The Chemistry of Trioxodinitrates. Part I. Decomposition of Sodium Trioxodinitrate (Angeli's Salt) in Aqueous Solution

By **Martin N. Hughes** and **Peter E. Wimbledon**, Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH

The kinetics of decomposition of sodium trioxodinitrate, $Na_2[N_2O_3]$, have been measured over the range pH 1—10 at several temperatures. At pH > 4, the rate-determining step is breakdown of $[HN_2O_3]^-$ to $[NO_2]^-$ and N_2O. The p*K* for $[HN_2O_3]^-$ at I = 0·25 mol dm^{-3} and 25 °C is 9·35, and $\lambda_{max.}$ = 237 nm. At lower pH values, the rate increases with increasing acidity with production of NO, which is the predominant product at pH 2. At these pH values, $k_{obs.}$, the measured first-order rate constant, increases with increasing concentration of $Na_2[N_2O_3]$. This is attributed to a reaction with trace amounts of HNO_2, giving NO and reforming $[NO_2]^-$, rather than to an enhanced instability of $H_2N_2O_3$. Extrapolation of $k_{obs.}$ to zero $[N_2O_3{}^{2-}]$ at pH < 3 gives $k_{obs.}{}^*$ which corresponds to decomposition *via* $[HN_2O_3]^-$; $k_{obs.}{}^*$ decreases with decreasing pH, showing that $H_2N_2O_3$ is stable compared to $[HN_2O_3]^-$ in the absence of nitrite and allowing the estimation of pK_1 *ca.*3·0. Addition of $[NO_2]^-$ to $Na_2[N_2O_3]$ at pH 5 results in the production of NO, the use of $[^{15}NO_2]^-$ showing that this is not attributable to the disproportionation of HNO_2 and also that both molecules of NO produced in the reaction are derived from the nitrogen atoms of $[N_2O_3]^{2-}$. The acid-catalysed HNO_2-catalysed reaction at lower pH obeys the rate equation Rate $\propto [H^+][HNO_2][H_2N_2O_3]$, but the value of the third-order rate constant is too high for a diffusion-controlled electrophilic nitrosation reaction. Added ethanol at these pH values has a very marked inhibitory effect on the rate, so it is suggested that formation of NO results from a free-radical chain reaction.

WHILE the structure of the anion of Angeli's salt, $Na_2[N_2O_3]$ [known as sodium hyponitrate, sodium trioxodinitrate(II), or sodium oxohyponitrite [1]] has now been determined [2] to be $[ON{=}NO_2]^{2-}$, there is still uncertainty over the mechanism of the decomposition of the salt in aqueous solution. The stoicheiometry of the reaction is known [3,4] to be dependent on pH. Dinitrogen oxide and nitrite ions are formed at high pH, while nitrogen mono-oxide is reported to be the only product in acidic solutions, although there is some uncertainty over the highest pH at which this occurs. The use of $[^{15}N_2O_3]^{2-}$ shows [5] that the nitrite product is derived from the nitrogen atom in $[N_2O_3]^{2-}$ that is bonded to two oxygen atoms, suggesting that one mode of decomposition involves N=N cleavage. Kinetic studies [4,6] on the decomposition are limited, but it has been suggested that the inhibition of decomposition by added hydroxide is indicative of the involvement of $[HN_2O_3]^-$ in the rate-determining step. Values for pK_1 and pK_2 have been determined [7] at several ionic strengths (pK_1 2.39, pK_2 9.36 at 0.25 mol dm^{-3} ionic strength), and it has been observed that decomposition in acidic solutions is fast. We have made a thorough study of the kinetics of decomposition over a wide range of pH and temperature, together with ^{15}N studies. Since the completion of this work, Bonner and Ravid [8] have reported a detailed study of the stoicheiometry of the reaction using $[O^{15}NNO_2]^{2-}$, together with some kinetic results. In general, our observations are in agreement with those of Bonner and Ravid, but we have made much more extensive kinetic studies, particularly at pH <3, and as a result have a different interpretation of the kinetics in more acidic solutions.

EXPERIMENTAL

Angeli's salt was prepared from hydroxylamine and ethyl nitrate [1] and recrystallised several times from dilute alkali (rather than water, to cut down self decomposition). The purity was checked by analysis (Found: N, 23.0. Calc.: 22.96%) and u.v. spectroscopy ($\varepsilon_{max.}$ 7 900 dm^3 mol^{-1} cm^{-1} at 248 nm; lit.,[1] 8 300). Angeli's salt is oxidised to nitrite quite readily in air, and so was stored in an atmosphere of nitrogen, while all solutions were thoroughly deoxygenated before use. Reproducible kinetic results were obtained for four preparations, but a fifth preparation gave *ca.* 30% lower rate constants although with a similar pH dependence. All other reagents were of the best grade available.

U.v. studies were made in silica cells in Unicam SP 500 and SP 800 spectrophotometers. Kinetic runs were started by addition of the appropriate amount of solid $Na_2[N_2O_3]$ to thermostatted solutions of appropriate pH and ionic strength. The reaction was followed by withdrawing known volumes of the reaction solution and running them into known volumes of 1.0 mol dm^{-3} sodium hydroxide solution, the final solutions being alkaline. Optical densities were measured at 248 nm. Initial concentrations of $[N_2O_3]^{2-}$ were measured by extrapolation of the absorption at 248 nm to zero time. Some runs were followed directly in the thermostatted cell compartment of the Unicam SP 500 by noting the change in absorption with time at 248 nm and pH 10, and at 237 nm ($\lambda_{max.}$ for $[HN_2O_3]^-$) and pH 4—10. Good agreement was obtained for the two methods for reactions at pH $\geqslant$4, but only the sampling technique could be used at pH <4.

The gaseous products of the reaction were studied by mass spectrometry (A.E.I. MS 20). Solid $Na_2[N_2O_3]$ was placed in one leg of a **Y** tube and all other components were in the second leg. After several cycles of freezing to liquid-nitrogen temperatures, evacuating, and thawing, for thorough degassing of the solution, the reaction was started (at room temperature) by tipping the **Y** tube.

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[7] P. E. Sturrock, J. D. Ray, and H. R. Hunt, *Inorg. Chem.*, 1963, **2**, 649.

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On completion of the reaction the solutions were frozen in solid carbon dioxide–acetone slush and the relative concentrations of the various products were measured. A similar technique was used for the ^{15}N studies in which the nitrite–trioxodinitrate reaction was studied by $[^{15}NO_2]^-$ (95% enriched; British Oxygen Company, 'Prochem'). For studies of the gaseous products of the trioxodinitrate–nitrite reaction, thoroughly mixed $Na_2[N_2O_3]$ and sodium nitrite were placed in one leg of the tube.

Table 1

Variation of nitrite production with pH at 25 °C

pH	5.06 *	4.83 *	4.68	4.50	4.46 *	4.03 *	4.14	3.66	3.20	2.70	2.33	1.76
$\Delta[NO_2^-]/\Delta[N_2O_3^{2-}]$	0.84	0.83	0.73	0.83	0.80	0.76	0.72	0.62	0.44	0.34	0.19	0.10

* Acetate buffer, other results in citrate buffer.

Buffers (borax, phosphate, acetate, and citrate) were prepared according to literature specifications. Values of pH were checked by the use of a Pye model 290 pH meter.

RESULTS

U.v. Studies on the Reaction Stoicheiometry.—The reaction was studied over the full pH range by repetitive scanning of the u.v. spectrum. In borate and phosphate buffers (pH 7.5—10 and 5.4—7.5 respectively) there was a decrease in the $Na_2[N_2O_3]$ absorption with time, either of the $[N_2O_3]^{2-}$ absorption ($\lambda_{max.}$ 248 nm) or of the $[HN_2O_3]^-$ absorption ($\lambda_{max.}$ 236—237 nm) as observed by Bonner and Ravid,[8] while there was an increase in absorption of a band with $\lambda_{max.}$ 212—215 nm due to $[NO_2]^-$. A sharp isosbestic point was observed at 223—226 nm, together with one between 190 and 200 nm. The quotient $\Delta[NO_2^-]/\Delta[N_2O_3^{2-}]$ was *ca.* 0.8 for pH >4.5, although it is unwise to attach too much significance to the deviation of this ratio from unity in view of the experimental uncertainty. In acetate and citrate buffers (pH 3.8—5.4 and 2.0—3.9 respectively) the situation is more complicated. The absorption due to $[HN_2O_3]^-$ decreased with time, but the absorption due to the production of $[NO_2]^-$ appeared at higher wavelength, overlapping with the $[HN_2O_3]^-$ absorption. The spectrum of $[NO_2]^-$ in these buffers is similar and we attribute this behaviour to formation of nitrosyl acetate or citrate, while at pH <3 molecular nitrous acid is formed. It is clear, however, that the production of nitrite decreased at pH <4 and that only trace amounts could be detected in perchloric acid solutions of pH <2 (Table 1).

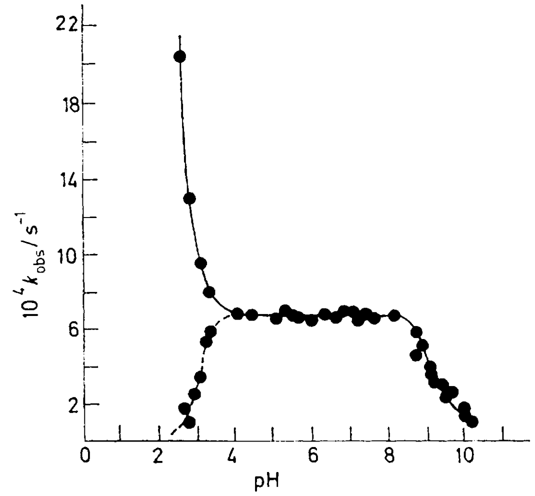
Analysis of Gaseous Products.—This showed that only dinitrogen oxide could be detected at pH >3, that N_2O in small amounts and nitrogen mono-oxide could be found in the range pH 2—3, and that NO is the predominant gaseous product at lower pH. These results confirm the general conclusions previously reported, except that, like Bonner and Ravid,[8] we did not observe production of NO at pH >3. However, as described later, when $[NO_2]^-$ was added, NO was produced at pH ⩽5, and this may explain the discrepancy in the literature in view of the ready oxidation of $[N_2O_3]^{2-}$ to $[NO_2]^-$, which will then interfere with subsequent reactions of $[N_2O_3]^{2-}$.

Kinetic Studies, pH ⩾4.—Most runs were carried out at 25 °C and 0.25 mol dm^{-3} ionic strength (maintained with sodium perchlorate). Occasionally, erratic runs were observed and were disregarded. Otherwise the reproducibility was fairly good. Over the range pH 4—10.5 the reaction is of first order in $[N_2O_3^{2-}]$, as evidenced by excellent plots of log *D* against time, the constancy of successive half-lives, and the independence of $k_{obs.}$, the measured first-order rate constant, of the concentration of trioxodinitrate. Many reactions were followed for four half-lives and the remainder for at least two half-lives. Values of $k_{obs.}$ (Table 2) were unaffected by the addition of ethanol (up to 4% v/v) and were independent of the nature and concentration of the buffer used. It may be seen that $k_{obs.}$ increased with decreasing pH until pH *ca.* 8, and was then independent of pH down to pH 4 (Figure). It is quite clear that in this pH range decomposition takes place through the anion $[HN_2O_3]^-$, values of $k_{obs.}$ following closely the variation of the quotient $[HN_2O_3^-]/\{[HN_2O_3^-] + [N_2O_3^{2-}]\}$ calculated from the literature value of pK_2 9.36. Alternatively, a graphical treatment of the data in the range

Table 2

Decomposition of trioxodinitrate in aqueous solution at pH >4, 25 °C, and I = 0.25 mol dm^{-3}. Buffers are detailed in the text

pH	$10^5[Na_2N_2O_3]$ / mol dm^{-3}	$10^4k_{obs.}$ / s^{-1}	pH	$10^5[Na_2N_2O_3]$ / mol dm^{-3}	$10^4k_{obs.}$ / s^{-1}
10.05	11.4	1.18	7.21	15.3	6.50
9.90	17.7	1.83	7.00	15.6	6.92
9.89	13.2	1.58	6.87	13.8	6.62
9.59	19.4	2.72	6.87	9.7	7.12
9.40	12.7	2.33	6.56	8.6	6.36
9.37	15.1	3.12	6.22	12.5	6.78
9.12	13.0	3.18	5.87	8.66	6.30
9.07	12.8	3.55	5.85	8.80	6.55
9.05	17.9	3.98	5.57	8.90	6.54
8.84	12.0	5.07	5.44	9.5	6.79
8.75	8.6	4.55	5.33	13.1	6.95
8.73	21.5	5.78	5.42	14.3	6.42
8.66	16.1	4.80	5.06	19.0	6.50
8.63	13.6	6.30	4.39	10.7	6.78
8.57	11.0	6.18	4.02	8.0	7.02
8.13	13.6	6.67			
7.64	12.0	6.44			
7.36	9.2	6.85			



Effect of pH on the decomposition of $[N_2O_3]^{2-}$ at 25 °C pH 8—10 allows the calculation of pK_2 9.35, in excellent agreement with the literature value. Equations (1) and

$$[HN_2O_3]^- \rightleftharpoons [N_2O_3]^{2-} + H^+ \qquad (1)$$

(2) hold. Cleavage of the N=N bond in $[HN_2O_3]^-$ gives

$$[HN_2O_3]^- \longrightarrow \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O + [NO_2]^- \qquad (2)$$

$[NO_2]^-$ and $[NO]^-$, one of which will be protonated depending on the site of protonation of $[HN_2O_3]^-$. The pK of $[HNO]^-$ [9] is 4.7, so for most of the present pH range the products of N=N cleavage will be $[NO_2]^-$ and $[NO]^-$. It is customary to assume that $[NO]^-$ dimerises to give *cis*-hyponitrite which decomposes rapidly to N_2O and water.[10]

Kinetic Studies at pH <4.—These were made at 25 °C and 0.25 mol dm^{-3} ionic strength. There was a rapid increase in the measured first-order rate constant at pH <3. An immediate explanation is that this reflects the conversion of $[HN_2O_3]^-$ into $H_2N_2O_3$ which decomposes more rapidly with the production of NO. However, while individual runs in this pH region gave excellent first-order plots, values of $k_{obs.}$ increased with increasing $Na_2[N_2O_3]$ (Table 3). Bonner and Ravid did not report this phenomenon. We attribute the behaviour to a reaction between a trioxodinitrate species and nitrous acid, which is catalytic in nitrous acid. The nitrite is present as an impurity in Angeli's salt but is difficult to determine quantitatively. When working with $Na_2[N_2O_3]$ containing zero or very low $[NO_2]^-$ a short induction period was observed, during which nitrite was formed by $[HN_2O_3]^-$ decomposition, followed by an increase in the reaction rate. We attempted to eliminate the nitrite reaction by the use of nitrite scavengers, but added excesses of urea or sulphamic acid had no effect, presumably because hydrogen trioxodinitrate is more reactive with nitrous acid. This is strange in view of the fact that the sulphamic acid–nitrous acid reaction is diffusion controlled.

TABLE 3

Decomposition of trioxodinitrate in aqueous solution at pH <4, 25 °C, and I = 0.25 mol dm^{-3}

pH	$10^5[Na_2N_2O_3]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	$10^4(k_{obs.} - k_{obs.}^*)^a$/s^{-1}	$k_2{}^b$/dm^3 mol^{-1} s^{-1}
3.51	5.1	5.07		
3.51	19.4	5.95		
3.51	31.2	7.20		
3.25	15.3	7.80	1.80	1.18
3.25	40.8	10.9	4.90	1.20
3.25	51.8	12.2	6.20	1.20
3.15	16.9	9.68	4.18	2.47
3.15	49.3	17.7	12.2	2.47
3.15	56.6	18.8	13.3	2.34
3.06	15.6	9.58	6.08	3.90
3.06	32.2	16.8	13.3	4.13
3.06	42.0	18.8	15.3	3.64
2.84	13.7	13.1	10.6	7.73
2.84	30.8	26.4	23.9	7.76
2.72	30.8	30.8	29.8	9.70
2.72	31.8	29.4	28.4	9.00
2.72	43.8	44.2	43.2	9.90
2.64	15.6	20.6	18.6	11.9
2.64	34.5	45.4	43.4	12.6
2.64	38.7	44.1	42.1	10.9
2.64	60.5	73.9	71.7	11.9
2.30	55.7	148	148	26.5
2.30	81.4	218	218	26.8
2.19	20.5	92.7	92.7	45.2
2.19	46.1	174	174	37.7
2.19	51.6	258	258	50.0
2.19	53.4	175	175	32.8
1.91	46.5	292	292	62.8
1.91	48.7	346	346	71.0
1.91	67.3	410	410	60.9
1.91	86.7	584	584	67.4

pH	3.25	3.15	3.06	2.84	2.72	2.64	2.39	2.19	1.91
$10^4k_{obs.}$/s^{-1}	6.00	5.50	3.50	2.50	*ca.* 1.0	*ca.* 2	*ca.* 0	*ca.* 0	*ca.* 0
k_2/dm^3 mol^{-1} s^{-1}	1.19	2.43	3.89	7.74	9.53	12.2	26.5	41.4	65.5
k_2(A) ^{c}/dm^3 mol^{-1} s^{-1}	1.86	3.53	5.32	9.45	11.1	13.9	28.2	43.4	67.2
$10^{-3}k_3$ ^{d}/dm^6 mol^{-2} s^{-1}	3.31	4.98	6.11	6.54	5.83	6.07	5.63	6.72	5.46
$10^{-3}k_3$(A) ^{e}/dm^6 mol^{-2} s^{-1}	6.13	8.36	9.47	8.71	7.30	7.34	6.17	7.22	5.67

[a] Values of $k_{obs.}^*$ were obtained by extrapolation of $k_{obs.}$ to zero $[N_2O_3{}^{2-}]$; at pH 2.30, 2.19, and 1.91, $k_{obs.} \approx 0$. [b] $k_2 = (k_{obs.} - k_{obs.}^*)/[Na_2N_2O_3]$. [c] Includes a correction for the varying amounts of HNO_2 with pH. [d] $k_3 = k_2(A)/[H^+]$. [e] Includes a correction for the varying amounts of $H_2N_2O_3$ with pH, mean value 7 400 dm^6 mol^{-2} s^{-1}.

Values of $k_{obs.}$ at pH <3 were dependent on the age and batch of $Na_2[N_2O_3]$ as these contain different amounts of $[NO_2]^-$. All the runs reported were made over a short period of time on one batch of $Na_2[N_2O_3]$. A standard run was repeated to ensure that the nitrite concentration was not varying enough to invalidate a comparison between these runs. Increase in the concentration of $[N_2O_3]^{2-}$ (and hence of catalytic $[NO_2]^-$) speeds up the NO-producing reaction and has no effect on $[HN_2O_3]^-$ decomposition. We believe that the dramatic change in stoicheiometry with pH is accounted for more satisfactorily by this new reaction than by the suggestion that it results from decomposition of $H_2N_2O_3$ rather than $[HN_2O_3]^-$. The different nature of the reaction giving NO is shown by the effect of added alcohol. This had no effect at pH 5.5, but at pH 2.38 the addition of 1% ethanol caused a 38% decrease in k_{obs}, while 2% ethanol caused a 80% decrease.

A plot of $k_{obs.}$ against $[Na_2N_2O_3]$ was linear at each pH. Extrapolation to zero concentration gives a value for $k_{obs.}$ corresponding to the rate constant for the $[HN_2O_3]^-$ decomposition (designated $k_{obs.}^*$). These values, shown on the Figure and in Table 3, indicate that self decomposition of $Na_2[N_2O_3]$ decreases at pH >3, *i.e.* $H_2N_2O_3$ is stable compared to $[HN_2O_3]^-$, and pK_1 *ca.* 3.0 in reasonable accord with the literature value. There is a similarity with hyponitrite [11] where $H_2N_2O_2$ and $[N_2O_2]^{2-}$ are stable compared to $[HN_2O_2]^-$. Values of ($k_{obs.} - k_{obs.}^*$) give first-order rate constants for the reaction producing NO. Values of $(k_{obs.} - k_{obs.}^*)/[Na_2N_2O_3] = k_2$ were constant at each pH (Table 2), showing that the reaction is first order in the concentration of nitrous acid (the dominant nitrite species at these pH values). This results from the fact that the nitrite concentration will be directly proportional to that

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[11] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 1239.

of $[N_2O_3]^{2-}$. Values of k_2 therefore represent a minimum value, true values being obtained by multiplying by $[Na_2N_2O_3]/[NaNO_2]$. Unfortunately this quotient is not accurately known, but the sample used in these runs contained *ca.* 5% nitrite. Also in Table 2 are values of $k_3 = k_2/[H^+]$ [equation (3)], corrected to allow for the conversion of $[NO_2]^-$ into HNO_2 and $[HN_2O_3]^-$ into $H_2N_2O_3$ over the pH range studied. The latter calculation was based on a pK_1 value for $H_2N_2O_3$ of 3.32, obtained by

$$\text{Rate} = k_3[H^+][HNO_2][H_2N_2O_3] \qquad (3)$$

a method of successive approximations. This gives $k_3 = 7\,400[Na_2N_2O_3]/[NaNO_2]$. The constancy of k_3 is only fair but is better than that obtained for the rate constant for equation (4), which also requires a very low pK_1 value for $H_2N_2O_3$ of *ca.* 1.

$$\text{Rate} \propto [H^+][HNO_2][HN_2O_3^-] \qquad (4)$$

The Nitrous Acid–Hydrogen Trioxodinitrate Reaction.—We attempted to confirm the existence of this reaction by observing the effect of added $[NO_2]^-$ on the rate and products of the decomposition of $Na_2[N_2O_3]$ over the range pH 2—4. At all acidities this resulted in an increased rate of decomposition, while at pH 4, where NO is not normally a product of the decomposition reaction, addition of $[NO_2]^-$ in equimolar amounts resulted in extensive production of NO. Tests on NO production *via* nitrous acid disproportionation in the range pH 2—5 showed that this is small compared to NO production in the HNO_2–$H_2N_2O_3$ reaction. This was confirmed by the use of $[^{15}NO_2]^-$, which resulted in the production of NO with only 15% of the labelled product present, showing that the NO is not produced *via* nitrous acid decomposition. It also appears probable by comparison with HNO_2 experiments that this ^{15}NO is derived from disproportionation of nitrous acid, and that both nitrogen atoms in $H_2N_2O_3$ end up in NO, so confirming the catalytic role of HNO_2.

The HNO_2–$H_2N_2O_3$ reaction at pH >4 followed a different course, the trioxodinitrate being stabilised by $[NO_2]^-$. This may reflect the absence of the molecular acids, and the existence of an equilibrium between $[HN_2O_3]^-$ and its decomposition product, addition of $[NO_2]^-$ therefore favouring the recombination of HNO with $[NO_2]^-$ rather than its dimerisation and decomposition. The reaction between HNO_2 and $H_2N_2O_3$ is being studied further at present.

Temperature Dependence at pH $\geqslant 4$.—The reaction has been studied in detail at 35 °C and briefly at other temperatures (Table 4). The pK_2 value at 35 °C is 9.30, indicative of a small value for the heat of ionisation of $[HN_2O_3]^-$. Values of the enthalpy and entropy of activation were **100** kJ mol^{-1} and 33.8 J K^{-1} mol^{-1}.

Table 4

Variation of rate with temperature

pH	θ_c/°C	$10^4k_{obs.}$/s^{-1}	pH	θ_c/°C	$10^4k_{obs.}$/s^{-1}
9.87	35	6.57	8.05	35	26.2
9.81	35	7.77	7.56	35	29.1
9.65	35	9.45	7.56	40	58.3
9.50	35	10.1	9.50	40	23.2
9.13	35	16.3	7.56	30	15.2
8.83	35	20.9	9.50	30	6.35

DISCUSSION

The interpretation of the results at pH >4 seems clear cut, and involves homolytic fission of $[HN_2O_3]^-$, followed probably by dimerisation and decomposition of $[NO]^-$ to N_2O. The site of protonation of the anion is not

$$H^+ + [N_2O_3]^{2-} \rightleftharpoons [HN_2O_3]^- \qquad (5)$$

$$[HN_2O_3]^- \longrightarrow HON + [NO_2]^- \longrightarrow \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O + [NO_2]^- \qquad (6)$$

known so it is possible that $[NO]^-$ and HNO_2 are produced. Alternatively, the enhanced instability of the $[HN_2O_3]^-$ ion may result from *N*-protonation giving $^-O{-}NH{-}\overset{+}{N}(O){-}O^-$ or $O{=}\overset{+}{N}{-}NH(O^-)_2$ and facilitating N–N bond cleavage.

The results at pH <4 are less easy to interpret. Bonner and Ravid attribute the increase in rate with decreasing pH to decomposition *via* $H_2N_2O_3$, the reaction at pH *ca.* 3 giving N_2O and $[NO_2]^-$. However, they suggest that protonation of HNO occurs at lower pH values and that this species reacts with $[NO_2]^-$ instead of dimerising, so accounting for the change in stoicheiometry. We prefer a scheme involving the reaction between HNO_2, $H_2N_2O_3$, and H^+, but agree that (*a*) NO is not formed by a simple dehydration reaction of $H_2N_2O_3$, and (*b*) that HNO_2 is implicated. The suggestion that NO is not produced by dehydration of $H_2N_2O_3$ is in accord with pulse-radiolysis studies[9] which show that NO is the anhydride of the species H_2NO_2.

In theory, the two mechanisms suggested for NO production could be distinguished by the use of $[^{15}NO_2]^-$. The reaction between equimolar amounts of $Na_2[N_2O_3]$ and $Na[^{15}NO_2]$ should give NO containing 25% ^{15}NO if Bonner and Ravid's scheme holds, and zero ^{15}NO in our scheme. We have found intermediate levels of ^{15}NO to be produced (*i.e. ca.* 15%), but cannot distinguish precisely enough between this and the amount of ^{15}NO produced by disproportionation to categorically rule out Bonner and Ravid's scheme. However, our kinetic results cast doubt on their mechanism, as it cannot accommodate the observed first-order dependence on the concentration of HNO_2, while the results in the presence of ethanol show the reaction at pH <4 to be more complicated than that suggested by them.

Rate equation (3) is a familiar one[12] in nitrous acid chemistry, and is usually interpreted in terms of the attack of $[H_2NO_2]^+$ on a substrate, although attack by $[NO]^+$ must also be considered. Ridd[12] noted that $[H_2NO_2]^+$ does not distinguish markedly between nucleophiles, but there appears to be a limit for negatively charged and neutral nucleophiles resulting from the effect of charge on the encounter rate between the reactants. The limiting rate for neutral nucleophiles (S) at 25 °C is given[13] by $k_3 = 5\,000$ dm^6 mol^{-2} s^{-1} in Rate $= k_3[H^+][HNO_2][S]$. In the present work $k_3 \approx 7\,400[Na_2N_2O_3]/[NaNO_2]$ and is probably *ca.* 100 000 dm^6 mol^{-2} s^{-1}, much greater than the limiting value. This suggests that the reaction of HNO_2 with $H_2N_2O_3$

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

[13] K. Al-Mallah, P. Collings, and G. Stedman, *J.C.S. Dalton*, 1974, 2469.

does not involve a simple electrophilic nitrosation. This is confirmed by the effect of added ethanol, which indicates the presence of a chain reaction, and by the failure of excess of sulphamate to inhibit the reaction.

There is a further parallel with hyponitrous acid. This reacts with nitrous acid[14,15] according to rate equation (7). The value of k_3 is *ca.* 400 times greater

$$\text{Rate} \propto [\text{HNO}_2][\text{H}_2\text{N}_2\text{O}_2] = k_3[\text{H}^+][\text{HNO}_2][\text{HN}_2\text{O}_2^-] \qquad (7)$$

than the limit for reaction with negative nucleophiles. As with hyponitrous acid, it appears then that the most probable mechanism for the decomposition of Angeli's salt at pH <3 is through a chain reaction that is initiated by nitrous acid attack, probably giving an oxygen-nitrosated species.

$$\text{H}^+ + \text{HNO}_2 \rightleftharpoons [\text{H}_2\text{NO}_2]^+ \rightleftharpoons [\text{NO}]^+ + \text{H}_2\text{O} \qquad (8)$$

$$[\text{NO}]^+ + \text{H}_2\text{N}_2\text{O}_3 \longrightarrow \text{ONON=NO(OH)} + \text{H}^+ \qquad (9)$$

$$\text{ONON=NO(OH)} \longrightarrow \text{NO}_2 + \text{N}_2\text{O} + \text{OH} \qquad (10)$$

$$\text{NO}_2 + \text{H}_2\text{N}_2\text{O}_3 \longrightarrow \text{HNO}_2 + \text{OH} + 2\text{NO} \qquad (11)$$

$$\text{OH} + \text{HNO}_2 \longrightarrow \text{H}_2\text{O} + \text{NO}_2 \qquad (12)$$

$$\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \tfrac{1}{2}\text{O}_2 \qquad (13)$$

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[14] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 4230.

[15] J. R. Buccholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1965, **87**, 2350.