The Chemistry of Trioxodinitrates. Part 2.[1] The Effect of added Nitrite on the Stability of Sodium Trioxodinitrate in Aqueous Solution

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In solutions of pH $\leqslant$ 3.29 added nitrite catalyses the decomposition of trioxodinitric acid to nitrogen mono-oxide. At 25 °C and I = 0.25 mol dm^{-3}, the rate law is Rate = $1.14 \times 10^4 [H^+][HNO_2][H_2N_2O_3]$, the reaction proceeding by initial nitrosation and a subsequent free-radical reaction. As the temperature is decreased, the rate law changes over a narrow temperature range to one involving a dependence on $[HNO_2]$ of order *ca.* 1.6 and having buffer-dependent and -independent terms. Further decrease in temperature has no effect on the rate of reaction. At pH $\geqslant$ 4.9, trioxodinitrate is stabilised by added nitrite. This may be understood in terms of an equilibrium between $[HN_2O_3]^-$ and the products of nitrogen–nitrogen bond fission, HNO and $[NO_2]^-$. It is suggested that $[HN_2O_3]^-$ undergoes fast tautomerisation to $[O{=}N{-}N(OH)O]^-$ which undergoes heterolytic cleavage in a slow step. Evidence is also presented for a previously unreported non-reversible decomposition path of $[HN_2O_3]^-$. At intermediate pH, added nitrite results first in stabilisation of trioxodinitrate, and then, at higher $[NO_2^-]$, in increased instability. These results confirm that the catalytic role of nitrous acid in the NO-producing decomposition of trioxodinitrate is *via* reaction with $H_2N_2O_3$ rather than with NOH or $[NOH_2]^+$.

IN Part 1 it was shown[1] that sodium trioxodinitrate decomposes in aqueous solutions by two paths. At pH $\geqslant$4 a unimolecular cleavage of the ion $[HN_2O_3]^-$ occurs giving nitrite and dinitrogen oxide. At lower pH the predominant path is a nitrous acid- and acid-catalysed decomposition to nitrogen mono-oxide, NO. The latter reaction is retarded by the addition of radical traps such as ethanol, suggesting the presence of a free-radical chain reaction. It arises from the presence of nitrite impurities in the trioxodinitrate or from $[NO_2]^-$ produced by the $[HN_2O_3]^-$ decomposition.[1] In this paper is presented a study of the nitrous acid-catalysed decomposition in the presence of added $[NO_2]^-$ and also of the retardation of the $[HN_2O_3]^-$ decomposition by high concentration of nitrite.

EXPERIMENTAL

Sodium trioxodinitrate (Angeli's salt) was prepared[2] from hydroxylamine and ethyl nitrate as described in Part 1. Instrumentation, kinetic methods, and buffers are described in Part 1.

RESULTS

Kinetic runs were carried out with an excess of nitrite over trioxodinitrate at a number of pH values in the range 2.7—5.2, at 0.25 mol dm^{-3} ionic strength, and usually at 25 °C. They were followed by monitoring the decrease in trioxodinitrate concentration by withdrawing samples, running them into known volumes of 4.0 mol dm^{-3} sodium hydroxide solution, and measuring optical densities at 248 nm. Each run gave a good first-order plot of log D against time, showing the reaction to be first order with respect to $[N_2O_3^{2-}]$ under all conditions. Values of $k_{obs.}$, the measured first-order rate constant, were independent of $[N_2O_3^{2-}]$, batch of preparation and, except where specified, buffer type and concentration. In Part 1, values of $k_{obs.}$ for the self decomposition at pH <3 did depend on the batch of preparation as varying amounts of adventitious nitrite were present. Under the present conditions with substantial amounts of added $[NO_2]^-$ already present such variations would be insignificant.

Values of $k_{obs.}$ were measured for a range of $[NO_2^-]$ at each pH value studied. The variation of $k_{obs.}$ with nitrite was dependent on pH. At the most acid pH values studied, $k_{obs.}$ increased with $[NO_2^-]$, but at the highest pH values $k_{obs.}$ decreased with increase of $[NO_2^-]$ showing that trioxodinitrate is stabilised by nitrite. At intermediate pH values, $k_{obs.}$ decreased and then increased as the nitrite concentration was increased. Examples of these types of behaviour are shown in Figures 1 and 2. Values of $k_{obs.}$ are given in Tables 1, 2, and 4. As the role of nitrous acid is a catalytic one, plots of log D against time were still excellent straight lines even when the ratio $[NO_2^-] : [N_2O_3^{2-}]$ was below that usually used for pseudo-first-order conditions.

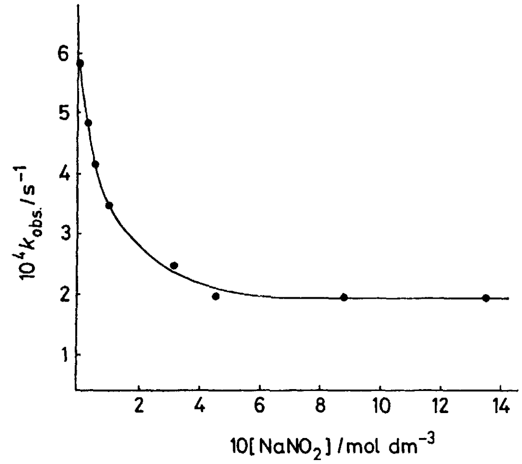

FIGURE 1 Stabilisation of trioxodinitrate by added nitrite at pH 4.92 and 25 °C

The Stabilisation Reaction.—As illustrated in Figure 1, at higher pH trioxodinitrate is stabilised by nitrite. Values of $k_{obs.}$ decrease with increase of nitrite and level off at high $[NO_2^-]$, so that further increase has no effect. Under these conditions of pH, trioxodinitrate is present as $[HN_2O_3]^-$ and self-decomposition is thought to give initially $[NO_2]^-$ and $[NO]^-$, one of which will be protonated, depending on the site of protonation in $[HN_2O_3]^-$. The present results

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[1] M. N. Hughes and P E. Wimbledon, *Chem. and Ind.*, 1975, 742; Part 1, *J.C.S. Dalton*, 1976, 703.

[2] C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 1952, 338.

suggest the presence of an equilibrium between $[HN_2O_3]^-$ and its cleavage products; *i.e.* $k_{obs.}$ is a measure of the rate of approach to equilibrium. The addition of nitrite drives equilibrium (1) to the left, *i.e.* the $[NO]^-$ or HNO reacts with $[NO_2]^-$ instead of dimerising, with resulting stabilisation of trioxodinitrate. These results are of interest in that they present good evidence for the N–N cleavage of $[HN_2O_3]^-$, and also show the presence of a previously unknown path

$$[HN_2O_3]^- \overset{\text{slow}}{\rightleftharpoons} HNO + [NO_2]^- \qquad (1)$$

$$HNO \rightleftharpoons [NO]^- + H^+;\ 2HNO \longrightarrow N_2O + H_2O\ (via\ H_2N_2O_2) \qquad (2)$$

for the self-decomposition of $[HN_2O_3]^-$ that apparently does not involve such cleavage. This latter conclusion arises from the limiting rate ($k_{min.}$) at high nitrite concentration, which appears to be independent of pH over a range where trioxodinitrate is completely present as the monoprotonated anion.

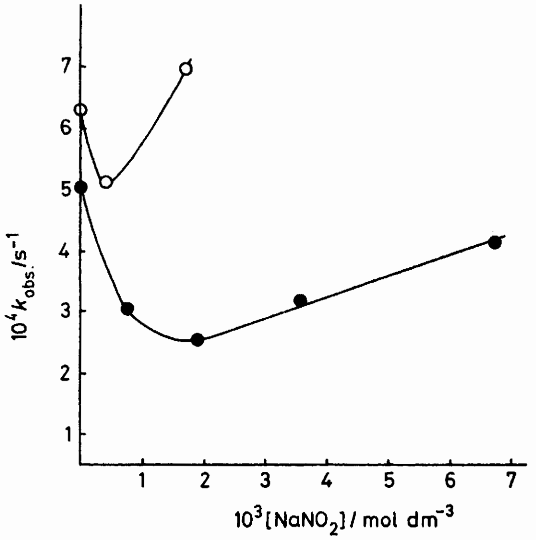

FIGURE 2 Stabilisation and reaction of trioxodinitrate with added nitrite at 25 °C and pH 3.98 (○) and 4.54 (●)

TABLE 1

Stabilisation of trioxodinitrate by nitrite at high pH, 25 °C, and I = 0.25 mol dm^{-3}

(*a*) pH 4.92

$10^5[Na_2N_2O_3]$/mol dm^{-3}	20.8	26.1	20.3	46.9	21.5	22.0
$10^5[NaNO_2]$/mol dm^{-3}	0	29	50.7	101	315	449
$10^4k_{obs.}/s^{-1}$	5.85	4.88	4.17	3.48	2.52	2.00
$10^5[Na_2N_2O_3]$/mol dm^{-3}	26.2	24.5				
$10^5[NaNO_2]$/mol dm^{-3}	888	1 348				
$10^4k_{obs.}/s^{-1}$	2.03	1.98				

(*b*) pH 5.27

$10^5[Na_2N_2O_3]$/mol dm^{-3}	18.3	1.80	25.1	16.9	27.7	24.7
$10^5[NaNO_2]$/mol dm^{-3}	0	54	138	236	464	634
$10^4k_{obs.}/s^{-1}$	6.01	4.92	4.08	2.93	1.82	1.70

TABLE 2

Rate constants for the catalytic reaction with nitrous acid at 25 °C

pH	$10^4[NO_2^-]$ / mol dm^{-3}	$10^3(k_{obs.} - k_0)$ / s^{-1}	$(k_{obs.} - k_0)/[NO_2^-]$ / dm^3 mol^{-1} s^{-1}
2.75	7.09	8.88	12.5
2.75	13.2	21.4	16.2
2.75	19.3	26.7	13.8
2.75	35.4	47.7	13.5
3.04	15.3	8.77	5.72
3.04	33.0	18.3	5.52
3.17	13.2	5.16	3.91
3.17	20.6	8.76	4.25
3.29	16.4	5.70	3.47
3.29	36.7	9.73	2.65

pH	$(k_{obs.} - k_0)/[NO_2^-]$ [a] / dm^3 mol^{-1} s^{-1}	$10^{-4}k_3^*$ [b] / dm^6 mol^{-2} s^{-1}
2.75	14.0	1.04
3.04	5.62	1.02
3.17	4.08	1.16
3.29	3.06	1.35

[a] Mean value. [b] k_3^* is defined in equation (5).

The Catalytic Reaction.—Subtraction of the value of $k_{obs.}$ at zero $[NO_2^-]$ (k_0) from values of $k_{obs.}$ at higher nitrite concentrations gives the first-order rate constant for the nitrous acid-catalysed decomposition (k*). All the rate constants for this reaction are designated by an asterisk. Under the conditions of pH used the decomposition in the absence of $[NO_2]^-$ is *via* $[HN_2O_3]^-$ exclusively, and so no complications arise from the possibility of the adventitious nitrite catalysing the decomposition at ' zero ' nitrite. At 25 °C a plot of $k_{obs.}$ against $[NO_2^-]$ was a straight line with an intercept on the $k_{obs.}$ axis corresponding to the self-decomposition *via* $[HN_2O_3]^-$. Values of $(k_{obs.} - k_0)/[NO_2^-]$ were constant showing the reaction to be first order with respect to $[NO_2^-]$.

The pH dependence of the rate constants indicated that the reactive species were HNO_2 and $H_2N_2O_3$ and that the reaction is acid catalysed. Corrections for the varying conversion of $[NO_2]^-$ and $[HN_2O_3]^-$ into HNO_2 and $H_2N_2O_3$ at different pH values were made by using values of pK_a 3.50 and 3.32 respectively. Rate constants used in equations (3)—(5) are defined in terms of the molecular acids; values of k_2* and k_3* are given in Table 2.

$$\text{Rate} = k^*[H_2N_2O_3] \qquad (3)$$

$$= k_2^*[HNO_2][H_2N_2O_3];\ k_2^* = k^*/[HNO_2] \qquad (4)$$

$$= k_3^*[H^+][HNO_2][H_2N_2O_3];\ k_3^* = k_2^*/[H^+] \qquad (5)$$

The mean value of k_3* is 1.14 × 10^4 dm^6 mol^{-2} s^{-1}. In Part 1 this was estimated [1] to be 7.4 × $10^3[Na_2N_2O_3]/[NaNO_2]$, the correction factor being introduced to allow for the fact that the nitrite was only present as an impurity. Comparison of the two sets of results indicates that the trioxodinitrate used previously [1] had *ca.* 40% nitrite present as impurity. This seems unreasonable, and it is more likely that the present rate constants are more reliable, in view of the difficulties experienced in Part 1. The previous discussion [1] of this rate law is unaffected by these changes in values of the rate constants. The presence of a free-radical reaction was confirmed in the present study by the use of added ethanol as in Part 1.

On attempting to study the reaction at 0 °C to evaluate the activation parameters, with excess of nitrite over trioxodinitrate, it was found to be no longer first order with respect to $[NO_2^-]$, excellent plots of log $(k_{obs.} - k_0)$ against log $[NO_2^-]$ being obtained with gradients of *ca.* 1.6. In addition the rate was dependent on the buffer concentration (acetate or citrate). A plot of $k_{obs.}$ against [citrate] was linear with an intercept on the $k_{obs.}$ axis. These results seemed to imply [3] that the nitrosating agent was now N_2O_3, *formed in buffer-dependent* and -independent paths. The existence of different rate laws at different temperatures implies a very large difference in activation energy for the two processes, a situation that does not appear to have been observed previously in nitrous acid chemistry. Accordingly a detailed study was carried out at a number of temperatures at several pH values (Table 3). At each pH the buffer concentration was constant and results were not extrapolated to zero buffer. At each temperature an excellent plot of log $[NO_2^-]$ against log $(k_{obs.} - k_0)$ was obtained and the orders thus determined ($[NO_2^-] = 0.01$—0.09 mol dm^{-3}) are shown in Table 3. It appears that the change in order with respect to $[NO_2^-]$ takes place over a narrow temperature range, and that the new order is close to 1.5 rather than 2. Further decrease in temperature below those at which the change in rate law occurred had little effect on the rate of reaction, showing that the reaction process corresponding to the new law appeared to have an activation energy close to zero. This appears to rule out the suggestion that this process merely involves a change in reactive nitrous acid species to N_2O_3. Some determinations were repeated in the presence of 2% ethanol, but the same change in order was observed, although all the values of the rate constants decreased. The presence of dissolved oxygen in the system appeared to have no effect on these phenomena.

TABLE 3

(*a*) Temperature dependence of the order of reaction with respect to nitrite

pH	θ_c/°C	Order	pH	θ_c/°C	Order
3.05	25	0.98	3.90	25	1.02
3.05	10	0.96	3.90	17.5	1.43
3.05	5	1.61	3.90	10	1.60
3.05	0	1.60	3.90	0	1.61

(*b*) Rate constants at various temperatures

$\frac{\theta_c}{°C}$	pH	$\frac{10^5[NaNO_2]}{mol\ dm^{-3}}$	$\frac{10^4k_{obs.}}{s^{-1}}$
10	3.90	220	1.53
0	3.90	220	1.40
10	3.90	500	2.95
0	3.90	500	2.51
10	3.90	880	7.00
0	3.90	880	7.36
5	3.05	220	13.7
0	3.05	220	12.1
5	3.05	500	45.3
0	3.05	500	45.0

TABLE 4

Effect of added nitrite at intermediate pH values, 25 °C, and $I = 0.25$ mol dm^{-3}

(*a*) pH 3.98

$10^5[NaNO_2]$/mol dm^{-3}	0	38.6	90.2	171	267	403
$10^5[Na_2N_2O_3]$/mol dm^{-3}	9.4	18.0	15.3	21.0	10.8	13.9
$10^4k_{obs.}$/s^{-1}	6.33	5.07	5.60	6.95	8.10	10.6

(*b*) pH 4.30

$10^5[NaNO_2]$/mol dm^{-3}	0	105	178	254	428	844
$10^5[Na_2N_2O_3]$/mol dm^{-3}	13.8	25.6	28.5	25.4	28.8	25.2
$10^4k_{obs.}$/s^{-1}	5.62	4.73	3.30	4.87	5.50	8.63

(*c*) pH 4.54

$10^5[NaNO_2]$/mol dm^{-3}	0	77.3	187	361	676
$10^5[NaN_2O_3]$/mol dm^{-3}	11.7	14.7	13.5	19.8	14.7
$10^4k_{obs.}$/s^{-1}	5.07	3.0	2.47	3.18	4.13

(*d*) pH 4.59

$10^5[NaNO_2]$/mol dm^{-3}	0	67.6	148	322
$10^5[Na_2N_2O_3]$/mol dm^{-3}	15.5	21.5	13.1	25.3
$10^4k_{obs.}$/s^{-1}	6.71	4.43	2.73	2.87

Results showing Retardation followed by Catalysis.—The behaviour described so far reflects protonation of the nitrite ion. If unprotonated it will react with HNO (or NOH) reforming $[HN_2O_3]^-$, but if protonated it will react with trioxodinitric acid giving NO. At appropriate pH values, increase of $[NO_2^-]$ results in enhanced stabilisation as the back reaction becomes increasingly important. Clearly there is a limit beyond which increase of $[NO_2^-]$ will have no effect, as the trioxodinitrate becomes stoicheiometrically present as $[HN_2O_3]^-$. However the catalytic reaction to give NO is not subject to such a limit, and so even at pH values at which only a small fraction of the nitrite is protonated increase in nitrite concentration will eventually result in reaction. Figure 2 shows the effects of pH and $[NO_2^-]$ on the stability and reactivity of trioxodinitrate.

A detailed analysis of these results is not possible as the rate constant for the nitrous acid-catalysed reaction at these high pH values is usually obtained as the difference between two large numbers. However, the results at pH 4.54 show that the reaction is first order with respect to $[NO_2^-]$ and the value of k_3^* is within an order of magnitude of the mean value obtained at lower pH values.

DISCUSSION

The stabilising action of nitrite on trioxodinitrate at certain pH values supports the suggestion that trioxodinitrate decomposes *via* a nitrogen–nitrogen bond-cleavage reaction. The existence of this reverse reaction between $[NO_2]^-$ and $[NO]^-$ has not been reported previously. We attempted to exploit this in a new synthesis of triododinitrate, in which nitrite was added to a sodium–liquid-ammonia system through which nitrogen mono-oxide was being passed. No reaction took place, other than the reduction of $[NO_2]^-$, possibly due to the more ready dimerisation of $[NO]^-$ or to the state of protonation of the species under these conditions.

Several points of mechanistic interest arise from the present observations, which indicate that the discussion [1] of the decomposition of the species $[HN_2O_3]^-$ in Part 1 was oversimplified. There is clear evidence to show that added $[NO_2]^-$ suppresses the dissociation of $[HN_2O_3]^-$, but the mechanistic scheme used previously, when modified to allow for the reverse reaction in the presence of added nitrite, cannot now be accommodated by the observed rate law. The scheme is as in equations (6)—(8), where $k_1 = k_{obs.}$ and $k_{min.}$ is the limiting rate constant at high $[NO_2^-]$. As the second term is quantitatively more important than the first under certain

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[3] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

$[NO_2^-]$, there should be substantial deviation from first-order kinetics for loss of trioxodinitrate. This is not observed as shown by values of consecutive half-lives.

$$[HN_2O_3]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNO + [NO_2]^- \qquad (6)$$

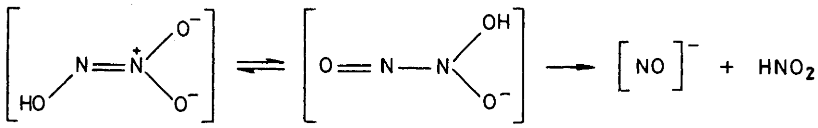
$$2HNO \xrightarrow{k_2} N_2O + H_2O \qquad (7)$$

$$[HN_2O_3]^- \xrightarrow{k_{\text{min.}}} \text{Products} \qquad (8)$$

$$\begin{aligned} -d[HN_2O_3^-]/dt &= k_{\text{min.}}[HN_2O_3^-] + (k_2/2)[HNO]^2 \\ &= k_{\text{min.}}[HN_2O_3^-] + \\ &\quad (k_1^2k_2[HN_2O_3^-]^2/2k_{-1}^2[NO_2^-]^2) \qquad (9) \end{aligned}$$

Such simple first-order kinetics can only be expected if the decomposition of $[NO]^-$ is also first order with respect to [HNO]. Clearly, dimerisation of HNO to give N_2O must take place, but this must be preceded by a slower unimolecular step involving HNO. Possibilities are a tautomerisation of HNO to NOH or a reaction of HNO with water, both of which appear unlikely to be slow.

A further difficulty relates to the cleavage of the ion $[HN_2O_3]^-$. It is customary to represent this as a homolytic cleavage of the N=N bond even though it generates a nitrite diradical species. However, the implication of this suggestion is that the reverse reaction also involves a nitrite diradical, which is unlikely. Accordingly it is suggested that the $[HN_2O_3]^-$ ion undergoes tautomerisation followed by slow heterolysis to give the products.



The results at pH values where retardation is followed by catalytic decomposition as the nitrite concentration is increased appear to resolve conclusively a point of disagreement over the interpretation of the role of nitrous acid in the catalytic decomposition of trioxodinitrate. Bonner and Ravid[4] suggested that the reaction takes place between nitrous acid and NOH or $[NOH_2]^+$ while the present workers suggested[1] direct reaction with $H_2N_2O_3$. However, in the present work, catalytic decomposition occurs at $[NO_2^-]$ for which the $[HN_2O_3]^-$ cleavage reaction is completely suppressed, implying that HNO_2 interacts with $H_2N_2O_3$, the low rate reflecting the small relative amounts of $H_2N_2O_3$ and HNO_2.

The results for the nitrous acid-catalysed decomposition of trioxodinitric acid to NO at 25 °C have been considered earlier, but of particular interest is the remarkable effect on the rate law and activation energy brought about by a small change in the reaction temperature. This effect has only been described in terms of a composite rate constant at this stage, and further work is in progress in which the effect of buffer catalysis and the nature of intermediates is being studied in more detail. While these observations must reflect the presence of a complex free-radical chain reaction, no satisfactory explanation is available at present.

We thank the S.R.C. for the award of a studentship (to P. E. W.), and a referee for helpful comments.

[6/2141 *Received, 22nd November*, 1976]

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[4] F. T. Bonner and B. Ravid, *Inorg. Chem.*, 1975, **14**, 558.