Stoicheiometry, Kinetics, and Mechanism of the Oxidation of Hyponitrous Acid by Iodine in Acetate Buffers

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The reaction of hyponitrous acid with iodine occurs as (i) in the pH range 4—6 and at $[I^-]$

$$H_2N_2O_2 + I_2 + \tfrac{1}{6}H_2O \longrightarrow 2HI + \tfrac{1}{2}N_2O + \tfrac{2}{3}NO + \tfrac{1}{3}HNO_3 \qquad \text{(i)}$$

< 0.025 mol dm^{-3}. One of the identified intermediates is HNO_2 which is the main source of NO. Several reactions involving HNO_2, $H_2N_2O_2$, and iodide may follow. The decomposition of $H_2N_2O_2$ is very significant at pH < 4 and $[I^-] > 0.025$ mol dm^{-3}, and the stoicheiometry $\Delta[H_2N_2O_2]/\Delta[I_2]$ changes from 1 : 1 to 2 : 1 or even 6 : 1. The rate law (ii) applies where K_d' is the first acid-

$$-d[I_2]_T/dt = kK_d'[H_2N_2O_2]_T[I_2]_T/[H^+](1 + K[I^-]) \qquad \text{(ii)}$$

dissociation constant of $H_2N_2O_2$ and K is the equilibrium constant for the formation of I_3^-; k was found to be $(2.1 \pm 0.1) \times 10^4$ dm^3 mol^{-1} s^{-1} at 35 °C employing $K_d' = 6.3 \times 10^{-8}$ mol dm^{-3} and $K = 549$ dm^3 mol^{-1}.

Our interest in the oxidation of hyponitrous acid $H_2N_2O_2$ arose because it is one of the probable intermediates in the oxidation of hydroxylamine[1,2] to nitrate and/or nitrate, and also since little is known about its redox chemistry. Only two reactions of hyponitrite, with nitrite[3–5] and with nitric oxide,[6] had been reported before we started systematic investigation on its redox chemistry. We have carried out its oxidation with thallium(III),[7] cerium(IV),[8] chloramine T (*N*-chlorotoluene-*p*-sulphonamide),[9] and Hexacyanoferrate(III).[10]

The main features of the mechanism of redox reactions of $H_2N_2O_2$ so far found can be expressed as in equations (1)—(4),

$$H_2N_2O_2 + Ox \longrightarrow H_2N_2O_3 \qquad (1)$$

$$H_2N_2O_3 \longrightarrow \tfrac{1}{2}N_2O + HNO_2 \qquad (2)$$

$$HNO_2 + H_2N_2O_2 \longrightarrow N_2 + HNO_3 + H_2O \qquad (3)$$

$$HNO_2 + Ox \longrightarrow HNO_3 \qquad (4)$$

where Ox is any oxidant. The stoicheiometry and identification and estimation of gaseous products and of HNO_3 revealed the steps which occur in a particular system. It is only in case of chloramine T(cat)[9] that $H_2N_2O_2$ appears to be directly oxidized to nitrate since no gas is evolved and the stoicheiometry $\Delta[\text{cat}]/\Delta[H_2N_2O_2]$ is equal to 4.

Molecular iodine is a mild oxidant. There is one reference[11] on its reaction with $H_2N_2O_2$ suggesting oxidation to nitrite and nitrate according to equation (5). However, no mechanism has

$$H_2N_2O_2 + 3I_2 + 3H_2O \longrightarrow HNO_2 + HNO_3 + 6HI \qquad (5)$$

been given and both HNO_2 and HNO_3 in the products are unlikely. A further investigation seemed desirable. Our study of this reaction in buffered systems shows that the fate of HNO_2 produced in reaction (2) is decided by its decomposition or probably other reactions and not by reaction (3) or (4).

Experimental

Materials.—Sodium hyponitrite was prepared by electrolytic reduction[12] of nitrite and its purity was found to be 70—96% by the precipitation method.[13] It contained Na_2CO_3 as an impurity but no sodium nitrite. The sample had $\lambda_{max.}$ at 248 nm in 0.1 mol dm^{-3} NaOH and its molar absorption coefficient was found to be 6 650 dm^3 mol^{-1} cm^{-1} on the basis of percentage purity (lit.,[14] 247 nm, $\varepsilon = 6\,550$ dm^3 mol^{-1} cm^{-1}). A value of 6 920 dm^3 mol^{-1} cm^{-1} has also been reported.[15] Solutions of $Na_2N_2O_2$ were prepared whenever required in aqueous 0.5 mol dm^{-3} $HClO_4$ to which alcohol (0.1 mol%) was added to prevent decomposition.[16] E. Merck iodine as employed to prepare solutions in E. Merck KI (in most cases 0.01 mol dm^{-3}). Acetate buffers of pH 3.65—5.96 were employed to vary $[H^+]$.

Kinetic Procedure.—Solutions of hyponitrite in one flask and buffer solution and iodine in another were separately equilibrated at 35 ± 0.1 °C in a thermostat. Nitrogen was flushed through both flasks for several minutes. The reaction was initiated by adding a known quantity of $Na_2N_2O_2$ solution to the second flask. Aliquots of 5 cm^3 were withdrawn at appropriate intervals and added to ice-cold water. The unreacted iodine was immediately titrated against a standard solution of thiosulphate using starch as indicator. Most reactions were carried out at pH > 4, but the upper limit was 5 since the rate becomes too large for conventional methods of analysis. However, a few reactions at 15 °C were carried out even at pH > 5 to pH 5.96. These reactions were rapid and hence the kinetics was followed by a modified method. Several identical reaction mixtures were prepared, allowed to react separately for predetermined times, and analyzed iodometrically. No aliquots were withdrawn in this method.

Initial rates were determined by the plane-mirror method[17] and second-order rate constants (k_2) calculated from them. Second-order plots were also made wherever conditions permitted the calculation of the second-order rate constants. The results in the two cases were similar and reproducible to ±3%.

The product gases were collected over (*a*) water, (*b*) water saturated with N_2O (obtained by the reaction[18] of NH_2OH and HNO_2), (*c*) water saturated with $FeSO_4$, and (*d*) water saturated with N_2O and $FeSO_4$. The gases N_2 and NO have negligible solubilities in water and hence will be collected in case (*a*). In case (*b*) all gases (N_2, N_2O, and NO) will be obtained. In case (*c*), nitrogen only will collect and in (*d*), N_2 and N_2O will be obtained.

For the determination of nitrate in the reaction mixtures with excess of iodine, the mixture was warmed with H_2O_2 to oxidize iodide and the iodine so liberated along with that already present was extracted with CCl_4. Excess of H_2O_2 was removed by heating and decomposition and then nitrate determined by the iron(II) method.[19]

Sodium trioxodinitrate(II) was prepared by Angeli's method[20] as described in Addison's paper.[21] The solid compound $Na_2N_2O_3$ after recrystallization was kept under ethanol in a refrigerator. In aqueous solution it decomposed slowly, but readily in acidic solutions.

Spectrophotometric results were obtained on a Cecil CE 599 Universal automatic scanning instrument.

Results

Stoicheiometry at [KI] < 0.025 mol dm^{-3} *and* pH > 4.—Experiments were carried out with an excess of iodine and the latter was determined with thiosulphate. The end product nitrate was determined as described earlier and $\Delta[H_2N_2O_2]/\Delta[HNO_3]$ was found to be 3:1 with an error of $\pm 6\%$. The results of different concentrations of KI and pH under atmospheric conditions and also under nitrogen are given in Table 1 and 1 mol of iodine reacts with 1 mol of hyponitrite if [KI] < 0.025 mol dm^{-3} and pH > 4. The number of moles of gases obtained from different amounts of hyponitrite are also given in Table 1. Under the specified conditions, nitrous oxide and nitric oxide are the major gaseous products and nitrogen is a minor product which could arise from side reaction (E). The number of moles of N_2O and NO per mol of $H_2N_2O_2$ are approximately $\frac{1}{2}$ and $\frac{2}{3}$ respectively. Based on these results and ignoring nitrogen, the overall reaction seems to be (6). On the

$$H_2N_2O_2 + I_2 + \tfrac{1}{6}H_2O \longrightarrow 2HI + \tfrac{1}{2}N_2O + \tfrac{2}{3}NO + \tfrac{1}{3}HNO_3 \quad (6)$$

basis of the NO/HNO_3 ratio and the effect of sulphamic acid, the probable intermediate is HNO_2 decomposing as per reaction (C). The compound $H_2N_2O_3$ has been suggested[7–10] as an intermediate in the oxidation of $H_2N_2O_2$, and HNO_2 is obtained from the decomposition of $H_2N_2O_3$. Although there is no strong evidence for reaction (B) in the present system, the decomposition[22–25] of $H_2N_2O_3$ is one of the most well characterized reactions studied in connection with hyponitrite chemistry and hence it has been included. Reaction (6) may be made up of (1) and (C).

Deviations from Normal Stoicheiometry.—The results with [KI] > 0.025 mol dm^{-3} and/or pH < 4 show that the stoicheiometry $\Delta[H_2N_2O_2]/\Delta[I_2]$ is >1. There are three possibilities: (*i*) more of $H_2N_2O_2$ is consumed, or (*ii*) less of I_2 is used up, or (*iii*) both may occur. Formation of iodine in a side reaction will also result in decreasing values of $[I_2]$. Thus the reactions subsequent to (A) likely to occur are (B)—(E) and (G) (see Table 1). These reactions affect the stoicheiometry to varying extents depending on the pH and $[I^-]$. From the amounts of gases collected under different conditions, it becomes obvious that decomposition of $H_2N_2O_2$ [reaction (G)] is very significant at low pH and/or large [KI]. Hughes and co-workers[3,5] have shown the significance of the decomposition of $H_2N_2O_2$ [reaction (G)] in the reaction of HNO_2 and $H_2N_2O_2$ and they further found[26] that reaction (G) is greatly catalysed by HNO_2, NO, and acidity leading to the variation in stoicheiometry. The direct reaction between NO and $H_2N_2O_2$ is also in accord with the catalysed decomposition of $H_2N_2O_2$.[6] Thus one can understand the decomposition at low pH, but why large [KI] enhances this is not clear. Separate experiments on the decomposition of $H_2N_2O_2$ at pH 4.63 in the absence and presence of KI show that the decomposition is catalysed by KI. Thus iodide is more effective for reaction (G) rather than for (D). Nevertheless reaction (D) also becomes significant when the pH is low and [KI] is large. Reaction (F) in the presence of sulphamic acid is a measure of the HNO_2 produced, and at pH 5.57 and $[I^-] = 0.01$ mol dm^{-3} nitrogen is quantitatively obtained as per reaction (F) along with N_2O as per reaction (B). However, at low pH and/or large $[I^-]$, $H_2N_2O_2$ is consumed in reactions other than (A) and the expected amount of nitrogen is not obtained from reaction (F) through (B). These results establish the intermediacy of HNO_2 in the reaction. Further, in the presence of sulphamic acid the stoicheiometry obtained (5.57 and 2.96) and that calculated from evolved nitrogen (6.00 and 3.00) are similar and show that the whole of the HNO_2 is consumed in reaction (F), and $H_2N_2O_2$ is used up in some other reaction in addition to the primary reaction (A).

Kinetics.—Experiments were carried out under the condition $[I^-] < 0.025$ mol dm^{-3} and pH > 4 for reasons stated in the previous section. Stoicheiometric experiments under these conditions have already shown that there is no decomposition of $H_2N_2O_2$. Kinetically also, since the second-order rate constants from the second-order plots are similar to those from the initial rates, there is no decomposition of $H_2N_2O_2$ under the specified conditions. Also the first-order rate constants[16,27] at 25 °C and pH 5.59 and 2.05 are 2.5×10^{-5} and 5.01×10^{-7} s^{-1} respectively which are much lower than 9.2×10^{-3} s^{-1} at 25 °C and pH 4.62.

Rate dependence on I_2 *and* $Na_2N_2O_2$. The concentration of iodine was varied from 2×10^{-4} to 2.5×10^{-3} mol dm^{-3} at fixed $[Na_2N_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3} [KI] $= 0.01$ mol dm^{-3}, pH 4.62, and 35 °C. A plot of initial rate *versus* $[I_2]$ yielded a straight line passing through the origin and hence the order in $[I_2]$ is one. The concentration of $Na_2N_2O_2$ was varied in the range 2.5×10^{-4}—3.0×10^{-3} mol dm^{-3} at fixed $[I_2] = 1.0 \times 10^{-3}$ mol dm^{-3}, [KI] $= 0.01$ mol dm^{-3}, pH 4.62, and 35 °C. A similar plot in this case too indicated an order of one in $[Na_2N_2O_2]$ and the second-order rate constant is 8.8 dm^3 mol^{-1} s^{-1}. Second-order plots yielded an average value of 8.8 ± 0.6 dm^3 mol^{-1} s^{-1} for the second-order rate constant. These results are given in Table 2.

Iodide and hydrogen-ion dependence. The concentration of iodide was varied from 0.005 to 0.045 mol dm^{-3}. It was not possible to investigate lower concentrations of KI than the limit shown since a minimum concentration has to be employed to dissolve iodine. Larger concentrations could not be employed because of complications due to side reactions involving iodide. The results are given in Table 3. The rate decreases with increasing $[I^-]$. A plot of rate *versus* $(1 + K[I^-])^{-1}$ was linear passing through the origin, where *K* refers to equilibrium (7).

$$I_2 + I^- \xrightarrow{K} I_3^- \quad (7)$$

Several values ranging from 550 to 1 000 dm^3 mol^{-1} have been reported[28] for *K*. The latest value[29] is 698 dm^3 mol^{-1} at 25 °C, but we have employed a value[28] of 549 dm^3 mol^{-1} at 35 °C for our calculations. There is large deviation from the linear plot at large concentrations (>0.025 mol dm^{-3}) of iodide.

Table 1. Stoicheiometry and mol fraction of gases in the reaction of $H_2N_2O_2$ and iodine in acetate buffers at 35 °C; volume of reaction mixture = 100 cm^3

$10^3[Na_2N_2O_2]$	$10^3[I_2]$	$[I^-]$			mol of gas per mol of $Na_2N_2O_2$				$\Delta[Na_2N_2O_2]/\Delta[I_2]$ calculated from		
mol dm^{-3}			pH	$\Delta[Na_2N_2O_2]/\Delta[I_2]$	N_2O	NO	N_2	Possible reactions (major/minor)	N_2O	NO	N_2
2.440	3.918	0.025	4.30	1.04[a]							
2.440	5.877	0.025	4.30	1.03[a]							
2.440	7.836	0.025	4.30	1.02[a]							
2.440	9.795	0.025	4.30	1.05[a]							
3.705	8.128	0.025	4.30	1.00[a]							
3.705	6.096	0.025	4.30	1.07[a]							
1.202	3.920	0.010	4.30	1.07							
1.202	5.880	0.015	4.30	1.04	0.493	0.665	0.035	(D) + (E) + (F)/(H)	1.01	1.00	—
1.202	7.840	0.020	4.30	1.04							
1.316	5.060	0.025	4.30	1.03	0.490	0.687	0.034	(D) + (E) + (F)/(H)	1.02	0.97	—
1.620	5.065	0.025	4.30	1.02	0.456	0.667	0.027	(D) + (E) + (F)/(H)	1.09	1.00	—
1.934	5.061	0.025	4.30	1.00	0.470	0.646	0.046	(D) + (E) + (F)/(H)	1.06	1.03	—
1.357	5.230	0.025	4.30	1.03	0.486	0.590	0.032	(D) + (E) + (F)/(H)	1.03	1.12	—
1.575	5.010	0.025	5.74	1.02	0.501	0.665	0.28	(D) + (E) + (F)/(H)	0.99	1.00	—
1.050	5.010	0.025	4.99	1.02	0.498	0.643	0.21	(D) + (E) + (F)/(H)	1.00	1.01	—
1.880	4.680	0.000	4.30	0.98[a,b]							
2.774	4.680	0.000	3.42	1.97[b]	0.654	0.341	—	(D) + (E) + (F) + (H)/—	—	1.95	—
1.900	4.160	0.010	5.57	1.01[c]	0.500	0.00	0.90	(D) + (E) + (I)/—	1.00	—	1.02
1.116	4.950	0.025	3.42	5.57[c]	0.914	0.00	0.17	(D) + (E) + (I) + (J)/—	—	—	6.00
1.183	5.010	0.200	4.27	2.96[c]	0.821	0.02	0.33	(D) + (E) + (I) + (J)/(G)	—	—	3.00
1.700	4.350	0.011	3.42	4.7	0.880	0.14	0.01	(D) + (E) + (J) + (F)/(G)	4.8	—	—
1.050	4.350	0.011	3.42	4.6	0.910	0.15	0.02	(D) + (E) + (J) + (F)/(G)	4.4	—	—
1.500	4.350	0.185	4.05	3.3	0.806	0.22	0.00	(D) + (E) + (F) + (J)/(G)	—	3.00	—
1.050	4.350	0.185	4.05	2.9	0.805	0.26	0.00	(D) + (E) + (F) + (J)/(G)	—	2.56	—
1.202	4.064	0.100	4.90	1.52							
1.126	4.000	0.500	5.23	2.55[a]							
1.126	6.000	0.100	5.23	1.28[a]							
1.126	4.060	0.050	5.23	1.12[a]							

Reactions: $H_2N_2O_2 + I_2 + H_2O \longrightarrow H_2N_2O_3 + 2H^+ + 2I^-$ (A); $H_2N_2O_3 \longrightarrow \frac{1}{2}N_2O + \frac{1}{2}H_2O + HNO_2$ (B); $3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$ (C); $2HNO_2 + 2H^+ + 2I^- \longrightarrow 2NO + I_2 + 2H_2O$ (D); $HNO_2 + H_2N_2O_2 \longrightarrow N_2 + HNO_3 + H_2O$ (E); $HNO_2 + NH_2SO_3H \longrightarrow N_2 + H_2SO_4 + H_2O$ (F); $H_2N_2O_2 \longrightarrow N_2O + H_2O$ (G).

[a] Nitrogen atmosphere. [b] Alcoholic iodine and no KI. [c] In the presence of 0.0416 mol dm^{-3} sulphamic acid.

Table 2. Initial rate (i.r.) dependence on $[Na_2N_2O_2]$ and $[I_2]$, and second-order rate constant (k_2) at $[I^-]$ = 0.01 mol dm^{-3}, pH 4.62 and 35 °C

$10^4[Na_2N_2O_2]$	$10^4[I_2]$		k_2/dm^3 mol^{-1} s^{-1}	
mol dm^{-3}		10^5i.r./mol dm^{-3} s^{-1}	i.r./$[Na_2N_2O_2][I_2]$	From second-order plots
2.50	10.0	0.22	8.8	8.7
5.00	10.0	0.45	8.9	8.8
10.0	10.0	0.89	8.9	8.8
15.0	10.0	1.33	8.9	9.0
20.0	10.0	1.76	8.8	8.8
25.0	10.0	2.25	9.0	8.7
30.0	10.0	2.69	9.0	8.9
20.0[a]	2.0	0.35	8.7	8.8
20.0	4.0	0.69	8.6	8.7
20.0	6.0	1.05	8.7	8.6
20.0	8.0	1.38	8.6	8.8
20.0	10.0	1.77	8.8	8.9
20.0	20.0	3.65	9.1	8.8
20.0	25.0	4.49	9.0	8.8
20.2[b]	10.0	1.90	4.5	
20.2[b]	20.0	1.93	4.8	
20.2[b]	25.0	2.33	4.7	

[a] Calculated from the pseudo-first-order rate constant of 0.0176 s^{-1}. [b] At 15 °C.

The pH of the system was varied from 3.65 to 4.99 at 35 °C and from 4.31 to 5.96 at 15 °C to investigate the $[H^+]$ dependence. The results are given in Table 4. A plot of rate *versus* $[H^+]^{-1}$ was linear passing through the origin, with data points at large $[H^+]$ (pH < 4) deviating. In general the reactions mentioned in Table 1, which affect the stoicheiometry, should not influence the rate and kinetics. However, the reactions at low pH (3.42) show a substantial decomposition of

Table 3. Iodide dependence in the reaction of hyponitrite and iodine at $[Na_2N_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[I_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, pH 4.0, and 35 °C

$10^2[I^-]$/mol dm^{-3}	10^6 i.r./mol dm^{-3} s^{-1}
0.50	13.7
0.60	12.0
0.80	10.0
1.0	8.0
1.5	5.3
2.0	4.2
2.5	3.4
3.0	2.4
3.5	1.2
4.5	0.23

Table 4. Hydrogen-ion dependence in the reaction of hyponitrite and iodine at 35 and 15 °C, $[Na_2N_2O_2] = 2.0 \times 10^{-3}$, $[I_2] = 2.0 \times 10^{-3}$, and $[I_2] = 0.025$ mol dm^{-3}

At 35 °C					
$10^5[H^+]$/mol dm^{-3}	22.4	16.9	15.8	11.8	10.7
10^6 i.r./mol dm^{-3} s^{-1}	0.63	1.03	1.47	2.60	2.83
$10^5[H^+]$/mol dm^{-3}	8.51	7.08	6.02	4.89	3.98
10^6 i.r./mol dm^{-3} s^{-1}	4.2	5.4	6.2	7.0	9.0
$10^5[H^+]$/mol dm^{-3}	3.02	2.81	2.57	2.24	1.99
10^6 i.r./mol dm^{-3} s^{-1}	12.3	13.0	14.7	16.0	19.0
$10^5[H^+]$/mol dm^{-3}	1.86	1.58	1.35	1.26	1.02
10^6 i.r./mol dm^{-3} s^{-1}	21.0	23.0	26.0	29.5	36.5
At 15 °C					
$10^5[H^+]$/mol dm^{-3}	4.89	1.99	1.00	0.616	0.234
10^6 i.r./mol dm^{-3} s^{-1}	1.5	3.6	6.5	10.0	30.0
$10^5[H^+]$/mol dm^{-3}	0.141	0.110			
10^6 i.r./mol dm^{-3} s^{-1}	48.0	62.0			

$H_2N_2O_2$ and this is likely to disturb the kinetics. All reactions mentioned after (A) in Table 1 are likely to be favoured by $[H^+]$ and hence the total effect on the rate may be significant, leading to deviations.

Results in the presence of sulphamic acid. Some kinetic experiments were conducted in the presence of sulphamic acid at pH 3.77 and also at the commonly employed pH of 4.62. The results are given in Table 5. A comparison with control experiments (in the absence of sulphamic acid) shows that the rate in the presence of sulphamic acid is about 15% larger at pH 3.77 but it is the same at 4.65 within experimental error. These results support what has been said in the previous paragraph.

Discussion

The pK_1 and pK_2 values of hyponitrous acid are reported[27,30] to be 7.2 and 11.5 respectively and hence it exists mainly as $H_2N_2O_2$ below pH 5, but the $[H^+]$ dependence shows that $HN_2O_2^-$ is reactive kinetically. Iodine in iodide solutions

$$H_2N_2O_2 \overset{K_d'}{\rightleftharpoons} HN_2O_2^- + H^+ \qquad (8)$$

would mainly exist as tri-iodide ion through equilibrium (7) with $K \approx 700$ dm^3 mol^{-1},[29] and the iodide dependence of the rate indicates free iodine molecules to be reactive. The concentrations of the reactive $HN_2O_2^-$ and I_2 would be approximately $K_d'[H_2N_2O_2]_T/[H^+]$ and $[I_2]_T/(1 + K[I^-])$ respectively.

The evolution of N_2O along with the formation of HNO_2 shows that the intermediate product from the oxidation of $H_2N_2O_2$ may be $H_2N_2O_3$ since the decomposition[22-25] of latter to give N_2O and NO_2^- (HNO_2) is well established. It has already been discussed that the fate of HNO_2 is decided by reaction (C) rather than (D) or (E) providing pH > 4 and $[I^-] < 0.025$ mol dm^{-3}. Although reaction (D) has been reported[31] to have large $[H^+]$ and $[I^-]$ dependences, it becomes significant only when both of them are large. The decomposition of HNO_2 to yield NO is also well known,[32] but is slow at low acidity. In our system, since HNO_2 was found only in traces after 24 h and the gas measurements were made after 24 h, HNO_2 is likely to decompose completely in this period. A possible other source of NO could be the decomposition of oxyhyponitrous acid or trioxodinitrate(II) in the presence of some agent in the system similar to haemoglobin,[33-35] myoglobin,[33-35] penta-amminenitrosylruthenium(II),[36] and hexa-ammineruthenium(III),[37] but the amounts of product gases from these reactions do not conform to equation (6) and one wonders what is the agent in the present system which traps NO and brings about this decomposition of $H_2N_2O_3$. Hence in all probability NO appears to be obtained only through decomposition of HNO_2. Based on the stoicheiometry, the product gases, the fate of HNO_2, and the orders of one in the two main reactants, the mechanism in equations (9)—(11) may

$$HN_2O_2^- + I_2 + H_2O \xrightarrow{k} \tfrac{1}{2}N_2O + NO_2^- + \tfrac{1}{2}H_2O + 2HI \qquad (9)$$

$$NO_2^- + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} HNO_2 \qquad (10)$$

$$HNO_2 \longrightarrow \tfrac{2}{3}NO + \tfrac{1}{3}HNO_3 + \tfrac{1}{3}H_2O \qquad (11)$$

be proposed. The rate of disappearance of I_2 according to this mechanism is given in equation (13). If $K_d' = 6.3 \times 10^{-8}$ mol

$$-d[I_2]_T/dt = k[HN_2O_2^-][I_2] = kK_d'[Na_2N_2O_2]_T[I_2]_T/[H^+](1 + K[I^-]) \qquad (12)$$

$$= k'[Na_2N_2O_2]_T[I_2]_T/[H^+](1 + K[I^-]) \qquad (13)$$

dm^{-3} and $K = 549$ dm^3 mol^{-1} are substituted, k is found to be $(2.1 \pm 0.1) \times 10^4$ dm^3 mol^{-1} s^{-1}.

One likely intermediate of the present reaction is trioxodinitrate(II), but there is no strong evidence for it. Whatever the intermediates, the kinetics shows that they should decompose or react in fast steps. It is well known that trioxodinitrate(II) decomposes slowly, the first-order rate constant[24,25] being 4.6×10^{-4} s^{-1} at 25 °C and pH 4.8. The first-order rate constant for the present redox reaction is 9.2×10^{-3} s^{-1} at 25 °C, pH 4.73, $[I_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, and $[I^-] = 0.01$ mol dm^{-3}. The redox reaction between prepared trioxodinitrate(II) and iodine is slow. Thus the decomposition as well as the redox reaction of trioxodinitrate(II) are slow processes compared to the present redox reaction. If trioxodinitrate(II) is formed in the present system a small concentration of $H_2N_2O_3$ will accumulate. The monoprotonated form of trioxodinitrate(II) absorbs[14] at 237 nm. A reaction mixture containing 5.0×10^{-5} mol dm^{-3} $[I_2]$, 1.0×10^{-4} mol dm^{-3} $[Na_2N_2O_2]$, and 1.25×10^{-4} mol dm^{-3} [KI] in acetate buffer of 4.62 gave after 5 min a sharp peak at 237 nm (with KI, $Na_2N_2O_2$, and buffer as blank) with an absorption of 1.12. Tri-iodide ion also gives a sharp peak at 231 nm with $\varepsilon = 1.4 \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}. A solution of $[I_2] = 5.0 \times 10^{-5}$ mol dm^{-3} in $[KI] = 1.25 \times 10^{-4}$ mol dm^{-3} in acetate buffer of pH 4.62, yields a sharp peak at 231 nm with an absorption of 0.69. Thus the absorption of the reaction mixture

Table 5. Reaction of $H_2N_2O_2$–I_2 in the presence of sulphamic acid at pH 3.77 and 4.62, 35 °C, $[Na_2N_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3}, and $[KI] = 1.0 \times 10^{-2}$ mol dm^{-3}

	10^6 i.r./mol dm^{-3} s^{-1}			
	pH 3.77		pH 4.62	
$10^3[I_2]$/mol dm^{-3}	No sulphamic acid	0.02 mol dm^{-3} sulphamic acid	No sulphamic acid	0.02 mol dm^{-3} sulphamic acid
0.8	1.3	1.5	14	14
1.0	1.6	1.9	18	18
1.5	2.4	2.7	27	27

at 237 nm cannot be explained merely on the basis of I_3^-, and part of it should be ascribed to some intermediate, probably $HN_2O_3^-$.

The reaction of thallium(III)[7] with $Na_2N_2O_2$ in 0.5 mol dm^{-3} $HClO_4$ also throws some light on the nature of this intermediate. The reaction occurs in two stages. The first occurs almost instantaneously according to the stoicheiometry $\Delta[Na_2N_2O_2]/\Delta[Tl^{III}]$ of 1 : 1. The second process is much slower and is characteristic of the reaction[38] of HNO_2 and Tl^{III}. The reaction of Tl^{III} with prepared trioxodinitrate(II) was found to be fast and the decomposition was slower than the redox process. If trioxodinitrate(II) were to be an intermediate in the oxidation of $Na_2N_2O_2$ with Tl^{III}, the stoicheiometry $\Delta[Na_2N_2O_2]/\Delta[Tl^{III}]$ of the first-stage reaction is expected to be 1:2. This was not found. Thus there is no evidence for trioxodinitrate(II) in the thallium(III) reaction, but there is some evidence for it in the present reaction.

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