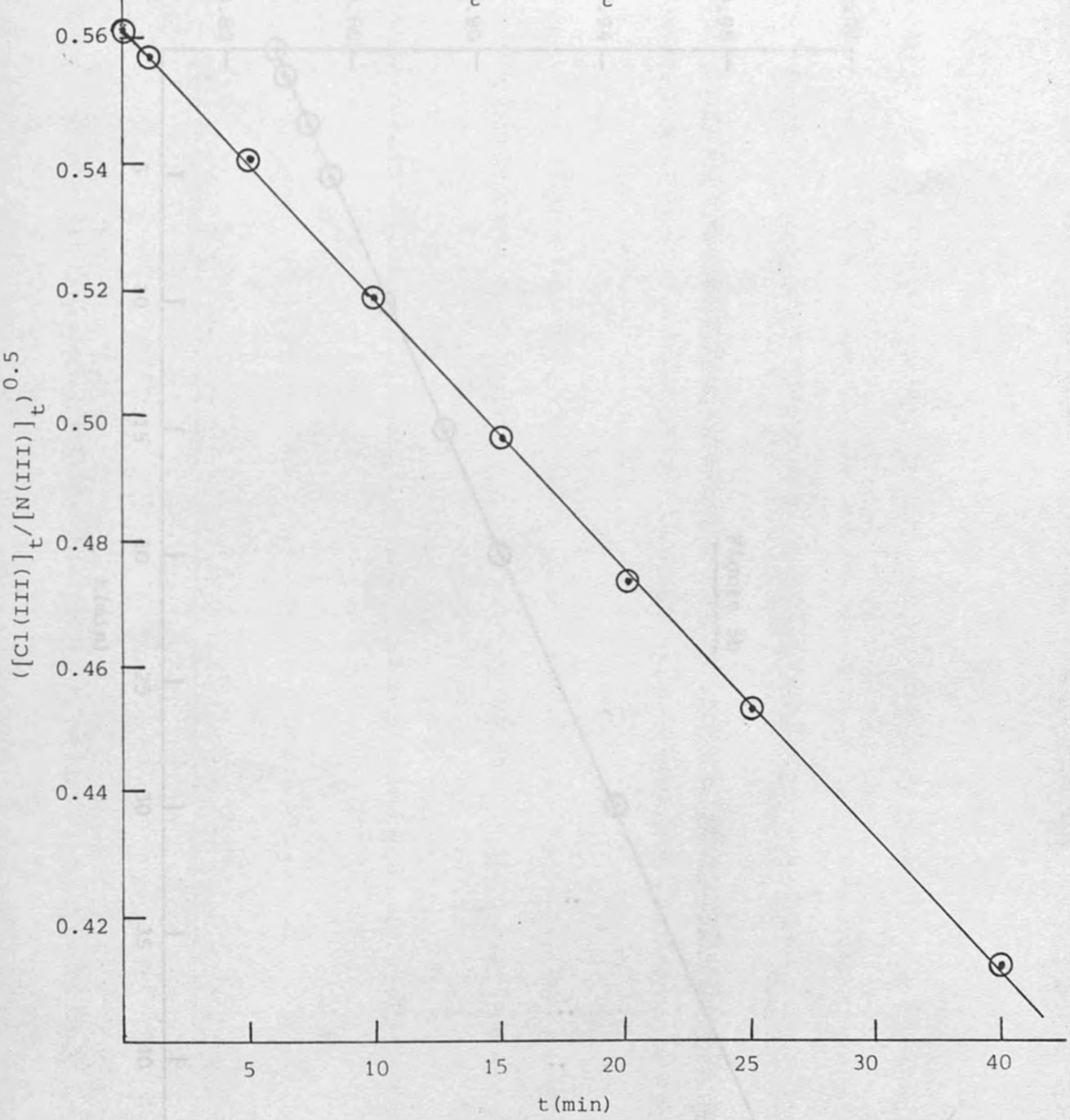
slope = -0.00288 min^{-1}

k_2 = 1.07 dm^3 mol^{-1} s^{-1}

k_r = 1.32 $dm^{7.5}$ $mol^{-2.5}$ s^{-1}

Figure 5a

Plot of $([Cl(III)]_t/[N(III)]_t)^{0.5}$ versus time



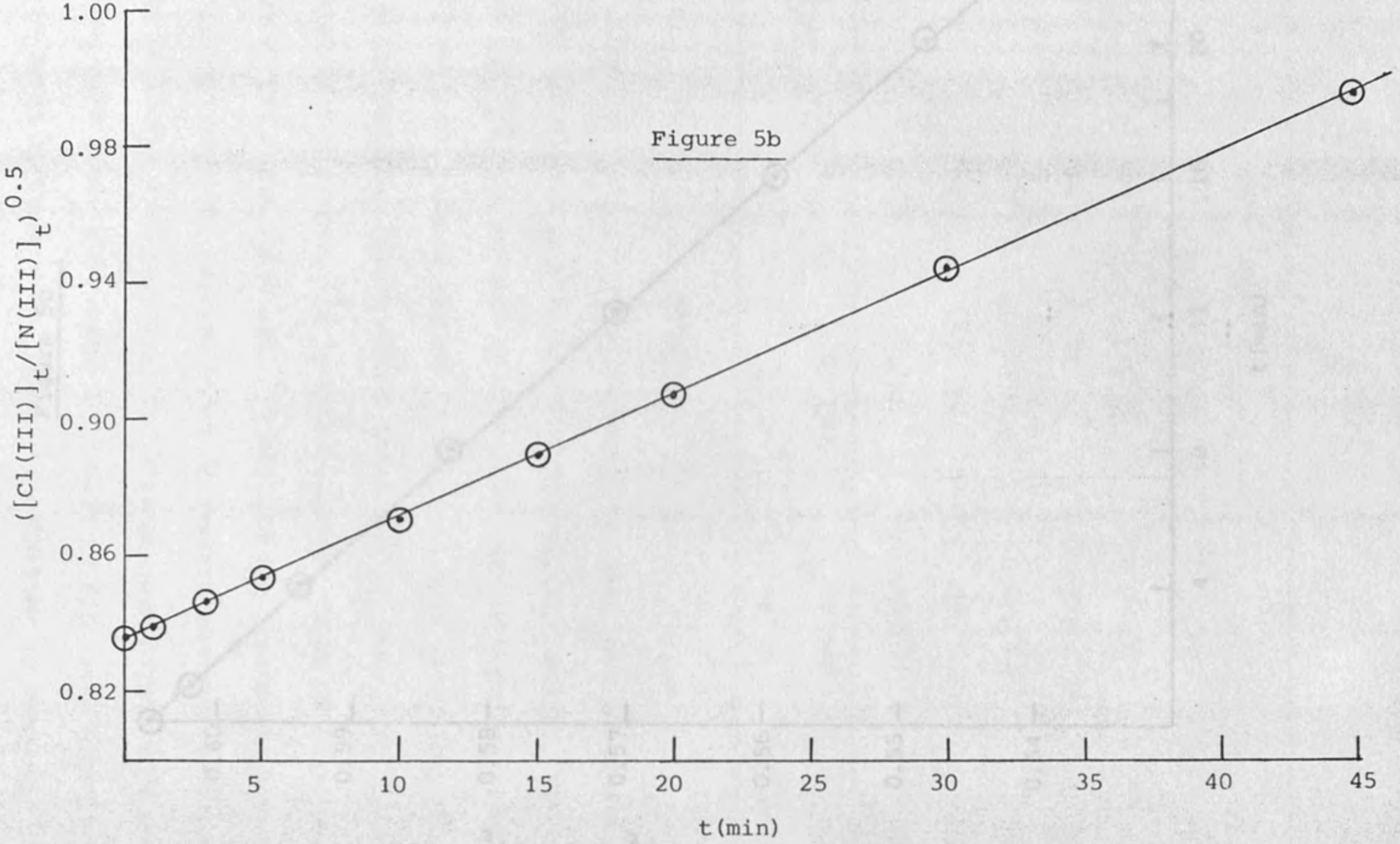
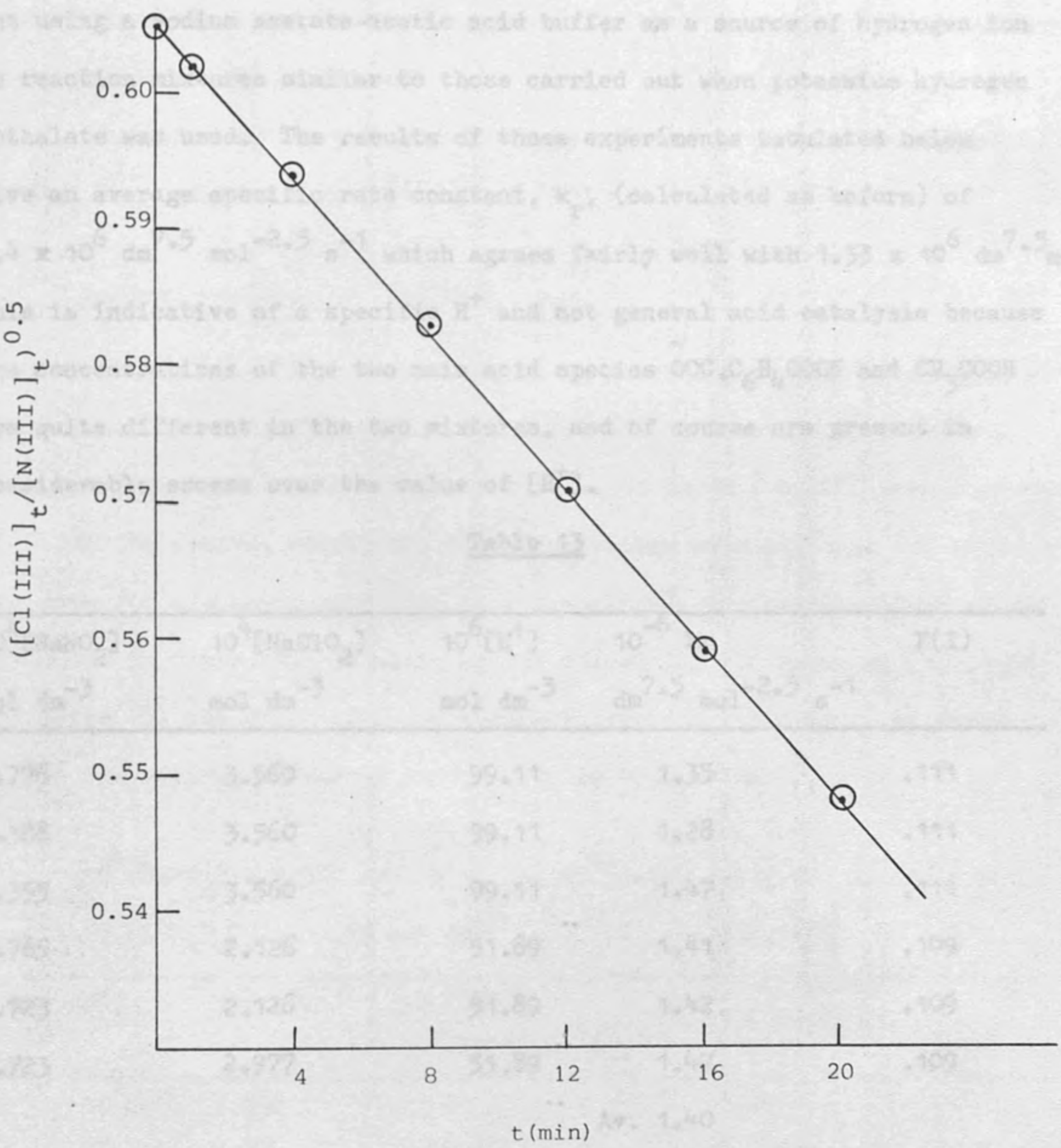


Figure 5b
1.00
0.98
0.94
0.90
0.86
0.82
$([Cl(III)]_t/[N(III)]_t)^{0.5}$
5
10
15
20
25
30
35
40
45
t(min)

Figure 5c



2.10 Kinetic runs using sodium acetate-acetic acid buffer

The experiments described so far have all involved the presence of H^+ but also the acid species $C_6H_4(COOH)_2$ and $\bar{O}OC.C_6H_4COOH$.

In order to determine whether H^+ is a specific catalyst or whether general acid catalysis is occurring, experiments have also been carried out using a sodium acetate-acetic acid buffer as a source of hydrogen ion in reaction mixtures similar to those carried out when potassium hydrogen phthalate was used. The results of those experiments tabulated below give an average specific rate constant, k_r, (calculated as before) of 1.4×10^6 $dm^{7.5}$ $mol^{-2.5}$ s^{-1} which agrees fairly well with 1.33×10^6 $dm^{7.5} mol^{-2.5} s^{-1}$ This is indicative of a specific H^+ and not general acid catalysis because the concentrations of the two main acid species $\bar{O}OC.C_6H_4COOH$ and CH_3COOH are quite different in the two mixtures, and of course are present in considerable excess over the value of $[H^+]$.

Table 13

$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$10^6[H^+]$ mol dm^{-3}	10^{-6} kr $dm^{7.5}$ $mol^{-2.5}$ s^{-1}	F(I)
6.776	3.560	99.11	1.35	.111
3.388	3.560	99.11	1.28	.111
1.355	3.560	99.11	1.47	.111
4.765	2.126	51.89	1.41	.109
2.723	2.126	51.89	1.42	.109
2.723	2.977	51.89	1.47	.109
			Av. 1.40	

2.11 The effect of temperature on the rate of reaction

Arrhenius suggested the following relationship between rate constant and temperature,

$$k = A\ e^{-E/RT} \qquad \ldots\ldots \quad (20)$$

where A and E are defined as temperature independent constants and their values for a reaction are characteristic for that reaction. Most reactions approximate to this behaviour.

The value of the activation energy (E) can be obtained experimentally. Taking $\log_{10}$ of each side of equation (20) gives,

$$\log k = \frac{-E}{2.303RT} + \log A \qquad \ldots\ldots \quad (21)$$

from which a plot of logk versus $^1/_T$ is in general a straight line with a slope equal to -E/2.303RT whence the value of E can easily be obtained.

Experiments in the temperature range 10 to 40 ± 0.02°C were conducted in which the nominal conditions of concentration were the same (no allowance was made for expansion with rise in temperature), the results of which are tabulated in table (14) in which k_2 was calculated via equation (18), and in figure (6) the graph of $\log k_2$ versus reciprocal temperature is shown.

The activation energy is found to be 42.4 kJ mol^{-1}.

Table 14

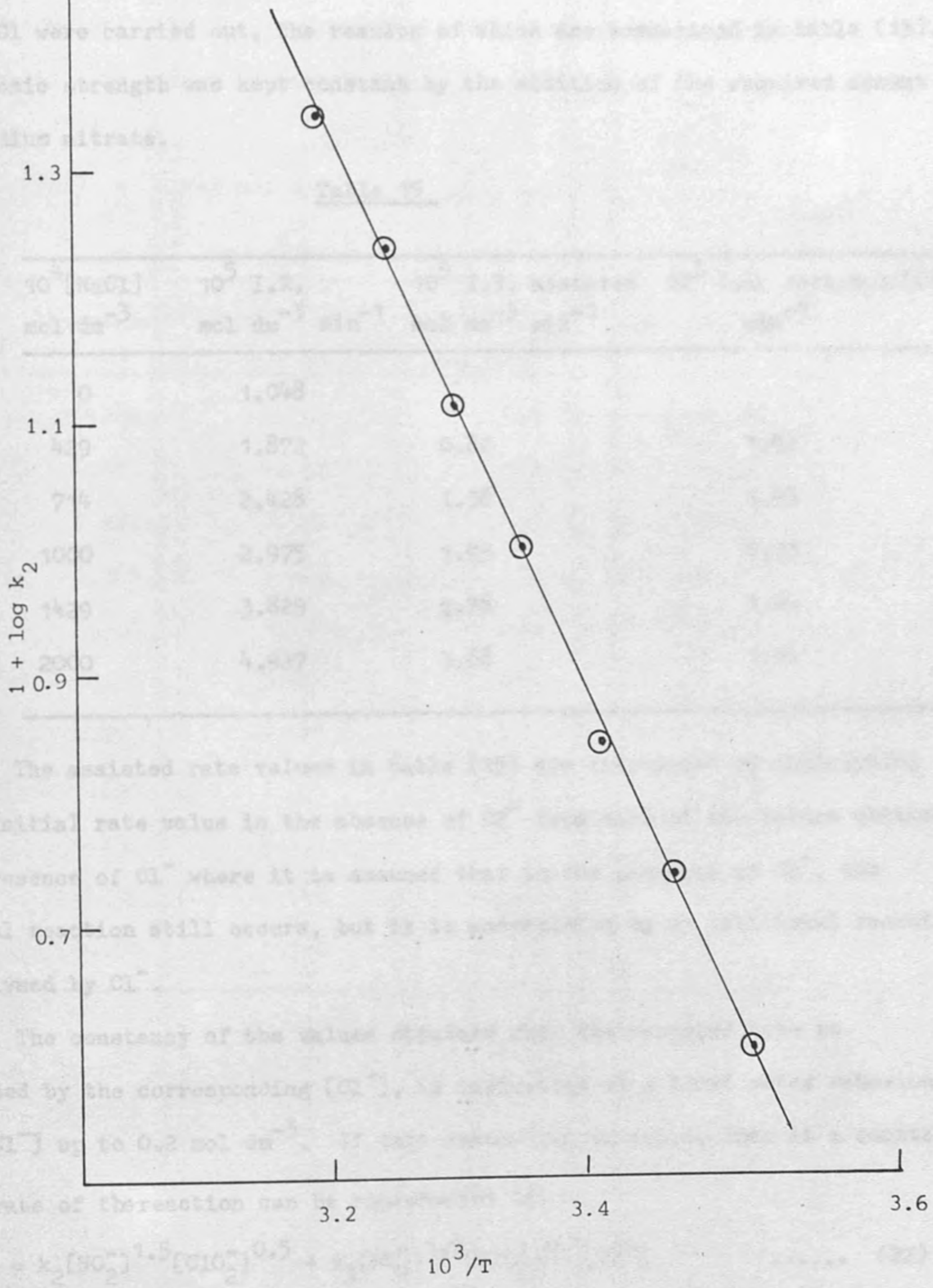
$10^4[NaNO_2] = 3.379$ mol dm^{-3} $10^4[NaClO_2] = 2.470$ mol dm^{-3}

$10^2[KHC_8H_4O_4] = 1.43$ mol dm^{-3} $10^6[H^+] = 86.51$ mol dm^{-3}

T°C	$10^3/T°K$	k2 $dm^3\ mol^{-1}\ s^{-1}$	$1 + \log k_2$
10	3.532	0.40	0.602
15	3.470	0.55	0.740
20	3.411	0.70	0.845
25	3.354	1.05	1.021
30	3.299	1.33	1.124
35	3.245	1.72	1.235
40	3.193	2.21	1.344

Figure 6

Plot of log k_2 versus $10^3/T$ for N(III)/Cl(III) reaction



2.12 Effect of Cl^- on the rate of reaction

To investigate the effect of chloride ion on the rate of reaction, several experiments starting in each with the same initial nitrite, chlorite and hydrogen ion concentrations, but different concentrations of Cl^- added as NaCl were carried out, the results of which are summarized in table (15). The ionic strength was kept constant by the addition of the required amount of sodium nitrate.

Table 15

10^4[NaCl] mol dm^{-3}	10^5 I.R. mol dm^{-3} min^{-1}	10^5 I.R. assisted mol dm^{-3} min^{-1}	10^3 I.R. assisted/[Cl^-] min^{-1}
0	1.048		
429	1.872	0.82	1.92
714	2.428	1.38	1.93
1000	2.975	1.93	1.93
1429	3.825	2.78	1.94
2000	4.927	3.88	1.94

The assisted rate values in table (15) are calculated by subtracting the initial rate value in the absence of Cl^- from each of the values obtained in presence of Cl^- where it is assumed that in the presence of Cl^-, the normal reaction still occurs, but it is accompanied by an additional reaction catalysed by Cl^-.

The constancy of the values obtained when the assisted rate is divided by the corresponding [Cl^-], is indicative of a first order behaviour in [Cl^-] up to 0.2 mol dm^{-3}. If this assumption is valid, then at a constant pH, the rate of the reaction can be represented by,

$$\text{Rate} = k_2[NO_2^-]^{1.5}[ClO_2^-]^{0.5} + k_3[NO_2^-]^{1.5}[ClO_2^-]^{0.5}[Cl^-] \qquad \ldots\ldots \quad (22)$$

$$= [NO_2^-]^{1.5}[ClO_2^-]^{0.5}\left\{k_2 + k_3[Cl^-]\right\} \qquad \ldots\ldots\ldots \quad (23)$$

and because [Cl^-] is present in at least 64-fold excess, it remains constant throughout a run, so that the experiments in the presence of Cl^- should still plot as straight lines when $([NaClO_2]/[NaNO_2])^{0.5}$ is plotted versus time. This is illustrated by plotting the results given in tables (16a and 16b) in figures (7a and 7b) as typical examples at 25°C in acetic acid sodium acetate buffer.

Table 16a

[KCl] = 0.143 mol dm^{-3} pH = 4.348

T = 25°C

t (min)	Absorbance	$10^4[NaNO_2]$ mol dm^{-3}	$10^4[NaClO_2]$ mol dm^{-3}	$([NaClO_2]/[NaNO_2])^{0.5}$
0	0.501	4.765	2.126	0.668
1	0.489	4.651	2.069	0.667
7	0.420	3.995	1.741	0.660
13	0.368	3.500	1.493	0.653
19	0.326	3.101	1.294	0.646
25	0.296	2.815	1.151	0.639
31	0.271	2.577	1.032	0.633
37	0.248	2.359	0.923	0.625
43	0.232	2.206	0.846	0.619
49	0.215	2.045	0.766	0.612
55	0.201	1.912	0.699	0.605

Table 16b

10^2[KCl] = 7.14 mol dm^{-3} pH = 3.980

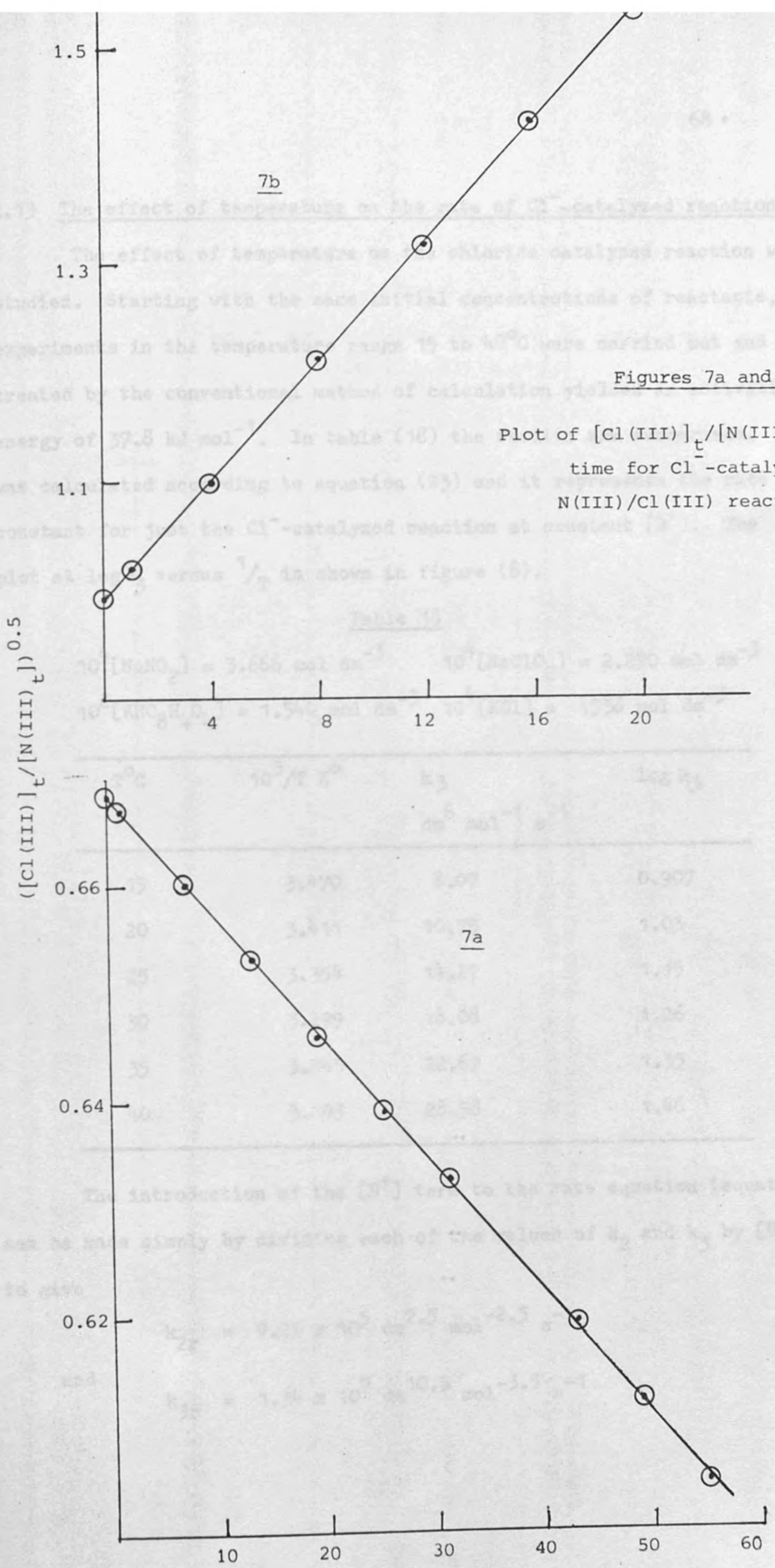
T = 25°C

t (min.)	Absorbance	10^4[NaNO$_2$] mol dm^{-3}	10^4[NaClO$_2$] mol dm^{-3}	([NaClO$_2$]/[NaNO$_2$])$^{0.5}$
0	0.369	3.586	3.560	0.996
1	0.337	3.275	3.404	1.019
4	0.256	2.488	3.011	1.100
8	0.186	1.808	2.671	1.215
12	0.143	1.417	2.476	1.321
16	0.112	1.132	2.333	1.435
20	0.097	0.943	2.238	1.540

The values of k_2 and k_3 can be deduced from equation (23) and are listed in table (17).

Table 17

10^4[NaCl] mol dm^{-3}	k_2 dm^3 mol^{-1} s^{-1}	k_3 dm^6 mol^{-2} s^{-1}
-	0.64	-
429		11.8
714		11.8
1000		11.9
1429		11.9
2000		11.9
		av. 11.9



Figures 7a and 7b

Plot of $[Cl(III)]_t/[N(III)]_t$ versus time for Cl^--catalysed N(III)/Cl(III) reaction

2.13 The effect of temperature on the rate of Cl^--catalyzed reactions.

The effect of temperature on the chloride catalyzed reaction was studied. Starting with the same initial concentrations of reactants, experiments in the temperature range 15 to 40°C were carried out and when treated by the conventional method of calculation yielded an activation energy of 37.8 kJ mol^{-1}. In table (18) the results are summarized. k_3 was calculated according to equation (23) and it represents the rate constant for just the Cl^--catalyzed reaction at constant $[H^+]$. The plot at $\log k_3$ versus $^1/_T$ is shown in figure (8).

Table 18

$10^4[NaNO_2]$ = 3.666 mol dm^{-3} $10^4[NaClO_2]$ = 2.290 mol dm^{-3}
$10^2[KHC_8H_4O_4]$ = 1.540 mol dm^{-3} $10^4[KCl]$ = 1538 mol dm^{-3}

T°C	10^3/T K°	k_3 dm^6 mol^{-1} s^{-1}	$\log k_3$
15	3.470	8.07	0.907
20	3.411	10.75	1.03
25	3.354	14.27	1.15
30	3.299	18.08	1.26
35	3.245	22.67	1.35
40	3.193	28.58	1.46

The introduction of the $[H^+]$ term to the rate equation (equation 23) can be made simply by dividing each of the values of k_2 and k_3 by $[H^+]^{1.5}$ to give

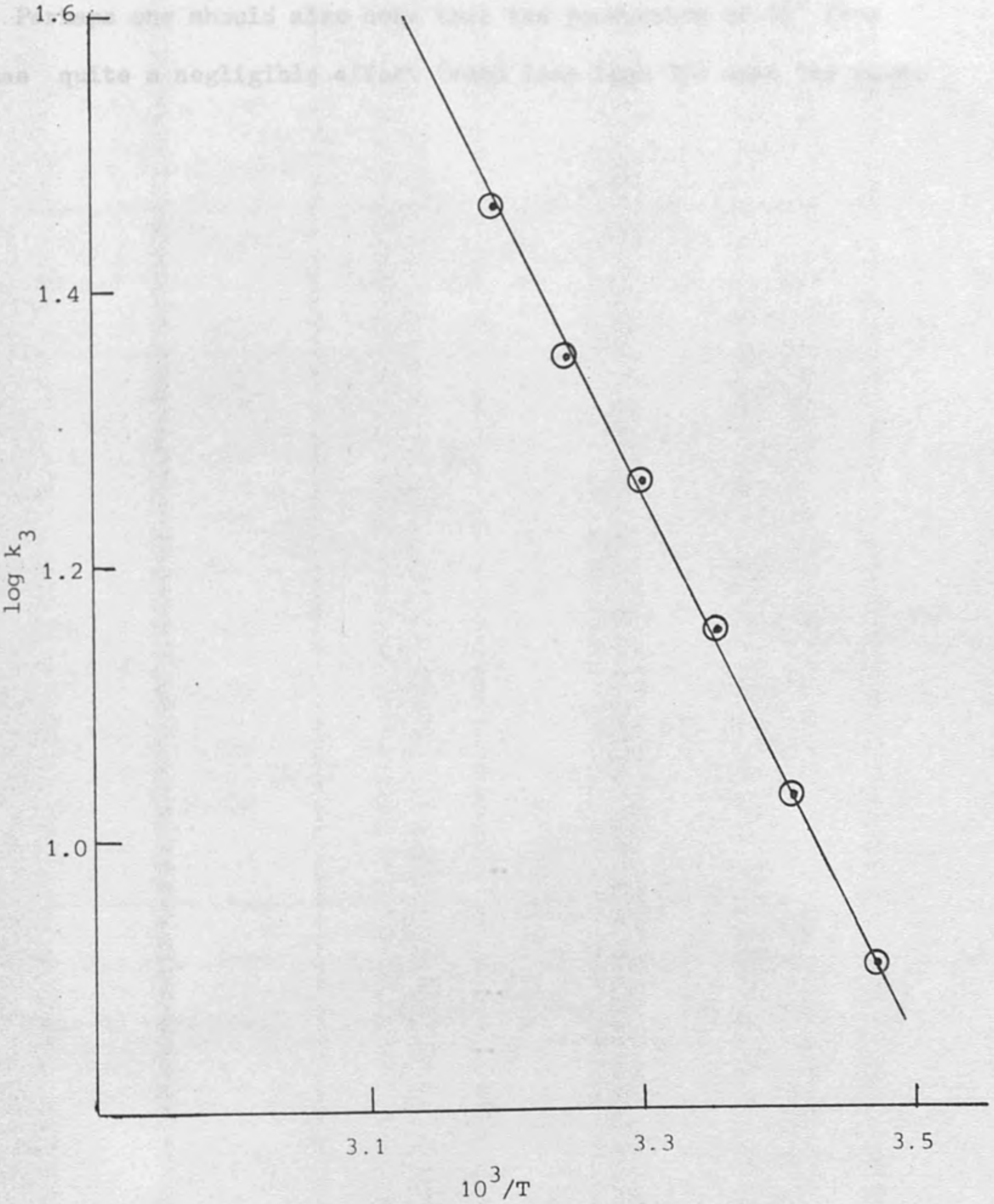
$$k_{2r} = 7.25 \times 10^5 \ dm^{7.5} \ mol^{-2.5} \ s^{-1}$$

and

$$k_{3r} = 1.34 \times 10^7 \ dm^{10.5} \ mol^{-3.5} \ s^{-1}$$

Figure 8

Plot of log k_3 versus $10^3/T$ for Cl^--catalysed N(III)/Cl(III) reaction



The conclusion that can be drawn from the results of the chloride catalyzed reaction experiments is that, it seems that the basic mechanism is unaltered by the presence of chloride ion. It merely helps the formed activated complex to give the products. This implies that Cl^- does not react significantly with ClO_2^- under the experimental conditions.

Perhaps one should also note that the production of Cl^- from ClO_2^- has quite a negligible effect (much less than 1%) upon the rate.

2.14 Effect of Br^- on the rate of reaction

Because of the effect found with Cl^- (and for other reasons, see later) the effect of Br^- was tested by deliberately adding definite amounts to a reaction mixture, the rate in each case was compared with the rate of reaction without Br^- addition. In the three experiments given in table (19), the reactant concentrations other than Br^- were the same.

Table 19

$10^4[NaNO_2] = 5.501$ mol dm^{-3} $10^4[NaClO_2] = 3.845$ mol dm^{-3}

$[H^+] = 8.619$ mol dm^{-3} T = 25°C

t (min.)	Control	$10^3[Br^-]$ 1.553 mol dm^{-3}	$10^5[Br^-]$ 7.766 mol dm^{-3}
	Absorbance		
0	0.574	0.574	0.574
1	0.559	0.562	0.555
3	0.530	0.535	0.533
5	0.501	0.502	0.500
10	0.443	0.439	0.443
15	0.394	0.392	0.388
20	0.354	0.353	0.348
30	0.292	0.291	0.295
45	0.233	-	-

The results obtained, indicate that Br^- has not produced any effect on the rate of reaction, even when $[Br^-]$ was about 3 times $[NaNO_2]$.

2.15 The reaction between hypochlorite and nitrite

The reaction between hypochlorite and nitrite has been reported to be very much acid dependent(44). It proceeds with almost complete transfer of the hypohalite oxygen to nitrite(45).

Lister and Rosenblum(23) studied the reaction in alkaline solution and gave the rate equation,

$$\text{Rate} = k[\text{HOCl}][\text{NO}_2^-]$$

where the H^+ is most likely to be attached to the hypohalite in agreement with Anbar and Taube(45).

An attempt was made to measure the rate of reaction between hypochlorite and nitrite under conditions similar to those used for the chlorite/nitrite reaction. With conventional techniques it was too fast to be measured. A reaction in which the concentrations of $NaNO_2$ and NaOCl were both about 10^{-4} mol dm^{-3} and for which $pH \sim 4$ was completed in less than a minute.

The conclusion from this observation is a confirmation that the reaction of Cl(I) with N(III) is much faster than that of Cl(III) with N(III) under similar reaction conditions, so the rate determining step for the N(III)/Cl(III) reaction is accomplished before Cl(I) is formed and no account of Cl(I)/N(III) need be taken in formulating a mechanism for the reaction with ClO_2^-.

2.16 Discussion

Rate is directly proportional to $[NO_2^-]^{1.5}$, $[H^+]^{1.5}$ and $[ClO_2^-]^{0.5}$. The rate determining step must therefore involve species which are stoichiometrically related to [N(III)] in the ratio 1.5:1, and to [Cl(III)] in the ratio 0.5:1.

The reacting solutions are mixed as nitrite and chlorite in a buffered medium in aqueous solution of pH $\sim$ 4. From the experimental results, the following reaction schemes compatible with the rate equation can be proposed.

A. The un-catalysed reaction:

(a) $HNO_2 \overset{K_a}{\rightleftharpoons} H^+ + NO_2^-$

(1) $HNO_2 + ClO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + ONOO^-$

(2) $ONOO^- \xrightarrow{k_2} NO_3^-$

(3) $HOCl + HNO_2 \xrightarrow{k_3} NO_3^- + Cl^- + 2H^+$

B. The chloride-catalysed reaction:

(a) $HNO_2 \overset{K_a}{\rightleftharpoons} H^+ + NO_2^-$

(1) $HNO_2 + ClO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + ONOO^-$

(2) $ONOO^- \longrightarrow NO_3^-$

(4) $HOCl + Cl^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HOClCl^-$

(5) $HOClCl^- + HNO_2 \xrightarrow{k_5} NO_3^- + 2H^+ + 2Cl^-$

In the above schemes, the proton transfer, step (a), may be assumed to be virtually infinitely fast. The form of the kinetic equation is unusual and puts definite restrictions upon the kinds of mechanism which could lead to the kinetic result. The proposed oxygen-transfer, step (1) is essentially the means, whereby the kinetic result can be explained. It is here assumed that this equilibrium is rapidly established, peroxonitrite and hypochlorous acid being formed, but that the position of equilibrium lies well to the reactant ($HNO_2 + ClO_2^-$) side. The known reactivity of peroxonitrite is in agreement with this. As will be discussed later, the details of this step seem to require that pK for peroxonitrous acid is less than 4.

Analysing the sequence of events given above, we have to note that $ONOO^-$ and HOCl will virtually be formed and lost at equal rates, therefore the concentrations which start from zero at zero time will always be virtually the same, i.e.

$$[HOCl] = [ONOO^-] = K_1^{0.5}[HNO_2]^{0.5}[ClO_2^-]^{0.5} \quad \ldots\ldots \quad (24)$$

$$\text{with } K_1 = k_1/k{-1}$$

and

$$\text{Predicted Rate (A)} = 2k_3[HOCl][HNO_2] \quad \ldots\ldots \quad (25)$$

$$= 2k_3\ K_1^{0.5}[HNO_2]^{1.5}[ClO_2^-]^{0.5} \quad \ldots\ldots \quad (26)$$

(Note that although, strictly, activity coefficients should be inserted in the expression for [HOCl], both numerator and denominator contain the activity coefficients for one molecular species and one univalent ion. They may be regarded as cancelling to unity).

The concentration of HNO_2, in a solution of pH∼4 where both HNO_2 and the "ineffective" NO_2^- are present in significant amounts is governed by

$$^1/_{K_a} = [HNO_2]\gamma_{HNO_2}/[H^+][NO_2^-]\gamma_{H^+}\ \gamma_{NO_2^-} \quad \ldots\ldots \quad (27)$$

and again assuming that the activity coefficient of an uncharged species is one and the activity coefficients of monocharged species (γ_1) are equal, the substitution of equation (27) into (26) yields:

$$\text{Predicted Rate (A)} = 2k_3\ K_1^{0.5}\ K_a^{-1.5}\gamma_1^3\ [NO_2^-]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5} \qquad \ldots\ldots\ (28)$$

$$\doteq k_r\ [NO_2^-]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5} \qquad \ldots\ldots\ (29)$$

at constant ionic strength, which is exactly what is observed, noting of course, that the concentrations in equation (29) are equilibrium values, whereas the observed rate equation deals in total concentrations of N(III) and ClO_2^-.

The same treatment of the chloride-catalyzed reaction leads to

$$\text{Predicted Rate(B)} = 2k_5[HOClCl^-][HNO_2] \qquad \ldots\ldots\ (30)$$

$$= 2k_5\ K_4[HOCl][Cl^-][HNO_2] \qquad \ldots\ldots\ (31)$$

$$= 2k_5\ K_4\ K_1^{0.5}[HNO_2]^{1.5}[ClO_2^-]^{0.5}[Cl^-] \qquad \ldots\ldots\ (32)$$

Thus,

$$\text{Predicted Rate(B)} = 2k_5\ K_4\ K_1^{0.5}\ K_a^{-1.5}\gamma_1^3\ [NO_2^-]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5}[Cl^-]\ , \qquad (33)$$

$$= k_r'\ [NO_2^-]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5}[Cl^-] \qquad \ldots\ldots\ (34)$$

which is also what is observed.

We must now consider how to reconcile the "made-up" and "equilibrium" concentrations referred to above in connection with equation (28) and (33).

The rate of reaction was followed and measured as the rate at which total N(III) is consumed, and well within analytical limits, N(III) consists solely of HNO_2 and NO_2^- at pH 4. So that,

$$[NO_2^-] = [N(III)] - [HNO_2] \qquad \ldots\ldots\ (35)$$

$$[NO_2^-] = [N(III)] - [H^+][NO_2^-]\ \gamma_1^2/K_a \qquad \ldots\ldots\ (36)$$

which on rearrangement yields,

$$[NO_2^-] = [N(III)]/(1 + [H^+]\ \gamma_1^2/K_a) \qquad \ldots\ldots\ (37)$$

and when equation (37) is substituted into equations (28) and (33), equations (38) and (39) result, written as

$$\text{Observed Rate(A)} = \frac{2k_3\, K_1^{0.5}\, K_a^{-1.5} \gamma_1^3}{\left(1 + \frac{[H^+]\,\gamma_1^2}{K_a}\right)^{1.5}} [N(III)]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5} \quad \ldots\ldots \quad (38)$$

and

$$\text{Observed Rate (B)} = \frac{2k_5\, k_4\, K_1^{0.5}\, K_a^{-1.5} \gamma_1^3}{\left(1 + \frac{[H^+]\,\gamma_1^2}{K_a}\right)^{1.5}} [N(III)]^{1.5}\, [H^+]^{1.5}\, [ClO_2^-]^{0.5}\, [Cl^-] \quad \ldots\ldots \quad (39)$$

If $K_a = 9 \times 10^{-4}$, the value of the term $(1 + [H^+]\,\gamma_1^2/K_a)^{1.5}$ varied from 1.13 at $[H^+] = 10^{-4}$ to 1.01 at $[H^+] = 10^{-5}$ mol dm^{-3} all at ionic strength of 0.016 mol dm^{-3}, under which conditions most of the present work had been performed. Thus the predicted and observed rates are in agreement, because this difference factor between "made-up" and "equilibrium" concentrations is relatively unchanging over the experimental range.

The predicted rate equation (equation 28) can also be used to explain the observed effect of ionic strength on the rate of the reaction. This is quite a sensitive test for the correctness or otherwise of the proposed mechanism and in turn has repercussion upon the properties of $ONOO^-$.

A graph obtained when log k_r is plotted versus a funtion of the ionic strength, F(I), has a negative slope of 1.45 (fig. 4). Dividing equation (28) by the concentration terms produces,

$$\text{Rate}/[NO^-]^{1.5}[H^+]^{1.5}[ClO_2^-]^{0.5} = 2k_3\, K_1^{0.5}\, K_a^{-1.5} \gamma_1^3 \quad \ldots\ldots \quad (40)$$

the left hand side of equation (40) is equal to k_r, the observed specific rate constant, and the constants, $2k_3\, K_1^{0.5}\, K_a^{-1.5}$ can be set equal to k_o, so that equation (40) can be written as

$$k_r = k_o\, \gamma_1^3 \quad \ldots\ldots \quad (41)$$

and

$$\log k_r = \log k_o + 3 \log \gamma_1 \qquad \ldots\ldots \quad (42)$$

For dilute aqueous solutions at 25°C, (equation 5)

$$\log \gamma = -0.509 \, Z^2 \, F(I)$$

hence, the mechanism leads to the expected result

$$\log k_r = \log k_o - 1.53 \, F(I) \qquad \ldots\ldots \quad (43)$$

A result in agreement with the observation, both in sign and magnitude.

Some discussion is necessary about step (2) in each mechanism.

It might have been written,

$$ONOO^- + HNO_2 \xrightarrow{k_2} HNO_2 + NO_3^-$$

this would still produce the correct kinetics as well as the stoichiometry for reaction A, but for various reasons this step has been rejected.

The liability of XOOH to undergo nucleophilic substitution increases with the strength of the negative inductive effect of X$^{-(46)}$, and the nucleophilic strength$^{(47)}$ for displacement on oxygen of XOOH decreases in the order $Br^- > NO_2^- > Cl^- >> H_2O$. Thus if HNO_2 were reacting with $ONOO^-$ it would be expected that Br^- would affect the rate of reaction whereas Br^- is not observed to have any effect even when present in greater concentration than HNO_2. Also Halfpenny and Robinson$^{(13)}$ observed that Br^- is oxidised by peroxonitrous acid, but not by the products formed by isomerization of peroxonitrous acid. Thus if $ONOO^-$ lasted long enough in the present system to react with Br^- it would presumably lead to Br_2 or HOBr which would then oxidise nitrite. The reaction with Br_2 known to be a fast reaction having been studied by Pendlebury and Smith$^{(48)}$ in the pH range 4.2 - 5.8. Again the fact that Br^- is not found to alter the rate indicates that $ONOO^-$ does not remain as such long enough to undergo significant bimolecular reactions with any solutes in the solution and hence the mechanism put forward shows step 2 as a rearrangement not involving other solutes.

So far, $ONOO^-$, HOCl and $HOClCl^-$ (formed in presence of excess Cl^-) have been proposed as intermediates in the reaction between nitrite and chlorite in aqueous acid solution.

$HOClCl^-$ as well as $HCl_2O_2^-$, Cl_2O_2 and $IClO_2^-$ have been proposed as intermediates in the reactions of oxyacids of chlorine(49,45,80). For example, $HOClCl^-$ seemed to Anbar and Taube(45) a possible intermediate for the H_2O-ClO^- exchange reaction catalyzed by Cl^-. Kieffer and Gordon(50) on the other hand, made a comparison between $HCl_2O_2^-$, Cl_2O_2 and $IClO_2^-$ and reported that Cl_2O_2 rapidly produces ClO_2 and ClO_3^- depending on its concentration. The proposed species $IClO_2^-$ undergoes primarily internal oxidation-reduction to form I_2 and ClO_2^- rather than oxidize I^- or ClO_2^-, but $HCl_2O_2^-$ readily oxidizes Cl^-. The intermediate peroxonitrite, however, isomerizes to nitrate as shown in step 2 of the proposed mechanism. Despite the several studies by many authors, the uncertainty as to whether the isomerization of peroxonitrous acid proceeds via homolytic or heterolytic cleavage of the O-O link is not yet solved. A detailed review of some of the published work seems inevitable.

Peroxonitrite, was long ago recognized as a yellow species, best known in the reaction between acidified hydrogen peroxide and nitrite.

Halfpenny and Robinson(13) have reviewed the work that revealed the existence of the species. The first reported isolation of a solid peroxonitrite is due to Hughes and Nicklin(51) and the spectrum of the acid form was recorded by Benton and Moore(52) and that of the anion by Yagil and Anbar(53), who also found various methods for its preparation.

According to Halfpenny and Robinson(13), addition of nitrite solution to a solution containing acidified hydrogen peroxide and benzene resulted in the formation of phenol and nitrobenzene. The acidification of peroxonitrite solution caused the polymerization of methyl methacrylate.

Those results led to the conclusion that free radicals are produced in the course of isomerization and not during the formation of HOONO. They formulated the following equations:

$$HNO_2 + H_2O_2 \longrightarrow HOONO + H_2O$$

$$HOONO \longrightarrow HO + NO_2$$

$$HO + NO_2 \longrightarrow HNO_3$$

and added that when H_2O_2 is abundant, the hydroxyl radicals provide a means of oxygen liberation by such a chain as

$$HO + H_2O_2 \longrightarrow H_2O + HO_2$$

$$HO_2 + H_2O_2 \longrightarrow HO + O_2 + H_2O$$

Abel,(54) denied the existence of peroxonitrous acid and believed that it was a "salt like" undissociated acid nitrosyl peroxide, $HO_2^-.NO^+$ formed by

$$H_2O_2 + HNO_2 \longrightarrow HO_2NO + H_2O$$

Hughes and Nicklin(51) studied the kinetics of the isomerization of HOONO in excess alkali and concluded that the rate can be represented by,

$$Rate = k_3[HOONO]$$

where $k_3 = k_2 K_a$ and $k_2 = k_1[OH^-]/K_w$, with K_a, K_w being the dissociation constant for peroxonitrous acid and the ionic product for water and k_1 is the pseudo first order rate constant for isomerization of peroxonitrite. The values of k_2 and k_3 at 25°C were given as 8.3×10^7 mol^{-1} dm^3 s^{-1} and 0.43 s^{-1} from which K_a was found to be 5.2×10^{-9} as an upper limit. They also added that the rate of isomerization of HOONO was independent of nitrite, nitrate, added alcohol (up to 10% v/v) and ionic strength which is contrary to the results reported by Papee and Petriconi(55). The rate was also said not to be acid-catalyzed as was suggested by Shilov and Stepanova(56), but the results do not preclude the incursion of an acid-catalyzed term into the rate equation at higher acidities. They(51) then concluded that the mode of isomerization of HOONO proceed via heterolsis of the O-O bond, and gave the following reasons:

First, one might not expect homolysis to account for 100% yield of nitrate as the possibility of other radical reactions can not be discounted. Secondly, reactions of inorganic and organic peroxides that involve the homolysis of the O-O bond have activation energies in the range 120-160 kJ mol^{-1}, whereas the value obtained for the isomerization of HOONO was 52 kJ mol^{-1}. The presence of electronically dissimilar groups either side of this link, suggests that homolysis might not be favoured.

To account for Halfpenny and Robinson's results, Hughes and Nicklin thought that hydroxylation by peroxonitrous acid may occur by direct attack on the double bond which can be followed by homolytic cleavage and suggested that heterolysis of the O-O link would probably give NO_2^+ and OH^- which would immediately react with each other to produce HNO_3. The alternative heterolytic fission giving OH^+ and NO_2^- would yield HNO_2 and this fission is therefore inoperative. On the other hand, the isomerization to give nitrate can be an intramolecular rearrangement of peroxonitrous acid.

A rate equation similar to that of Hughes and Nicklin was also suggested by Keith and Powel(57) who studied the rate of isomerization of the peroxo-acid in the pH range 4 to 9 in buffer solutions, and found that the rate was independent of the buffer concentration, consistent results being obtained with acetate, phosphate, arsenate and pyrophosphate buffers. They accordingly concluded that there were no complications arising from specific reactions of peroxonitrite with buffer species.

A rate constant of 0.1 s^{-1} at (1 ± 1°C) and a pK_a of 6.6 for HOONO were given by Keith and Powel.

A non-radical mechanism seemed more plausible to Benton and Moore$^{(52)}$ who studied the rate of isomerization of HOONO in perchloric acid (0.01 to 1 mol dm^{-3}) and found that the first order rate constant at 0.055°C can be given as, $10^2k = (5.27 \pm 0.10) + (59 \pm 0.8)[H^+]\ s^{-1}$. They also deduced a pK_a of 9.4 for HOONO, but said this was clearly too high.

Mahoney$^{(58)}$ on the other hand, claimed to show that the isomerization of HOONO does proceed via homolysis of the O-O bond and determined the evolved oxygen. He noted that the evolution of O_2 was strongly retarded by acetate, benzoate ions and isopropyl alcohol.

Mahoney's rate expression was given by,

$$-[d[NO_2]/dt]/[+\ d[O_2]/dt] = a + b\ [NO_2^-]_t/[H_2O_2]$$

with which the following reaction scheme is consistent.

$$H^+ + NO_2^- \overset{k_1}{\underset{k-1}{\rightleftharpoons}} HNO_2$$

$$HNO_2 + H^+ \overset{k_2}{\underset{k-2}{\rightleftharpoons}} NO^+ + H_2O$$

$$NO^+ + H_2O_2 \xrightarrow{k_3} HOONO + H^+$$

$$HOONO \xrightarrow{k_4} HO + NO_2$$

$$HO + NO_2^- \xrightarrow{k_5} HO^- + NO_2$$

$$HO + H_2O_2 \xrightarrow{k_6} HO_2 + H_2O$$

$$2HO_2 + H_2O \xrightarrow{k_7} H_2O_2 + O_2$$

$$2NO_2 + H_2O \xrightarrow{k_8} HNO_2 + HNO_3$$

As a further support for the homolysis mechanism he considered the cycle

$$\begin{tikzcd}
HO - NO_2(aq) \arrow[d, "\Delta H_1"] & HO(aq) + NO_2(aq) \arrow[l, "\Delta H_4"'] \\
H^+(aq) + O\bar{O}NO(aq) \arrow[r, "\Delta H_2"] & HOONO(aq) \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

and assumed that ΔH_4 in aqueous solution is equal to the gas-phase value, -205 kJ mol^{-1}, and that ΔH_1 is $+ 162 \pm 8$ kJ mol^{-1}, a value given by Ray$^{(59)}$ (who also suggested a radical type mechanism). A value of $\Delta H_2 + \Delta H_3 = 42 \pm 8$ kJ mol^{-1} was calculated which compares favourably with the value, 52 kJ mol^{-1} given by Hughes and Nicklin.

Furthermore, Graetzel, Henglin and Taniguchi$^{(60)}$ reported that HOONO disappears by a first order reaction with a rate constant, 1.9×10^3 s^{-1} and the undisociated form isomerizes to form HNO_3. They gave a value of 5.3 for pK_a of the acid.

As evidence of the non-radical mechanism of the isomerization of HOONO, Shevchuk and Vysotskaya$^{(61)}$ found that the rates of oxidation of methanol and ethanol by $H_2O_2 - Fe^{2+}$ and by radiolysis of H_2O are about 100 times that for HOONO oxidation.

Returning to consider evidence on these matters coming from the present work. The mechanism suggested for the reaction between nitrite and chlorite does not directly comment upon whether the isomerization of peroxonitrite proceeds via homolysis or heterolysis, but it favours a pK_a value for HOONO $\ll 4$ so that peroxonitrite is present mainly in the anionic form, otherwise the mechanistic steps will not lead to the correct order with respect to $[H^+]$ because if step (1) in the reaction schemes is written as

$$HNO_2 + H^+ + ClO_2^- \rightleftharpoons HOONO + HOCl$$

the rate equation would be

$$\text{Rate} = 2k_3\, K_1^{0.5} K_a^{-1.5} \gamma_1^{3.5} [NO_2^-]^{1.5} [H^+]^2 [ClO_2^-]^{0.5}$$

giving an order of 2 in $[H^+]$ rather than the experimental value of 1.5. Alternatively if step (1) took place as indicated but pK for peroxonitrous acid were > 4, then a large fraction of the species would be present in the acid form, just as HOCl is at this pH. The low concentration of $\overset{-}{O}ONO$ would not meet the kinetic interpretation requirement that

$$[\overset{-}{O}ONO] = [HOCl].$$

Although no evidence about the nature of isomerization of peroxonitrous acid can be found from the proposed mechanism for the nitrite/chlorite reaction, some experimental evidence has been obtained. A reacting mixture containing 0.02 mol dm^{-3} of each of NO_2^- and ClO_2^- at pH ~ 3.8 at room temperature (i.e. a fast reacting mixture with expected half life about 3 minutes) was passed through the cavity cell of a Varian E4 spectrometer. Although a wide range band (~ 5000 G, X band) was explored, no e.s.r. signals were detected, indicating that insignificant amounts of any radicals are present during the reaction. This is relevant to both the main reaction whose mechanism has therefore been written to involve only non-radical intermediates, and to the reaction of peroxonitrite (assuming it is present).

The actual formation of peroxonitrite during the reaction between nitrite and chlorite has been demonstrated by the following experiment, the conditions of which are by no means critical. To a solution of nitrite (~ 4 g in ~ 30 cm^3 H_2O), a solution of chlorite (~ 3g in ~ 20 cm^3 H_2O) is added followed immediately by the addition of ~ 3 cm^3 of 2M acid. The orange-yellow colour, characteristic of peroxonitrite which appears and disappears again within a few seconds can be observed.

This evidence as a whole, therefore suggests that peroxonitrite heterolyses to nitrate.

Another possible kind of mechanism may be considered. The products of decomposition of $HClO_2$ are reported(62,49,63,64) to be ClO_3^-, ClO_2 and Cl^-. Nitrite might therefore be reacting with one of these rather than directly with $HClO_2$. Alternatively, since hypochlorite and chlorite react together to form ClO_3^- and Cl^-, this reaction might be a precursor to the reaction of nitrite with ClO_3^-.

However, the rate of decomposition of $HClO_2$ is reported to be very acid dependent and is very small in comparison with the rate observed for N(III)/Cl(III) at $pH > 3$. The idea of the intervention of ClO_3^- into a rate determining step with N(III) may be dismissed because the rate of ClO_3^-/NO_2^- is known to be slow at pH 4.

The concentration of ClO_2 arising from $HClO_2$ decomposition is reported to approach zero in the pH range 3.6 - 4, and putting this together with the fact that the concentration of $HClO_2$ is about 0.01 $[ClO_2^-]$ because $pH \sim 4$ and $pK_{ClO_2} \sim 2$, we see that $[HClO_2]$ is in any case extremely small ($\sim 10^{-6}$ mol dm^{-3}) in the present reaction mixtures; hence $[HClO_2]$ in the present mixture is quite insignificant. Also it seems quite clear that any produced H^+ and Cl^- are not present in kinetically significant amounts.

On the other hand, if it is assumed that ClO^- (or HOCl) is involved in the rate determining step, then

$$N(III) + Cl(III) \longrightarrow Cl(I) + N(V)$$
$$Cl(I) + N(III) \longrightarrow Cl(-1) + N(V)$$

which means that $\frac{1}{2}$ of the N(III) would be oxidized in a fast reaction yielding Cl(I) which will then react in a slow step, a result that is not observed. This experimental observation is in harmony with the established fact that ClO^- reacts much faster than ClO_2^- with NO_2^- under similar conditions.

Finally, the involvement of nitrosyl chloride which might be formed according to

$$H^+ + HNO_2 + Cl^- \rightleftharpoons NOCl + H_2O$$

in the reaction path does not seem to produce the correct kinetics.

The above considerations all support the mechanism actually proposed.

It is tempting to consider exoerimental methods of testing the proposed mechanism.

The most novel step proposed is the transfer of oxygen to produce peroxonitrite, and it is of interest to enquire whether this could be unequivocally demonstrated. The rates of ^{18}O exchange between anions and solvent water have been investigated for the stable reactant and product species involved here. If the rates of these exchanges are all significantly lower than any demonstrable transfer of ^{18}O from reactant $NaClO_2$ to product NO_3^- this would be consistent with the proposed mechanism.

Various difficulties, however, present themselves and this kind of experiment has not yet been attempted.

There is the practical matter that under the kinetic conditions, removal of NO_3^- from the solution at 25°C is difficult, either it must be fractionally distilled out (which would cause exchange) or the reaction would need to be carried out to produce much higher concentrations of nitrate which might be selectively precipitated with known complex nickel cations. Further there are the theoretical difficulties concerning both the interpretation of observation of exchange, and of no exchange. Exchange might also result from the reaction of HOCl with nitrite. Further the isomerization of peroxonitrite has, as has been discussed, an undetermined mechanism-production of labled peroxonitrite might finally yield unlabled nitrate.

3. The Reaction Between N(III) and I(VII)

For reasons which will become apparent the work attempted on a study of this reaction will be presented in chronological order rather than in an arrangement dictated by hindsight.

3.1 Optimum conditions for the reaction

In general, reactivity of periodate is considerably higher than Br(VII) or Cl(VII) possibly because of the higher coordination number of groups which may be attached to I$^{(65)}$. Hence although ClO_4^- is known to be unreactive as an oxidizing agent towards N(III), I(VII) might well be able to react at an observable rate. The most suitable conditions, under which it appeared the reaction could be studied were worked out from the results of several experiments that were conducted using a variety of conditions of reactants in neutral and aqueous acid solutions. The optimum conditions for the reaction at 25°C were found to be when the $[NaNO_2] = 10^{-4}$ mol dm^{-3}, $[KIO_4] = 10^{-3}$ mol dm^{-3}, and $[H^+] = 1$ to 2 mol dm^{-3} when added (unless otherwise stated) as HCl (B.D.H. technical grade). The acid solutions were standardized against anhydrous sodium carbonate.

"Analar" grade chemicals were used when available without further purification (on a percentage basis technical HCl has a specification not inferior to other analar reagents).

The technique adopted was similar to that used in the previous work. Sodium nitrite and potassium periodate solutions were pipetted into a 250 cm^3 stoppered conical flask. The acid and any other solutions were measured into another 250 cm^3 flask. The stoppered flasks were immersed in the thermostat, controlled to $\pm$ 0.02°C and allowed to reach thermal equilibrium. The reaction was started when the contents of the acid-containing flask were poured into the flask containing NO_2^-/IO_4^- and the clock started. Mixing was ensured by repeatedly pouring the contents of one flask into the other, and the reaction rate measured was that at which the N(III) species was consumed. The same method for N(III) analysis given earlier was used.

3.2 Reproducibility of measurements and the effect of physical conditions

The possibility of complications arising from surface reactions, photochemical reactions, traces of metal ions contaminating "pure" chemicals. dissolved gases as well as the reproducibility of measurements were tested by the performance of experiments whose results are given in table (20). The table shows the measured absorbances at time intervals for experiments (a), (b), (c), (d) and (e) in each of which the experimental conditions were respectively:

(a) Normal laboratory conditions (control experiment).

(b) The flask was packed with short lengths of glass tubing so as to treble the area of glass surface exposed to the reacting solution.

(c) The flask was wrapped in metal foil to exclude light.

(d) 1.667×10^{-3} mol dm^{-3} Na_2 EDTA was added to the reaction mixture.

(e) O_2 free N_2 was bubbled through the reactant solutions for about 30 minutes before mixing, and continued during the kinetic run.

The observation that purging with N_2 gave a faster apparent rate was further investigated by carrying out the experiments (a'), (b'), (c'), (d'), (e'), (f') for a reaction under the same chemical conditions, but involving:

(a') Normal laboratory conditions.

(b') N_2 bubbled through the solutions as in (e) i.e. about 8 cm^3/min.

(c') Ar was bubbled through the solutions at about the same rate.

Table 20

$10^4[NaNO_2] = 4.256$ mol dm^{-3} $10^3[KIO_4] = 2.453$ mol dm^{-3}

[HCl] = 1.691 mol dm^{-3} T = 25°C

t (min.)	Absorbance (a)	 (b)	 (c)	 (d)	 (e)
0	0.446	0.446	0.446	0.446	0.446
1	0.429	0.427	0.430	0.430	0.432
3	0.401	0.405	0.405	0.403	0.387
5	0.369	0.371	0.373	0.372	0.340
8	0.329	0.330	0.331	0.330	0.278
12	0.275	0.277	0.276	0.274	0.205
16	0.225	0.228	0.227	0.223	0.149
20	0.181	0.181	0.177	0.178	0.105
25	0.131	0.133	0.133	0.132	-

(d') Ar used at a flow rate of about 7 cm^3/min.

(e') Ar used at a flow rate of about 19 cm^3/min.

(f') Ar was bubbled at a flow rate of about 7 cm^3/min through the reacting solutions before mixing; but blowm across the surface once the reaction (total volume, 60 cm^3) had started in a nominal 50 cm^3 stoppered flask, so that the mixture occupied most of the volume in the flask and argon was then being gently blown at the surface of the solution to exclude contamination with air. The results are given in table (21),

Table 21

$10^4[NaNO_2] = 4.036$ mol dm^{-3} $10^3[KIO_4] = 3.758$ mol dm^{-3}

$[HCl] = 1.691$ mol dm^{-3} $T = 25^{\circ}C$

t (min.)	(a')	(b')	(c')	(d')	(e')	(f')
0	0.432	0.432	0.432	0.432	0.432	0.432
1	0.404	0.400	0.404	-	-	-
3	0.364	0.351	0.356	0.370	0.328	0.370
5	0.321	0.299	0.311	0.303	0.266	-
8	0.264	0.233	0.251	0.244	0.192	0.274
12	0.195	0.159	0.178	0.174	0.122	-
16	0.132	0.103	0.118	0.109	0.075	0.141
20	0.081	0.062	0.069	-	-	0.088

The results of table (20) exclude the possibility of interference of physical conditions and of metals contaminating "pure" chemicals. Table (21) indicates that blowing an inert gas through the reaction mixture increases the measured rate. This could not be due to participation of either N_2 or Ar in the reaction between N(III) and I(VII) under the conditions shown. It is most likely to be due to the presence of a volatile component in the reaction. HNO_2 is a volatile acid and is one of the reactants; and clearly loss of this would result from excessive purging, and would apparently involve a higher rate of loss of N(III).

From the results of tables (20) and (21), the conclusion drawn is that the reaction between N(III) and I(VII) can be studied spectrophotometrically under normal laboratory conditions.

3.3 Stoichiometry of the reaction

A spectrophotometric method for the determination of periodate in presence of iodate has been reported by Bhattacharyya and Chetia$^{(66)}$. In this method about 6 mg of aluminium sulphate and 10 cm^3 of 1 mol dm^{-3}

ammonium chloride are added to a measured amount of KIO_3 and KIO_4. Aluminium is precipitated by passing ammonia gas, and the precipitate is filtered and washed with about 50 cm^3 H_2O, then dissolved by percolating 20 cm^3, 3 mol dm^{-3} H_2SO_4 and the solution is made up to 50 cm^3 with H_2O. The absorbance of the final solution is measured against a blank at 210 nm.

The mechanism involved$^{(66)}$ in the process of carrying periodate down to $Al(OH)_3$ may be due to some form of internal adsorption where the periodate ion is internally adsorbed in the lattice of the carrier.

The authors found that Beer's law in the concentration range, 1 to 18 x 10^{-5} mol dm^{-3} is obeyed and gave the value, 2.87 x 10^3 m^2 mol^{-1} for the molar absorption coefficient of periodate. However, from the graph they produced by plotting the absorbance of a solution, 5 x 10^{-5} mol dm^{-3} KIO_4 dissolved in 1.2 mol dm^{-3} H_2SO_4 at various wavelengths, a value for the molar absorption coefficient of 3.2 x 10^3 m^2 mol^{-1} at 210 nm at which the periodate solution showed maximum absorption has been recalculated by the present author.

The product of oxidation of nitrite is expected to be nitrate and the product of reduction of periodate by nitrite is likely to be iodate because the rate of reaction of IO_3^- with N(III) is known to be slower than that observed here with periodate. The above mentioned method was used to determine the molar ratio at which nitrite reacts with periodate.

To decide which of the two (ε) numerical values to be used in the present calculations, an estimation of its value was first made. Three solutions of KIO_4 in 1.2 mol dm^{-3} H_2SO_4 were prepared and the absorption of each together with the absorption of a sample treated with aluminium sulphate at 210 nm were measured and the results are given below.

Table 22

	$10^5[KIO_4]$ mol dm^{-3}	Absorbance	ε m^2 mol^{-1}
(1)	9.763	0.320	3280
(2)	7.810	0.254	3250
(3)	6.508	0.212	3260
(4)*	6.508	0.209	3210
		av.	3250

* (KIO_4 treated with aluminium sulphate).

Reaction mixtures were then prepared and left for a period of time until no nitrite would be detected. Samples were then taken and treated as in reference (66). The results of those experiments are list in table (23).

Table 23

$10^3[KIO_4]$ mol dm^{-3} (put in)	$10^4[NaNO_2]$ mol dm^{-3} (put in)	$10^3[KIO_4]$ mol dm^{-3} (determined)	$\frac{[NaNO_2](\text{reacted})}{[KIO_4](\text{reacted})}$
2.441	7.027	1.754	1.023
2.441	5.019	1.954	1.030
2.441	5.019	1.970	1.066
1.953	5.019	1.431	0.961
1.627	2.008	1.423	0.984
1.627	5.019	1.046	0.864
			av. 0.988

Nitrite reacts with periodate, mole for mole. The stoichiometric equation representing the reaction can be written as,

$$HNO_2 + H_5IO_6 \longrightarrow 2H^+ + NO_3^- + IO_3^- + 2H_2O$$

3.4 Determination of the order with respect to each reactant

The order with respect to each reactant was determined by several experiments. The reaction conditions in each set were kept constant except for the concentration of the reactant under study.

Initial rates (calculated as given in the appendix), were used in the determination of order from the plots of log I.R versus log concentrations of reactant and where possible confirmed by other methods.

At the acidity, 1 to 2 mol dm^{-3}, used in this part of the work, $NaNO_2$ and KIO_4 put in at the concentrations, 10^{-4} and 10^{-3} mol dm^{-3} respectively will be considered as HNO_2 and H_5IO_6 without further calculation.

3.4.1 Order with respect to N(III)

Table 24

$10^3[KIO_4] = 3.172$ mol dm^{-3} [HCl] = 1.752 mol dm^{-3} T = 25°C

$10^4[HNO_2]$ mol dm^{-3}	$10^2[HNO_2]^{0.5}$ $mol^{0.5}$ $dm^{-1.5}$	10^5 I.R mol dm^{-3} min^{-1}	$\frac{10^2\ I.R}{[HNO_2]}$	$\frac{10^3\ I.R}{[HNO_2]^{0.5}}$
8.073	2.841	3.18	3.94	1.12
6.458	2.541	2.88	4.46	1.13
4.844	2.201	2.47	5.10	1.12
4.036	2.009	2.33	5.77	1.16
3.229	1.797	2.06	6.38	1.15
1.615	1.271	1.45	8.98	1.14

The apparent order with respect to $[HNO_2]$ is 0.5 and the constancy of $I.R/[HNO_2]^{0.5}$ for a five-fold variation in $[HNO_2]$ shows that only one reaction path is involved. The order appears to be a true one for this path; it is not the fortuitous result of parallel reactions of first and zero order in N(III) because this would lead to a significant variation in the figures in the last column.

3.4.2 Order with respect to I(VII)

Table 25

$10^4[NaNO_2] = 4.036$ mol dm^{-3} [HCl] = 1.691 mol dm^{-3}

T = 25°C

$10^3[H_5IO_6]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}
4.698	2.83
4.134	2.65
3.759	2.42
3.195	2.04
2.814	1.81
2.255	1.45
1.879	1.23

The slope of the line produced by plotting log I.R versus log $[H_5IO_6]$ is one, (Fig. 9a). When $[H_5IO_6]$ was plotted versus I.R, the straight line obtained passed through the origin (Fig. 9b). The apparent order with respect to I(VII) is one.

3.4.3 Order with respect to H^+

In this series of experiments, the ionic strength was kept constant by the addition of the required amount of NaCl (HW "analar" grade). This device also meant that [Cl$^-$] was constant throughout these experiments.

Table 26

$10^4[NaNO_2] = 4.036$ mol dm^{-3} $10^3[KIO_4] = 2.819$ mol dm^{-3}

$[Cl^-] = 2.254$ mol dm^{-3} T = 25°C

$[H^+]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}
2.254	3.20
2.029	2.91
1.803	2.58
1.578	2.29
1.353	1.93
1.127	1.60

The plots shown in Figs. (10a) and (10b) indicate an apparent order of one with respect to $[H^+]$.

3.4.4 Order with respect to Cl^-

Two sets of experiments were carried out. In the first, HCl was used as a source of H^+, thus Cl^- was provided as well. In the second, $HClO_4$ (B.D.H. "analar" grade) was used. It was thought that the use of $HClO_4$ might give a more precise indication of any role played in the reaction by Cl^-. In each set, NaCl (HW "analar") was used. Constant ionic strength was not maintained in the first set except that the ionic strength was high throughout. In the second set, the ionic strength was maintained by $NaClO_4$. The results of the two sets of experiments are given in table (27) and (28), and the plots of log I.R versus log $[Cl^-]$ in Figs. (11a) and (11b) their slopes are 0.97 and 1.42. This seems to imply an order with respect to $[Cl^-]$ of about one when Cl^- is all produced by HCl, but about 1.4 when derived entirely from NaCl.

The change of ionic strength from 1.75 to 2.15 mol dm^{-3} (table 27) is not expected to have drastic effect on the reaction. However, this point will be clarified later.

Table 27

$10^4[NaNO_2] = 5.651$ mol dm^{-3} $10^3[KIO_4] = 3.172$ mol dm^{-3}

$[H^+] = 1.752$ mol dm^{-3} T = 25°C

$[Cl^-]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	10^5 I.R/$[Cl^-]$ min^{-1}
2.152	3.08	1.43
2.052	2.93	1.43
1.952	2.83	1.45
1.852	2.67	1.44
1.752	2.33	1.33

The constancy of I.R/$[Cl^-]$ further confirms the order of one in Cl^-.

Table 28

$10^4[NaNO_2] = 4.792$ mol dm^{-3} $10^3[KIO_4] = 2.415$ mol dm^{-3}

$[H^+] = 1.560$ mol dm^{-3} T = 25°C

$[Cl^-]$ mol dm^{-3}	10^6I.R mol dm^{-3} min^{-1}	10^6 I.R assisted mol dm^{-3} min^{-1}	10^6I.R/$[Cl^-]$ min^{-1}	10^6 I.R/$[Cl^-]^{3/2}$ dm$^{1.5}$mol$^{-0.5}$ min^{-1}
-	2.72	-	-	-
0.333	3.29	0.57	1.72	2.99
0.667	6.68	3.96	5.941	7.27
1.000	10.02	7.30	7.30	7.30
1.333	13.46	10.74	7.50	6.98
1.667	17.33	14.61	8.76	6.79

The approximate order of 1.5 with respect to $[Cl^-]$ is further confirmed by the constancy (except for the first value at 0.333 mol dm^{-3} $[Cl^-]$) of the value obtained when I.R assisted is divided by $[Cl^-]^{1.5}$.

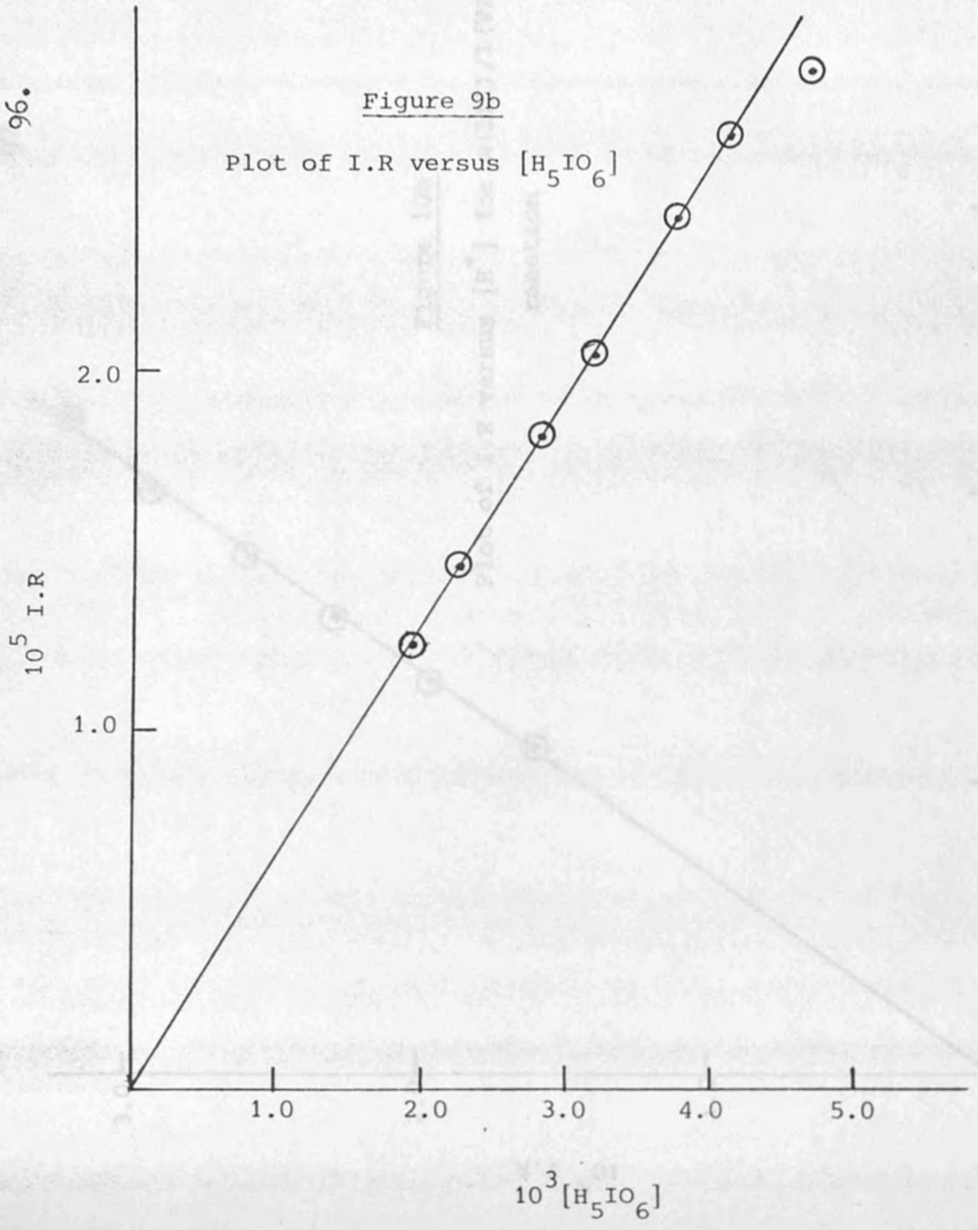


Figure 9b

Plot of I.R versus $[H_5IO_6]$

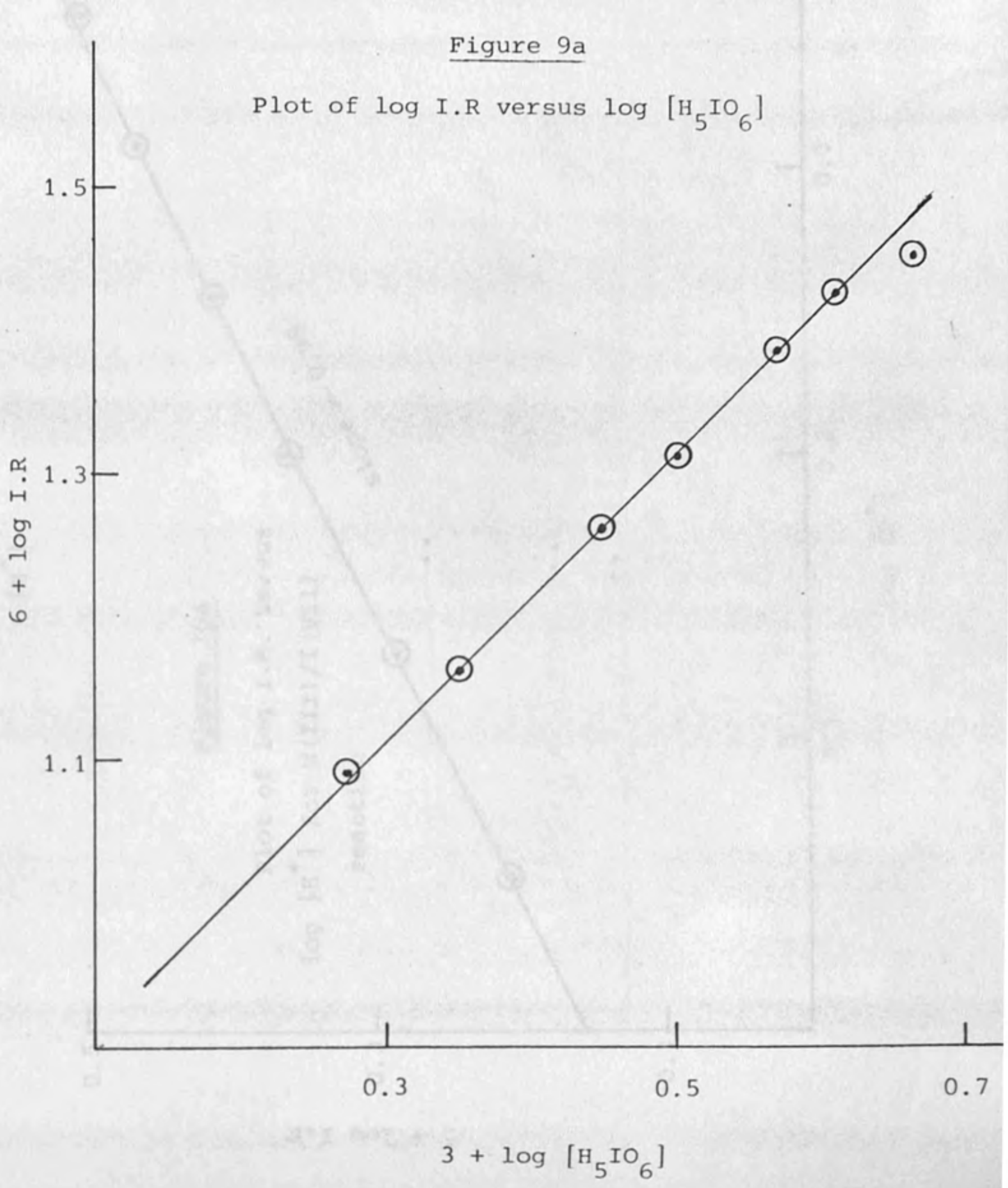


Figure 9a

Plot of log I.R versus log $[H_5IO_6]$

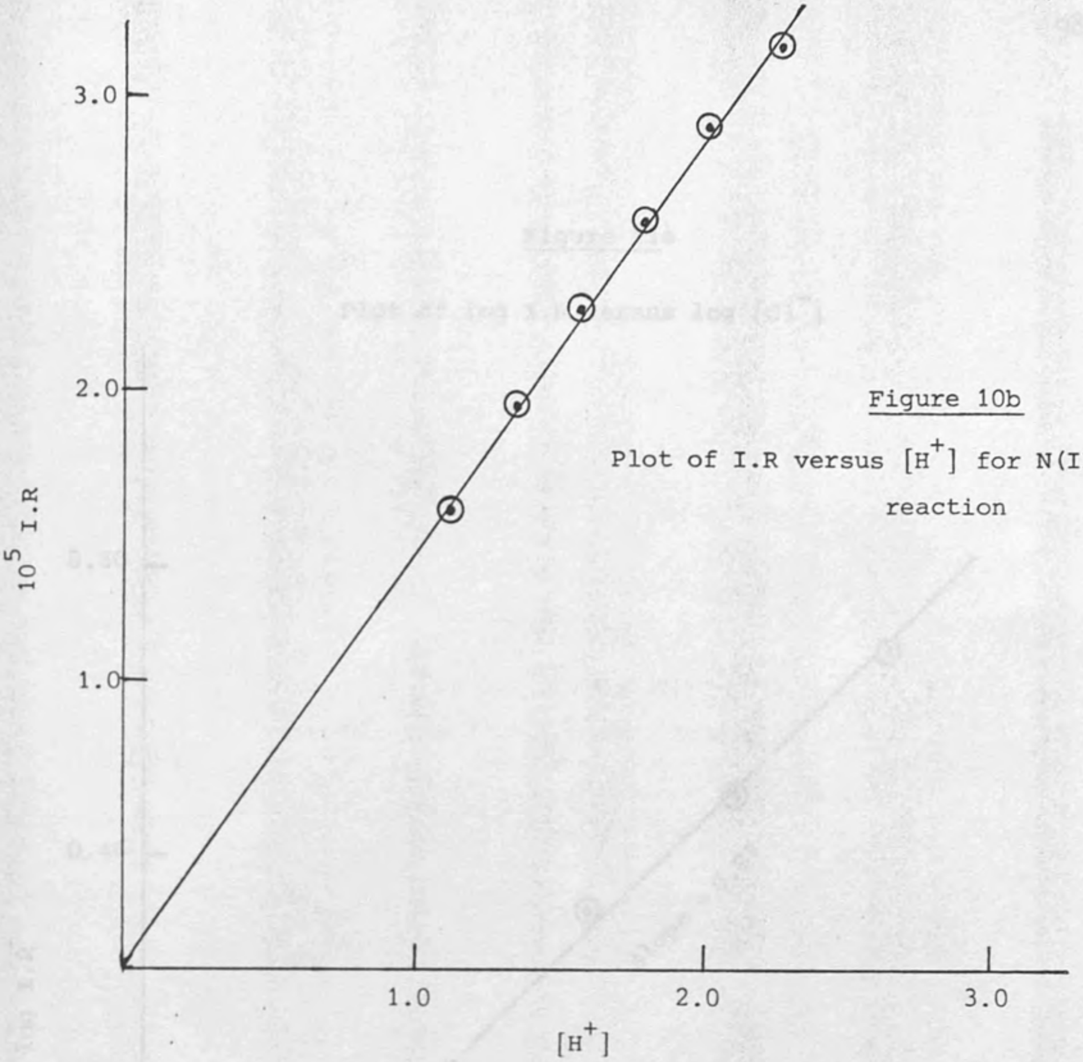


Figure 10b

Plot of I.R versus [H$^+$] for N(III)/I(VII) reaction

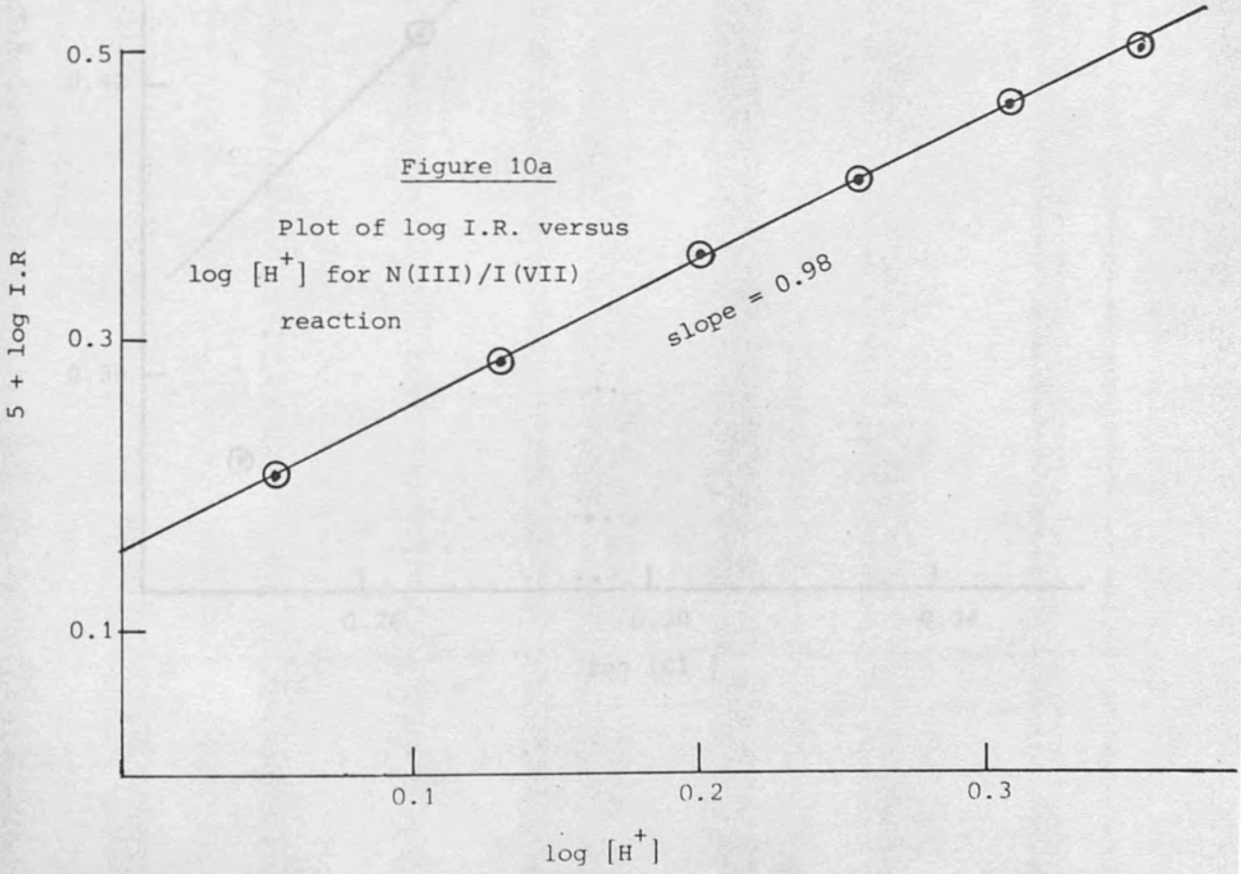


Figure 10a

Plot of log I.R. versus log [H$^+$] for N(III)/I(VII) reaction

Figure 11a

Plot of log I.R versus log $[Cl^-]$

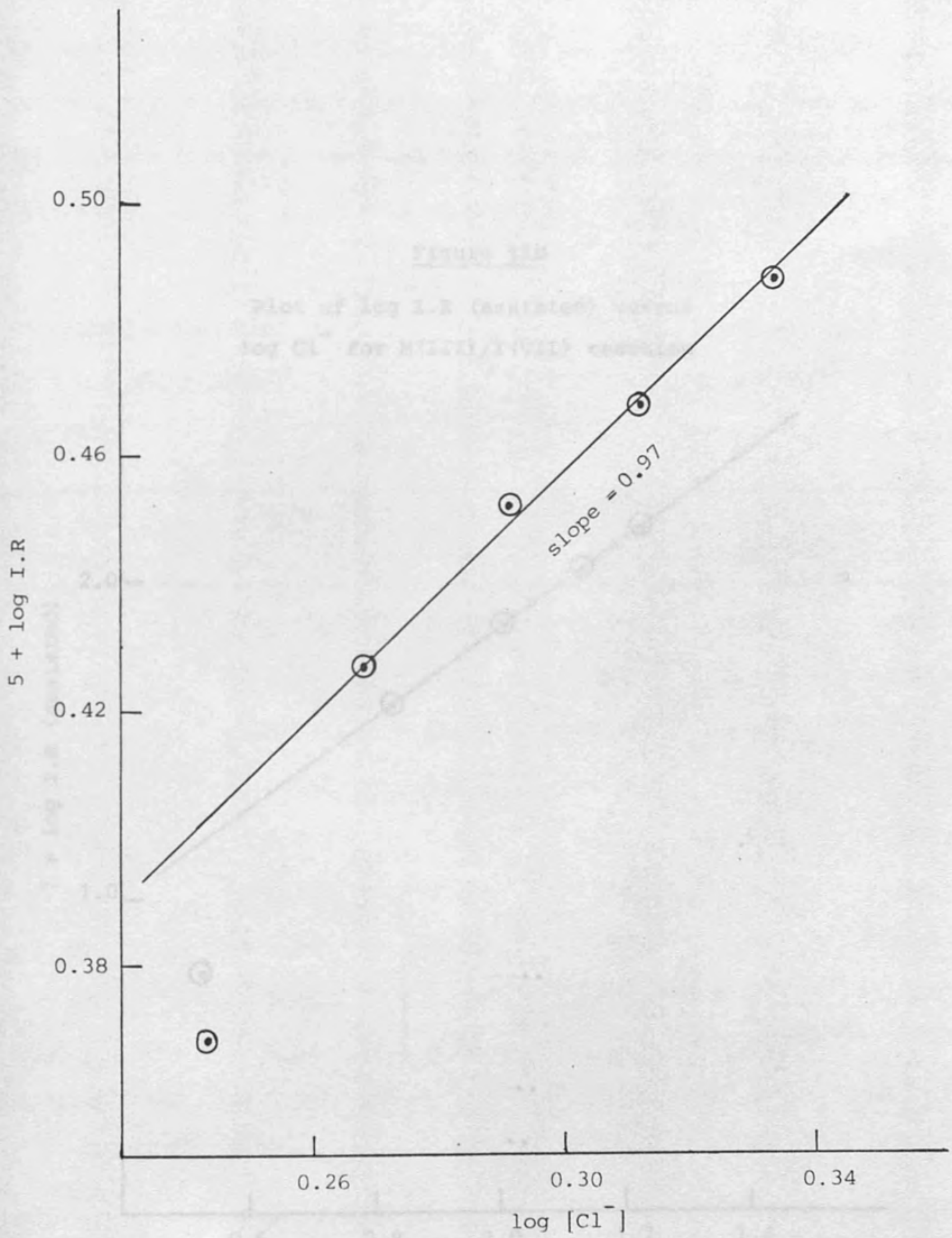
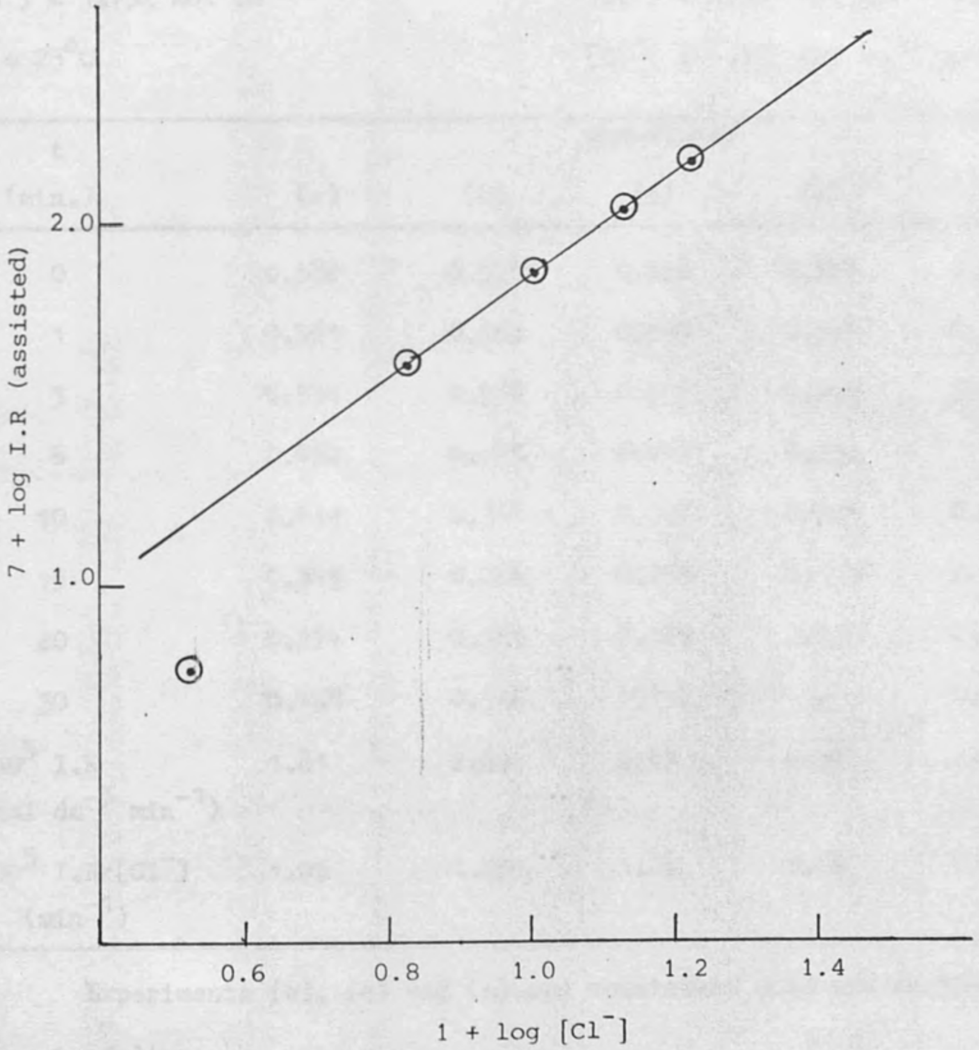


Figure 11b

Plot of log I.R (assisted) versus log Cl^- for N(III)/I(VII) reaction



3.5 The effect of added salts on the rate of reaction

3.5.1 Effect of monovalent cations

Starting with the same initial concentrations of reactants the experiments (a), (b), (c), (d) and (e), where in addition to the reactants in (a), reaction mixtures (b), (c), (d) and (e) respectively had additionally 0.4 mol dm^{-3} of LiCl (M.B. laboratory chemical), NaCl (HW "analar" grade), KCl (B.D.H. "analar" grade) and CsCl (B.D.H. laboratory reagent chemical) were accomplished. Their results are given below:

Table 29

$10^4[NaNO_2] = 5.651$ mol dm^{-3} $10^3[KIO_4] = 2.379$ mol dm^{-3}

$[H^+] = 1.752$ mol dm^{-3} $[Cl^-] = 2.152$ mol dm^{-3} (in (b) to (e))

$T = 25^\circ C$ $[Cl^-] = 1.752$ mol dm^{-3} (in (a))

t (min.)	Absorbance (a)	(b)	(c)	(d)	(e)
0	0.588	0.588	0.588	0.588	0.588
1	0.561	0.563	0.565	0.548	0.564
3	0.531	0.518	0.517	0.465	0.515
6	0.482	0.445	0.442	0.354	-
10	0.419	0.362	0.358	0.229	0.352
15	0.343	0.266	0.266	0.110	0.253
20	0.274	0.183	0.185	0.034	0.170
30	0.158	0.116	0.118	-	0.101
10^5 I.R (mol dm^{-3} min^{-1})	1.81	2.69	2.67	4.48	2.74
10^5 I.R/$[Cl^-]$ (min^{-1})	1.03	1.25	1.24	2.08	1.27

Experiments (b), (c) and (e) are consistent with one another but (d) is out of line.

In table (30), a summary of the results of the experiments in which [KCl] is varied, otherwise using the reactant conditions of table (29), (a).

Table 30

$10^4[NaNO_2] = 5.651$ mol dm^{-3} $10^3[KIO_4] = 2.379$ mol dm^{-3}

$[H^+] = 1.752$ mol dm^{-3} $T = 25^\circ C$

$[K^+]$ mol dm^{-3}	$[Cl^-]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	10^5 I.R/$[Cl^-]$ min^{-1}
0.0024	1.752	1.81	1.03
0.067	1.819	2.44	1.34
0.133	1.882	2.91	1.55
0.200	1.952	3.54	1.81
0.267	2.019	3.90	1.93
0.333	2.085	4.38	2.10
0.400	2.152	4.48	2.08

Although these results have been recorded, they are at this point inexplicable - it will later be seen that a gradual accumulation of anomalous results is understandable in terms of an impurity in several of the "analar" reagents.

3.5.2 Effect of added anions

To a reaction mixture similar to that described in experiment (a), Table (29), 0.4 mol dm^{-3} $NaNO_3$ was added and the experiment was carried out in duplicate. The measured absorbance at the time intervals given are shown in table (31).

Table 31

t (min)	0	1	3	6	10	15	20	25
Av. A	0.588	0.572	0.541	0.483	0.407	0.328	0.255	0.186
10^5 I.R = ($mol\ dm^{-3}\ min^{-1}$)		1.88						
10^5 I.R/[Cl^-] = (min^{-1})		1.07						

A comparison between the result in table (31) and the results of experiments (a) and (c) in table (29); leads to two obvious points; firstly, NO_3^- up to 0.4 mol dm^{-3} does not significantly affect the rate of reaction. Secondly, the catalysis, possibly due to Na^+, when this ion is added as NaCl is absent when the same concentration of Na^+ is supplied as $NaNO_3$.

Although much of the general kinetic behaviour of this reaction is now clear one conclusion which can be reached from several of the preceding sets of results is that some undetected catalytic (or inhibitory) influence is at work in some experiments. The next set of experiments was one thought prudent to try in attempting to locate any source of anomaly.

3.5.3 Effect of transition metal ions

Although the addition of about 1.7 x 10^{-3} mol dm^{-3} Na_2 EDTA to a reaction mixture did not produce any effect on the rate of reaction (page 88), it might be that some of the additional reagents added have contained kinetically significant traces of metal ions. This possibility was investigated by the deliberate addition of some metal ions to a reaction mixture, each in amount similar to the amount of $NaNO_2$ present in the mixture. The results obtained are given below.

*Table 32

10^4[NaNO$_2$] = 7.027 mol dm^{-3} 10^3[KIO$_4$] = 2.42 mol dm^{-3}

[HCl] = 1.752 mol dm^{-3} T = 25°C

t (min)	No additives	Cu^{2+} 7.67 x 10^{-4} mol dm^{-3}	Co^{2+} 7.428 x 10^{-4} mol dm^{-3}	Cr^{3+} 6.915 x 10^{-4} mol dm^{-3}	Fe^{2+} 7.213 x 10^{-4} mol dm^{-3}
	Absorbance				
0	0.734	0.734	0.734	0.734	0.734
1	0.703	0.708	0.708	0.707	0.584
3	0.671	0.682	0.679	0.679	0.560
6	0.609	0.617	0.618	0.618	0.511
10	0.542	0.552	0.551	0.548	0.454
15	0.458	0.465	0.465	0.462	0.385
20	0.379	0.386	0.387	0.384	0.317
25	0.306	0.315	0.315	0.313	0.267

* No EDTA is added.

The presence of Cu^{2+}, Co^{2+} and Cr^{3+} added as $CuSO_4$, $Cr_2(SO_4)_3$ and $Co(NO_3)_2$ produced no effect on the rate of reaction.

The effect of Fe^{2+} is similar to its effect on the NO_2^-/ClO_2^- reaction, in that about 25% of the nitrite reacted immediately, but in this reaction, the N(III) species subsequently continued to disappear at a measurable rate.

The results so far obtained, can be used to establish a rate expression for the reaction between nitrite and periodate in aqueous hydrochloric acid solution. It should be noted that in all experiments, the rate of reaction was much faster than the rate of decomposition of nitrous acid$^{(5)}$.

Since, experimental results showed that

$$\text{Rate } \alpha \ [HNO_2]^{0.5}, [H_5IO_6], [H^+] \text{ and } [Cl^-]$$

a rate equation such as

$$\text{Rate} = k[HNO_2]^{0.5}[H_5IO_6][H^+][Cl^-] \qquad \ldots\ldots \quad (44)$$

should give a constant value for the reaction rate constant. Calculations based on this rate law for the experiments conducted at 25°C are given in table (33), collecting results previously given together with some others.

The average value 1.86×10^{-3} $dm^{7.5}$ $mol^{-2.5}$ s^{-1} for k was calculated. The majority of rate constant values do not vary by more than 3% from the average.

Perhaps it should be emphasised at this point that although this value of the rate constant will subsequently be shown to be of little importance, the kinetics so far elucidated are valid.

Up to this stage of the investigation only one source had been used for each chemical used. At this point, however, use of a fresh supply of hydrochloric acid was necessary. No alterations in general technique or apparatus were made.

Table 33

$10^4[HNO_2]$ mol dm^{-3}	$10^2[HNO_2]^{0.5}$ $mol^{0.5}$ $dm^{-1.5}$	$10^3[H_5IO_6]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	$[Cl^-]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	10^3k $dm^{7.5}mol^{-2.5}s^{-1}$
4.256	2.063	2.453	1.691	1.691	1.60	1.84
4.036	2.009	3.758	1.691	1.691	2.38	1.84
8.073	2.841	3.172	1.752	1.752	3.18	1.92
6.458	2.541	3.172	1.752	1.752	2.88	1.94
4.844	2.201	3.172	1.752	1.752	2.47	1.92
4.036	2.009	3.172	1.752	1.752	2.33	1.98
3.229	2.797	3.172	1.752	1.752	2.06	1.96
1.615	1.271	3.172	1.752	1.752	1.45	1.95
4.036	2.009	4.698	1.691	1.691	2.83	1.75
4.036	2.009	4.134	1.691	1.691	2.65	1.86
4.036	2.009	3.759	1.691	1.691	2.42	1.87
4.036	2.009	3.195	1.691	1.691	2.04	1.85
4.036	2.009	2.814	1.691	1.691	1.81	1.87
4.036	2.009	2.255	1.691	1.691	1.45	1.86
4.036	2.009	1.879	1.691	1.691	1.23	1.90
4.036	2.009	2.819	2.254	2.254	3.20	1.85
4.036	2.009	2.819	2.029	2.254	2.91	1.87
4.036	2.009	2.819	1.803	2.254	2.58	1.87
4.036	2.009	2.819	1.578	2.254	2.29	1.89
4.036	2.009	2.819	1.333	2.254	1.93	1.89
4.036	2.009	2.819	1.127	2.254	1.60	1.85
7.027	2.651	2.420	1.752	1.752	2.14	1.81
5.651	2.377	3.172	1.752	2.152	3.08	1.80
5.651	2.377	3.172	1.752	2.052	2.93	1.78
5.651	2.377	3.172	1.752	1.952	2.83	1.83
5.651	2.377	3.172	1.752	1.852	2.67	1.83
5.651	2.377	3.172	1.752	1.752	2.33	1.68

3.5.4 Various experiments

Following on from the partially unexplained results in the presence of "inert" 1:1 electrolyte additives, a set of experiments was carried out adding di- and tri-valent ions partly in the hope that 'anomalies' with 1:1 electrolytes might be magnified and easily investigated with more higher charged species. Even with small amounts of additives, however, a new irreproducibility appeared in the results.

Table (34) lists the results of nine experiments,

(1) Is a control with no additives.

(2) Contained 4.16 x 10^{-3} mol dm^{-3} $Ba(NO_3)_2$.

(3) Contained 4.16 x 10^{-3} mol dm^{-3} $LaCl_3$.

(4)-(8) Further control experiments using fresh sources of $NaNO_2$ and KIO_4.

(9) $NaIO_4$ was used as the source of periodate.

Table 34

Experiment No.	$10^4[HNO_2]$ mol dm^{-3}	[HCl] mol dm^{-3}	$10^3[H_5IO_6]$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	10^3 k $dm^{7.5}$ $mol^{-2.5}$ s^{-1}
1	5.019	1.739	2.420	3.04	3.09
2	5.019	1.739	2.420	3.04	3.09
3	5.019	1.739	2.420	3.36	3.42
4	5.816	1.621	2.412	3.44	3.08
5	4.766	1.621	2.414	2.62	3.15
6	4.766	1.621	3.219	3.41	3.08
7	5.850	1.617	3.348	3.71	2.92
8	4.766	1.081	2.414	0.76	2.06
9	4.766	1.081	2.481	0.76	2.00

Rate constants were calculated from the rate expression (equation 44), and it is obvious that the rate constant obtained from most of these experiments is different from 1.86×10^{-3} $dm^{7.5}$ $mol^{-2.5}$ s^{-1} previously obtained by a factor of about 1.6. However, it is noticeable that when the concentration of hydrochloric acid was reduced from about 1.6 to 1.1 mol dm^{-3}, the rate constant dropped as well.

The only experimental difference unaccounted for between this set and the earlier experiments is the hydrochloric acid. Since both sources of HCl had been of technical grade; accordingly an analar grade sample was tried.

Results obtained with this acid are given in Table (35). The average rate constant found now was 7.11×10^{-3} $dm^{7.5}$ $mol^{-2.5}$ s^{-1}, about four times the average value, 1.86×10^{-3} $dm^{7.5}$ $mol^{-2.5}$ s^{-1} found with technical grade HCl, although each set is internally repeatable.

Table 35

Experiment No.	$10^4[NaNO_2]$ mol dm^{-3}	[HCl] mol dm^{-3}	$10^3[H_5IO_6]$ mol dm^{-3}	10^5 I.R mol $dm^{-3}min^{-1}$	10^3 k $dm^{7.5}$ $mol^{-2.5}s^{-1}$
1	5.830	1.632	3.348	9.52	7.08
2*	5.850	1.625	3.348	8.70	7.00
3	5.819	1.628	2.939	7.95	7.05
4	5.819	1.628	2.498	6.69	7.27
5	5.819	1.628	3.219	8.83	7.15
				av.	7.11

[* In this experiment a sample of the acid (1.632 mol dm^{-3}) used in experiment (1) was passed through a cation exchange (analar grade amberlite resin, I.R. 120 (H^+)), collected and restandardised and used in experiment(2). The possibility of cation interference in the rate of reaction seems excluded].

At first sight a change of 4-fold in rate caused by a difference in impurity levels in commercial samples of hydrochloric acid is surprising. Had the reaction been of a free radical nature the variation in rate could have been more readily acceptable. However, one has to note the discrepancy between the concentrations of reagents used. An impurity present in 0.01% in the acid, will be of comparable concentration to the nitrite in the reaction mixture. In principle such an impurity might be inhibiting the reaction in technical HCl or catalysing the reaction in analar HCl, and perhaps the expectation would be the former.

To demonstrate that the samples of hydrochloric acid are the source of the irreproducibility, experiments (a), (b), (c), (d) and (e) were performed and the results are listed in Table (36). The acid used was composed of a mixture of the analar and technical grades. The acids used were:

(a) 1.632 mol dm^{-3} analar grade HCl.

(b) As (a); reaction mixture also contained 8.33×10^{-3} mol dm^{-3} Na_2 EDTA.

(c) 1.617 mol dm^{-3} technical grade HCl.

(d) 1.509 mol dm^{-3} technical acid + 0.109 mol dm^{-3} analar acid (1.618 mol dm^{-3} in HCl).

(e) 1.293 mol dm^{-3} technical acid + 0.326 mol dm^{-3} analar acid (1.619 mol dm^{-3} in HCl).

The two acid solutions were purged with N_2 for more than one hour to remove possible traces of Cl_2 or H_2O_2 standardised and used.

The purging and the EDTA are without influence, but the rate of reaction varies roughly linearly with acid composition.

Table 36

10^4[$NaNO_2$] = 5.850 mol dm^{-3} 10^3[KIO_4] = 3.348 mol dm^{-3}

T = 25°C

t(min)	Absorbance				
	a	b	c	d	e
0	0.624	0.624	0.624	0.624	0.624
1	0.526	0.532	0.572	0.567	0.532
3	0.369	0.371	0.515	0.492	0.466
5	0.234	0.233	0.446	0.417	0.371
7	0.132	0.136	0.387	0.350	0.290
9	0.057	0.062	0.331	0.285	0.218
12	-	-	0.243	0.201	0.128
10^5 I.R (mol dm^{-3} min^{-1})	9.16	9.16	3.71	4.17	5.15

Specifications of commerical samples of hydrochloric acid mention the impurities, arsenic, antimony, bromide and iodide. The results in Table (37) indicate the non-interference of Sn^{2+} in the reaction.

Table 37

10^4[$NaNO_2$] = 5.850 mol dm^{-3} 10^3[KIO_4] = 3.348 mol dm^{-3}

[HCl] = 1.617 mol dm^{-3} T = 25°C

t(min)	Absorbance		
	a	b	c
1	0.572	0.568	0.569
3	0.515	0.505	0.504
5	0.446	0.439	0.439
7	0.387	0.381	0.381
9	0.331	0.321	0.324
12	0.243	0.237	0.234

(a) Control experiment.

(b) 9.69 x 10^{-5} mol dm^{-3} $SnCl_2$ added.

(c) 1.632 x 10^{-4} mol dm^{-3} $SnCl_2$ added.

Crude experiments involving the deliberate addition of arsenite, iodide and bromide (to reactant solutions in technical HCl) were carried out at room temperature (~ 20°C).

Table (38) lists (a) a control experiment, (b) one with about 10^{-4} mol dm^{-3} AS_2O_3 added, (c) approximately 10^{-4} mol dm^{-3} NaI added and (d) approximately 10^{-4} mol dm^{-3} NaBr added.

Table 38

$10^4[NaNO_2] = 4.012$ mol dm^{-3} $10^3[KIO_4] = 2.009$ mol dm^{-3}

$[HCl] = 1.297$ mol dm^{-3} $T \approx 20°C$

t (min)	No additives	As_2O_3	NaI	NaBr
2	0.418	0.416	0.411	0.403
5	0.398	0.392	0.395	0.345
10	0.363	0.360	0.361	0.259
15	0.328	0.329	0.326	0.185

The clue given by these results is that perhaps it is Br^- which is the impurity contaminating HCl, and this impurity has a catalytic effect. The implication is that the analar acid is more contaminated than technical acid. This conclusion was further studied.

3.6 Effect of Br^- on the rate of reaction

In "aristar" grade hydrochloric acid, the reaction between N(III) and I(VII) was found to be very slow. For example, Table (39) shows the absorbance data at the given intervals of time for two experiments, (a) and (b). In (a), KIO_4 was not present, so that the change in absorbance with time is due to decomposition of nitrous acid. In (b), the reacting solution contained 3.397×10^{-3} mol dm^{-3} KIO_4 in addition to reactants in (a).

Table 39

$10^4[NaNO_2] = 6.077$ mol dm^{-3} $[HCl]_{(aristar)} = 1.630$ mol dm^{-3}

T = 25°C

t(min)	Absorbance a	Absorbance b
1	0.623	0.613
5	0.609	0.603
10	0.593	0.576
15	0.581	0.562
25	0.560	0.532
35	0.542	0.506
10^6 I.R (mol dm^{-3} min^{-1})	3.70	6.04

Aristar grade hydrochloric acid was then used in order to determine the effect of Br$^-$ on the rate of reaction and in all experiments reported hereafter, so that a rate expression that correctly describes the experimental results could be deduced. The assumption being made is that in all experiments run in media in which Cl$^-$ is supplied by other than aristar HCl that (an at present unknown concentration of)Br$^-$ caused catalysis, and that Br$^-$ was an essential component of the reaction mixture.

In a series of experiments and under constant reactant concentrations (N(III), I(VII), H$^+$ and Cl$^-$), the effect of Br$^-$ was studied by the addition of NaBr. The results are summarised in Table (40).

Table 40

$10^4[NaNO_2] = 6.077$ mol dm^{-3} $10^3[KIO_4] = 3.397$ mol dm^{-3}

$[HCl] = 1.630$ mol dm^{-3} T = 25°C

Experiment No.	$10^5[Br^-]$ mol dm^{-3}	10^5 I.R mol dm^{-3}min^{-1}	10^5 I.R assisted mol dm^{-3} min^{-1}	k dm$^{10.5}$ mol$^{-3.5}$s^{-1}
	no additive	0.60	-	-
1	0.906	1.46	0.86	71.1
2	1.812	2.33	1.73	71.5
3	2.718	3.16	2.56	70.6
4	3.624	3.91	3.31	68.4
5	5.436	5.43	4.83	66.6
6	7.248	6.07	5.47	56.5
7	9.060	6.67	6.07	50.2

An apparent order of one with respect to $[Br^-]$ was obtained from the slope of the line (0.97) resulting from the plot of log $[Br^-]$ versus log I.R assisted and the line produced when I.R. assisted was plotted versus $[Br^-]$ passed through the origin (Figures 12a and 12b). This first order behaviour, however, shows signs of falling off above about 6×10^{-5} mol dm^{-3} Br^- in these reaction mixtures.

When (absorbance)$^{0.5}$ is plotted against time for each experiment containing Br^-, straight lines are obtained (Fig. 13) for more than 80% completion of the reaction. Thus assuming that the rate expression

$$\text{Rate} = k\,[HNO_2]^{0.5}[H_5IO_6][H^+][Cl^-][Br^-] \qquad \ldots\ldots \quad (45)$$

is valid, the values of k calculated from each experiment are given in the last column of Table (40).

The observation that the rate constant drops as $[Br^-]$ rises was confirmed in other experiments using various experimental conditions at 25°C as shown in Table (41).

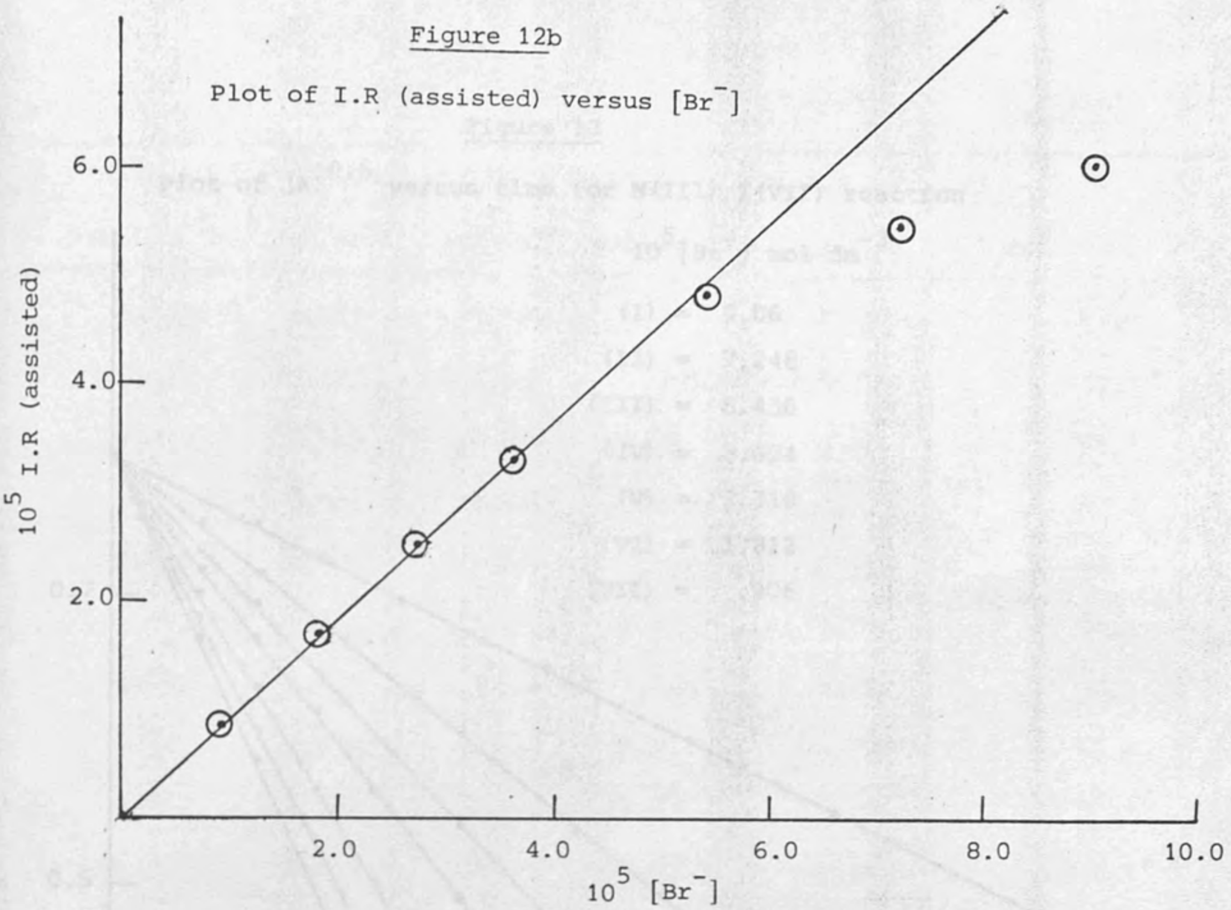


Figure 12b

Plot of I.R (assisted) versus [Br$^-$]

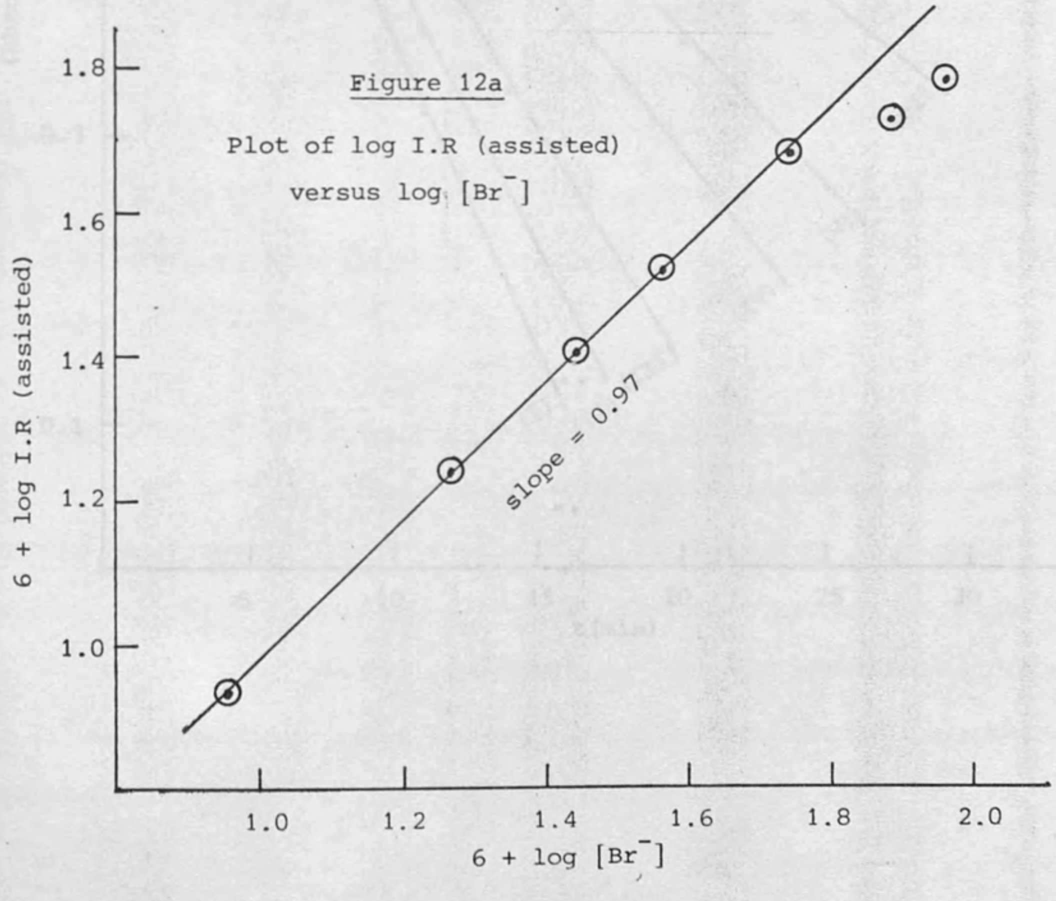


Figure 12a

Plot of log I.R (assisted) versus log [Br$^-$]

Figure 13

Plot of $(A)^{0.5}$ versus time for N(III)/I(VII) reaction

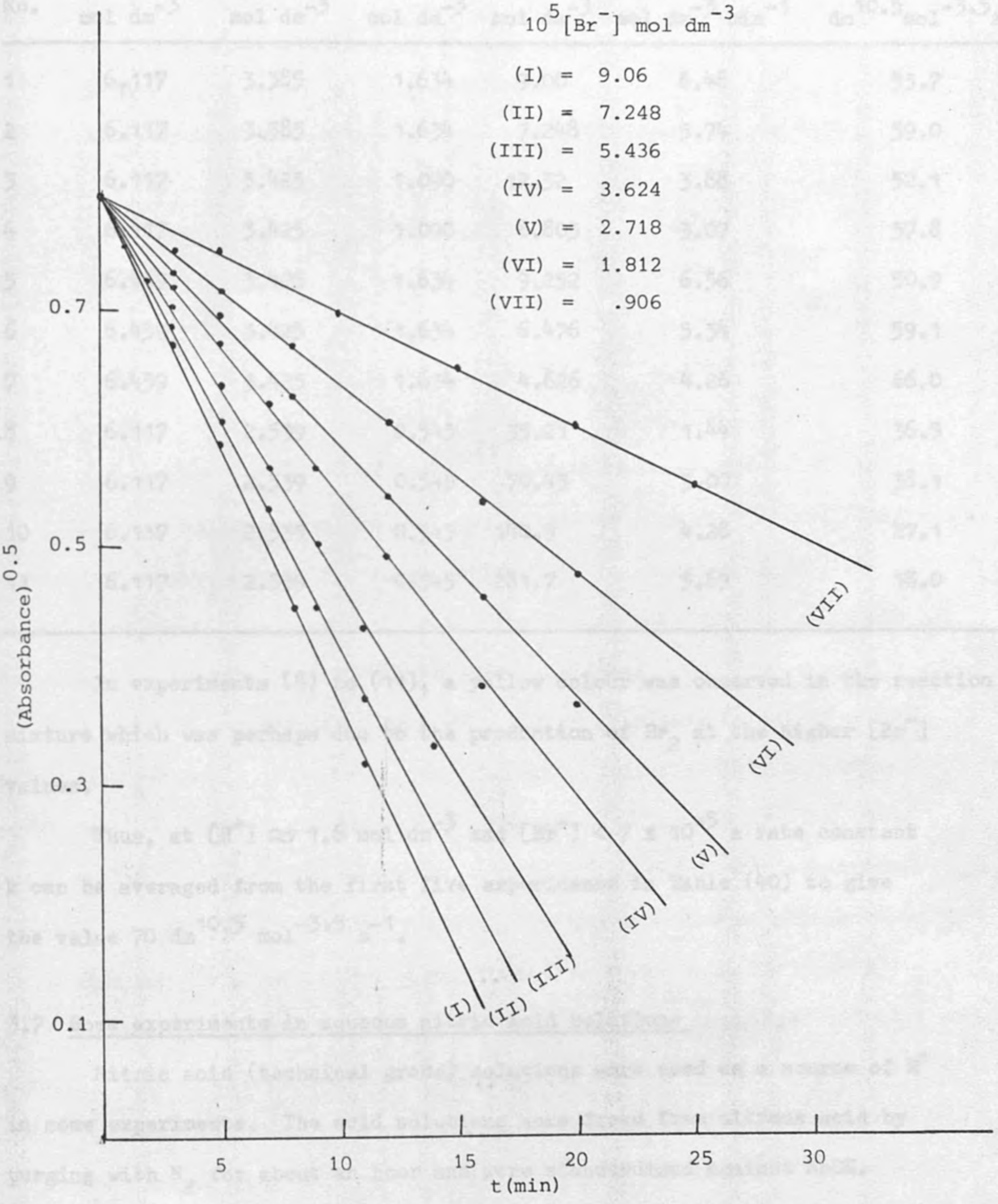


Table 41

Exp. No.	$10^4[NaNO_2]$ mol dm^{-3}	$10^3[KIO_4]$ mol dm^{-3}	[HCl] mol dm^{-3}	$10^5[Br^-]$ mol dm^{-3}	10^5 I.R assisted mol dm^{-3} min^{-1}	k dm$^{10.5}$mol$^{-3.5}$s^{-1}
1	6.117	3.385	1.634	9.00	6.48	53.7
2	6.117	3.385	1.634	7.248	5.74	59.0
3	6.117	3.425	1.090	12.32	3.88	52.1
4	6.117	3.425	1.090	8.803	3.07	57.8
5	6.459	3.425	1.634	9.252	6.56	50.9
6	6.459	3.425	1.634	6.476	5.34	59.1
7	6.459	3.425	1.634	4.626	4.26	66.0
8	6.117	2.539	0.545	35.21	1.44	36.5
9	6.117	2.539	0.545	70.43	3.00	38.1
10	6.117	2.539	0.545	140.9	4.28	27.1
11	6.117	2.539	0.545	281.7	5.69	18.0

In experiments (8) to (11), a yellow colour was observed in the reaction mixture which was perhaps due to the production of Br_2 at the higher $[Br^-]$ values.

Thus, at $[H^+] \approx 1.6$ mol dm^{-3} and $[Br^-] < 7 \times 10^{-5}$ a rate constant k can be averaged from the first five experiments in Table (40) to give the value 70 dm$^{10.5}$ mol$^{-3.5}$ s^{-1}.

3.7 Some experiments in aqueous nitric acid solutions

Nitric acid (technical grade) solutions were used as a source of H^+ in some experiments. The acid solutions were freed from nitrous acid by purging with N_2 for about an hour and were standardised against NaOH.

The results of the two experiments (a) and (b) are given in Table (42). No Cl^- is deliberately added to these reaction mixtures; run (a), however, includes 1.812×10^{-4} mol dm^{-3} Br^- (b) includes 3.624×10^{-4} mol dm^{-3} Br^-.

Table 42

$10^4[NaNO_2] = 4.340$ mol dm^{-3} $10^3[KIO_4] = 3.397$ mol dm^{-3}

$[HNO_3] = 1.535$ mol dm^{-3} $T = 25^\circ C$

t(min)	Absorbance a	 b
1	0.449	0.452
5	0.445	0.432
10	0.423	0.391
15	0.412	0.357
20	0.392	0.329
25	0.381	0.302

Although no control experiment was performed, the results are, however, indicative of two points; the first is that, in the absence of Cl^-, the reaction proceeds at a measurable rate; the second point is that the rate of reaction varies with $[Br^-]$ in nitric acid solutions.

One earlier observation was that addition of alkali chlorides caused catalysis. It would, of course, be possible to interpret this as cation catalysis but this was doubted. When, for example, 0.4 mol dm^{-3} Na^+ was added as $NaNO_3$ it produced no effect. Since Br^- is a reported contaminant of NaCl, and Br^- catalyses the reaction, the increase in rate attributable to cations may be actually due to Br^- (see also later, e.g. Table (47)).

In Table (43), the results of experiments, (a'), (b'), (c') and (d') are given. These experiments were accomplished in aqueous nitric acid solutions under the same conditions. A constant concentration of Cl^- was used in each case derived from different sources of sodium chloride as follows:-

(a') NaCl (B.D.H. "ultrar" grade).

(b') NaCl (B.D.H. "analar" grade).

(c') NaCl (HW "analar" grade).

(d') NaCl (M.B. technical grade).

Table 43

$10^4[NaNO_2] = 5.850$ mol dm^{-3} $10^3[KIO_4] = 3.348$ mol dm^{-3}

$[HNO_3] = 1.535$ mol dm^{-3} T = 25°C

$[Cl^-] = 1.0$ mol dm^{-3}

t (min)	No additives	Absorbance (a')	(b')	(c')	(d')
1	0.599	0.593	0.579	0.590	0.567
5	0.595	0.589	0.512	0.552	0.455
10	0.588	0.573	0.414	0.506	0.310
15	0.585	0.564	0.336	0.466	0.185
20	0.586	0.550	0.259	0.420	0.086
25	0.581	0.542	0.188	0.382	-

The plots of (absorbance)$^{\frac{1}{2}}$ against time produced good straight lines (except in d' where the points were scattered).

The differences in the rate of N(III) disappearance between (a') and any other experiment, and between (b') and (c') are likely to be due to differences in the amount of Br^- contaminating each salt. According to the catalogues of the suppliers, the impurities contaminating NaCl ('analar' grade (B.D.H) and(HW)) are exactly the same and present in the same amounts, which does not seem to be the case. However, "ultrar" grade NaCl may be used as a source of Cl^- without the complications created by the impurities.

3.8 Order with respect to H^+ and Cl^-

The results which led to the conclusion of a first order dependence of rate on $[H^+]$ and $[Cl^-]$ (Tables 26 and 27) were obtained from experiments that were carried out using HCl (B.D.H. technical and NaCl (HW analar) grade chemicals. Because the contaminant Br^- has been shown to be a participant in the reaction, a repetition of the earlier experiments using "bromide free" chemicals was carried out. It is worth noting that the consistency of the results in Table (26) and (27) arises because the addition of NaCl to maintain the ionic strength as HCl was varied presumably balanced out the concentration of contaminant.

The order with respect to $[H^+]$ was obtained from a series of experiments using "aristar" grade HCl and "ultrar" grade NaCl to keep constancy of ionic strength, in the presence of added Br^-. The results of the experiments are given in Table (44).

Table 44

$10^4[NaNO_2] = 6.418$ mol dm^{-3} $10^3[KIO_4] = 2.582$ mol dm^{-3}

$[Cl^-] = 1.413$ mol dm^{-3} $10^5[Br^-] = 9.06$ mol dm^{-3}

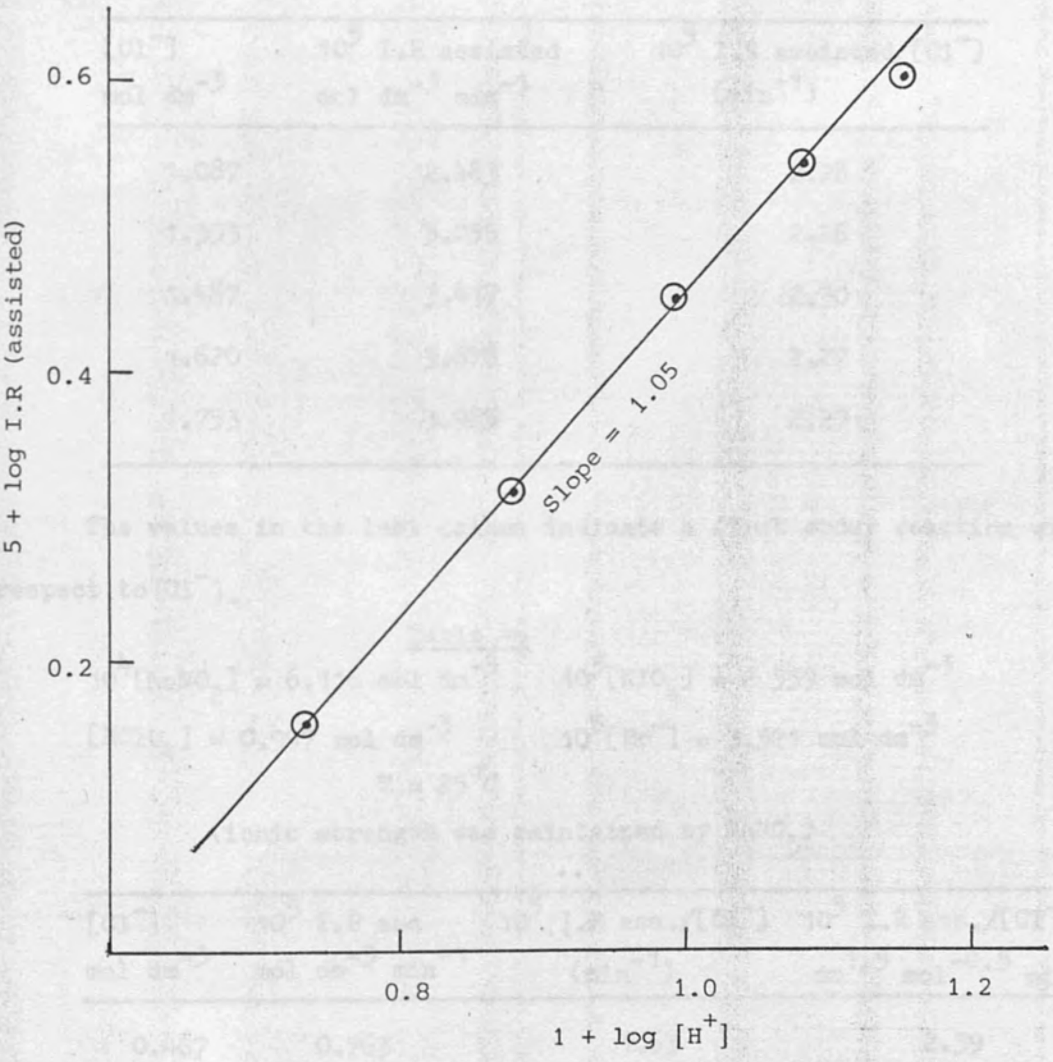
$T = 25^\circ C$

$[H^+]$ mol dm^{-3}	10^5 I.R assisted mol dm^{-3} min^{-1}
0.543	1.44
0.761	2.07
0.978	2.81
1.195	2.49
1.413	4.01

The slope of the line produced from the plot of log I.R assisted against log $[H^+]$ was 1.05 (Fig. 14). The order with respect to $[H^+]$ is one as was found with the earlier bromide-contaminated solutions.

Figure 14

Plot of log I.R assisted versus log $[H^+]$



The order with respect to Cl^- was investigated by two sets of results obtained from experiments conducted in HCl (aristar) and in $HClO_4$ (analar) where Cl^- in the latter was added as NaCl (ultrar). Br^- was added as NaBr in each set of experiments. The results of the first set of experiments are shown in table (45) and at the second set in table (46).

Table 45

$10^4[NaNO_2] = 6.418$ mol dm^{-3} $10^3[KIO_4] = 2.582$ mol dm^{-3}

$[H^+] = 1.087$ mol dm^{-3} $10^5[Br^-] = 9.06$ mol dm^{-3}

T = 25°C

(ionic strength was maintained by $NaNO_3$)

$[Cl^-]$ mol dm^{-3}	10^5 I.R assisted mol dm^{-3} min^{-1}	10^5 I.R assisted/$[Cl^-]$ (min^{-1})
1.087	2.483	2.28
1.353	3.055	2.26
1.487	3.417	2.30
1.620	3.678	2.27
1.753	3.985	2.27

The values in the last column indicate a first order reaction with respect to $[Cl^-]$.

Table 46

$10^4[NaNO_2] = 6.116$ mol dm^{-3} $10^3[KIO_4] = 2.559$ mol dm^{-3}

$[HClO_4] = 0.997$ mol dm^{-3} $10^5[Br^-] = 3.521$ mol dm^{-3}

T = 25°C

(ionic strength was maintained by $NaNO_3$)

$[Cl^-]$ mol dm^{-3}	10^5 I.R ass mol dm^{-3} min^{-1}	10^5 I.R ass./$[Cl^-]$ (min^{-1})	10^5 I.R ass./$[Cl^-]^{1.5}$ dm$^{1.5}$ mol$^{-0.5}$ min^{-1}
0.467	0.763	1.63	2.39
0.667	1.265	1.89	2.32
1.000	2.176	2.19	2.18

The order with respect to [Cl$^-$] in aqueous $HClO_4$ solutions is, however, 1.5, which is the same observation as before (see Table 28).

3.9 The effect of monovalent cations

The possible involvement of K^+, Na^+ and Cs^+ in the reaction was further investigated by a set of experiments, (a), (b) and (c). In addition to the reactants, experiments (a), (b) and (c) contained 0.2 mol dm^{-3} $NaNO_3$, KNO_3 and $CsNO_3$. "Aristar" HCl aqueous solutions were used. The results given below show that none of the added cations produced any effect on the rate of reaction confirming again that Br$^-$ contamination was the cause of enhanced rates in the earlier experiments.

Table 47

$10^4[NaNO_3] = 6.117$ mol dm^{-3} $10^3[KIO_4] = 2.539$ mol dm^{-3}

[HCl] = 1.09 mol dm^{-3} $10^5[NaBr] = 8.105$ mol dm^{-3}

T = 25°C

t (min.)	no additives	Absorbance (a)	 (b)	 (c)
0	0.656	0.656	0.656	0.656
1	0.628	0.627	0.624	0.627
3	0.581	0.578	0.579	0.576
5	0.537	0.541	0.538	0.542
8	0.483	0.478	0.485	0.481
12	0.399	0.389	0.401	0.395
17	0.316	0.320	0.319	0.319

3.10 The effect of I^- on the rate of reaction

The semiqualitative test of the effect of I^- implied the lack of effect of I^- on the rate of reaction (see page 110). However, when NaI was added to reaction mixtures (2 to 6 x 10^{-4} mol dm^{-3}), a yellow colour appeared immediately. This is likely to be due to the formation of I_2 as a result of the reaction between I^- and periodate which is known to be very fast(35) when $[H^+]$ exceeds 1 mol dm^{-3}.

The rate of disappearance of N(III) in a reaction mixture containing 6 x 10^{-5} mol dm^{-3} NaI, was followed. The absorbance-time data is given in Table (48).

Table 48

$10^4[NaNO_2]$= 6.077 mol dm^{-3} $10^3[KIO_4]$ = 3.397 mol dm^{-3}

$[HCl]_{(aristar)}$ = 1.63 mol dm^{-3} T = 25°C

t (min.)	1	5	10	15	25	35
A	0.619	0.604	0.588	0.569	0.538	0.510

The lack of effect of I^- is confirmed by the results shown above. The rate appears to be just that of N(III) decomposition.

3.11 The effect of temperature on the rate of reaction

Two sets of experiments were carried out. In the first, the reaction mixture contained only HCl (technical), $NaNO_2$ and KIO_4 and rates were measured in the temperature range 15 - 40°C. In the second NaCl (HW analar) was added and rates were measured in the temperature range 25 - 40°C.

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

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

Initial rates were plotted against $I/_T$ (Figs. 15a and 15b) and the values of E were estimated as

Gradient = $-E/2.303R$

The results of the two sets of experiments are summarised in Tables (49) and (50). The nominal value for E, obtained from the first set is 65.3 kJ mol^{-1} and from the second set is 64.8 kJ mol^{-1}.

Table 49

$10^4[NaNO_2] = 6.709$ mol dm^{-3} $10^3[KIO_4] = 3.221$ mol dm^{-3}

$[HCl] = 1.739$ mol dm^{-3}

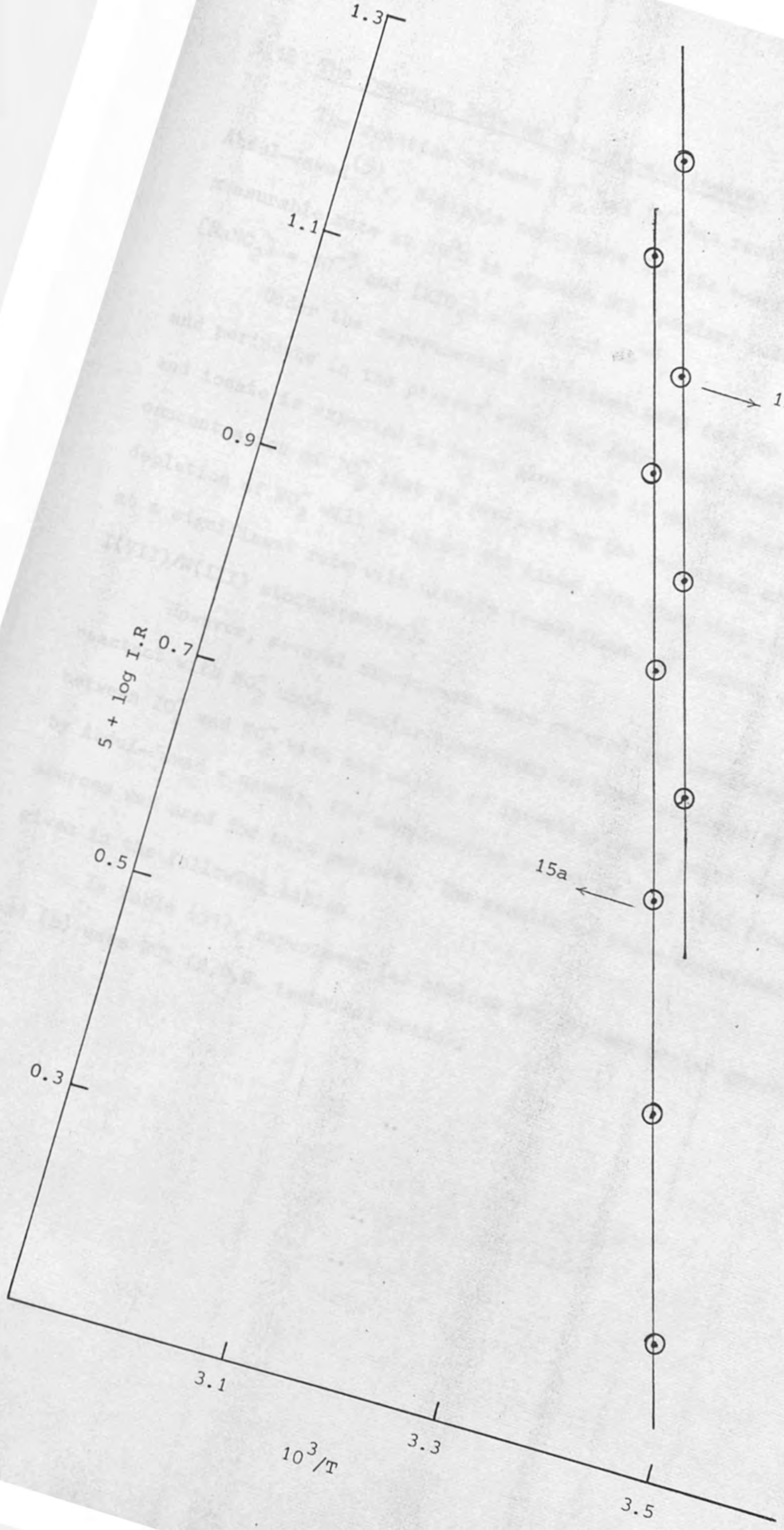
10^5 I.R mol dm^{-3} min^{-1}	5 + log I.R	1000/T°
1.65	0.218	3.470
2.64	0.421	3.411
4.03	0.606	3.354
6.37	0.804	3.299
9.47	0.976	3.245
14.6	1.164	3.193

Table 50

$10^4[NaNO_2] = 6.709$ mol dm^{-3} $10^3[KIO_4] = 3.221$ mol dm^{-3}

$[HCl] = 1.739$ mol dm^{-3} $[NaCl] = 0.467$ mol dm^{-3}

10^5 I.R. mol dm^{-3} min^{-1}	5 + log I.R	1000/T°
5.02	0.703	3.354
7.77	0.890	3.299
11.68	1.067	3.245
17.88	1.252	3.193



Figures 15a and 15b

Plot of log I.R versus $10^3/T$ for N(III)/I(VII) reaction

3.12 The reaction between nitrite and iodate

The reaction between NO_2^- and IO_3^- has recently been studied by Abdul-Jawad$^{(5)}$. Suitable conditions for the reaction to proceed at a measurable rate at 25°C in aqueous HCl (analar) solutions were $[H^+] = 1.4 - 2.26$, $[NaNO_2] = 10^{-3}$ and $[KIO_3] = 10^{-2}$ mol dm^{-3}.

Under the experimental conditions used for the reaction between nitrite and periodate in the present work, the subsequent reaction between nitrite and iodate is expected to be so slow that it may be disregarded because the concentration of IO_3^- that is produced by the reduction of IO_4^- at complete depletion of NO_2^- will be about 100 times less than that required to react at a significant rate with nitrite (consistent, of course, with the I(VII)/N(III) stoichiometry).

However, several experiments were carried out involving IO_3^- as the reactant with NO_2^- under similar conditions to those employed for the reaction between IO_4^- and NO_2^- with the object of investigating a point briefly noted by Abdul-Jawad - namely, the accelerating effect of Br^-. HCl from different sources was used for this purpose. The results of these experiments are given in the following tables.

In Table (51), experiment (a) employs HCl (Fisons analar grade) and (b) uses HCl (B.D.H. technical grade).

Table 51

$10^4[NaNO_2] = 5.850$ mol dm^{-3} $10^3[KIO_3] = 3.450$ mol dm^{-3}

[HCl] (a) = 1.632 mol dm^{-3} [HCl] (b) = 1.617 mol dm^{-3}

T = 25°C

t (min.)	Absorbance a	 b
0	0.624	0.624
1	0.593	0.616
3	0.537	0.596
6	0.458	0.570
10	0.363	0.532
15	0.258	0.495
20	0.173	-
25	-	0.426
10^5 I.R (mol dm^{-3} min^{-1})	2.77	0.89

Firstly, the values of I.R, 2.77×10^{-5} and 0.89×10^{-5} mol dm^{-3} min^{-1} can be compared with the I.R values, 9.16×10^{-5} and 3.71×10^{-5} mol dm^{-3} min^{-1} respectively obtained for experiments carried out using the same $[NaNO_2]$, [HCl] values but with $[IO_4^-]$ comparable to $[IO_3^-]$.

This shows that under similar conditions, the reaction between NO_2^- and IO_4^- is about four times faster than the reaction with IO_3^-. But as noted above, IO_3^- in our work is only formed in concentration comparable with $[NO_2^-]$ which is 10 times lower than $[IO_4^-]$.

Secondly, the hydrogen ion reactant in (a) and (b) above was derived from different HCl samples and provides a first clue that may be Br^- in minute traces also catalyses the N(III)/I(V) reaction.

Some absorbance-time data for reaction between NO_2^- and IO_3^- or IO_4^- under similar reaction conditions are given in Table (52). HCl (aristar) solutions were used and 4.53×10^{-5} mol dm^{-3} NaBr was added to reaction mixtures in experiments (b) and (c) and 9.06×10^{-5} mol dm^{-3} in experiment (a). Experiments (a) and (b) are concerned with the N(III)/I(V) reaction, (c) follows the N(III)/I(VII) reaction.

Table 52

$10^4[NaNO_2] = 6.418$ mol dm^{-3} $10^3[KIO_3] = 2.587$ mol dm^{-3} (a) and (b)

$[HCl] = 1.09$ mol dm^{-3} $10^3[KIO_4] = 2.582$ mol dm^{-3} (c)

T = 25°C

t (min.)	Absorbance a	 b	 c
1.5	0.664	0.667	0.654
3	0.663	0.661	0.631
5	0.653	0.653	0.601
8	0.641	0.643	0.551
12	0.634	0.634	0.491
17	0.608	0.609	0.421
25	0.595	0.593	0.320

Again, under similar conditions, IO_4^- reacts faster than IO_3^- with NO_2^-. (a) and (b) appear to show that $[Br^-]$ has no effect but this is because the rate observed here is merely that of N(III) decomposition.

By increasing the acidity of the N(III)/I(V) medium, the effect of Br^- can be studied in Table (53).

*Table 53

$10^4[NaNO_2] = 3.448$ mol dm^{-3} $10^3[KIO_3] = 6.117$ mol dm^{-3}

$[HCl] = 2.179$ mol dm^{-3} $T = 25^\circ C$

t (min.)	Absorbance a	 b
0	0.656	0.656
1	0.569	0.582
3	-	0.526
5	0.384	0.466
8	0.265	0.387
11	0.171	0.310
15	0.082	0.226

*Experiment (a) contained 8.883×10^{-5} mol dm^{-3} Br^- and experiment (b) contained 3.521×10^{-5} mol dm^{-3} Br^-.

Clearly Br^- does influence the rate of the N(III)/I(V) reaction.

Many years ago, Kurtenacker(25) studied the reaction between iodate and nitrite in acid solution kinetically. A rate-determining step such as

$$IO_3^- + NO_2^- \longrightarrow IO_2^- + NO_3^-$$

was suggested, and he also concluded that chloride and bromide ions have an accelerating effect, this effect being stronger with the bromide ion. In his work nitrite and sulphuric acid were mixed and thermostated and later added to iodate. At the concentrations used, $[NO_2^-] = 0.0167$ mol dm^{-3} and $[H_2SO_4] = 0.09$ mol dm^{-3}, the decomposition products of nitrous acid would have accumulated before admixture with IO_3^- and might have contributed to the subsequent reaction steps. Indeed results now found with a reaction mixture similar in its components to reaction mixtures used by Kurtenacker do imply that what he was dealing with may not be the reaction of NO_2^- (or HNO_2) with iodate, but may be the reaction between the decomposition products of nitrous acid and iodate.

In his method, the rate of disappearance of iodate was determined iodometrically. In Table (54) results obtained in the present work from experiments under similar conditions are recorded. The rate of disappearance of N(III) was followed by the same method (page 30) but in these experiments, sampling was made in two volumetric flasks, because the concentration of N(III) was too high to be directly determined by withdrawing samples and treating them in the normal way. Thus, 2 cm^3 samples of the reaction mixture were withdrawn and diluted to 50.0 cm^3 then as rapidly as possible, 2 cm^3 samples of the diluted solutions were taken into a 100 cm^3 volumetric flask for analysis.

*Table 54

$10^2[NaNO_2] = 1.670$ mol dm^{-3} $10^3[KIO_3] = 1.582$ mol dm^{-3}

$10^2[H_2SO_4]^{\dagger} = 8.970$ mol dm^{-3} T = 25°C

t (min.)	Absorbance			
	a	b	c	d
1	0.658	0.659	0.664	0.648
5	0.649	0.646	0.647	0.624
10	0.628	0.635	0.638	0.615
20	.595	0.588	0.590	0.584
35	.560	0.544	0.549	0.536
55		0.494		

*(a) KIO_3 and Br^- were not added. It merely represents the decomposition of HNO_2.

*(b) No Br^- was added to the reactants (acid-nitrite-iodate).

*(c) Reaction mixture contained 1.869×10^{-4} mol dm^{-3} Br^-.

*(d) Reaction mixture contained 4.673×10^{-5} mol dm^{-3} Br^-.

† B.D.H. "aristar" grade sulphuric acid.

The reaction between periodate and nitrite in sulphuric acid solution was also found to be very sensitive to traces of Br^- and faster than the iodate reaction under similar conditions. The results of these experiments are shown in Table (55).

*Table 55

$10^4[NaNO_2] = 6.459$ mol dm^{-3} $10^3[KIO_4] = 2.568$ mol dm^{-3}

$[H_2SO_4] = 1.346$ mol dm^{-3} $10^3[KIO_3] = 3.164$ mol dm^{-3}

$[Cl^-] = 0.667$ mol dm^{-3} $10^5[NaBr] = 4.673$ mol dm^{-3}

t (min.)	Absorbance a	b	c
0	0.681	0.681	0.681
1	0.669	0.675	0.672
3	0.665	0.666	0.644
5	0.652	0.659	0.615
10	0.637	0.648	0.558
15	0.630	0.635	0.493
20	-	0.620	0.444
25	0.604	-	-

* In experiment (a) the reactant was IO_3^- In (b) and (c) the reactant was IO_4^- , (b) contained no Br^-, (c) had Br^- as indicated above.

Conclusions:

The rate expression that describes the dependence of the rate of reaction between N(III) and I(VII) on the concentration of each participant can be expressed by

$$\text{Rate} = k\,[N(III)]^{0.5}[I(VII)][H^+][Br^-][Cl^-],$$

where k is the specific rate constant and its value at $[H^+] \simeq 1.6$ and $[Br^-] < 7 \times 10^{-5}$ mol dm^{-3} is 70 dm$^{10.5}$ mol$^{-3.5}$ s^{-1} at 25°C.

Perhaps the most important outcome of the investigation of this reaction is its sensitivity to the presence of 10^{-6} mol dm^{-3} Br$^-$. Thus it could be used as a simple (if not the simplest(68)) method for determination of traces of bromide that contaminate chlorides. However, no doubt this needs further careful study of the reaction in different aqueous acidic media in particular, in acids other than HCl such as HNO_3, $HClO_4$ and H_2SO_4. The collection of the results of such studies may make the reaction applicable for quantitative estimation of traces of Br$^-$.

Assuming that the bromide ion contaminating "aristar" grade hydrochloric acid is effectively zero (remembering that the reaction in aqueous solutions of this acid is very slow), an estimate of the amount of Br$^-$ contaminating HCl (first and second B.D.H. technical samples) and HCl (Fisons analar) can be made by dividing the average rate constant obtained from experiments using each acid (and neglecting the variation in $[H^+]$ from ~ 1.6 to ~ 1.7 mol dm^{-3}) by the rate constant 70 obtained by using HCl (aristar grade).

For the first technical HCl sample used

$$[Br^-] = 1.86 \times 10^{-3}/\ 70 \simeq 2.7 \times 10^{-5} \text{ mol dm}^{-3}$$

and for the second

$$3.078 \times 10^{-3}/70 \simeq 4.4 \times 10^{-5} \text{ mol dm}^{-3}$$

but, in the "analar" grade

$$7.11 \times 10^{-3}/\ 70 \simeq 1 \times 10^{-4} \text{ mol dm}^{-3}$$

and the values of $[Br^-]$ are those that were present in the reaction mixture, i.e. relative to 1.7 mol dm^{-3} HCl.

This result shows that, hydrochloric acid "technical" produced by one company is quite variable in its Br$^-$ content. On the other hand, the "analar" grade hydrochloric (Fisons) contained about four times as much Br$^-$ impurity as the technical grade.

The extension of recognition of Br^- catalysis by traces of this contaminant in the N(III)/I(V) reaction means that unfortunately the results of Kurtenacker and Abdul-Jawad on this reaction need re-appraisal. One matter, however, may well be cleared up by the present observation. It seemed surprising that the reaction between N(III) and I(V) in H_2SO_4 medium (disregarding criticisms of the technique employed by Kurtenacker) was observed to proceed smoothly at acidities lower by a power of 10 than in HCl-work of Abdul-Jawad. This may now be interpreted as a general improvement in the quality of chemicals in the 60-year gap between these two investigations, with consequent reduction in Br^- contamination.

3.13 Discussion

Based on the experimental results

$$\text{Rate} \ \alpha \ [N(III)]^{0.5}, [I(VII)], [H^+], [Cl^-] \text{ and } [Br^-]$$

The order with respect to N(III) is definitely indicated to be 0.5, rather than a fortuitous combination of parallel processes involving a zero order term and a first order term. In the rate determining step a species which is stoichiometrically related to $(N(III))^{0.5}$ must be involved. We must note, however, that no half power of H^+ is involved. This could be explained by such reactions as

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

which providing a small concentration of monomeric N(III) which is the effective reactant, with $N(III)_2$ virtually ineffective.

N(III) could be, nitrite (NO_2^-), nitrous acid (HNO_2), nitrous acidium ion ($H_2NO_2^+$), nitrosonium ion (NO^+), dinitrogen trioxide (N_2O_3), nitrosyl halide (NOX) or even a combination of these.

Thus the catalysis by Br^- and Cl^- could mean that reactions such as

$$2H^+ + 2X^- + N(III)_2 \rightleftharpoons 2N(III)X + H_2O$$

or

$$H^+ + X^- + N(III)_2 \rightleftharpoons N(III)X + N(III)$$

would explain the order of 0.5 with respect to N(III).

The involvement of several pre-equilibria before the rate determining step, introduces complications in deciding upon a unique mechanism for the reaction between nitrite and periodate in aqueous hydrochloric acid solution, and it does not seem possible yet to come to a definite conclusion. One can, however, produce possible mechanisms.

For example, the following reaction schemes produce the correct stoichiometry and kinetics for the reaction.

Scheme A

(1) $$H^+ + HNO_2 \underset{k-1}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+$$

(2) $$H_2NO_2^+ + HNO_2 \underset{k-2}{\overset{k_2}{\rightleftharpoons}} HN_2O_3^+ + H_2O$$

(3) $$H^+ + HN_2O_3^+ + 2Br^- \underset{k-3}{\overset{k_3}{\rightleftharpoons}} 2NOBr + H_2O$$

(4) $$H_5IO_6 + Cl^- \underset{k-4}{\overset{k_4}{\rightleftharpoons}} H_3IO_5Cl^- + H_2O$$

(5) $$NOBr + H_3IO_5Cl^- \xrightarrow{k_5} 2H^+ + NO_3^- + HIO_3 + Br^- + Cl^-$$

(6) $$NOBr + H_2O \xrightarrow{k_6} HNO_2 + H^+ + Br^-$$

(with some of these steps being possibly composite ones)

overall reaction

$$HNO_2 + H_5IO_6 \longrightarrow 2H^+ + NO_3^- + IO_3^- + 2H_2O$$

By assuming the steady state approximation, the rate of formation of NOBr can be set equal to zero. Thus (neglecting $[H_2O]$),

$$d[\mathrm{NOBr}]/dt = k_3[\mathrm{HN_2O_3^+}][\mathrm{H^+}][\mathrm{Br^-}]^2 - k_{-3}[\mathrm{NOBr}]^2 - k_5[\mathrm{NOBr}][\mathrm{H_3IO_5Cl^-}] - k_6[\mathrm{NOBr}] = 0 \quad \ldots\ldots \quad (46)$$

from which

$$k_{-3}[\mathrm{NOBr}]^2 + [\mathrm{NOBr}]([\mathrm{H_3IO_5Cl^-}]k_5 + k_6) - k_3[\mathrm{HN_2O_3^+}][\mathrm{H^+}][\mathrm{Br^-}]^2 = 0 \quad \ldots\ldots \quad (47)$$

This quadratic equation can be solved to give

$$[\mathrm{NOBr}] = \frac{-(k_6 + k_5[\mathrm{H_3IO_5Cl^-}]) + \sqrt{(k_6 + k_5[\mathrm{H_3IO_5Cl^-}])^2 + 4k_{-3}(k_3[\mathrm{HN_2O_3^+}][\mathrm{H^+}][\mathrm{Br^-}]^2}}{2k_{-3}} \quad \ldots\ldots \quad (48)$$

so that, if

$$\left(4k_{-3}(k_3[\mathrm{HN_2O_3^+}][\mathrm{H^+}][\mathrm{Br^-}]^2\right)^{0.5} \gg (k_6 + k_5[\mathrm{H_3IO_5Cl^-}]$$

then

$$[\mathrm{NOBr}] \approx K_3^{0.5}[\mathrm{HN_2O_3^+}]^{0.5}[\mathrm{H^+}]^{0.5}[\mathrm{Br^-}] \quad \ldots\ldots \quad (49)$$

Assume rate = $k_5[\mathrm{NOBr}][\mathrm{H_3IO_5Cl^-}]$ ...... (50)

$$\therefore \quad \text{Rate} = k_5K_4K_3^{0.5}[\mathrm{HN_2O_3^+}][\mathrm{H^+}]^{0.5}[\mathrm{Br^-}][\mathrm{H_5IO_6}][\mathrm{Cl^-}] \quad \ldots\ldots \quad (51)$$

i.e.

$$\text{Rate} = k[\mathrm{N_2O_3}]^{0.5}[\mathrm{H_5IO_6}][\mathrm{H^+}][\mathrm{Cl^-}][\mathrm{Br^-}] \quad \ldots\ldots \quad (52)$$

where $k = k_5K_4K_3^{0.5}$

However, reaction steps such as

$$\mathrm{HNO_2 + HNO_2 \rightleftharpoons N_2O_3 + H_2O}$$

$$\mathrm{N_2O_3 + 2H^+ + 2Br^- \rightleftharpoons 2NOBr}$$

in which NOBr is formed to further react with $\mathrm{H_3IO_5Cl^-}$ will also produce the same result when treated as above.

Alternatively, the reaction scheme, (Scheme B),

(1) $\mathrm{H^+ + HNO_2 \underset{k-1}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+}$

(2) $\mathrm{H_2NO_2^+ + HNO_2 \underset{k-2}{\overset{k_2}{\rightleftharpoons}} HN_2O_3^+ + H_2O}$

(3) $\mathrm{HN_2O_3^+ + Br^- \underset{k-3}{\overset{k_3}{\rightleftharpoons}} NOBr + HNO_2}$

$$(4) \quad H_5IO_6 + Cl^- \underset{k-4}{\overset{k_4}{\rightleftharpoons}} H_3IO_5Cl^- + H_2O$$

$$(5) \quad NOBr + H_3IO_5Cl^- \xrightarrow{k_5} 3H^+ + NO_3^- + IO_3^- + Br^- \; Cl^-$$

still produces the correct stoichiometry and kinetic behaviour for the N(III)/I(VII) system. Thus applying the steady state approximation to NOBr,

$$d[NOBr]/dt = k_3[HN_2O_3^+][Br^-] - k_3[NOBr][HNO_2] - k_5[NOBr][H_3IO_5Cl^-] = 0 \qquad \ldots\ldots \; (53)$$

from which

$$[NOBr] = \frac{k_3[HN_2O_3^+][Br^-]}{k_{-3}[HNO_2] + k_5[H_3IO_5Cl^-]} \qquad \ldots\ldots \; (54)$$

but,

$$\text{Assume rate} = k_5[NOBr][H_3IO_5Cl^-] \qquad \ldots\ldots \; (55)$$

$$= \frac{k_3k_5[HN_2O_3^+][Br^-][H_3IO_5Cl^-]}{k_{-3}[HNO_2] + k_5[H_3IO_5Cl^-]} \qquad \ldots\ldots \; (56)$$

and if

$$k_{-3}[HNO_2] > k_5[H_3IO_5Cl^-]$$

then

$$\text{Rate} = \frac{k_3k_5[HN_2O_3^+][Br^-][H_3IO_5Cl^-]}{k_{-3}[HNO_2]} \qquad \ldots\ldots \; (57)$$

where,

$$[HN_2O_3^+] = K_1K_2[H^+][HNO_2]^2 \qquad \ldots\ldots \; (58)$$

and

$$[H_3IO_5Cl^-] = K_4[H_5IO_6][Cl^-] \qquad \ldots\ldots \; (59)$$

thus,

$$\text{Rate} = k_5K_1K_2K_3K_4[HNO_2][H_5IO_6][H^+][Cl^-][Br^-] \qquad \ldots\ldots \; (60)$$

and $[HNO_2] \alpha [N(III)]^{0.5}$

so that,

$$\text{Rate} = k[N(III)]^{0.5}[H_5IO_6][H^+][Cl^-][Br^-] \quad ...... \quad (61)$$

where $k = k_5K_1K_2K_3K_4$

Again, the reaction steps

$$HNO_2 + HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$N_2O_3 + H^+ + Br^- \rightleftharpoons NOBr + HNO_2$$

will produce the same result when treated as above, and several other possibilities have been identified.

Note that NOBr is more reactive$^{(67)}$ than either N_2O_3 or NOCl (the rate constant for hydrolysis of NOBr = 8×10^6 at $0^\circ C$, and the rate constant for hydrolysis of NOCl = $(9 \pm 0.3) \times 10^2$ at $25^\circ C$.

The formation of nitrosyl iodide$^{(67)}$ has not yet been achieved, indeed it is thought to be incapable of existence. This may be used to explain the lack of effect of I^- on the rate of reaction, and perhaps supports the assumption that a species of the formula NOX (X = Br or Cl) is the reactive species.

4. The Reaction Between N(III) and Cl(V)

As mentioned earlier, the reaction between nitrite and chlorate in buffered aqueous acid solution has been recently studied by Abdul-Jawad(5). The general conclusions are:

1. Nitrite and chlorate react in the molar ratio 3:1 yielding Cl^- and NO_3^- as products.
2. The rate equation for the reaction is
   Rate = $220[HNO_2][ClO_3^-][H^+]$ mol dm^{-3} min^{-1} of N(III) at zero ionic strength and 25°C.
3. The rate of reaction is insensitive to specific cationic or anionic effects. However, the rate increases as the ionic strength decreases.

In this part of the present work the effect of change of solvent medium, in particular of change of dielectric constant on the rate of reaction between nitrite and chlorate was studied by using mixtures of water and 1,4-dioxan.

The dielectric constant of dioxan is low when compared with that of water (2.1 and 78.3 respectively at ordinary temperatures), and dioxan is completely miscible in all proportions with water(68). Water and dioxan thus provide a good mixture of solvents with which the dielectric constant can be varied widely.

In dilute acid solutions ($H^+ < 0.02$ mol dm^{-3}), N(III) will be present as HNO_2 and NO_2^- through the protonation equilibrium,

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

The equilibrium constant for this reaction is well known for the medium water, but a study of the Cl(V)/N(III) reaction in aqueous dioxan will necessarily require determination of the concentrations of the acid and anionic forms of 'nitrite' in these media.

"Analar" grade chemicals and "technical grade" hydrochloric acid were used. Analar dioxan was freed from possible traces of H_2O_2 by being run through chromatographic alumina before being used.

4.1 Properties of the solvent mixtures

Some properties of the water-dioxan solutions used are given in Table (56).

Table 56

V_{H_2O} cm^3	V_{dioxan} cm^3	V(total) cm^3	Wt.(total) g	Wt. % dioxan	D
60.00	0	60.00	59.82	0	78.30
40.00	20.00	59.70	60.44	34.02	48.38
20.00	40.00	59.25	61.06	67.34	20.45

The actual total volume of water-dioxan mixtures was measured by separate experiments using a standard flask to determine the change in volume when the two liquids were mixed. It was found that 34.04 wt. % dioxan mixtures had 0.994 of the volume of the separate liquid components, and that 67.34 wt. % dioxan in water mixtures had 0.985 of the additive value, all measurements being made at 25°C. In practice this diminution in volume has been taken into account in expressing concentrations in terms of mol dm^{-3}. The values of dielectric constant (D) were calculated from the results of Akerlof and Short$^{(69)}$.

4.2 The ionization constant of nitrous acid in the different media

The latest and most reliable values of the ionization constant of nitrous acid in water seem to be the results of Lumme and Tummavuori$^{(70,71)}$. They also summarized the early work on the ionization of the acid. Their observation that the decomposition of 0.01 mol dm^{-3} nitrite solution is catalysed by 0.001 mol dm^{-3} of a mineral acid and even by acetic acid, was used to explain why earlier reported values differed by about 0.2 - 0.4 pK units from their own values obtained at about the same temperature and ionic strength.

Values for the ionization constant in water-dioxan solutions have not been reported, so it was necessary to evaluate these so that they could be used when needed in a kinetic run.

The ionization constant of nitrous acid was spectrophotometrically determined in water and water-dioxan solutions. Nitrite and nitrous acid absorb in the same wavelength region (400-300 nm), but with different molar absorption coefficients at the same wavelengths. Thus a mixture of the two species can be analysed from the observed absorption of the mixture which is governed by the equation,

$$A = (\varepsilon_1 c_1 + \varepsilon_2 c_2)\, l \qquad \ldots\ldots \quad (62)$$

The absorption spectrum of nitrite ion in the region 400-300 nm consists of one featureless band with a peak at 354 nm. That of nitrous acid in the same region whilst having a somewhat similar envelope shows five peaks at 386, 372, 358, 346 and 336 nm with three well marked intervening troughs at 380, 364 and 357 nm (see Fig. 17). General aspects of these features are maintained over the three media investigated although very minor shifts in the wavelengths of absorption may occur, e.g. the strongest absorption appears to lie at 372 nm in water, while the corresponding peak, now slightly surpassed in molar absorption coefficient by the other strong band is at 373 nm in 34 wt. % dioxan,.and at 374 nm is 68 wt. % dioxan.

In order to get maximum accuracy the two wavelengths in the region 373 and 352 nm were chosen because of the disparity in the molar adsorption coefficients of the anion and acid forms at these two wavelengths.

4.2.1 The molar absorption coefficients of NO_2^- and HNO_2

The molar absorption coefficients ε_1 and ε_2 were determined for NO_2^- and HNO_2 in aqueous and mixed solvents. The results of the measurements are listed below.

4.2.1.(a) The absorption coefficient of NO_2^-.

The absorptions of solutions of nitrite (containing a trace of NaOH) and the calculated molar absorption coefficient values are given in Table (57a, 57b, and 57c).

Table 57a

(measurements in aqueous solutions)

$10^2[NaNO_2]$ mol dm^{-3}	A_{373}	ε_{373} m^2 mol^{-1}	$A_{352.5}$	$\varepsilon_{352.5}$ m^2 mol^{-1}
1.967	0.295	15.0	0.450	22.9
1.574	0.238	15.1	0.363	23.1
1.180	0.179	15.2	0.274	23.2
0.787	0.119	15.1	0.182	23.1
		av. 15.1		av. 23.1

Table 57b

(measurements in 34 wt. % dioxan)

$10^2[NaNO_2]$ mol dm^{-3}	A_{373}	ε_{373} m^2 mol^{-1}	$A_{352.5}$	$\varepsilon_{352.5}$ m^2 mol^{-1}
2.130	0.399	18.7	0.584	27.4
1.704	0.320	18.8	0.466	27.3
1.278	0.240	18.8	0.349	27.3
0.852	0.160	18.8	0.234	27.5
		av. 18.8		av. 27.4

Table 57c

(measurements in 67 wt. % dioxan)

$10^2[NaNO_2]$ mol dm^{-3}	A_{360}	ε_{360} m^2 mol^{-1}	A_{354}	ε_{354} m^2 mol^{-1}
1.997	0.601	30.1	0.588	29.4
1.598	0.484	30.3	0.472	29.5
1.198	0.365	30.5	0.353	29.5
0.799	0.244	30.5	0.235	29.4
		av. 30.3		av. 29.5

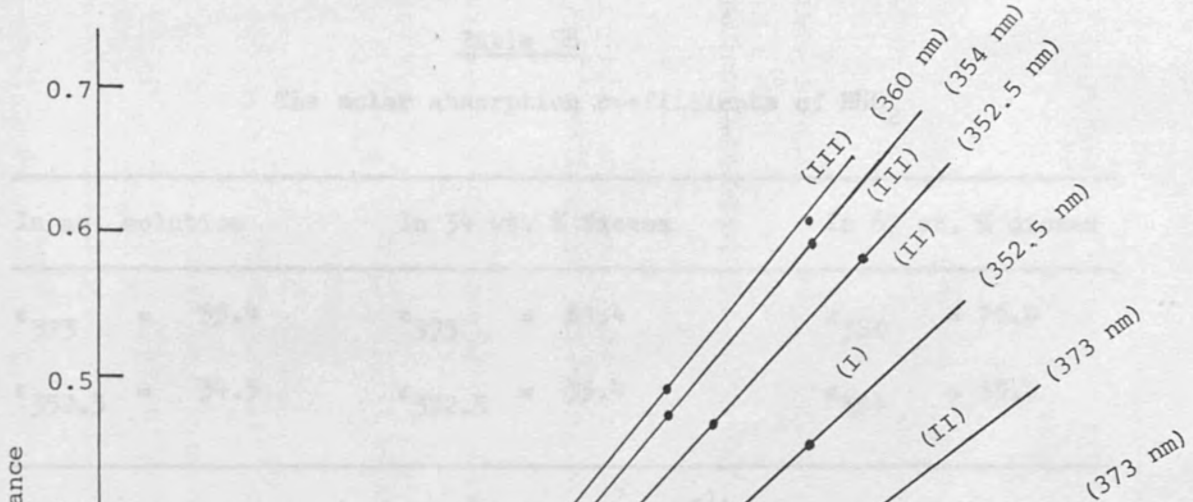
The plots of $[NaNO_2]$ versus absorbance given in the above three tables are shown in Fig. (16), further indicating that Beer's law is obeyed.

4.2.1.(b) The molar absorption coefficient of HNO_2

The ε values for nitrous acid in the three solvents were determined as follows. To a known amount of nitrite solution, excess of HCl was added and the spectrum of the acid was recorded in the wavelength region 400 - 310 nm. In order to minimise errors due to loss of HNO_2 through decomposition, the spectrum of the acid was recorded at intervals of time, the absorption at each desired wavelength was determined from the spectrum at measured times after acidification of the nitrite. The absorption values were then plotted against time and the curve was extrapolated to $t = 0$ to give A_o which was taken to correspond to the initial acid concentration. For example, the following observations were made on a solution in 34 wt. % dioxan containing 7.493×10^{-3} mol dm^{-3} $NaNO_2$ and 3.667×10^{-1} mol dm^{-3} HCl.

Figure 16

Plot of absorbance versus $[NaNO_2]$ in water/dioxan mixtures



Time (min):	0	0.5	2	5	10	15
A_{372} :	(0.464)	0.459	0.449	0.436	0.416	0.401
A_{351} :	(0.268)	0.266	0.260	0.251	0.238	0.230

The molar absorption coefficient values determined for the acid in the three solvents are given in Table (58).

Table 58

The molar absorption coefficients of HNO_2

In aq. solution	In 34 wt. % dioxan	In 67 wt. % dioxan
$\varepsilon_{373} = 55.4$	$\varepsilon_{373} = 61.4$	$\varepsilon_{360} = 70.9$
$\varepsilon_{352.5} = 34.5$	$\varepsilon_{352.5} = 35.4$	$\varepsilon_{354} = 33.2$

(units of ε are $m^2\ mol^{-1}$)

In Fig. (17), the spectra recorded in aqueous solutions for,

I: 2.248×10^{-2} mol dm^{-3} $NaNO_2$ (+ trace NaOH)

II: 1.124×10^{-2} mol dm^{-3} $NaNO_2$ + 3.667×10^{-3} mol dm^{-3} HCl

III: 1.124×10^{-2} mol dm^{-3} $NaNO_2$ + 3.667×10^{-1} mol dm^{-3} HCl

are shown to illustrate the method used in the calculations of the ionization constant of HNO_2. The spectrum of nitrous acid (III), corresponds well with that published by Longstaff and Singer(9a) in 0.05 mol dm^{-3} HNO_3, 4 mol dm^{-3} $HClO_4$ and 4 mol dm^{-3} H_2SO_4, and clearly involves virtual complete conversion to HNO_2 (max ε at 372 $\sim$ 50 - 54 in the different media).

By comparing the spectra of gaseous mixtures of NO, NO_2 and H_2O and of NO, NO_2 and D_2O, Porter(72) has shown that the bands in the region of 329 to 384 nm do correspond to HNO_2. The strong bands in the gas phase

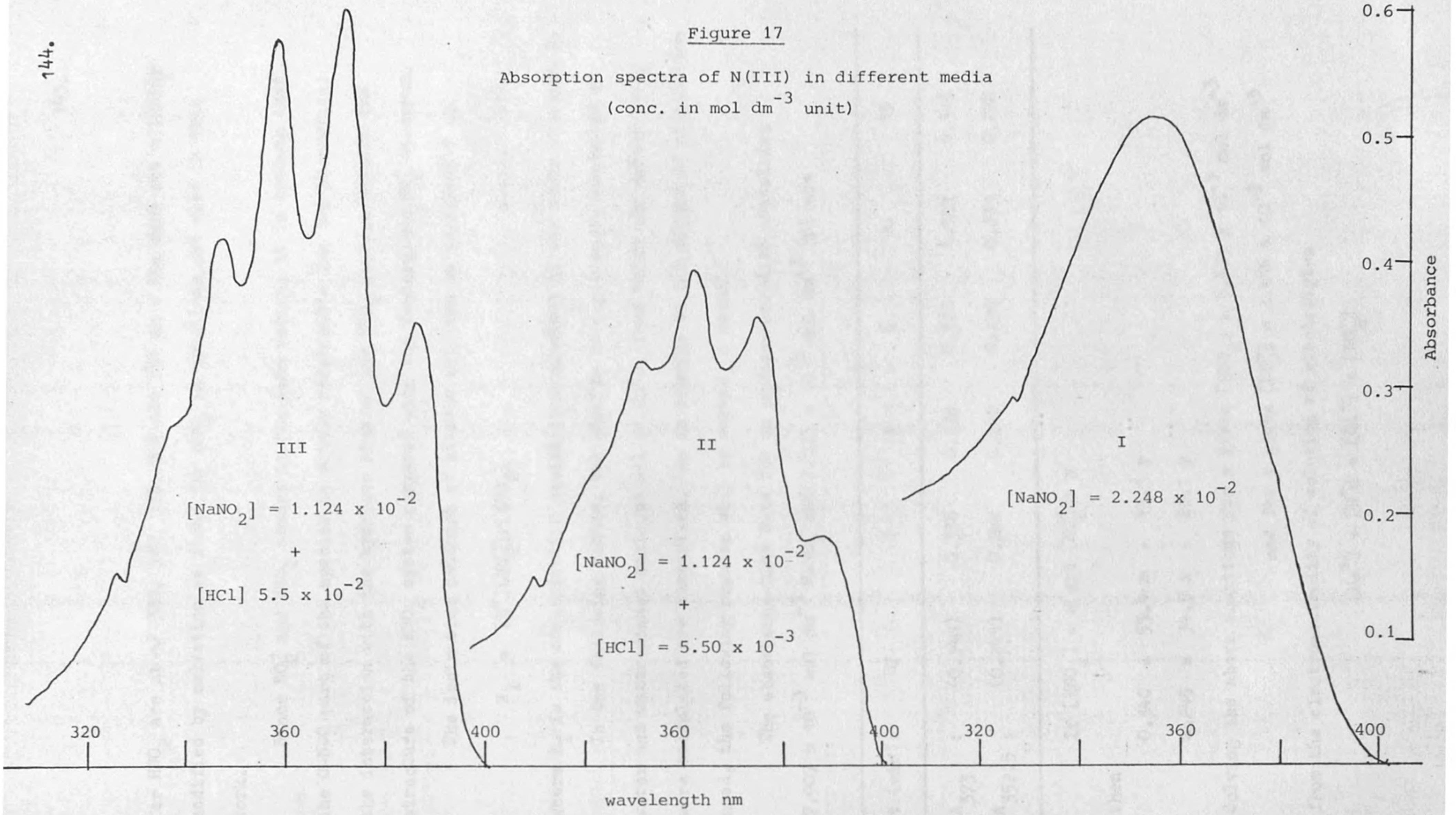


Figure 17

Absorption spectra of N(III) in different media (conc. in mol dm^{-3} unit) for HNO_2 are at ~ 329, 340, 353, 368 and 384 nm - the same set slightly modified by solvation as found for HNO_2 in solutions and used in this work.

Since NO_2^- and HNO_2 absorb in the same region, it is obvious that the O-N-O part of the species is mainly responsible for the absorption; the interaction with the hydrogen atom of the HNO_2 perhaps causing the structure of the HNO_2 system compared with the featureless NO_2^- spectrum.

The ionization constant of nitrous acid can be represented by

$$K_I = [H^+][NO_2^-]/[HNO_2] \qquad \ldots\ldots \quad (63)$$

where K_I is the concentration equilibrium constant at the ionic strength I.

In the following tables, the results of experiments conducted in water and water-dioxan mixtures all at 25°C, from which the values of K_I were calculated are summarised. As an example of the method of calculation used, the following results will be worked in detail.

The absorbance-time data for an aqueous solution containing 7.907×10^{-3} mol dm^{-3} $NaNO_2$ and 7.333×10^{-3} mol dm^{-3} HCl are

t (min):	0	1	3	6	10	15
A_{373} :	(0.340)	0.338	0.332	0.328	0.322	0.318
$A_{352.5}$:	(0.245)	0.242	0.240	0.236	0.231	0.228

If $[HNO_2] = x$ and $[NO_2^-] = y$

then

$$0.340 = 55.4\,x + 15.1\,y$$

$$0.245 = 34.5\,x + 23.1\,y$$

Solving the above equations for x gives $[HNO_2] = 5.479 \times 10^{-3}$ mol dm^{-3}

and for y gives $[NO_2^-] = 2.416 \times 10^{-3}$ mol dm^{-3}

from the electroneutrality of solution of electrolytes

$$[Na^+] + [H^+] = [Cl^-] + [NO_2^-]$$

so that

$$[H^+] = 0.007333 + 0.002416 - 0.007907$$

$$[H^+] = 1.842 \times 10^{-3} \text{ mol dm}^{-3}$$

but

$$pK_I = -\log K_I = -\log([H^+][NO_2^-]/[HNO_2])$$

hence , $pK_I = 3.09$

$$\text{where, } I = \tfrac{1}{2}\left\{[NO_2^-] + [Na^+] + [H^+] + [Cl^-]\right\}$$

$$= 0.01 \text{ mol dm}^{-3}$$

As a check, the total N(III) concentration (NO_2^- + HNO_2), calculated is 7.895×10^{-3}, while the amount put in is 7.907×10^{-3} mol dm^{-3} which shows that the discrepancies between the calculated and initial concentrations of N(III) are small and this result gives some confidence in the use of the values determined for the molar absorption coefficients.

Table 59a

(in aqueous solution)

$10^3[NaNO_2]$ mol dm^{-3} (put in)	$10^3[HCl]$ mol dm^{-3} (put in)	A_o (373)	A_o (352.5)	$[HNO_2]$ mol dm^{-3} (calc.)	$[NO_2^-]$ mol dm^{-3} (calc.)	$10^2F(I)$	pK_I
11.24	5.500	0.364	0.314	4.834×10^{-3}	6.370×10^{-3}	9.529	3.08
7.907	7.333	0.340	0.245	5.479×10^{-3}	2.416×10^{-3}	8.841	3.09

Table 59b

(in 34 wt. % dioxan)

$10^3[NaNO_2]$ mol dm^{-3} (put in)	$10^3[HCl]$ mol dm^{-3} (put in)	A_o (373)	A_o (352.5)	$[HNO_2]$ mol dm^{-3} (calc.)	$[NO_2^-]$ mol dm^{-3} (calc.)	$10^2F(I)$	pK_I
15.37	14.75	0.820	0.518	1.252×10^{-2}	2.727×10^{-3}	11.239	3.34
15.37	3.689	0.440	0.448	3.556×10^{-3}	1.179×10^{-2}	10.644	3.44
7.715	4.373	0.319	0.245	4.061×10^{-3}	3.706×10^{-3}	8.046	3.48
6.173	4.373	0.291	0.205	4.051×10^{-3}	2.248×10^{-3}	7.350	3.60
4.630	4.373	0.254	0.163	3.821×10^{-3}	1.033×10^{-3}	6.49	3.68

Table 59c

(in 67 wt. % dioxan)

$10^3[NaNO_2]$ mol dm^{-3} (put in)	$10^3[HCl]$ mol dm^{-3} (put in)	A_o (361)	A_o (354)	$[HNO_2]$ mol dm^{-3} (calc.)	$[NO_2^-]$ mol dm^{-3} (calc.)	$10^2F(I)$	pK_I
6.229	5.295	0.381	0.203	4.669×10^{-3}	1.637×10^{-3}	7.508	3.61
4.672	4.413	0.304	0.156	3.895×10^{-3}	9.171×10^{-4}	6.670	3.81
4.672	4.413	0.304	0.156	3.895×10^{-3}	9.171×10^{-4}	22.78*	3.81
4.672	10.59	0.331	0.157	4.608×10^{-3}	1.401×10^{-4}	21.98	3.75
3.115	4.413	0.228	0.110	3.131×10^{-3}	1.965×10^{-4}	6.243	4.03
3.115	2.648	0.196	0.103	2.446×10^{-3}	7.427×10^{-4}	5.424	4.08

* ionic strength was made by $NaNO_3$

In 67 wt. % dioxan it is still being assumed that Na^+, NO_2^-, H^+ and Cl^-, other than the material combined as HNO_2, act as free unassociated ions.

Comments on the results in Tables 59a, 59b and 59c

1. The average value of pK_I in aqueous solution 3.085 compares favourably with 3.05 calculated by the same equation used by Lumme and Tummavuori (see appendix). This indicates that the method is satisfactory.

2. pK_I decreases as the dielectric constant of the solution increases. This behaviour is known for all acids studied in mixed solvents of different dielectric constants.

3. pK_I in 34 wt. % dioxan is ionic strength dependent and when pK_I was plotted versus F(I) a straight line was produced (Figure 18). This figure was used for determining pK_I at any ionic strength by interpolation.

In 67 wt. % dioxan, pK_I is not affected by variation of ionic strength (perhaps because the calculated values of ionic strength are far too high in this medium).

4.3 The ionization constant of benzoic acid

As a further test of the reliability of the spectrophotometric technique used for the determination of the ionization constant of nitrous acid, the same technique was used in the determination of the ionization constant of benzoic acid in water and water-dioxan solutions and the results were compared with those reported in the literature.

Unfortunately, it was not possible at the wavelength used, 275 nm (at which the acid-form shows a maximum absorption), to use mixed solvents of higher than a volume:volume ratio of 3:1 water:dioxan, because it was not possible to determine accurately the molar absorption coefficient of the benzoate ion in such media.

The molar absorption coefficient of the acid form (HB) was determined from solutions of the acid containing an excess of HCl (1:15, HB:HCl). The absorption coefficient of benzoate (B^-) was determined from a solution of the acid containing a large excess of NaOH (1:50, HB:NaOH).

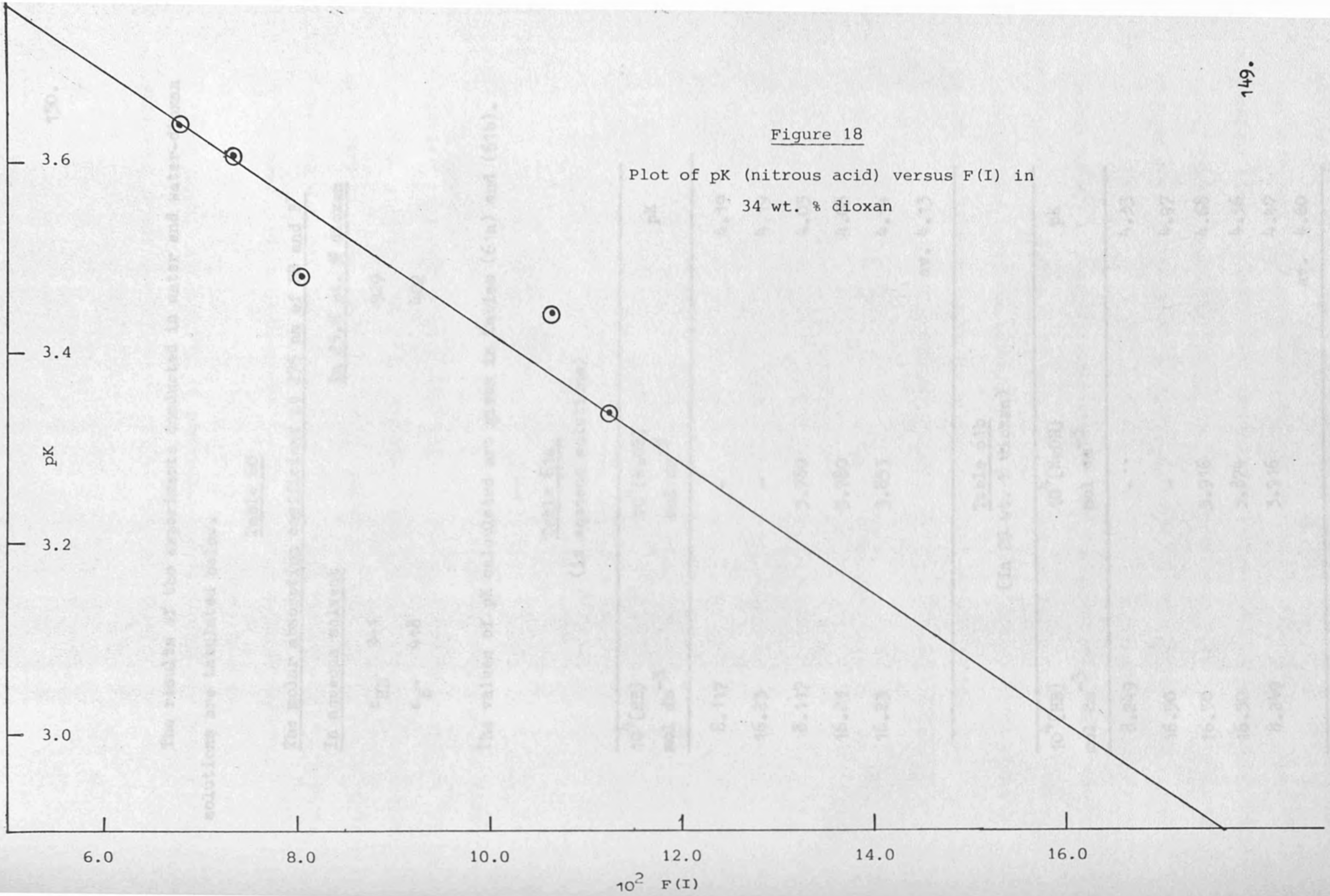


Figure 18

Plot of pK (nitrous acid) versus F(I) in 34 wt. % dioxan

The results of the experiments conducted in water and water-dioxan solutions are tabulated below.

Table 60

The molar absorption coefficient at 275 nm of HB and B^-

	In aqueous solvent	In 25.6 wt. % dioxan
ε_{HB}	941	929
ε_{B^-}	418	402

The values of pK calculated are given in Tables (61a) and (61b).

Table 61a

(in aqueous solutions)

10^4[HB] mol dm^{-3}	10^4[NaOH] mol dm^{-3}	pK
8.117	-	4.19
16.23	-	4.19
8.117	5.780	4.05
16.23	5.780	4.08
16.23	3.853	4.14
	av.	4.13

Table 61b

(In 25 wt. % dioxan)

10^4[HB] mol dm^{-3}	10^4[NaOH] mol dm^{-3}	pK
8.249	-	4.33
16.50	-	4.97
16.50	3.916	4.68
16.50	5.874	4.56
8.249	3.916	4.47
	av.	4.60

The ionic strength in each set of experiments, was always less than 10^{-3} so that the ionic strength correction to pK_o is never greater than 0.01. This has been ignored.

The average value, 4.13 is in good agreement with the literature value 4.16. The average value 4.60 in water-dioxan solutions was compared with the results of Lynch and La Mer (73). In Table (62), the results of this work and those of Lynch and La Mer are listed and the graph obtained when $1/_D$ is plotted versus pK is shown in Fig. (19). This shows that a smooth curve passes through the points.

Table 62

100/D	pK
1.277	4.13*
1.577	4.60*
2.915	6.11
4.762	7.87
8.547	9.57

*the present results.

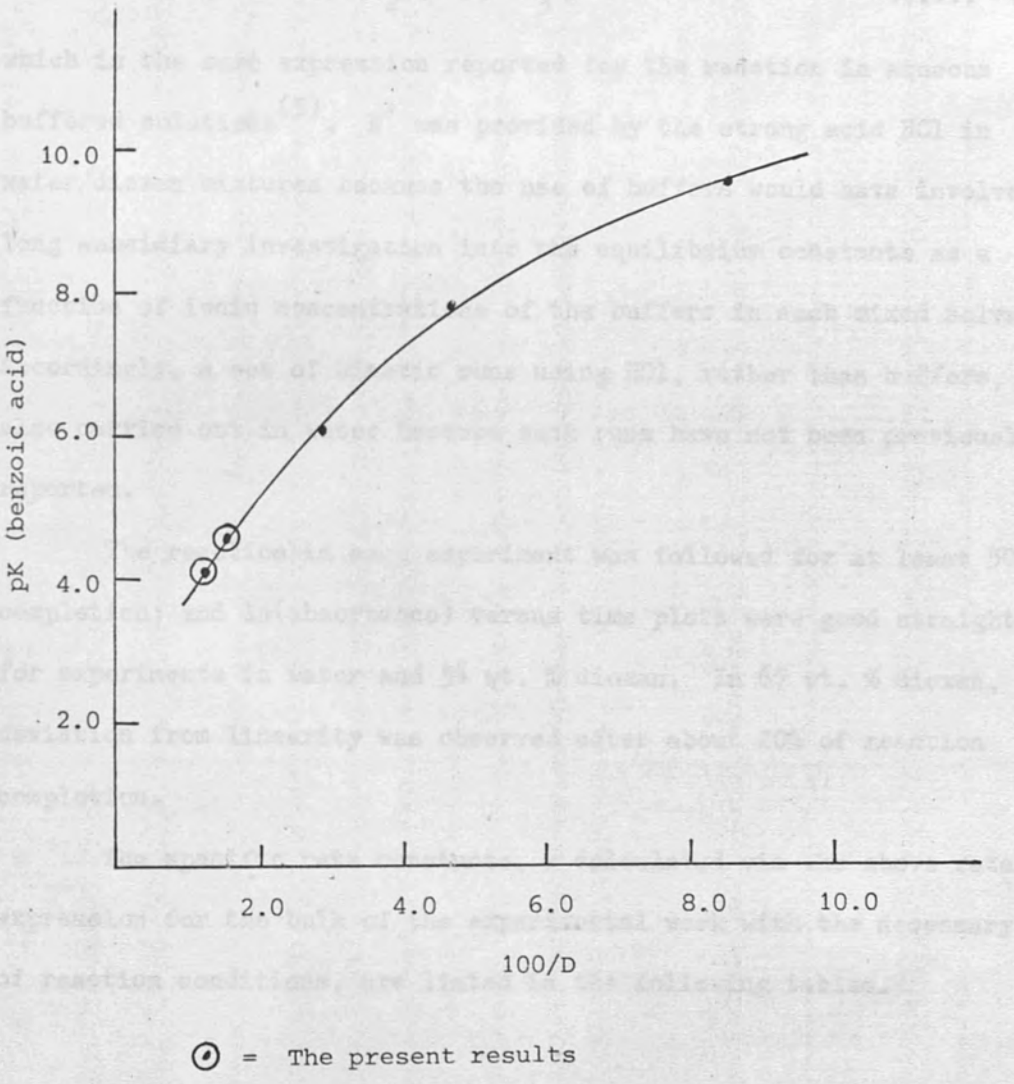
4.4 Kinetics of the reaction between nitrite and chlorate

The rate expression for the reaction was established in each solvent by conducting a series of experiments to determine the order with respect to each reactant. This was made from the results of experiments under otherwise constant reaction conditions, but various concentrations of the reactant being investigated.

The technique adopted was essentially the same as that used before. Nitrite and chlorate were measured into a 250 cm^3 stoppered conical flask, the acid and any other reactant into another flask, and both were thermostated at 25°C. The reaction was started by thoroughly mixing the reactants and samples were then taken for analysis (page 30) at time intervals read from a stopclock.

Figure 19

Plot of pK (benzoic acid) versus 100/D



4.4.1 The rate equation for the reaction

The rate expression that can be written for the reaction in water/dioxan solutions is

$$\text{Rate} = k[\text{HNO}_2][\text{H}^+][\text{ClO}_3^-] \qquad \ldots\ldots \quad (67)$$

which is the same expression reported for the reaction in aqueous buffered solutions(5). H^+ was provided by the strong acid HCl in water/dioxan mixtures because the use of buffers would have involved a long subsidiary investigation into the equilibrium constants as a function of ionic concentrations of the buffers in each mixed solvent. Accordingly, a set of kinetic runs using HCl, rather than buffers, was also carried out in water because such runs have not been previously reported.

The reaction in each experiment was followed for at least 50% completion; and ln(absorbance) versus time plots were good straight lines for experiments in water and 34 wt. % dioxan. In 67 wt. % dioxan, deviation from linearity was observed after about 20% of reaction completion.

The specific rate constants, k calculated via the above rate expression for the bulk of the experimental work with the necessary details of reaction conditions, are listed in the following tables.

4.4.1.(a) In aqueous acid solutions

Table 63

10^4[NaNO$_2$] mol dm^{-3}	10^2[HCl] mol dm^{-3}	10^3[KClO$_3$] mol dm^{-3}	10^4[HNO$_2$] mol dm^{-3}	10^6 I.R mol dm^{-3} min^{-1}	k dm^{6}mol^{-2}s^{-1}
6.269	1.850	4.119	5.783	6.25	2.37
4.701	1.864	4.119	4.369	4.70	2.33
3.918	1.871	4.119	3.655	3.91	2.32
3.134	1.879	4.119	2.935	3.12	2.28
1.567	1.893	4.119	1.479	1.54	2.23
3.918	1.872	6.591	3.639	6.08	2.25
3.918	1.872	4.943	3.639	4.57	2.27
3.918	1.872	3.296	3.639	3.04	2.25
3.918	1.872	1.648	3.639	1.54	2.28
3.918	2.509	6.587	3.716	8.51	2.32*
3.918	2.145	6.587	3.685	7.20	2.30*
3.918	1.782	6.587	3.641	5.94	2.32*
3.918	1.238	6.587	3.535	4.12	2.38*
3.918	0.875	6.587	3.401	2.85	2.42*

* F(I) = 0.187
F(I) = 0.145
I was maintained by NaNO$_3$

4.4.1.(b) The effect of ionic strength on the rate of reaction

The rates of reactions in which the concentrations of reactants were initially the same, but in which ionic strength was varied by addition of NaNO$_3$ were determined and their results are given in Table (64). The straight line produced when log k, the rate constant was plotted versus F(I) (Fig.20) has a slope, -1.04. Extrapolation of the line to F(I) = 0 gives the value

3.46 $dm^6\ mol^{-2}\ s^{-1}$ for k which compares favourably with 3.67 $dm^6\ mol^{-2}\ s^{-1}$ obtained by Abdul-Jawad. Furthermore, the gradient of the graph of log k versus F(I) obtained by Abdul-Jawad was, -1.3.

Table 64

k $dm^6\ mol^{-2}\ s^{-1}$	F(I)
2.47	0.126
2.32	0.145
2.29	0.187
2.02	0.229
1.93	0.247
1.83	0.265

4.4.1.(c) The effect of transition metal ions on the rate of reaction

The effect of transition metal ions on the rate of nitrite/chlorate reaction has not been tested before.

In a series of experiments, the initial concentrations of each of nitrite, chlorate and hydrochloric acid were the same, but concentrations of transition metal ions about equal to that of nitrite were added to reaction mixtures, and the rate in each case was compared with the rate of a control experiment. The absorbance-time data for these experiments are tabulated below. The last column of the table lists the data of a reation mixture to which the di-valent cation, Pb^{++} was added.

Figure 20

Plot of log k versus F(I) for N(III)/Cl(V) reaction

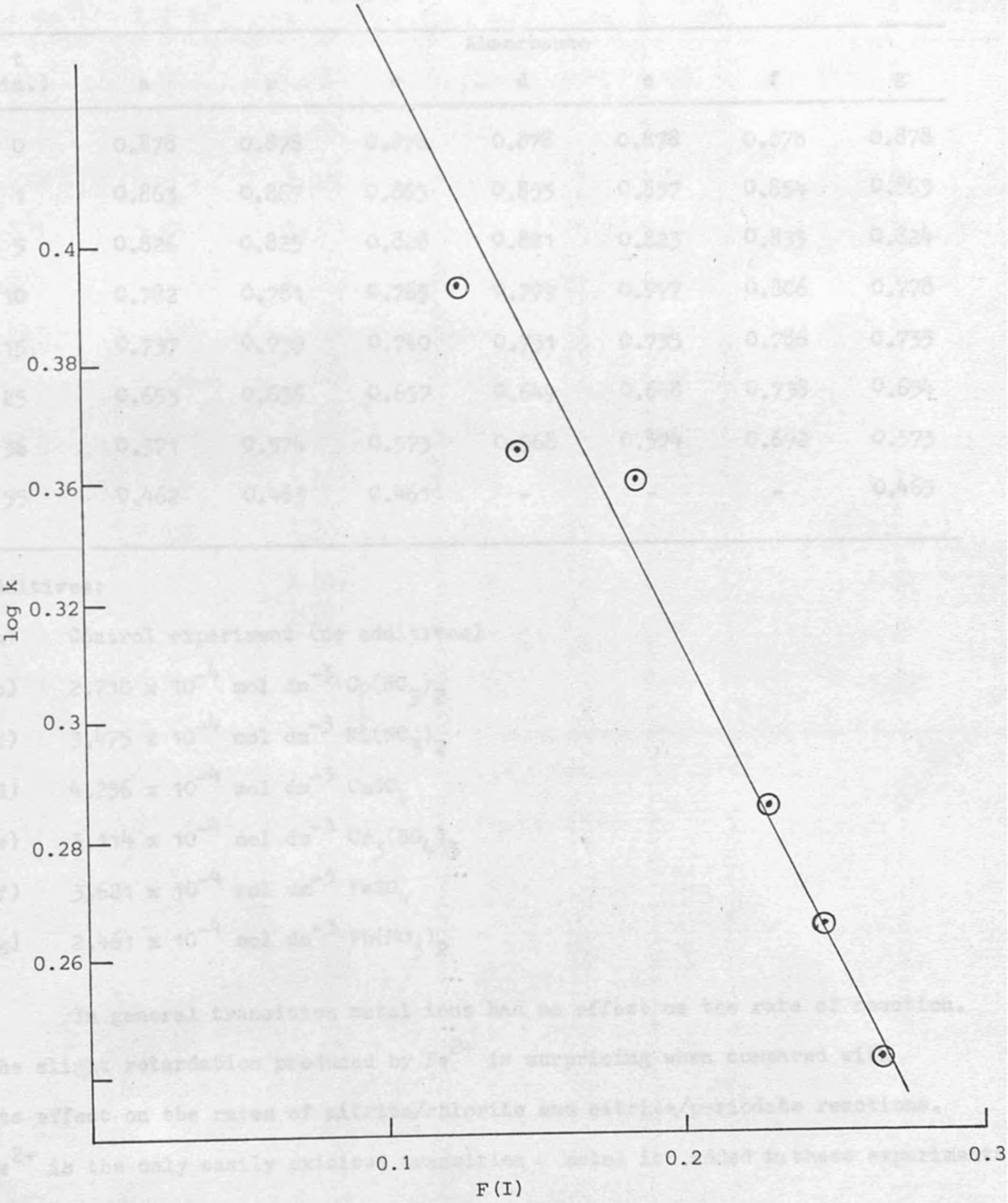


Table 65

$10^4[HNO_2] = 3.130$ mol dm^{-3} $10^3[KClO_3] = 4.465$ mol dm^{-3}

$10^2[HCl] = 1.974$ mol dm^{-3} F(I) = 0.130

T = 25°C

t (min.)	Absorbance a	b	c	d	e	f	g
0	0.878	0.878	0.878	0.878	0.878	0.878	0.878
1	0.863	0.867	0.865	0.855	0.857	0.854	0.865
5	0.826	0.825	0.828	0.821	0.823	0.835	0.824
10	0.782	0.781	0.785	0.779	0.777	0.806	0.778
15	0.737	0.739	0.740	0.731	0.735	0.786	0.735
25	0.653	0.656	0.657	0.649	0.648	0.738	0.654
36	0.571	0.574	0.573	0.568	0.574	0.692	0.573
55	0.462	0.463	0.461	-	-	-	0.465

Additives:

(a) Control experiment (no additives)

(b) 2.710×10^{-4} mol dm^{-3} $Co(NO_3)_2$

(c) 3.475×10^{-4} mol dm^{-3} $Ni(NO_3)_2$

(d) 4.256×10^{-4} mol dm^{-3} $CuSO_4$

(e) 3.114×10^{-4} mol dm^{-3} $Cr_3(SO_4)_3$

(f) 3.621×10^{-4} mol dm^{-3} $FeSO_4$

(g) 2.461×10^{-4} mol dm^{-3} $Pb(NO_3)_2$

In general transition metal ions had no effect on the rate of reaction. The slight retardation produced by Fe^{2+} is surprising when compared with its effect on the rates of nitrite/chlorite and nitrite/periodate reactions. Fe^{2+} is the only easily oxidised transition metal ion added in these experiments.

4.4.2 In 34 weight % dioxan

Table 66

10^4[NaNO$_2$] mol dm^{-3}	10^2[HCl] mol dm^{-3}	10^3[KClO$_3$] mol dm^{-3}	10^4[HNO$_2$ mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	k dm^6 mol^{-2} s^{-1}
9.589	1.886	8.304	8.839	2.94	3.53
7.671	1.903	8.304	7.135	2.43	3.58
5.753	1.920	8.304	5.400	1.86	3.60
3.835	1.937	8.304	3.633	1.25	3.55
4.821	1.926	9.965	4.549	1.88	3.58
4.821	1.926	8.304	4.549	1.52	3.48
4.821	1.926	6.643	4.549	1.27	3.65
4.821	1.926	4.982	4.549	0.97	3.68
4.821	1.926	3.321	4.549	0.65	3.75
4.794	3.902	8.304	4.609	2.98	3.33*
4.794	2.775	8.304	4.538	2.24	3.58*
4.794	1.930	8.304	4.437	1.56	3.65*
4.794	1.367	8.304	4.309	1.06	3.60*

F(I) = .145) assuming electrolytes fully ionised in water are
)
* F(I) = .186) also fully ionised in this medium

4.4.3. In 67 weight % dioxan

Table 67

10^4[NaNO$_2$] mol dm^{-3}	10^3[HCl] mol dm^{-3}	10^3[KClO$_3$] mol dm^{-3}	10^4[HNO$_2$] mol dm^{-3}	10^5 I.R mol dm^{-3} min^{-1}	k dm^6 mol^{-2} s^{-1}
3.678	8.881	4.109	3.486	1.140	14.93
1.839	9.052	4.109	1.776	0.555	14.00
4.598	8.798	6.574	4.317	2.132	14.23
4.598	8.798	4.931	4.317	1.619	14.40
4.598	8.798	4.109	4.317	1.354	14.45
4.598	8.798	3.287	4.317	1.111	13.97
3.678	18.09	4.109	3.579	2.306	14.45
3.678	14.39	4.109	3.555	1.810	14.35
3.678	12.56	4.109	3.538	1.563	14.27
3.678	10.72	4.109	3.516	1.334	14.35

F(I) = 0.145 (with the same assumption as in Table 66).

4.4.4 The effect of temperature on the rate of reaction

Frost and Pearson$^{(74)}$ have considered the effect of dielectric constant on the activation energy for some reactions and concluded that "The relative insensitivity of the activation energy to the dielectric properties of the medium is not unexpected. Of much greater importance in determining the activation energy for a reaction, are the repulsive energies between the reactants as they are brought together. The forces are of the van der Waals type and result from the interaction of filled electron levels in different molecules. Such interactions are attractive for moderate distances needed for making and breaking of chemical bonds. The strength of such bonds are also of importance in determining the activation energy. Hence most of the factors that determine the energy barrier to forming the activated complex are properties of the reactants and the solvent plays only a secondary role. Since the solvent lowers the energy of both the reactants and the activated state by solvation, even this effect tends to cancel. Though the solvation would be expected to be greater for the polar complex, the experimental evidence seems to be that the activation energy is frequently somewhat greater in the more polar solvents".

For the reaction between nitrite and chlorate, the activation energies in water, 34 weight % dioxan and in 67 weight % dioxan were evaluated from three sets of experiments. The results of each set with the corresponding plot at log k versus $1/_T$ are given in Tables (68a), (68b) and (68c) and Figures (21a),(21b) and (21c), from which the values of E were

68.3 kJ mol^{-1} in aqueous solution (67.3 kJ mol^{-1} found by Abdul-Jawad)
64.3 kJ mol^{-1} in 34 wt. % dioxan
and 59.0 kJ mol^{-1} in 67 wt. % dioxan

Table 68a

(in aqueous solution)

$10^4[HNO_2] = 3.646$ mol dm^{-3} $10^3[KClO_3] = 6.587$

$10^2[HCl] = 1.782$ mol dm^{-3}

10^6 I.R mol dm^{-3} min^{-1}	k dm^6 mol^{-2} s^{-1}	1 + log k	$1000/_T$
1.54	0.60	0.778	3.532
2.50	0.97	0.987	3.470
3.99	1.55	1.190	3.411
6.23	2.42	1.380	3.354
10.29	4.00	1.602	3.299
15.89	6.18	1.791	3.245
24.44	9.52	1.979	3.193

The plot of log k against $1000/_T$ is shown in Fig.(21a).

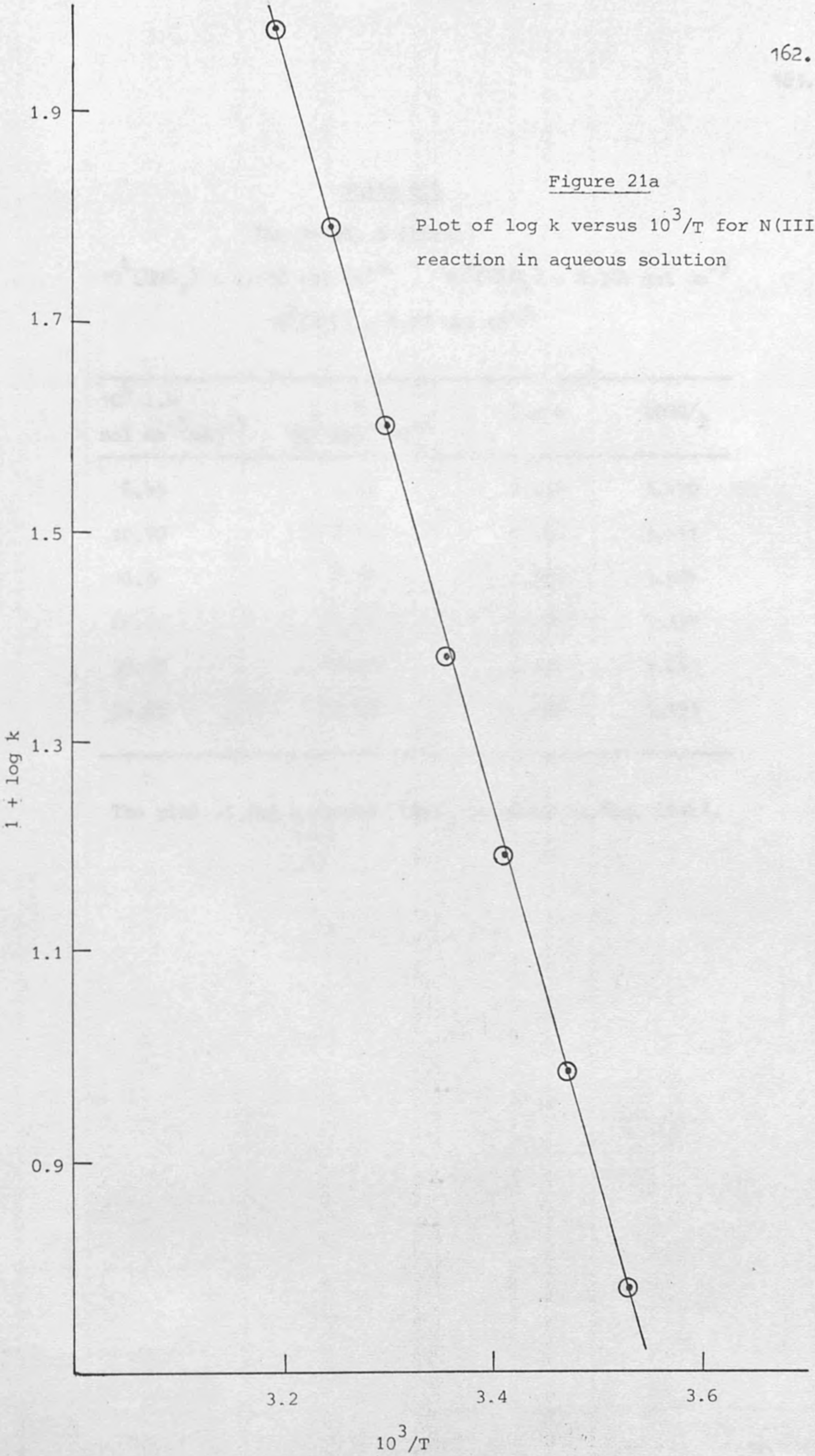


Figure 21a

Plot of log k versus $10^3/T$ for N(III)/Cl(V) reaction in aqueous solution

Table 68b

(in 34 wt. % dioxan)

$10^4[HNO_2] = 4.538$ mol dm^{-3} $10^3[KClO_3] = 8.304$ mol dm^{-3}

$10^2[HCl] = 1.93$ mol dm^{-3}

10^6 I.R mol dm^{-3}min^{-1}	k dm^6 mol^{-2} s^{-1}	log k	1000/$_T$
6.43	1.47	0.167	3.470
10.50	2.41	0.382	3.411
16.32	3.74	0.573	3.354
26.17	6.00	0.778	3.299
38.11	8.73	0.941	3.245
54.65	12.52	1.098	3.193

The plot of log k versus 1000/$_T$ is shown in Fig. (21b).

Figure 21b

Plot of log k versus $10^3/T$ for N(III)/Cl(V) reaction in 34 wt. % dioxan

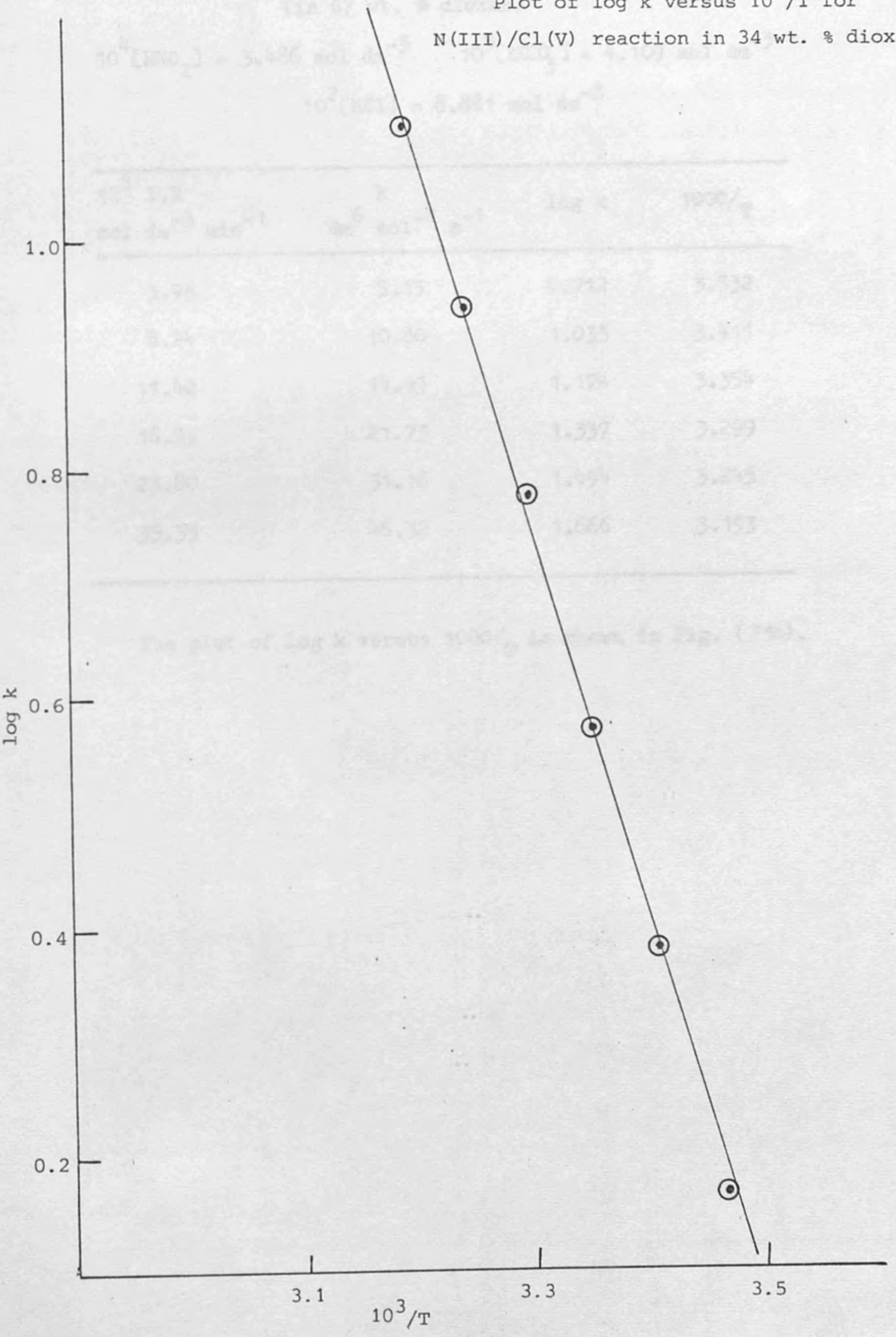


Table 68c

(in 67 wt. % dioxan)

$10^4[HNO_2] = 3.486$ mol dm^{-3} $10^3[KClO_3] = 4.109$ mol dm^{-3}

$10^2[HCl] = 8.881$ mol dm^{-3}

10^6 I.R mol dm^{-3} min^{-1}	k dm^6 mol^{-2} s^{-1}	log k	$1000/_T$
3.93	5.15	0.712	3.532
8.24	10.80	1.033	3.411
11.40	14.93	1.174	3.354
16.59	21.73	1.337	3.299
23.80	31.18	1.494	3.245
35.35	46.32	1.666	3.193

The plot of log k versus $1000/_T$ is shown in Fig. (21c).

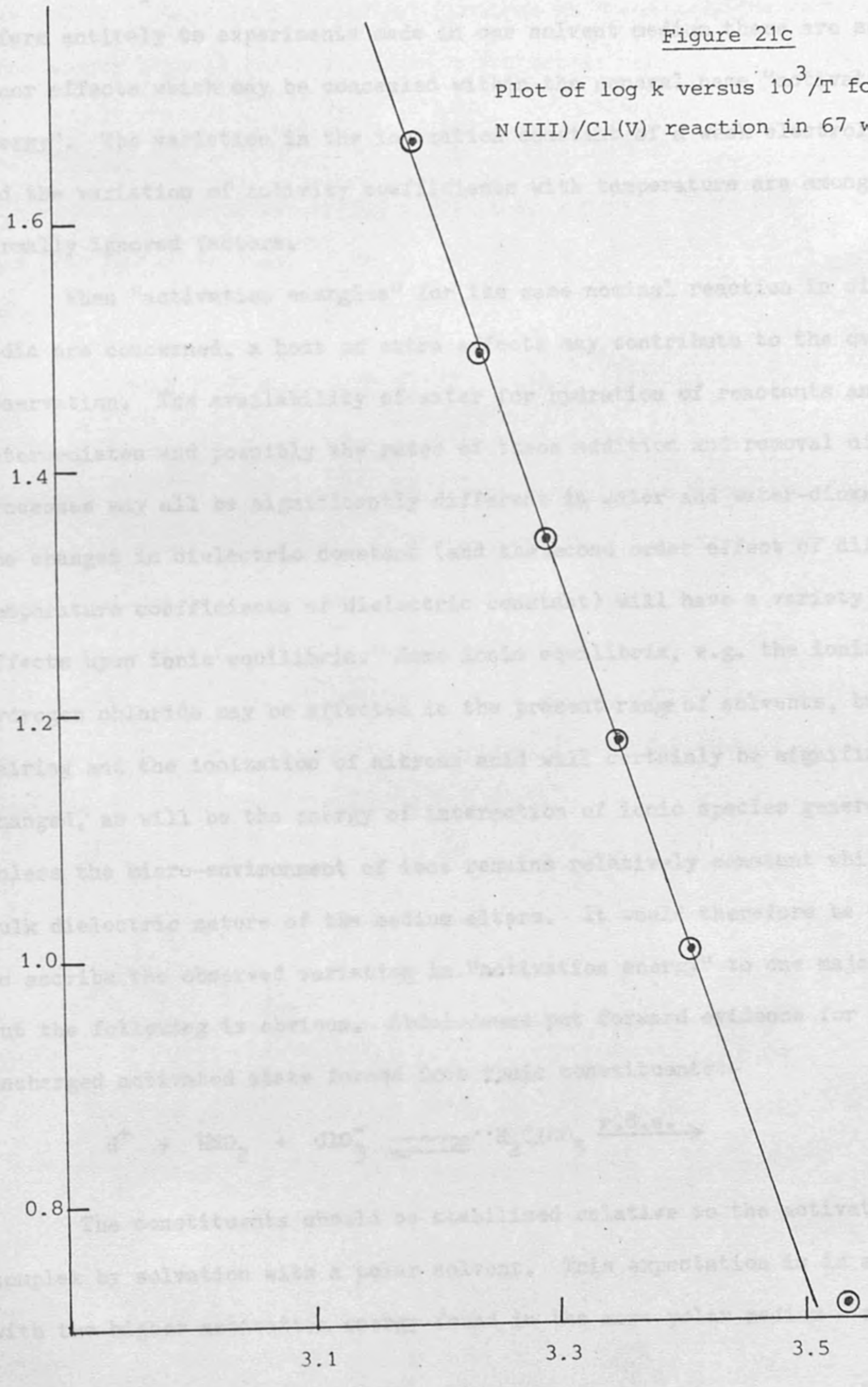


Figure 21c

Plot of log k versus $10^3/T$ for N(III)/Cl(V) reaction in 67 wt. % dioxan

Of course these measured changes in the variation of calculated log k with $1/_T$ are the resultant of many effects. Even when this variation refers entirely to experiments made in one solvent medium there are several minor effects which may be concealed within the general name "activation energy". The variation in the ionization constant of a weak electrolyte and the variation of activity coefficients with temperature are amongst these normally ignored factors.

When "activation energies" for the same nominal reaction in different media are concerned, a host of extra effects may contribute to the overall observation. The availability of water for hydration of reactants and intermediates and possibly the rates of these addition and removal of water processes may all be significantly different in water and water-dioxan. The changes in dielectric constant (and the second order effect of different temperature coefficients of dielectric constant) will have a variety of effects upon ionic equilibria. Some ionic equilibria, e.g. the ionization of hydrogen chloride may be affected in the present range of solvents, but ion-pairing and the ionization of nitrous acid will certainly be significantly changed, as will be the energy of interaction of ionic species generally, unless the micro-environment of ions remains relatively constant whilst the bulk dielectric nature of the medium alters. It would therefore be difficult to ascribe the observed variation in "activation energy" to one major cause, but the following is obvious. Abdul-Jawad put forward evidence for an uncharged activated state formed from ionic constituents:-

$$H^+ + HNO_2 + ClO_3^- \rightleftharpoons H_2ClNO_5 \xrightarrow{r.d.s.}$$

The constituents should be stabilised relative to the activated complex by solvation with a polar solvent. This expectation is in accord with the higher activation energy found in the more polar medium - agreeing with Frost and Pearson's theoretical argument (and at the same time with their survey of experimental results), and, using the argument the other way round, perhaps this dielectric constant evidence provides some extra consistency support for Abdul-Jawad's mechanism.

4.5 Discussion

The effect of dielectric constant on the rate of reaction between two ions may be written(74) as

$$\ln k = \ln k_o' - \frac{NZ_AZ_Be^2}{DRTr} \qquad \ldots\ldots \quad (65)$$

where k_o' is the specific rate constant in a medium of infite dielectric constant. This equation predicts a linear plot of ln k against $1/_D$ with a positive slope if the charges of the ions are of opposite sign and a negative slope if the charges are of the same sign.

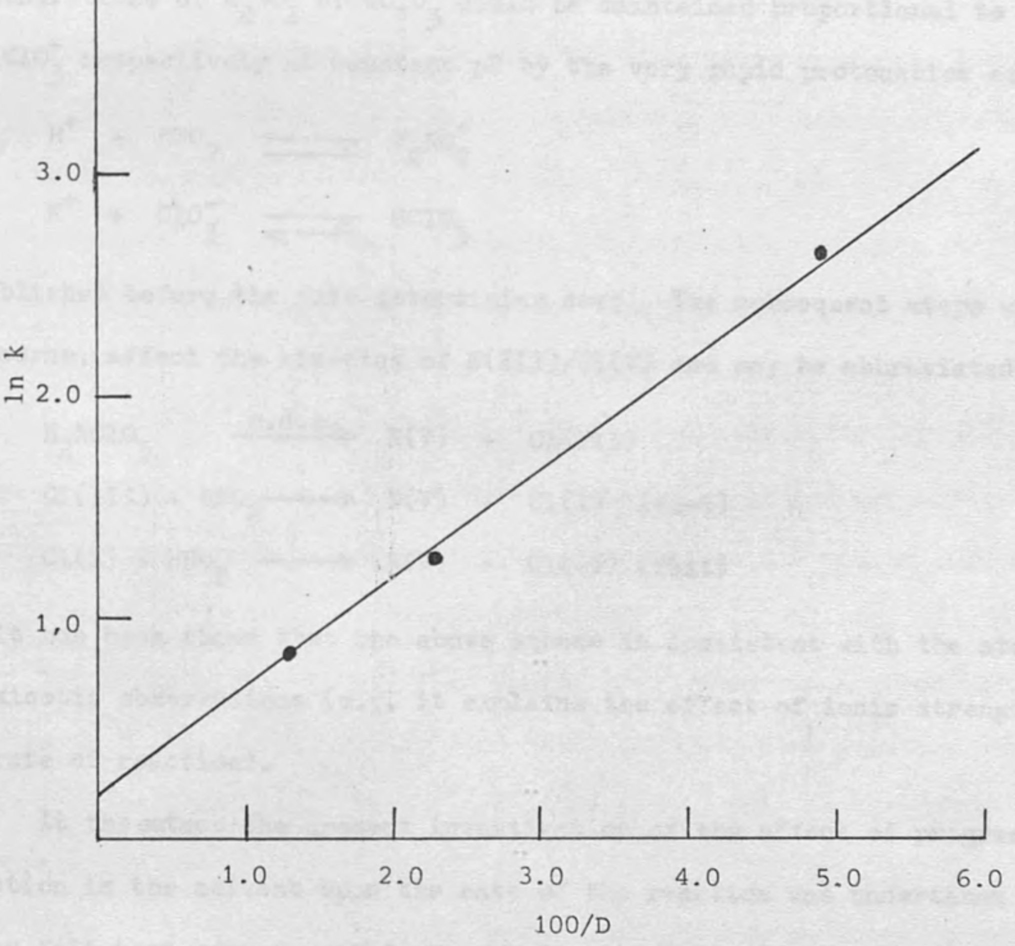
Variation of the specific rate constant of the reaction between nitrite and chlorate with the dielectric constant of the medium is given in Table (69), and the plot of ln k versus $100/_D$ produced a straight line (Fig. 22) with a positive slope. Extrapolation to D = ∞ gives the value 1.35 $dm^6\ mol^{-2}\ s^{-1}$ for k.

Table 69

k $dm^6\ mol^{-2}\ s^{-1}$	D	$100/_D$	ln k
2.31	78.30	1.277	0.837
3.58	48.38	2.067	1.275
14.31	20.45	4.890	2.661

Figure 22

Plot of ln k versus 100/D for N(III)/Cl(V) reaction



The mechanism postulated by Abdul-Jawad(5) for the reaction between nitrite and chlorate is through the establishment of an overall equilibrium to give the complex H_2NClO_5 as:

$$\left.\begin{array}{ll}(1) & H^+ + HNO_2 + ClO_3^- \\ (2) & H^+ + HNClO_4^- \\ (3) & H_2NO_2^+ + ClO_3^- \\ (4) & HNO_2 + HClO_3\end{array}\right\} \rightleftharpoons H_2NClO_5 \xrightarrow{r.d.s.}$$

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 the very rapid protonation equilibria,

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

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

established before the rate determining step. The subsequent steps will not, of course, affect the kinetics of N(III)/Cl(V) and may be abbreviated thus:-

$$H_2NClO_5 \xrightarrow{r.d.s.} N(V) + Cl(III)$$

$$Cl(III) + HNO_2 \longrightarrow N(V) + Cl(I) \quad \text{(fast)}$$

$$Cl(I) + HNO_2 \longrightarrow N(V) + Cl(-I) \quad \text{(fast)}$$

and it has been shown that the above scheme is consistent with the stoichiometry and kinetic observations (e.g. it explains the effect of ionic strength on the rate of reaction).

At the outset the present investigation of the effect of progressive variation in the solvent upon the rate of the reaction was undertaken because it was felt that very few studies of this kind had been reported although a variety of medium-effects might be operative.

Ways in which the present reaction may be different from the few oxidation reactions examined in this way are (a) essentially the others have been electron-exchange reactions such as the Np(V)/Np(VI) reaction in ethylene glycol-water mixtures(75), (b) at least one of the reactants in the present case is a weak electrolyte in all the systems studied and hence the underlying pre-equilibria may be affected by change of medium. Taking up this last point, Feakins(76) has observed that dioxan-water mixtures should be more basic than water. Accepting this point one anticipates an intrinsic increase in dissocation constants for weak acids as the dioxan component is increased in the mixture. However, it is also necessary to consider the relatively large effects of solvation, and whilst all the species HNO_2, H^+ and NO_2^- have sites which can interact with the oxygen or hydrogen atoms of the solvent, the ionic species are undoubtedly the more involved in solvation. This slective effect should lower the dissocation constant as dioxan concentration is increased. The diminution in volume observed when water is mixed with dioxan implies an appreciable interaction between the two components of the solvent, so that ions would be in competition with dioxan for the water. Thus at the outset it was not at all clear how change of solvent would affect the concentration of HNO_2. Unless there were a change in mechanism as the medium changed, alterations in $[HNO_2]$ would be directly reflected in the rate.

The basicity of dioxan-water should be relevant in another way. In addition to H^+ being required to form HNO_2, the mechanism requires an extra H^+ per activated complex. This H^+ could be more freely available in the more basic solvent.

Of course, when the solvent medium changes many potentially relevant properties alter, for example, the viscosity variation might be kinetically significant, but it seems likely that the variation in dielectric constant (so marked in the present system even while the mole:mole ratio of dioxan-water has only been altered from 0:1 to about 1:2) is a major factor which could affect the rate (equation 65). It may be noted at this point that although many reactions are known which approach this kind of behaviour of variation with dielectric constant (as represented by equation 65), the Np(V)/Np(VI) electron exchange referred to above seems anomalous in that no variation in k was observed as D varied ~ 90 to ~ 60.

One further, rather obvious, comment can be included in the initial thoughts about the reaction before experiments were begun. Although the reaction is an oxidation, electron transfer probably takes place internally in the activated complex. Such electron transfer might be virtually uninfluenced by the medium, hence the fact that the reaction happens to involve oxidation might be quite unimportant as far as change of dielectric constant is concerned.

When we turn to the results we find that a variation in D from 80 to 20 has little effect upon overall rate, the major identified features being a rise in pK (HNO_2), (rather as expected), leading to a rise in $[HNO_2]$, coupled with a rise in overall rate constant. This rise in rate constant is calculated for the "actually existing" reactant species.

It is unfortunately not possible, however, to use this result in a unique way to learn much more about the mechanism. It is already established that $2H^+$, NO_2^- and ClO_3^- are in overall equilibrium with an activated state H_2NClO_5. This is probably a three step event. The present experiments have enabled one to find the effect of change of D upon the obvious step, the protonation of NO_2^-, but it has not been possible to measure similar effects upon all the conceivable pre-equilibrium steps; and the overall observed effect of change of D is the sum of its effect upon both pre-equilibria and the rate determining step.

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

$$H_2NO_2^+ + ClO_3^- \rightleftharpoons H_2NClO_5 \xrightarrow{r.d.s.}$$

represents the detail, the first step might be little affected by change of D whereas step two would be enhanced by a fall in D - this would be consistent with the observation; but for example

$$HNO_2 + ClO_3^- \rightleftharpoons HNClO_5^-$$

$$H^+ + HNClO_5^- \rightleftharpoons H_2NClO_5 \xrightarrow{r.d.s.}$$

has the same charge characteristics and therefore would not be eliminated by the observations.

All that can be said is that the observed effect is in accord with the more probable mechanistic details.

The possible reaction between nitrite and perchlorate

The redox reactions of perchlorate are known to be extremely slow despite the advantageous redox potentials frequently obtaining. Since H^+ has been supplied by $HClO_4$ in some experiments it was necessary to investigate the N(III)/Cl(VII) reaction. The inertness of ClO_4^- with regard to its redox reaction with nitrite in immediately seen under the experimental conditions given in Table (70), which gives the time-absorbance data for the experiments that were carried out.

*Table 70

$10^4[NaNO_2] = 4.159$ mol dm^{-3} T = 25°C

(5 ml samples were taken for analysis)

t (min)	Absorbance a	b	c	d	e
1	1.057	1.054	1.053	1.055	1.058
5	1.053	1.047	1.049	1.053	1.056
10	1.049	1.040	1.043	1.049	1.051
15	1.033	1.020	1.010	1.013	1.011
25	1.016	0.999	-	-	-
35	0.989	-	0.983	0.980	0.983
60	-	-	0.951	0.959	0.958

* reactants other than nitrite were,

	$[NaClO_4]$ mol dm^{-3}	[HCl] mol dm^{-3}	[KCl] mol dm^{-3}
(a)	1.387×10^{-3}	2.005×10^{-2}	-
(b)	1.387×10^{-3}	2.005×10^{-1}	-
(c)	4.162×10^{-3}	2.005×10^{-1}	-
(d)	1.041×10^{-1}	2.005×10^{-1}	-
(e)	-	2.005×10^{-1}	1.001×10^{-1}

When the results of experiments c, d, and e are compared they indicate that these observed changes in absorbance with time are due to the decomposition of nitrous acid in the presence of acid. Thus ClO_4^- does not react with nitrite under conditions where ClO_3^- reacts with nitrite rapidly.

Since the observed rates of reaction of chlorine oxyacids with N(III) are in order,

$$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$$

it is clear that the use of $HClO_4$ to provide hydrogen ion, or of perchlorates to provide ionic strength has no detected complicating effect upon the rates of these other reactions.

Appendix

Methods of Calculation

(i) Determination of Initial Rates

Initial rates have been determined by three (occasionally four) methods and weighted averages taken. These methods are:-

(a) Extrapolation of the experimental absorbance versus time points to $t = 0$, and a tangent put through the curve at $t = 0$.

(b) Differences between the experimental absorbance readings were divided by the time interval and were then plotted at the mid point of each time interval. The graph extrapolated to $t = 0$, gives absorbance/unit time as the intercept at $t = 0$, (this method was found to be more reliable than (a)).

(c) Depending on the order with respect to N(III), initial rates were determined from the corresponding plots of absorbance data versus time. Three cases were considered in this method.

(1) When the apparent order in N(III) is 0.5, and we write C for [N(III)], initial rates were calculated via:

$$\text{I.R} = -2\text{Co} \times \text{factor} \times \text{gradient of } A^{0.5}/\text{time} \qquad \text{......} \quad (66)$$

because in this case if,

$$-dC/dt = k\, C^{0.5} \qquad \text{......} \quad (67)$$

then

$$-dC \times C^{-0.5} = k\, dt \qquad \text{......} \quad (68)$$

which on integration and rearrangement gives

$$C^{0.5} = -\frac{k}{2}\, t + \text{constants} \qquad \text{......} \quad (69)$$

Equation (69) is of the form

$$y = m\, x + \text{constant} \qquad \text{......} \quad (70)$$

where

$$\text{gradient} = m = -\frac{k}{2} \qquad \text{......} \quad (71)$$

or $k = -2 \times \text{gradient}$ ...... (72)

if $C^{0.5}$ is plotted versus t. But absorbance $(A)^{0.5}$ was plotted versus t, i.e. we have multiplied (69) by a factor:-

$(\varepsilon/50)^{0.5} \times C^{0.5} = -\frac{k}{2}t \times (\varepsilon/50)^{0.5} + \text{constant}$ ...... (73)

so gradient observed $= -\frac{k}{2}(\varepsilon/50)^{0.5}$ ...... (74)

hence, $k = -2(50/\varepsilon)^{0.5} \times \text{gradient}$ ...... (75)

(the factor $(\varepsilon/50)^{0.5}$ was used because 2cm^3 of reaction mixture was diluted to 100 cm^3 and the absorbance of a 1 cm length observed).

(2) If the apparent order in N(III) is one, initial rates were calculated by multiplying each initial concentration of N(III) by (minus) the gradient of the corresponding graph of ln A versus time, i.e.

$I.R = -Co \times \text{gradient}$ ...... (76)

(3) When the order is apparently 1.5, the following equation was used in calculating initial rates,

$I.R = 2\,Co^{1.5} \times \text{factor} \times \text{gradient of } C^{-0.5}/t$ ...... (77)

because, as before

$-dC/dt = k\,C^{1.5}$ ...... (78)

then

$-C^{1.5}dC = k\,dt$ ...... (79)

and

$C^{-0.5} = \frac{k}{2}\,t + \text{constant}$ ..... (80)

and mutliplying both sides of equation (80) by $(\varepsilon/50)^{0.5}$, yields

$(\varepsilon C/50)^{-0.5} = \frac{k}{2}(\varepsilon/50)^{-0.5}\,t + \text{constant} = A^{-0.5}$ ...... (81)

from which

$$k = 2 \text{ gradient} \times \left(\frac{50}{\varepsilon}\right)^{-0.5}$$

(d) In some cases a quadratic function was fitted to the early results as

$$A = Ao + Bt + Et^2 \qquad \ldots\ldots \quad (83)$$

where A and Ao refer to the absorbance at t = t and t = o respectively, B and E are constants.

Differentiation of the equation produces

$$dA/dt = B + 2\,Et \qquad \ldots\ldots \quad (84)$$

which at t = o indicates the initial rate via,

$$-dA/dt = -B \qquad \ldots\ldots \quad (85)$$

As a modification to the quadratic functions, absorbance readings were sometimes fitted to an exponential function, such as

$$A = Ao\ e^{-2.303\ pt} \qquad \ldots\ldots \quad (86)$$

(p is a constant)

or $$dA/dt = -2.303\ p\ Ao\ e^{-2.303\ pt} \qquad \ldots\ldots \quad (87)$$

$$(\text{because } de^{\mu}/dt = e^{\mu}\ .\ d\mu/dt) \qquad \ldots\ldots \quad (88)$$

so that, $$dA/dt = -2.303\ pA \qquad \ldots\ldots \quad (89)$$

or, initial rate of $dA/dt = -2.303\ pA_o$ ...... (90)

In practice this was also used to find Ao to put into the final expression. Actual observations of A_1 and A_2 are used to find the best values of p; then since t_1, t_2 are known, values of Ao can be calculated as

$$Ao = A_1 \times 10^{pt_1} \quad \text{etc.} \qquad \ldots\ldots \quad (91)$$

and an average value of Ao used in $(dA/dt)_{t=o}$.

(ii) pH Measurements and Calculations of Hydrogen Ion Concentrations

pH measurements were carried out by using a Pye Dynacap pH meter in conjunction with an Ingold glass and calomel electrode. The meter was calibrated by means of 0.5 mol dm^{-3} potassium hydrogen phthalate solution and was checked at other points of the pH scale.

The concentration of H^{+} was calculated as follows:

By definition

$$pH = -\log_{10} a_{H^+} \qquad \ldots\ldots \quad (92)$$

$$= -\log_{10} [H^+]\, \gamma_{H^+} \qquad \ldots\ldots \quad (93)$$

and if it is accepted that

$$-\log \gamma = A\, Z^2\, F(I) \quad \text{(equation 5)}$$

then

$$pH = -\log [H^+] - \log \gamma_{H^+} \qquad \ldots\ldots \quad (94)$$

$$= -\log [H^+] + 0.509\, F(I) \qquad \ldots\ldots \quad (95)$$

hence

$$-\log [H^+] = pH - 0.509\, F(I) \qquad \ldots\ldots \quad (96)$$

(iii) Calculation of the Concentration of Nitrous Acid

In aqueous acidic media of nitrite, the equilibrium

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

is rapidly established and the concentration equilibrium constant K is given by

$$K = [NO_2^-][H^+]/HNO_2] \qquad \ldots\ldots \quad (97)$$

The value of K at ionic strength I, can be deduced using the results of Tummavuori and Lumme, i.e.

$$pK = pK_o - 2A\, I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + \beta I \qquad \ldots\ldots \quad (98)$$

in which, for example,

$$pK_o = 3.136$$

$$A = 0.5115$$

$$\alpha = 2.074$$

and $\beta = 0.0669$

at 25°C (other appropriate figures were used for other temperatures)

Since total [N(III)] dissolved as NO_2^- in a solution at pH∼4, becomes $[HNO_2] + [NO_2^-]$; equation (97) can be written as

$$K = K_I = \frac{([NO_2^-]_o - [HNO_2])[H^+]}{[HNO_2]} \qquad \ldots\ldots \quad (99)$$

from which,

$$[HNO_2] = \frac{[NO_2^-]_o[H^+]}{K_I + [H^+]} \qquad \ldots\ldots \quad (100)$$

In dilute aqueous hydrochloric acid solution (in which the reaction between N(III) and Cl(V) was studied in water/dioxan mixtures), the concentration of nitrous acid and hydrogen ion were calculated by,

$$[HNO_2] = \frac{[NO_2^-]_o[H^+]_o}{K_I + [NO_2^-]_o + [H^+]_o} \qquad \ldots\ldots \quad (101)$$

and $[H^+] = [H^+]_o - [HNO_2]$ $\qquad \ldots\ldots$ (102)

because no buffer was used to maintain $[H^+]$ at a constant value.

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الخلاصـــــــــــة

(Abstract in Arabic)

يتضمن هذا البحث دراسة ميكانيكية بعض تفاعلات التأكسد والاختزال بين النترايت وكل من —

آــ الكلورايت حيث ان معادلة التفاعل هى —

٢ يدنا$_٢$ + كلا$_٢^-$ ← نا$_٣^-$ + كل$^-$+ ٢ يد$^+$

بــ البيرأيوديت ومعادلة التفاعل هى —

٢ يدنا$_٢$ + يد$_٥$يوا$_٦$ + يد$^+$ ← نا$_٣^-$ + يوا$_٣^-$ + ٢ يد$_٢$ا + ٢ يد$^+$

جــ الكلورات ومعادلة التفاعل هى .—

٣ يدنا$_٢$ + كلا$_٣^-$ ← ٣ نا$_٣^-$ + كل$^-$ + ٤ يد$^+$

فيمايتعلق بالتفاعلات بين النترايت وكل من الكلورايت والبيرأيوديت اللذين يدرسا لأول مرة فقد تم ايجاد معادلة سرعة التفاعل فى كل حالة وبناء عليه امكن اقتراح الخطوات التى تتم اثناء عملية التفاعل ومناقشة هذه الخطوات التى تؤدى الى تكوين نواتج كل تفاعل .

من الملاحظات الهامة من الناحية التطبيقية هو ان مقدارا ضئيلا من ايون البرومايد يؤدى الى زيادة سرعة التفاعل بين النترايت والبيرأيوديت زيادة ملحوظة لذا فأنه من الممكن لهذا التفاعل ان يكون احد الطرق المستعملة فى تحديد المقادير الضئيلة من هذا الايون والتى توجد عادة كشوائب فى مركبات الكلورايد المختلفة بل لربما ان هذا التفاعل هو من اسهل الطرق التى يمكن استعمالها لهذه الغاية .

اما فيمايخص التفاعل بين النترايت والكلورات فقد تمت دراسته فى محاليل من الماء / والديوكسين بغرض دراسة تأثير تغيير بعض صفات وسط التفاعل على سرعته . هذا وقد تم ايضا تعيين ثابت التأين لحامض النيتروز فى محاليل مشابهه .

ملاحظة — تمت هذه الدراسة فى كلية بدفورد / جامعة لندن بهدف الحصول على شهادة الدكتوراة فى الكيمياء صيف عام ١٩٧٧ .