Mechanism of the Nitrite–Iodide Reaction

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The kinetics of the reaction between nitrite and iodide in acid medium were studied spectrophotometrically. The observed rate equation was:

$$v = k_1[HNO_2][H^+][I^-]^2 + k_2[HNO_2]^2[H^+]^2[I^-]^2$$

In perchloric acid medium at $25 \pm 0.1°C$, with an ionic strength of 0.2, the values of the rate constants were: $k_1 = 3.7 \pm 0.4 \times 10^3\ mol^{-3}\ dm^9\ s^{-1}$; $k_2 = 3.7 \pm 0.3 \times 10^{10}\ mol^{-5}\ dm^{15}\ s^{-1}$. As explanation, two parallel reaction paths were assumed, involving the formation of NOI and $H_2N_2O_3I^+$, the reaction of which with a further iodide leads to the redox step.

It was demonstrated that in the presence of citric acid the rate increases, while the bromide ion exerts an inhibitory effect. It was established that the zinc(II) catalysis assumed earlier by other authors is caused by a pH shift in the solution. At constant pH the zinc(II) ion decreases the rate.

Introduction

Of the redox reactions of nitrite we earlier investigated the kinetics of its oxidation by chromate[1] and permanganate[2]. As a continuation of this theme we have now begun a kinetic study of the reduction of nitrite by iodide ion. In acid medium the reaction takes place in accordance with the following stoichiometry:

$$2\ HNO_2 + 2\ I^- + 2\ H^+ \rightarrow I_2 + 2\ NO + 2\ H_2O \quad (1)$$
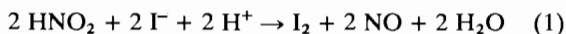
It was previously established by Bobtelsky and Kaplan[3] that the rate of the reaction is proportional to the concentrations of the nitrite, the iodide and the hydrogen ion, but their investigations were not carried out with the aim of determining the mathematical form of the rate equation. More recently, at about the time of the completion of our experimental work, Ferranti et al.[4] reported their detailed kinetic study of this reaction. Their experimental method differed from ours: the reaction was chemically frozen and the reaction mixture was analyzed by titration. The results obtained with the two different methods in part agree well, and in part supplement each other. Consideration of the experimental results, however, leads us to a different interpretation of the mechanism of the reaction.

Experimental

Method

The reaction was followed spectrophotometrically by measurement of the absorbance of the iodine formed. To eliminate the disturbing effect of the I_2–I_3^- equilibrium, measurements were made at 454 nm, the isosbestic point of I_2 and I_3^- (here $\varepsilon_{I_2} = \varepsilon_{I_3^-} = 1.083$ $mol^{-1}\ dm^3\ cm^{-1}$). In the course of the experiments care was taken to exclude oxygen: the acidic iodide solution was placed in a cell fitted with a rubber cap, nitrogen was bubbled through the solution for 15 min at an intense rate, and sodium nitrite solution which had similarly been swept with nitrogen was injected by syringe into the cell. The concentration conditions were selected so that the half-time of the reactions should be more than 5 min. Measurements were made at $25 \pm 0.1°C$, in 2 cm cells. The initial rates were determined graphically from the absorbance vs. time curves. The reaction rate is given by the change in the reaction coordinate according to the above stoichiometric equation: $v = d[I_2]/dt$.

Materials

Analytically pure, commercially available chemicals were used. The sodium perchlorate used to adjust the ionic strength was prepared from sodium hydrogen carbonate and perchloric acid. The concentration of the sodium nitrite stock solution was determined permanganometrically, and that of the sodium iodide bromatometrically.

Instruments

Hitachi Perkin–Elmer 139 spectrophotometer and Radelkis OP precision pH-meter were employed.

Results

The reaction was studied in the following concentration intervals:

sodium nitrite: 3.00×10^{-5}–4.50×10^{-4} mol dm^{-3}; sodium iodide: 1.00×10^{-4}–1.60×10^{-3} mol dm^{-3}; perchloric acid: 1.10×10^{-5}–5.40×10^{-3} mol dm^{-3}.

With the reagent concentrations constant, the increase of the ionic strength from 0.01 to 0.1 leads to a strong decrease in the reaction rate; further increase to 0.3, however, results in relatively little change (Figure 1). Subsequent measurements were thus made at an ionic strength of 0.2.

At constant nitrite and hydrogen ion concentrations the reaction rate varies linearly with the square of the iodide ion concentration (Figure 2). Accordingly:

$$v = c_1[I^-]_t^2 \tag{2}$$

where c_1 is a constant independent of the iodide concentration.

At constant iodide and hydrogen ion concentrations the order with respect to the nitrite concentration on a logarithmic plot lies between 1 and 2. The rate expression was therefore written as the sum of first and second-order terms as regards the nitrite concentration:

$$v = c_2 c_N + c_3 c_N^2 \tag{3}$$

where c_2 and c_3 are constants independent of the nitrite concentration, and c_N is the total nitrite concentration.

Expression (3) is confirmed by the fact that a plot of v/c_N against c_N is linear (Figure 3).

At constant nitrite and iodide concentrations a logarithmic plot gives a value larger than 2 for the order with respect to the hydrogen ion concentration. Since the hydrogen ion concentration also affects the nitrous acid concentration, the rate equation was written in the following form:
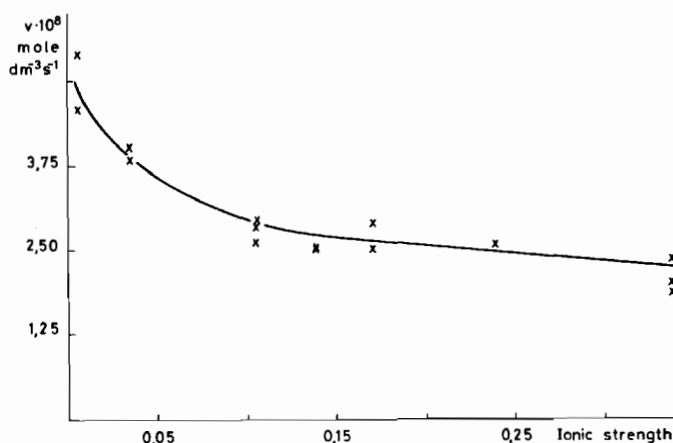
$$v = c_4[HNO_2][H^+] + c_5[HNO_2]^2[H^+]^2 \tag{4}$$

Figure 1. Dependence of the reaction rate on the ionic strength. $[I^-]_t = 4.00 \times 10^{-3}$ mol dm^{-3}; $c_H = 1.67 \times 10^{-3}$ mol dm^{-3}; $c_N = 1.00 \times 10^{-4}$ mol dm^{-3}.
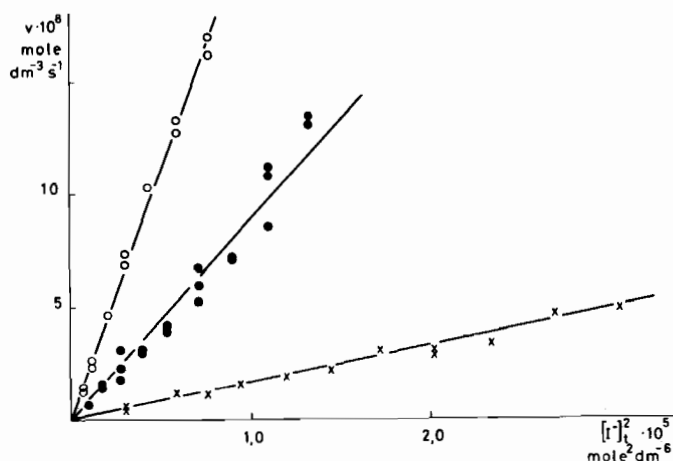

Figure 2. The reaction rate as a function of the square of the iodide ion concentration. X: $c_H = 1.93 \times 10^{-3}$ mol dm^{-3}, $c_N = 1.49 \times 10^{-4}$ mol dm^{-3}; O: $c_H = 3.86 \times 10^{-3}$ mol dm^{-3}, $c_n = 1.65 \times 10^{-4}$ mol dm^{-3}; O: $c_H = 5.80 \times 10^{-3}$ mol dm^{-3}, $c_N = 1.49 \times 10^{-4}$ mol dm^{-3}.
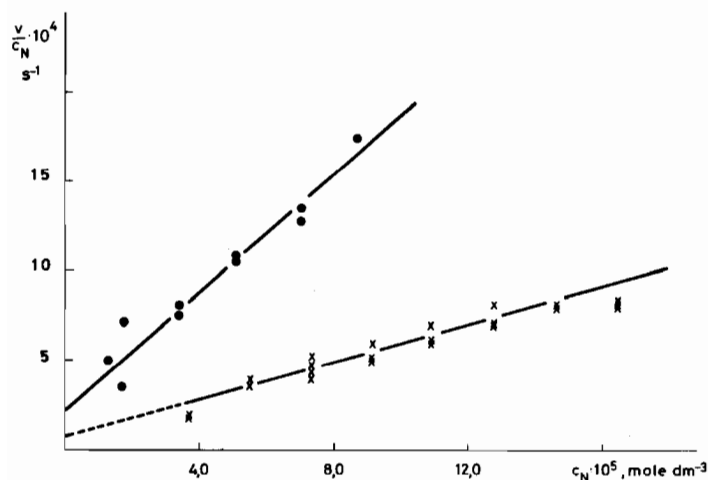
Figure 3. Determination of the first and second-order rate constants at constant hydrogen ion and iodide ion concentrations.
O: $c_H = 5.78 \times 10^{-3}$ mol dm^{-3}, $[I^-]_t = 4.15 \times 10^{-3}$ mol dm^{-3}; X: $c_H = 3.86 \times 10^{-3}$ mol dm^{-3}, $[I^-]_t = 3.87 \times 10^{-3}$ mol dm^{-3}.
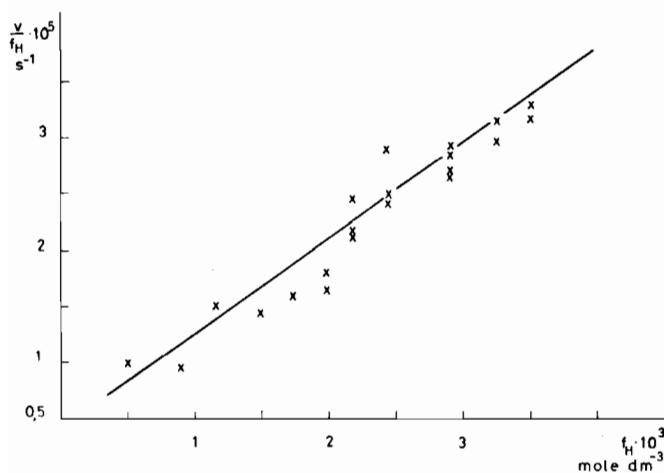
Figure 4. The v/f_H values as a function of f_H. $c_N = 1.06 \times 10^{-4}$ mol dm^{-3}; $[I^-]_t = 4.17 \times 10^{-3}$ mol dm^{-3}.

Taking into account the dissociation equilibrium (5):

$$HNO_2 \underset{}{\overset{K_d}{\rightleftharpoons}} H^+ + NO_2^-$$
$$(K_d = 1.17 \times 10^{-3} \text{ mol dm}^{-3}) \quad (5)$$
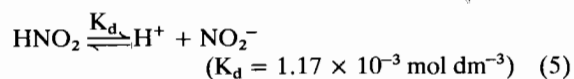
and expressing the concentration of nitrous acid with the total nitrite concentration (c_N), substitution into (4) gives:

$$v = c_4 c_N \frac{[H^+]^2}{K_d + [H^+]} +$$

$$c_5 c_N^2 \frac{[H^+]^4}{(K_d + [H^+])^2} \quad (6)$$

Denoting $[H^+]^2/(K_d + [H^+])$ by f_H, and plotting v/f_H as a function of f_H, a straight line is obtained (Figure 4), which confirms equations (4) and (6).

On the above basis the full rate equation can be written as follows:

$$v = k_1'[HNO_2][H^+][I^-]^2 + $$
$$k_2'[HNO_2]^2[H^+]^2[I^-]^2 \quad (7)$$

From the individual functions the constants were determined graphically, and from these k_1' and k_2' were calculated:

$k_1' = 3.7 \pm 0.4 \times 10^3$ mol^{-3} dm^9 s^{-1}
$k_2' = 3.7 \pm 0.3 \times 10^{10}$ mol^{-5} dm^{15} s^{-1}

With these constants the rate-dependences were calculated via equation (7). The calculated curves fit well to the experimentally determined values (Figures 5 and 6).

It was found experimentally that the reaction rate decreases strongly *on the action of the bromide ion*
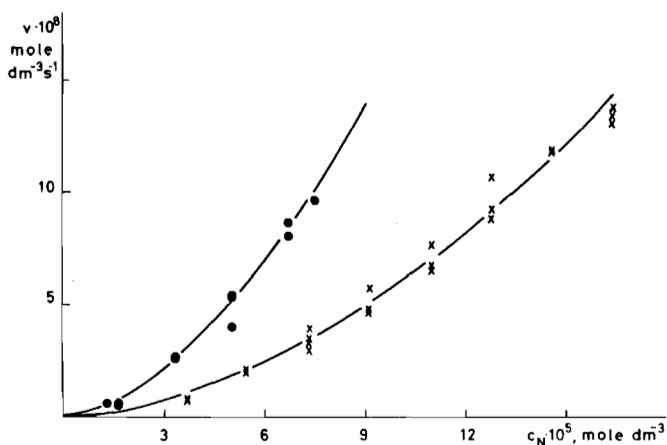
Figure 5. Reaction rate *vs.* nitrite concentration functions (drawn curves) calculated from the rate equation. The points indicate the experimentally measured values. X: $[I^-]_t = 3.87 \times 10^{-3}$ mol dm^{-3}, $c_H = 3.86 \times 10^{-3}$ mol dm^{-3}; O: $[I^-]_t = 4.15 \times 10^{-3}$ mol dm^{-3}, $c_H = 5.78 \times 10^{-3}$ mol dm^{-3}.
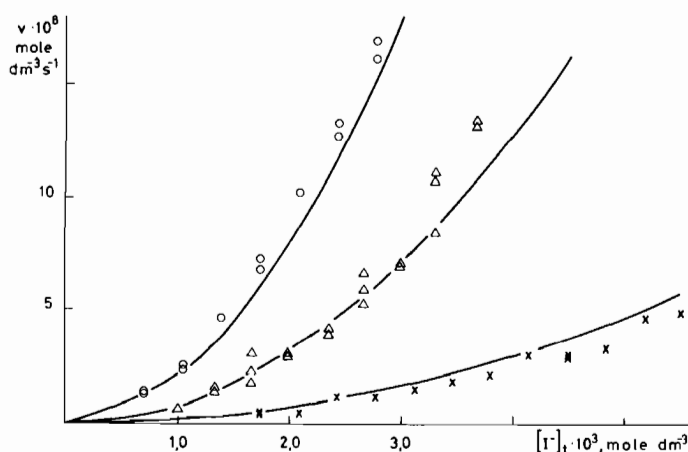

Figure 6. Dependence of the reaction rate on the iodide ion concentration. The drawn curves were calculated from the rate equation, and the points are the experimentally found values. X: $c_N = 1.49 \times 10^{-4}$ mol dm^{-3}, $c_H = 1.93 \times 10^{-3}$ mol dm^{-3}; $\triangle$: $c_N = 1.65 \times 10^{-4}$ mol dm^{-3}, $c_H = 3.86 \times 10^{-3}$ mol dm^{-3}; O: $c_N = 1.49 \times 10^{-4}$ mol dm^{-3}, $c_H = 5.80 \times 10^{-3}$ mol dm^{-3}.
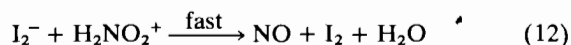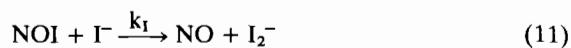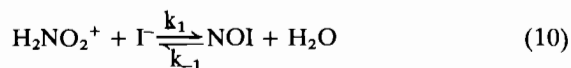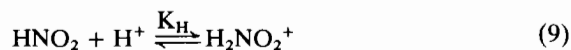
(Figure 7). At constant reagent concentrations and an ionic strength of 1.0 the reaction rate varies with the bromide ion concentration according to the expression:

$$v = \frac{c_6}{1 + c_7[Br^-]} \qquad (8)$$

where c_6 and c_7 are constants independent of the bromide ion concentration. However, the reaction orders with respect to the iodide, the nitrite and the hydrogen ion are practically unchanged in the presence of bromide: in 5×10^{-3} mol dm^{-3} perchloric acid in the absence of bromide the order for nitrite is 1.70 ± 0.05 and that for iodide is 2.05 ± 0.05, while with a bromide concentration of 0.2 mol dm^{-3} these values are 1.8 ± 0.1 and 2.1 ± 0.1, respectively.

Mechanism of the Reaction

The fourth-order term in the rate equation (7) is explained by the following reaction steps:

$$HNO_2 + H^+ \underset{}{\overset{K_H}{\rightleftharpoons}} H_2NO_2^+ \qquad (9)$$

$$H_2NO_2^+ + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOI + H_2O \qquad (10)$$

$$NOI + I^- \xrightarrow{k_I} NO + I_2^- \qquad (11)$$

$$I_2^- + H_2NO_2^+ \xrightarrow{fast} NO + I_2 + H_2O \qquad (12)$$

In other systems the NOI assumed in the mechanism has been detected in the gas phase in photoflash experiments[6], while the existence of I_2^- has been dem-
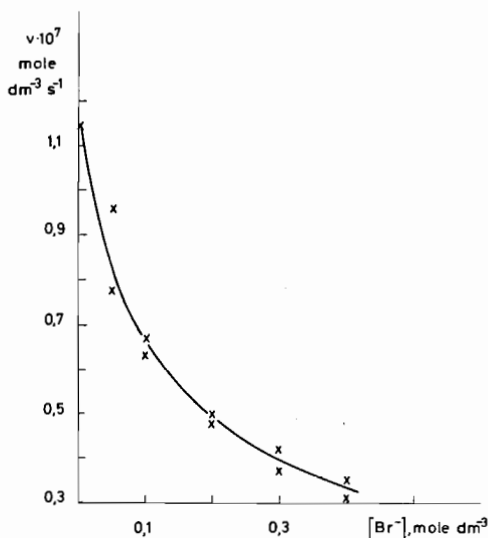
Figure 7. Dependence of the reaction rate on the bromide concentration. $c_N = 6.70 \times 10^{-5}$ mol dm^{-3}; $c_H = 5.0 \times 10^{-3}$ mol dm^{-3}; $[I^-]_t = 4.00 \times 10^{-3}$ mol dm^{-3}; $I_c = 1.0$.

onstrated spectrophotometrically in solution[7]. If (9) is regarded as a fast pre-equilibrium and a stationary state is assumed for NOI, we obtain the expression:

$$v_1 = \frac{k_1 k_1 K_H [HNO_2][H^+][I^-]^2}{k_{-1}a_w + k_1[I^-]} \tag{13}$$

where a_w is the activity of water. If $k_1[I^-] \ll k_{-1}a_w$, then (13) reduces to the experimentally found equation:

$$k_1' = k_1 k_1 K_H / k_{-1} a_w$$

The sixth-order term coincides with the full rate expression given by Ferranti *et al.* As explanation they assume a bimolecular reaction of the NOI formed:

$$NOI + NOI \xrightarrow{k_3} 2\,NO + I_2 \tag{14}$$
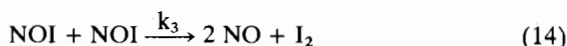
Here, however, a second-order dependence for every reactant is obtained only if process (10) is also regarded as a fast pre-equilibrium. This leads to the rate equation:

$$v_2 = k_3 \frac{K_{NOI}^2}{a_w^2} [HNO_2]^2[I^-]^2[H^+]^2$$

In this expression:

$$K_{NOI} = K_H k_1 / k_{-1} a_w$$

i.e. the formation constant of nitrosyl iodide. Taking into consideration that the experimentally determined value of k_2' is 3.7×10^{10}, and also that k_3, as a bimolecular rate constant, cannot be greater than 10^{10}, we have $K_{NOI} > 100$. However, this seems an improbably high value if it is compared with the formation constants of analogous compounds[8, 9]: $K_{NOBr} = 5 \times 10^{-2}$, $K_{NOCl} \sim 10^{-3}$.

There are a further two experimental findings which do not fit in the above mechanism. One of these is that although the reaction rate can be described by a similar equation in a citrate + phosphate buffer mixture, nevertheless the apparent rate constant values change to different extents. Thus, with a disodium hydrogen phosphate concentration of 0.024 mol dm^{-3} and a citric acid concentration of 0.029 mol dm^{-3}, the sixth-order rate constant is about 5 times that found in the absence of the buffer ($k_{2,B}' = 1.9 \times 10^{11}$ mol^{-5} dm^{15} s^{-1}), whereas the fourth-order constant is practically unchanged. This fact indicates that the sixth-order process does not take place via the same intermediate (in this case nitrosyl iodide).

The fact of bromide inhibition also induces us to assume reaction steps. It can readily be seen that if the formation of NOI is a fast process, then its concentration can be influenced by the bromide ion only as a result of a change in the amounts of the starting reagents. Nevertheless, as a consequence of the relatively low formation constant of nitrosyl bromide, the free nitrous acid concentration is scarcely decreased under the concentration conditions employed.

Accepting reaction path (14), another type of explanation was attempted. It was assumed that the nitrosyl iodide decomposes on the action of bromide ion:

$$NOI + Br^- \xrightarrow{k_{Br}^I} NOBr + I^- \tag{15}$$

$$NOBr + H_2O \xrightarrow{fast} HNO_2 + H^+ + Br^- \tag{16}$$
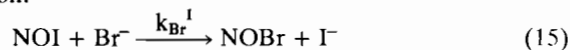
and that this process decreases the stationary concentration of nitrosyl iodide. $d[NOI]/dt$ may be expressed by (9), (10), (14) and (15):

$$\frac{d[NOI]}{dt} = k_1 K_H [HNO_2][H^+][I^-] - k_{-1}a_w[NOI] - k_{Br}^I[Br^-][NOI] - k_3[NOI]^2 \tag{17}$$

Disregarding the term $k_3[NOI]^2$ in (17) (which means that process (14) does not affect the stationary concentration of nitrosyl iodide significantly), in a stationary state:

$$[NOI] = \frac{k_1 K_H [HNO_2][H^+][I^-]}{k_{-1}a_w + k_{Br}^I[Br^-]} \tag{18}$$

Hence:

$$v_2 = \frac{k_3 k_1^2 K_H^2 [HNO_2]^2[H^+]^2[I^-]^2}{(k_{-1}a_w + k_{Br}^I[Br^-])^2} \tag{19}$$

Rearranging:

$$\frac{1}{\sqrt{v_2}} = \frac{k_{-1}a_w}{\sqrt{k_3 k_1 K_H}[HNO_2][H^+][I^-]} + \frac{k_{Br}^I[Br^-]}{\sqrt{k_3 k_1 K_H}[HNO_2][H^+][I^-]} \tag{20}$$

Since $v \sim v_2$ under the conditions used, then a plot of $1/\sqrt{v}$ against the bromide concentration should be
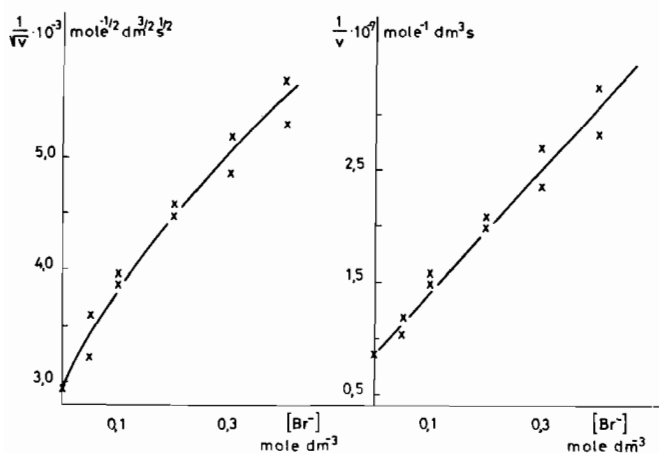
Figure 8. $1/\sqrt{v}$ and $1/v$ values as functions of the bromide ion concentration.

linear. Figure 8 shows that the experimental function definitely curves (it must be noted that an increasing importance of the fourth-order term cannot explain the curvature as the order relative to the nitrite does not change).

Taking all the above factors into account, we consider the following steps to be probable in the sixth-order reaction. As the first step we assume the formation of N_2O_3, which also figures in other second-order reactions of nitrite:

$$2\,HNO_2 \;\rightleftharpoons\; N_2O_3 + H_2O \qquad (21)$$
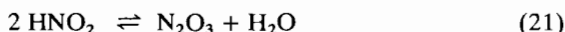
To explain the proton dependence, this is taken as being in the diprotonated form (its overall formation constant is designated as K_{2H}'):

$$N_2O_3 + 2\,H^+ \;\rightleftharpoons\; H_2N_2O_3{}^{2+} \qquad (22)$$
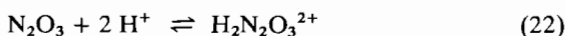
which gives rise to an association with one iodide ion:

$$H_2N_2O_3{}^{2+} + I^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2N_2O_3I^+ \qquad (23)$$
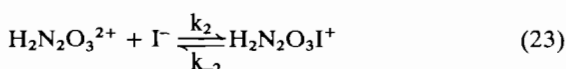
(this may also be written in its dehydrated form: $N_2O_2I^+$). Reaction of this association with a further iodide ion leads to the redox change:

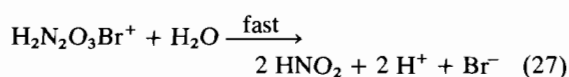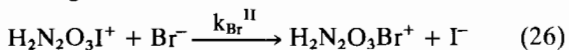$$H_2N_2O_3I^+ + I^- \xrightarrow{\;k_{II}\;} 2\,NO + I_2 + H_2O \qquad (24)$$
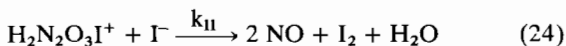
In the case of a stationary concentration of $H_2N_2O_3I^+$, reaction steps (21)–(24) give the rate equation:

$$v_2 = \frac{k_{II}k_2K_{2H}[HNO_2]^2[H^+]^2[I^-]^2}{k_{-2} + k_{II}[I^-]} \qquad (25)$$

where $K_{2H} = K_{2H}'/a_w$.

To explain the bromide dependence we assume that the $H_2N_2O_3I^+$ decomposes on the action of the bromide ion to give species ineffective as regards influencing the reaction:

$$H_2N_2O_3I^+ + Br^- \xrightarrow{\;k_{Br}{}^{II}\;} H_2N_2O_3Br^+ + I^- \qquad (26)$$

$$H_2N_2O_3Br^+ + H_2O \xrightarrow{\;fast\;} \\ 2\,HNO_2 + 2\,H^+ + Br^- \qquad (27)$$

If (27) is taken into consideration, the rate equation is:

$$v_2 = \frac{k_{II}k_2K_{2H}[HNO_2]^2[H^+]^2[I^-]^2}{k_{-2} + k_{II}[I^-] + k_{Br}{}^{II}[Br^-]} \qquad (28)$$

from which by rearrangement we obtain the function:

$$\frac{1}{v_2} = \frac{k_{-2} + k_{II}[I^-]}{k_{II}k_2K_{2H}[HNO_2]^2[H^+]^2[I^-]^2} + \\ \frac{k_{Br}{}^{II}}{k_{II}k_2K_{2H}[HNO_2]^2[H^+]^2[I^-]^2}[Br^-] \qquad (29)$$

It can be seen from Figure 8 that the reciprocal of the reaction rate is indeed a linear function of the bromide concentration (it should be noted that the bromide ion should also play a role in the fourth-order reaction path, according to reaction (15). If both rate terms are taken into account and certain simplifying assumptions are made, such a function is in fact obtained).

It has to be considered further that according to this mechanism the rate of the slowest step of the (21)–(23) reactions, which is probably (21), must be not smaller than that of (24), the redox reaction with iodide, that is the experimentally measured rate. The rate of the dinitrogen trioxide formation can be calculated from independent data, *e.g.* from the second-order rate constant of the permanganate–nitrite reaction[2]:

$$v_{N_2O_3} \approx (66 \pm 5)[HNO_2]^2$$

In the case of nitrite–iodide reaction at the highest measured rate $[HNO_2] = 2.25$ mol dm^{-3}.

Consequently $v_{N_2O_3} = 1.5 \pm 0.1 \times 10^{-6}$ mol dm^{-3} s^{-1} which is considerably higher than the measured rate ($-d[HNO_2]/dt = 3.4 \times 10^{-7}$ mol dm^{-3} s^{-1}).

Accordingly, in the absence of bromide and the buffer the following rate expression holds:

$$v = \frac{k_I k_1 K_H [HNO_2][H^+][I^-]^2}{k_{-1} a_w + k_I [I^-]} +$$

$$\frac{k_{II} k_2 K_{2H}' [HNO_2]^2 [H^+]^2 [I^-]^2}{k_{-2} + k_{II} [I^-]} \quad (30)$$

It can be seen that at relatively low iodide concentrations (if the terms containing the iodide concentration in the denominators are neglected) our experimentally found rate equation is obtained (equation (7)).

Expression (30) can also be used to interprete the results of Bobtelsky and Kaplan. They worked at a lower hydrogen ion concentration (pH ~ 5) and a higher iodide concentration (0.5 mol dm^{-3}). The former means that the second rate term can be neglected in comparison with the first, while as a result of the latter concentration condition the second of the terms in the denominator assumes major importance and the overall function obtained is first-order with regard to iodide.

The relations given provide an opportunity of roughly estimating the orders of magnitude of the constants in the expressions. It follows from the above that:

$k_{-1} a_w \ll k_I [I^-]_1$, if $[I^-]_1 = 0.5$ mol dm^{-3}, and
$k_{-1} a_w \gg k_I [I^-]_2$, if $[I^-]_2 = 10^{-3}$ mol dm^{-3}.
Thus, $k_{-1} \sim 10^{-4} k_I$.
By comparison of the derived and the experimentally found rate equations:

$$k_2' = k_{II} \frac{k_2 K_{2H}}{k_{-2}}$$

Here:

$$K_{2H} k_2 / k_{-2} = K_{II}$$

the formation constant of the assumed $H_2N_2O_3I^+$. Since $k_{II} \leq 10^{10}$ and $k_2' = 3.7 \times 10^{10}$, we have $K_{II} \geq 3.7$ (this value appears surprisingly high).

From the linearized form of the bromide dependence the quotient of the slope, a, and the intercept, b, gives the relation:

$$\frac{a}{b} = \frac{k_{Br}^{II}}{k_{-2}} = 7.40$$

Ferranti *et al.* further determined the apparent activation energy from the temperature dependence of the rate, and obtained a negative value. This again indicates that the redox reaction is preceded by a set of pre-equilibria.

We also investigated another interesting phenomenon connected with the reaction. Bobtelsky and Kaplan observed that the reaction is catalyzed by a number of heavy metal ions, such as zinc(II). This led to the consideration that the nitro complexes produced may be more reactive than the free ion. In our experiments under identical conditions (in acetate buffer), however, it turned out that the pH shift resulting from the hydrolysis of the zinc(II) is responsible for the rate increase. When the pH is maintained at a constant value the rate decreases substantially in the presence of the zinc(II) ion. Ferranti *et al.* observed the rate decreasing effect of thorium(IV). It appears from these results that the binding of nitrite to metal ions reduces its reactivity also in this reaction.

Acknowledgements

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