Contribution from the Department of Chemistry,
State University of New York at Stony Brook, Stony Brook, New York 11794

Decomposition of Sodium Trioxodinitrate ($Na_2N_2O_3$) in the Presence of Added Nitrite in Aqueous Solution[1]

MOHAMMAD JAVAID AKHTAR, CHARLES A. LUTZ, and FRANCIS T. BONNER*[2]

Received February 2, 1979

Scrambling of the two nitrogen atoms of trioxodinitrate in the presence of carboxylic acid buffers has been observed. Kinetic measurements show that the rate of trioxodinitrate decomposition is not notably affected by added nitrite at high acetate buffer concentration (0.25 M OAc^-) but is strongly reduced by nitrite in dilute buffer (0.05 M OAc^-) at ionic strength 0.25 M and pH 4.9. Stable isotope tracer experiments confirm that this kinetic stabilization is due to equilibrative recombination of the primary decomposition fragments NO^- and HNO_2. Nitrite catalysis of the decomposition reaction is observed at pH 4.1 and is found to be strikingly enhanced by increasing concentration of carboxylic acid buffer. Mass spectrometric examination of the NO and N_2O products of $Na_2N_2O_3$ decomposition in the presence of $^{15}NO_2^-$ and of $Na_2(O^{15}NNO_2)$ in the presence of nitrite at natural isotopic abundance shows the probable participation of several processes in addition to N–N bond cleavage followed by HNO dimerization: (1) attack of nitrite (or a species of nitrite origin) at the N atom of $HN_2O_3^-$ bound to two oxygens, yielding 2 mol of NO, one of which derives from the attacking species; (2) interaction between nitrite and trioxodinitrate in which the former is quantitatively reduced to NO; (3) interaction between nitrite and trioxodinitrate yielding 2 mol of NO, both nitrogen atoms deriving from $H_2N_2O_3$ (catalytic, radical chain reaction); (4) attack of nitrite (or a nitrite derived species) at the single oxygen N atom of trioxodinitrate, yielding N_2O in which one atom derives from the attacking species.

In a previous communication from this laboratory[3] it was shown that the thermal decomposition of sodium trioxodinitrate(II) ($Na_2N_2O_3$) in aqueous solution proceeds via cleavage of the N=N bond between nitrogens to form HNO (or NOH or NO^-) and NO_2^- (or HNO_2), the former species then undergoing a rapid dimerization reaction to produce N_2O. This process occurs over the pH range ca. 4–8 in which the monobasic anion $HN_2O_3^-$ predominates; the dibasic anion $(N_2O_3)^{2-}$ is much more stable than $HN_2O_3^-$. Below pH 4 the rate of decomposition increases sharply, and the reaction product converts from N_2O + nitrite to NO in a rather narrow pH range below 3. Since the product shift occurs at so low a pH, it is clear that increasing concentration of the free acid $H_2N_2O_3$ is not the direct cause of itself, since pK_1 has a measured value of 2.5.[4]

Subsequent to the publication of our earlier study[3] Hughes and Wimbledon[5] have reported further, detailed investigations of trioxodinitrate decomposition. Their results essentially confirm our conclusions about the process at pH ≥4, but their considerably more extensive kinetic measurements in the low pH range have led to the conclusion that the free acid $H_2N_2O_3$ is a relatively stable species by itself, a situation analogous to hyponitrous acid.[6] Hughes and Wimbledon ascribe both the increase in decomposition rate and the diversion of products from (N_2O + NO_2^-) to NO at low pH to interaction between nitrous acid and $H_2N_2O_3$ in a radical chain reaction. We are in agreement that our own earlier suggestion that NO production occurs through interaction between protonated HNO and nitrous acid is most probably incorrect.

Hughes and Wimbledon have found that the pH at which substantial NO product is formed in trioxodinitrate decomposition can be strikingly increased by the addition of nitrite, an effect which we had observed independently and which explains a number of discrepancies in the existing literature. In this paper we report a combination of stoichiometric, kinetic, and ^{15}N tracer studies of the nitrite–trioxodinitrate interaction.

Experimental Section

$Na_2N_2O_3$ was synthesized as described previously[3] with the exception that improved yields were secured by the substitution of extensive washing of product with ether and hot methanol for aqueous recrystallization. Extinction coefficients at 250 nm in 1.0 M NaOH solution were in good agreement with literature values,[7] and examination of crystalline product by laser Raman spectroscopy indicated negligible nitrite contamination. Isotopically labeled $Na_2(O^{15}NNO_2)$ was prepared by the same general method, using $^{15}NH_2OH{\cdot}HCl$ (Prochem) and $C_4H_9ONO_2$ in 1:1 stoichiometric ratio to yield a product containing ^{15}N at 19.6% abundance in the indicated position. Kinetic measurements were carried out by the method described by Hughes and Wimbledon,[5a] in which reaction mixture aliquots are removed at measured time intervals and quenched in a fixed volume of strong base and extinction is measured on each at 250 nm (Cary 14 spectrophotometer). Experiments were carried out at fixed ionic strength 0.25 M and two different levels of buffer concentration, the higher level based upon 0.25 M sodium acetate (also citrate) and the lower level based upon 0.05 M sodium acetate with $NaClO_4$ added at 0.20 M. Analyses of product gas mixtures were carried out, where required, by gas chromatography employing a vacuum line–GC interface described elsewhere.[8] Decomposition experiments were carried out by vacuum line techniques, with thorough degassing of solutions by several freeze–pump–thaw cycles in advance of each reaction initiation. Both kinetic and decomposition experiments were carried out with temperature controlled at 25.0 ± 0.05 °C. Experiments employing labeled nitrite were carried out with $Na^{15}NO_2$ at 30.2% ^{15}N abundance (Isomet) and in one instance 99% (Stohler Isotope Chemicals). Separation of N_2O and NO was accomplished by repeated distillation of product gas through a helical trap held at 113 K (2-methylbutane) to retain N_2O. Mass spectrometry was performed on an AEI MS-30 instrument, with an appropriate gas inlet system at the reference side. Recovery of undecomposed trioxodinitrate from solution was carried out by quenching with NaOH, followed by addition of thallium(I) nitrate or perchlorate, yielding the relatively insoluble bright yellow salt $Tl_2N_2O_3$.[9] Nitrogen in this precipitate was released as NO by addition of 0.5 M H_2SO_4[10] under vacuum line conditions. Under conditions of high nitrite concentration this method did not work well, and a method involving destruction of nitrite by reaction with azide was substituted, as will be described in a later section.

Results and Discussion

Nitrogen Scrambling Effects of Buffer Species. In previously reported studies of $Na_2(O^{15}NNO_2)$ decomposition at various pH values,[3] it was demonstrated that the nitrogen in N_2O product derives exclusively from the atom bound to a single oxygen atom in trioxodinitrate and that this nitrogen is randomly distributed among the species $^{15}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, and $^{14}N^{14}N^{16}O$, showing the participation of an unbound intermediate. The results were unambiguous at pH 8.5 in borate buffer and at pH 3.0 in perchlorate, but a single measurement at pH 5.0 in acetate buffer suggested the possibility that some nitrogen atoms from the $-NO_2$ side of trioxodinitrate may appear in product N_2O. The existence of this effect has now been confirmed in the series of experiments reported in Table I. Samples of labeled compound were allowed to undergo decomposition in the buffer solutions indicated, and the isotopic composition of N_2O

0020-1669/79/1318-2369$01.00/0 © 1979 American Chemical Society

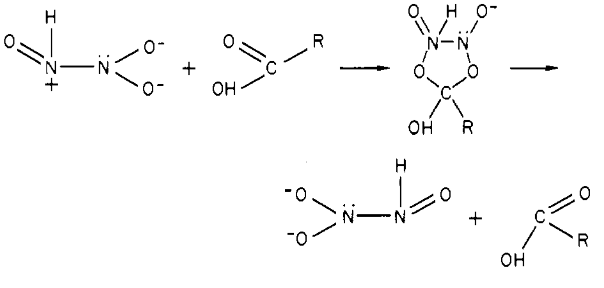
Table I. Composition of N_2O Product of $Na_2(O^{15}NNO_2)$ Decomposition at 25 °C[a]

buffer (M)	pH	ionic strength, M	reaction time, min	% mass			% ^{15}N, 44–46	% ^{15}N, 30–31
				46	45	44		
acetate (3)	6.0	3.0	60	3.18	30.2	66.5	18.3	17.7
acetate (3)	4.9	3.0	60	1.60	24.2	74.1	13.7	12.8
acetate (0.25)	4.9	0.25	60	1.87	25.2	72.8	14.5	13.7
acetate (0.05)	4.9	0.25	23	2.70	28.2	69.1	16.8	16.5
acetate (0.05)	4.9	0.25	80	2.38	27.0	70.7	15.8	15.3
citrate (0.25)	4.9	0.25	60	1.74	25.7	72.6	14.5	13.4
pyrophosphate	4.9	0.25	20	2.4	23.8	73.8	14.3	14.7
acetate (0.25)	4.1	0.25	60	1.60	24.5	73.9	13.8	12.2

[a] Initial $^{15}N = 19.6\%$ at indicated position.

product is reported as the percentage of total N_2O observed at each of the masses 46, 45, and 44, the overall percent of ^{15}N, and the percentage of ^{15}N in the mass 30 and 31 peaks produced by electron impact on N_2O in the mass spectrometer. The incorporation of N atoms from the $-NO_2$ side of $Na_2N_2O_3$ is made manifest by the fact that the overall ^{15}N percentage is lower than the initial percentage at the labeled position in every case. The one result reported in ref 3 is essentially similar to these.

The magnitude of the buffer effect increases with decreasing pH; while the effect is not strongly ionic strength dependent, the results at the same ionic strength but different acetate concentration levels indicate a substantial dependence upon the latter quantity. The fact that citrate and acetate produce closely similar effects implies that the carboxyl group is more important than its attachments; the single experiment with pyrophosphate indicates an effect of the same magnitude. The percentages at masses 44, 45, and 46 are close to but not identical with the values calculated for random distribution of N atoms at the observed, overall ^{15}N abundance in the N_2O product of each experiment. In particular, the abundance of $^{15}N^{15}N^{16}O$, mass 46, is slightly less than the random value in all cases except those of dilute acetate and pyrophosphate. The presence of a small degree of nonrandomness is confirmed by the fact that the ^{15}N content of electron-impact-produced NO is slightly smaller than that of parent N_2O in most cases, again with the exceptions of dilute acetate and pyrophosphate.



(1)

The main feature of this effect, for carboxylic acids, can be interpreted in terms of an exchange of oxygen atoms between the carboxyl group and trioxodinitrate, through a five-membered cyclic intermediate or transition state, followed by the breaking of N–O and C–O bonds in a concerted process (eq 1). (In eq 1, our placement of the proton on nitrogen rather than oxygen and choice of trioxodinitrate tautomer[11] are speculative.) This process would have the effect of reversing the position of isotope label, as observed; if formation of the unbound intermediate (HNO or NO^-) is the sole route to N_2O product, it would therefore account for an isotopic distribution containing N atoms from both sides of trioxodinitrate which is random at the resulting overall ^{15}N abundance level. To account for the small degree of nonrandomness in N_2O formation, we would have to postulate a small amount of direct N_2O formation from the bound intermediate. This would account for the fact that electron impact NO is in most cases somewhat lower in ^{15}N than parent N_2O but presumably would preserve the equality of production of the two isomers at mass 45. Finally, the fact that the extent of this effect increases with decreasing pH implies that it is probably the protonated buffer species, rather than its conjugate anion, that is primarily responsible.

Effects of Nitrite on Rate of Decomposition. Hughes and Wimbledon[5b] have postulated an equilibrium exchange process between monobasic trioxodinitrate anion and its primary decomposition products NO^- and HNO_2:

$$HN_2O_3^- \rightleftarrows NO^- + HNO_2 \qquad (2)$$

This conclusion is based upon measurements which show an apparent kinetic stabilization of trioxodinitrate by addition of NO_2^- at pH 4.92 and 5.27. The choice of NO^- and HNO_2 over HNO and NO_2^- as primary products is based on the implausibility of a reverse reaction involving the nitrite biradical species that would result from homolysis of the N=N bond, hence an assumption of tautomerism yielding $[O{=}NNO(OH)]^-$, followed by heterolysis at the N–N bond.[5b]

In Table II we show rate constant measurements in the pH regimes 4.9, 4.1, and 3.0. At pH 4.9 in acetate buffer at the higher concentration level 0.25 M, the decomposition rate is essentially unaffected by the addition of nitrite up to a very high stoichiometric excess (series a). If the acetate concentration is lowered to 0.05 M, however, a reduction of rate constant with increasing nitrite concentration is observed that is similar to, but less steep than, that reported by Hughes and Wimbledon[5b] at the same pH (series b). With citrate buffer at the higher concentration level, an initial decline in rate constant followed by a rapid rise is observed (series c), similar to the results reported by Hughes and Wimbledon at the somewhat lower pH 4.5. The buffer employed, citrate or acetate, and the buffer concentration level are not clear in ref 5b; apparent differences between their results and ours are doubtless ascribable to differences in one or both of these factors. In pyrophosphate buffer at pH 4.9 a distinct but relatively modest depression of rate constant is caused by added nitrite (series d).

At pH 4.1 and the higher acetate concentration (series e) a linear increase in rate results from increasing nitrite concentration (Figure 1). At the lower acetate concentration 0.05 M there may be a slight initial decline in rate, as observed by Hughes and Wimbledon at pH 4.0, followed by a linear increase again (series f). It is notable that equivalent concentrations of added nitrite produce a very much larger increase in decomposition rate at the higher than at the lower acetate concentration. One measurement at high nitrite and pH 4.1 in 2% ethanolic medium shows a decrease in rate by a factor greater than 2, confirming the presence of a radical chain reaction under these conditions as reported by Hughes and Wimbledon for the much lower pH 2.4.[5a] Finally, at pH 3.0 in the complete absence of acetate, the decomposition rate is seen to increase linearly with concentration of added nitrite (series g).

Table II. First-Order Rate Constants for $HN_2O_3^-$ Decomposition in the Presence of Added NO_2^-, 25.0 ± 0.05 °C

(a) pH 4.90, 0.25 M Acetate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	22.1	22.0	26.1	20.3	23.0	23.0	23.0[a]	26.2
$10^5[NaNO_2]$	0.0	0.0	29.0	53.0	449	449	449	888
10^4k_{obsd}, s^{-1}	6.26	7.06	6.42	6.79	4.93	4.52	5.30	6.50
(b) pH 4.90, 0.05 M Acetate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	26.1	24.6	22.1	46.9	20.1			
$10^5[NaNO_2]$	0.0	61.7	101.4	223.2	449.0			
10^4k_{obsd}, s^{-1}	5.92	4.24	3.35	2.79	2.49			
(c) pH 4.90, 0.25 M Citrate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	22.0	26.1	22.3	50.0	24.0	22.0	27.9	24.6
$10^5[NaNO_2]$	0.0	29.0	55.0	111.0	318	449	899	1370
10^4k_{obsd}, s^{-1}	5.97	4.15	3.53	2.73	2.69	3.46	5.30	9.14
(d) pH 4.90, Pyrophosphate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	22.1	26.2	20.5	22.1				
$10^5[NaNO_2]$	0.0	29.0	53.6	449				
10^4k_{obsd}, s^{-1}	7.04	6.93	6.27	4.26				
(e) pH 4.10, 0.25 M Acetate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	22.1	18.0	15.0	21.3	21.0	22.0		
$10^5[NaNO_2]$	0.0	38.6	90.1	171	267	449		
10^4k_{obsd}, s^{-1}	8.30	10.6	13.3	18.8	30.1	46.8		
(f) pH 4.10, 0.05 M Acetate, $\mu = 0.25$ M								
$10^5[Na_2N_2O_3]$	24.6	18.0	15.0	24.6	22.1	24.6[a]		
$10^5[NaNO_2]$	0.0	38.6	90.0	270	456	451		
10^4k_{obsd}, s^{-1}	7.65	7.69	8.66	16.5	21.5	9.65		
(g) pH 3.0, 0.25 M $NaClO_4$								
$10^5[Na_2N_2O_3]$	24.6	23.6	22.1	24.6	22.1			
$10^5[NaNO_2]$	0.0	16.8	26.9	34.0	40.1			
10^4k_{obsd}, s^{-1}	12.8	25.4	36.5	41.3	49.0			

[a] 2% ethanol added.

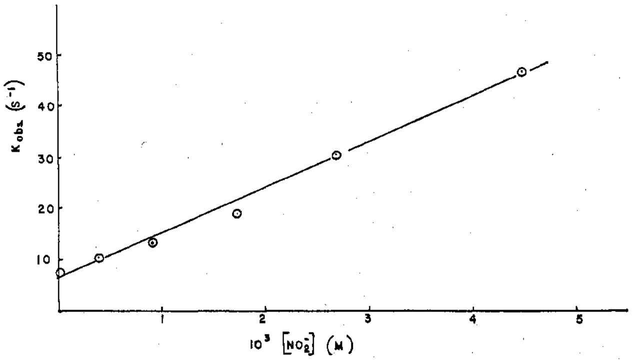


Figure 1. First-order rate constant vs. $[NaNO_2]$ at pH 4.1 (high acetate).

Our results are thus in essential agreement with those of Hughes and Wimbledon in showing that there is (a) kinetic stabilization of trioxodinitrate decomposition at pH 4.9 and (b) nitrite catalysis of the reaction at pH 4.1 and below. In addition, however, our measurements demonstrate a striking effect of acetate buffer concentration. We are in agreement that the most plausible explanation for the stabilization effect is equilibrative recombination of the primary products of cleavage and that NO^- and HNO_2 are the most probable primary products. If the NO^- species should be identical with that observed by pulse radiolysis, it would have a strong protonation tendency at these pH values, since that species has a measured pK of 4.7.[12] This identity cannot be taken for granted, however, since an HNO species with properties which distinguish it from the intermediate observed in trioxodinitrate decomposition has been observed in another reaction system.[13]

The strong effect of acetate concentration in enhancement of the nitrite catalysis reaction, seen at pH 4.1, suggests that nitrosyl acetate is an active species in this process. Hughes and Wimbledon have suggested nitrosation of $H_2N_2O_3$ by NO^+ as a chain initiator at low pH;[5a] their results and ours at pH 4.1 and 3.0 are consistent with this hypothesis. We believe the effect of carboxylic acid buffer concentration is probably due to the presence of nitrosyl carboxylate as a nitrosation agent; the spectroscopic properties of nitrite in solution have been observed by us[3] and by Hughes and Wimbledon[5a] to be altered by acetate, an effect ascribable to nitrosyl acetate. The presence of nitrosyl carboxylate appears to extend upward the pH range in which nitrite catalysis occurs. The observed intermediate behavior, i.e., initially declining and then rising rate, would thus be interpretable in terms of a competition between the kinetic stabilization effect of nitrite and the catalytic effect of the nitrosyl species. At pH 4.9, in these terms, the two opposing effects roughly compensate to produce apparent non nitrite dependence at high acetate, but kinetic stabilization predominates at low buffer concentration. The interesting difference in behavior between acetate and citrate buffers could then be simply explained as a concentration difference between nitrosyl acetate and nitrosyl citrate at equivalent buffer and nitrite concentrations and pH levels. Finally, it must be noted that the postulated catalysis at pH 4.9 cannot be a radical chain process like that at pH 4.1, as seen from the fact that ethanolic medium does not reduce the decomposition rate at high acetate and nitrite concentrations (Table II, series a).

Isotopic Composition of Trioxodinitrate following Partial Decomposition in the Presence of $^{15}NO_2^-$. To test the postulate of Hughes and Wimbledon that there is an equilibrium between $HN_2O_3^-$ and the primary decomposition products NO^- and HNO_2, we have carried out several experiments with $Na_2N_2O_3$ at natural abundance in solution in the presence of $Na^{15}NO_2$. In the first of these, no buffer was employed, so that the pH was high; the initial concentrations of $Na_2N_2O_3$ and $NaNO_2$ were 0.107 and 0.213 M respectively; the NO_2^- contained 30.2% ^{15}N. After 20 min Tl(I) was added to precipitate $Tl_2N_2O_3$, which was then treated with H_2SO_4 for quantitative conversion to NO.[10] Upon examination in the mass spectrometer, the NO was found to contain ^{15}N at natural abundance level. A second experiment was carried out at pH 5.5 in acetate buffer at $\mu \simeq 10$ M, with initial

$[Na_2N_2O_3]$ = 0.205 M and $[NaNO_2]$ = 0.170 M. Five minutes decomposition time was allowed; the solution was then quenched with NaOH and $Tl_2N_2O_3$ precipitated. Again, the NO recovered from this product contained no trace of enrichment from the $^{15}NO_2^-$. A third experiment was carried out at pH 4.3 in acetate buffer at $\mu \simeq 1.0$ M, this time with initial $[Na_2N_2O_3]$ = 0.205 M and $[NaNO_2]$ = 0.158 M, the latter containing 38.8% ^{15}N. This reaction was quenched after 8 min, and the NO produced from recovered $Tl_2N_2O_3$ showed a very slight enrichment in ^{15}N (observed value 0.89%; natural abundance 0.37%).

The results reported above indicate that under the conditions employed, the extent of reverse reaction 2 is vanishingly small, during a period of time in which substantial decomposition occurs, in each case. However, none of these corresponds to conditions in which strong rate reduction has been observed. In order to attempt a similar test under such conditions, e.g., pH 4.9, high excess of nitrite, it was necessary to work at a much lower $Na_2N_2O_3$ concentration, and the $Tl_2N_2O_3$ precipitation method was not feasible. Therefore a method was employed in which a reaction mixture ($[Na_2N_2O_3]$ = 0.0082 M, $[NaNO_2]$ = 0.0435 M, pH 4.9, acetate buffer) was first quenched with NaOH, and nitrite was then destroyed by addition of sodium azide followed by dropwise addition of acetic acid to pH 4.6, yielding the known reaction

$$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O \qquad (3)$$

After 3–5 min was allowed for completion of the above reaction, the solution was quenched again, outgassed in a Y-tube on the vacuum line, and then mixed with sufficient 3 M H_2SO_4 to release NO from the remaining, undecomposed $Na_2N_2O_3$. In a control experiment the gas products of the final step were found by gas chromatography to be N_2, N_2O, and NO. When the same procedure was followed starting with $NaNO_2$ solution alone, no NO product was formed, showing that $Na_2N_2O_3$ is the sole precursor source of this gas. We are uncertain about the origin of the N_2 and N_2O in the final H_2SO_4 reaction; presumably it represents incomplete destruction of HNO_2 in the preceding azide reaction, but the important point is that the reaction conditions employed do not give rise to NO by nitrite disproportionation. When the same complete procedure was employed in a control experiment using $Na_2N_2O_3$ as starting solution without added nitrite, the H_2SO_4 addition step produced NO as major product, plus minor amounts of N_2 and N_2O.

An experiment was carried out by using $Na_2N_2O_3$ at natural abundance and $NaNO_2$ containing 9.93% ^{15}N, both at the concentrations given in the paragraph above, in acetate buffer ($[CH_3COO^-]$ = 0.05 M) at ionic strength 0.25 M. The reaction mixture was quenched with NaOH (to pH 12) after 20 min and treated consecutively with NaN_3 and H_2SO_4 as described above. Isotopic analysis of the separated NO gas from the final step showed it to contain 3.8% ^{15}N. If the equilibration reaction (eq 2) were to proceed to completion in the earliest stages of the reaction and involved only one of the two nitrogen atoms in $HN_2O_3^-$, the conditions employed would yield nitrogen (in nitrite plus one side of $HN_2O_3^-$) containing 8.4% ^{15}N; if both nitrogen atoms are involved, 7.3%. Our observed value of 3.8% in NO shows that nitrogen from nitrite has indeed become incorporated in trioxodinitrate, confirming the hypothesis of Hughes and Wimbledon. If we assume only one nitrogen atom in $HN_2O_3^-$ is involved, the process has proceeded very far toward equilibrium: since the NO arises from both trioxodinitrate nitrogens, if one is at natural abundance the other must contain 7.2% ^{15}N.

In the same experiment described above, the N_2O produced in the azide reaction was also examined by mass spectrometry and found to contain 3.0% ^{15}N, corresponding to roughly 6% in the nitrite since the nitrogen in HNO_2 is known to go exclusively to N_2O in reaction 3.[14] This represents a greater apparent depletion of ^{15}N in HNO_2 than can be accounted for by the equilibration process and undoubtedly reflects the presence of N_2O from the $HN_2O_3^-$ decomposition process, continuing during the time allowed for the azide reaction, and strongly implying that the nitrogen bound to a single oxygen atom in $HN_2O_3^-$ does not exchange with nitrite. Analysis of the N_2O coproduced with NO in the final H_2SO_4 addition step showed an essentially similar mass spectrum, with an only slightly higher ^{15}N content.

Table III. Reaction Product Ratio as a Function of Initial $Na_2N_2O_3$ and $NaNO_2$ Concentrations at 25 °C; μ = 0.25 M

	$10^2 \times [Na_2N_2O_3]$	$10^2 \times [NaNO_2]$	NO/N_2O (av)
(a) pH 4.9, $[CH_3COO^-] = 0.25$	1.25	1.25	0.01
	0.82[a]	1.50	0.05
	1.25[a]	2.50	0.91
	1.25	3.74	1.40
	1.25	5.00	2.61
	0.41	2.02	0.20
(b) pH 4.9, $[CH_3COO^-] = 0.05$	0.0	2.49	*b*
	1.25	0.0	0.0
	1.25	2.49	0.016
	2.86	2.21	0.020
	1.25	5.00	0.090
	0.622	5.01	0.38
	0.322[a]	5.01	0.88
(c) pH 4.1, $[CH_3COO^-] = 0.25$	2.46	0.435	10.8
	1.23[a]	0.435	9.5
	0.82	0.435	9.3
	2.50	1.25	50.1
	0.615	0.435	7.9
	0.410	0.725	15.8
	1.25	2.50	44.1
(d) pH 4.1, $[CH_3COO^-] = 0.05$	1.25	2.49	5.30
	1.22	1.25	2.90
	2.51	1.22	2.50
	1.25[a]	0.623	1.50

[a] Conditions selected for tracer experiments. [b] No products detected.

A second experiment was carried out under conditions identical with those employed above but with $NaNO_2$ at natural abundance and $Na_2(O{*}NNO_2)$ containing 19.6% ^{15}N at the indicated position. After 20 min reaction time, the consecutive azide and H_2SO_4 reactions yielded an NO product containing 9.9% ^{15}N, corresponding to 19.4% at one side of the trioxodinitrate. In conjunction with the previous experiment this shows conclusively that the reverse reaction process (eq 2) involves only the nitrogen in trioxodinitrate that is bound to two oxygen atoms. It also shows that the scrambling of nitrogen atoms that is promoted by acetate in the absence of excess nitrite is essentially completely inhibited under the conditions of this experiment, in which rapid recombination of primary products occurs.

The N_2O coproduced with NO in this experiment was found to contain about 1% ^{15}N, which we believe is attributable to inclusion of N_2O from "normal" decomposition (HNO dimerization) along with N_2O of natural abundance from the azide reaction.

Distribution of Product Gases NO and N_2O. A series of experiments was carried out in which the ratios of product gases NO and N_2O were determined at pH 4.9 and 4.1, in acetate buffer at two concentration levels, with ionic strength 0.25 M and with varying ratios of initial trioxodinitrate and nitrite concentrations (Table III). The ratios reported are average values of analyses of gas samples withdrawn at several times in the course of each decomposition reaction, carried out over a total interval of about 60 min. Major trends were not observed in most cases, but in the case of the last experiment in series d the ratio shifted from 1.0 at 5 min to 2.0 at 20 min.

Table IV. Tracer Experiments, pH 4.9, Acetate Buffer, $\mu = 0.25$ M, 25 °C

	expt 1	expt 2		expt 3		expt 4		expt 5		expt 6	
	60 min	20 min	60 min	20 min	60 min	20 min	60 min	20 min	120 min	20 min	120 min
$[CH_3COO^-]$	0.25	0.25		0.25		0.25		0.05		0.05	
$10^2[Na_2N_2O_3]$	0.82	1.25		1.25		1.25		0.303		0.303	
$10^2[NaNO_2]$	1.45	2.49		2.49		2.49		5.07		5.07	
% ^{15}N in NO_2^-	30.2	30.2		99.0		0.37		30.2		0.37	
% ^{15}N in $O^*NNO_2^{2-}$	0.37	0.37		0.37		19.6		0.37		19.6	
46 (N_2O)	0.0045	0.0090	0.0074	0.092	0.096	0.0073	0.0065	0.0142	0.0160	0.0015	0.0021
45 (N_2O)	0.277	0.285	0.267	1.00	1.00	0.243	0.239	0.416	0.416	0.201	0.208
44 (N_2O)	1.00	1.00	1.00	0.444	0.444	1.00	1.00	1.00	1.00	1.00	1.00
31 (N_2O)	0.0475	0.051	0.050	0.222	0.237	0.047	0.048	0.084	0.065	0.037	0.036
30 (N_2O)	0.441	0.408	0.422	0.368	0.422	0.422	0.459	0.418	0.352	0.420	0.401
% ^{15}N in N_2O	11.2	11.7	11.0	38.5	36.7	10.3	10.1	15.5	15.7	8.5	8.8
% ^{15}N, 30–31 (N_2O)	9.7	11.2	10.7	37.6	36.0	9.98	9.58	16.7	15.6	8.1	8.2
% ^{15}N in NO	*a*	*b*	17.0	*b*	49.9	3.45	3.60	26.6	26.1	*b*	0.95

[a] Negligible NO product. [b] Not determined.

Table V. Tracer Experiments, pH 4.1, Acetate Buffer, $\mu = 0.25$ M, 25 °C

	expt 1	expt 2		expt 3			expt 4[c]		expt 5[c]	
	60 min	5 min	60 min	5 min	20 min	60 min	5 min	20 min	5 min	20 min
$[CH_3COO^-]$	0.25	0.25		0.25			0.05		0.05	
$10^2[Na_2N_2O_3]$	1.25	1.23		1.23			1.25		1.25	
$10^2[NaNO_2]$	1.25	0.435		0.435			0.623		0.623	
% ^{15}N in NO_2^-	30.2	30.2		0.37			30.2		0.37	
% ^{15}N in $O^*NNO_2^{2-}$	0.37	0.37		19.6			0.37		19.6	
46 (N_2O)	*a*	0.001	*b*	0.0237	0.017	0.020	0.0033	0.0022	0.0092	0.0092
45 (N_2O)		0.132	0.100	0.399	0.299	0.322	0.243	0.195	0.262	0.262
44 (N_2O)		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
31 (N_2O)		0.0052	0.0040	0.031	0.022	0.015	0.035	0.028	0.043	0.041
30 (N_2O)		0.139	0.144	0.240	0.170	0.122	0.351	0.338	0.381	0.365
% ^{15}N in N_2O		5.9	4.5	15.7	12.7	13.5	10.0	8.3	11.0	11.0
% ^{15}N, 30–31 (N_2O)		3.6	2.7	11.5	11.4	11.0	9.1	7.6	10.2	10.1
% ^{15}N in NO	13.0	5.9	7.0	10.9	10.5	8.1	*b*	10.0	5.7	6.7

[a] Negligible N_2O product. [b] Not determined. [c] $NO/N_2O = 1.0$ at 5 min, 2.0 at 20 min.

The results of these experiments show that NO becomes a prominent product at high nitrite concentration at pH 4.9. Comparison of the two levels of buffer concentration shows that acetate plays a major role in promotion of NO as product; e.g., at $[NaNO_2]/[Na_2N_2O_3] = 4.0$, NO/N_2O is 2.6 under the high acetate conditions in which added nitrite has little effect on decomposition rate but only 0.090 at low acetate concentration, in which kinetic stabilization is observed (Table II). At pH 4.1 and high acetate, NO is the predominant product under all conditions examined and remains in excess of N_2O but is strikingly suppressed by lowering of the acetate concentration; e.g., at $[NaNO_2]/[Na_2N_2O_3] = 0.5$, NO/N_2O is reduced from 50 to 2.5 by the reduction in buffer concentration.

We note in Table III that the proportion of NO product depends upon the level of $Na_2N_2O_3$ concentration, as well as $[NaNO_2]:[Na_2N_2O_3]$ ratio. In other experiments we have noted that the acetate concentration dependence is capable of raising the level of pH at which NO is coproduced with N_2O to a surprisingly high level; e.g., appreciable NO has been observed at pH 6.0 in concentrated acetate buffer, with high added nitrite concentration.

Tracer Experiments on Nitrite–Trioxodinitrate Interaction. A single tracer experiment has been reported by Hughes and Wimbledon[5a] in which $Na_2N_2O_3$ decomposition in the presence of $Na^{15}NO_2$ at pH 4.0 resulted in an NO product which contained substantial ^{15}N. In preliminary experiments under rather different conditions we found both NO and N_2O product gases to contain ^{15}N. These were carried out at pH 5.8 in high concentration acetate buffer, employing $NaNO_2$ at 30.2% ^{15}N. With equimolar amounts of $NaNO_2$ and $Na_2N_2O_3$ (each 0.02 M) very little NO was produced, but the N_2O contained 5.2% ^{15}N. With $[NaNO_2] = 0.055$ and $[Na_2N_2O_3] = 0.030$, the gas product was about 30% NO, containing 17.1% ^{15}N; the coproduct N_2O contained 7.0% ^{15}N.

In Tables IV and V we show the results of tracer experiments conducted at pH 4.9 and 4.1, respectively. In all cases ionic strength is 0.25 M and two levels of acetate buffer concentration are employed. Both $Na^{15}NO_2$ and $Na_2(O^{15}NNO_2)$ have been used in separate experiments, and stoichiometric ratio conditions have been chosen, as shown in Table III, to provide roughly equal amounts of NO and N_2O where feasible, with the exception of one experiment at each pH in which NO was negligible at 4.9 and N_2O at 4.1. In each table the mass spectra for separated N_2O are given in detail, normalized to the most abundant peak (44 or 45), followed by overall percentages of ^{15}N found in N_2O and in the NO produced by electron impact on N_2O (% ^{15}N, 30–31). The percentages of ^{15}N found in separated NO, where it has appeared as a significant product, are shown in the bottom row.

The data of Tables IV and V reveal an extraordinary degree of complexity in the trioxodinitrate–nitrite interaction process, and the difficulty in their interpretation is compounded by the effects of (1) normal decomposition, (2) N scrambling in carboxylic buffers (Table I), (3) production of NO by nitrite disproportionation (not substantial at pH 4.9, but significant at 4.1), and (4) kinetic stabilization exchange. Given the high degree of complexity presented, a quantitatively detailed discussion is not warrented, but we shall attempt to point out what appear to be major features:

(1) At pH 4.9 and high acetate, NO product derives somewhat more than half its nitrogen from added nitrite and only a minor proportion from the single oxygen side of trioxodinitrate. Coproduced N_2O derives slightly more than one-third its nitrogen from added nitrite and just over half from the single oxygen side of $Na_2N_2O_3$.

(2) At pH 4.9 and low acetate, nitrogen in NO derives

almost entirely from nitrite, less than 1% from *N in $Na_2(O*NNO_2)$; N_2O nitrogen derives half from nitrite and somewhat less than half from *N in $Na_2(O*NNO_2)$.

(3) At pH 4.1 and high acetate, nitrogen derives initially from nitrite at about 20% in both NO and N_2O, a proportion that increases with time in NO and declines in N_2O. Initial N content in NO is more than 50% from *N in $Na_2(O*NNO_2)$, and about 80% in N_2O; both decline with time.

(4) At pH 4.1 and low acetate, both NO and N_2O derive about one-third of their nitrogen atoms from nitrite; N_2O derives somewhat more than half and NO about one-third from *N in $Na_2(O*NNO_2)$.

(5) N_2O of mass 45 is produced essentially symmetrically (i.e., includes $^{14}N^{15}NO$ and $^{15}N^{14}NO$ in equal amounts) at pH 4.9. At pH 4.1 there is significant asymmetry, favoring $^{15}N^{14}NO$, at high acetate. At low acetate a similar but relatively slight asymmetry is observed.

(6) N_2O of mass 46, $^{15}N^{15}NO$, is observed above natural abundance level under all conditions examined. The ratio of observed proportion of total N_2O at 46 to that calculated for a random distribution of atoms at the overall ^{15}N abundance determined in each case is as follows: about 0.5 at pH 4.9, high acetate (both labels); 0.4 at pH 4.9, low acetate and $^{15}NO_2^-$ label, 0.2 with $Na_2O^{15}NNO_2$; 0.2 at pH 4.1, high acetate and $^{15}NO_2^-$ label; 0.8 with $Na_2O^{15}NNO_2$; 0.3 at pH 4.1, low acetate, $^{15}NO_2^-$ label; and 0.6 with trioxodinitrate label.

These features appear to indicate the occurrence of simultaneous processes as follows.

NO Production. At pH 4.9 and high acetate the data clearly indicate an attack of nitrite (or a nitrite-derived species) at the trioxodinitrate nitrogen bound to two oxygen atoms. Nitrogen atom scrambling due to buffer introduces some nitrogen from the other side into NO (seen with $Na_2O^{15}NNO_2$). Because of this, NO formed from the postulated interaction between $^{15}NO_2^-$ and $HN_2O_3^-$ should contain less than half its nitrogen from nitrite but is found to contain somewhat more than half. This indicates occurrence of an additional process that yields NO quantitatively from nitrite. Disproportionation of nitrite would do so, of course, but does not occur to an appreciable extent under the conditions employed.

At pH 4.9 and low acetate, the NO appears to be produced predominantly via the second of the two processes postulated above. Exchange between nitrite and one atom of $HN_2O_3^-$ is expected in this case via reaction 2; rapid equilibration would reduce the ^{15}N content of added nitrite to 28.5%, and the content of observed NO is just short of that value. While we have observed NO production by disproportionation chromatographically at these conditions, the amount produced within the allowed reaction time is nowhere near enough to account for the quantities found in the presence of $Na_2N_2O_3$. It would appear there is an interaction which produces NO of nitrite origin; the fate of the trioxodinitrate nitrogen in this interaction is not known to us. In the experiment with $Na_2O^{15}NNO_2$, the small amount of ^{15}N in NO is substantially less than the amount found at high acetate concentration. This can be ascribed to inhibition of the N scrambling under conditions which produce kinetic stabilization, as noted in a previous section.

At pH 4.1, in the region of nitrite catalysis, a new route to NO production has become prominent in which 2 mol of NO are produced, both deriving from trioxodinitrate, as judged by the small proportion arising from nitrite and the roughly 50% arising from $Na_2O^{15}NNO_2$. Here NO of disproportionation origin is expected to be significant, and its effects are seen in a rising ^{15}N content of NO from $H^{15}NO_2$ and in a falling in the case of $Na_2(O^{15}NNO_2)$, at high acetate. The difference between high and low acetate at this pH appears to be one of different proportions of sources.

N_2O Production. At pH 4.9 N_2O appears to be produced by attack of nitrite, or a species derived from nitrite, at the single oxygen nitrogen atom of trioxodinitrate; the precursor to N_2O in this interaction must be bound between nitrogen atoms and remains bound during symmetric formation of N*NO and *NNO. The presence of significant mass 46, however (feature 6 above), indicates that some N_2O is formed via an unbound intermediate in the case of high acetate. This supposition is confirmed by the fact that more than half the nitrogen atoms from the single-oxygen side become incorporated into N_2O, even despite the expected effects of buffer scrambling at these conditions. It is possible that some of the doubly labeled N_2O product arises from dissociation of the intermediate, but we assume most of it comes from the "normal" route of nitroxyl dimerization.

When acetate concentration is lowered at pH 4.9, we encounter conditions under which kinetic stabilization has been observed; the N_2O product in this case appears to arise largely via the process postulated above, i.e., interaction between nitrite and the single oxygen N atom of $HN_2O_3^-$. The suppression of nitroxyl dimerization in this case is manifest in the substantial reduction of mass 46 (see feature 6 above).

At pH 4.1, on the other hand, nitroxyl dimerization appears to be a major source of N_2O, as indicated by the elevation of 46 content in the $Na_2O^{15}NNO_2$ label experiments at both high and low acetate and the high percentage of ^{15}N in the N_2O products. N_2O resulting from the other postulated pathway is also present, in this case with an apparent asymmetry of derivation whose source is not clear. The difference between N_2O product at low and high acetate seems to be one of proportions from what we presume are the two major sources.

In summary, we believe our evidence indicates occurrence of the following processes in trioxodinitrate decomposition in the presence of added nitrite, under the conditions explored: (1) "normal" cleavage followed by nitroxyl dimerization; (2) attack of nitrite or a species derived from nitrite at the $-NO_2$ side of $HN_2O_3^-$ to produce 2 mol of NO, one from nitrite and one from the $-NO_2$ side of $HN_2O_3^-$; (3) an interaction between nitrite and trioxodinitrate in which the nitrite nitrogen is reduced quantitatively to NO; (4) an interaction between nitrite and trioxodinitrate yielding 2 mol of NO in which both nitrogen atoms come from trioxodinitrate; this appears coincidentally with the nitrite catalysis of trioxodinitrate decomposition; (5) interaction between nitrite, or a species derived from nitrite, and the single oxygen nitrogen atom of trioxodinitrate, yielding N_2O bearing one nitrogen atom from each source.

Our evidence does not provide grounds for extensive speculation on the mechanistic details of the complex of processes postulated above. Processes 2 through 5 may all be caused by nitrosation reactions; there are two distinct kinds of both oxygen and nitrogen atoms that should be susceptible to nitrosation; hence the possibility of multiple processes exists. The nitrosating agents presumably include $H_2NO_2^+$ and, at higher acidities, NO^+; in addition, in view of the strong effects of carboxylic acid buffers that we have observed, we believe nitrosyl acetate plays an important role. The effects of different attacking species seem clearly illustrated in the fact that at pH 4.9 a greater quantity of NO is produced in concentrated acetate than in dilute (Table III), and isotopic tracer results reveal a dramatic shift in origin of the NO nitrogen in the two cases. For the route which produces isotopically diluted NO, the agent may be NO(OAC), for the other, $H_2NO_2^+$.

Process 4 appears to arise in coincidence with the radical chain reaction associated with nitrite catalysis. The mechanism discussed by Hughes and Wimbledon[5a] would produce NO with nitrogen coming largely from the two atoms in trioxodinitrate, at least in its early stages. None of the other reactions appears to involve radical intermediates, at least if (4) is properly identified as the radical catalysis reaction. We are considerably puzzled about reaction 3 but do not believe our results can be explained as disproportionation; hence some such postulate is necessary. With respect to this and the other reactions, interpretation is inhibited by the fact that we are not wholly certain of the products other than gas products. For example, one can imagine more than one mechanism in which nitrate would be produced as a solution product; we have examined solutions after reaction at pH 4.9 for nitrate, both by spectrophotometry and by sensitive spot tests. While we have not detected it, its production is not ruled out because of the low concentration levels and the known difficulty of detection at such levels.

Acknowledgment. We wish to thank Dr. Charles Iden and the Stony Brook Mass Spectrometry Facility for assistance with isotopic analyses. C.A.L. wishes also to acknowledge the National Science Foundation's support of summer research participation at Stony Brook, to thank Dr. D. Ritter for making laboratory facilities available at the University of Washington, and to acknowledge the support of the Research Corp. for work done there.

Registry No. $Na_2N_2O_3$, 13826-64-7.

References and Notes

(1) Research supported by the National Science Foundation, Grant No. CHE 76-08766.
(2) Author to whom correspondence should be addressed.
(3) Bonner, F. T.; Ravid, B. *Inorg. Chem.* **1975**, *14*, 558.
(4) Sturrock, P. E.; Ray, J. D.; Hunt, H. R., Jr. *Inorg. Chem.* **1963**, *2*, 649.
(5) (a) Hughes, M. N.; Wimbledon, P. E. *J. Chem. Soc., Dalton Trans.* **1976**, *8*, 703. (b) *Ibid.* **1977**, *9*, 1650.
(6) Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 1239.
(7) Vosper, A. J. *J. Chem. Soc. A.*, **1968**, 2403.
(8) Pearsall, K. A., M.S. Thesis, State University of New York at Stony Brook, 1978.
(9) To the best of our knowledge this is the first report of this compound. In addition to the properties cited, $Tl_2N_2O_3$ is subject to ready photodecomposition.
(10) Hunt, H. R., Jr.; Cox, J. R., Jr.; Ray, J. D. *Inorg. Chem.* **1962**, *1*, 938.
(11) Hope, H.; Sequeira, M. R. *Inorg. Chem.* **1973**, *12*, 286.
(12) Grätzel, M.; Taniguchi, S.; Henglein, A. *Chem. Ber.* **1970**, *74*, 1003.
(13) Bonner, F. T.; Dzelzkalns, L. S.; Bonucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487.
(14) Clusius, K.; Effenberger, E. *Helv. Chim. Acta* **1955**, *38*, 1843.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Kinetic Study of the Cerium(IV)–Bromous Acid Reaction in Acid Sulfate Solution. Implications for the Belousov–Zhabotinskii Oscillating Reaction[1]

JAMES C. SULLIVAN* and RICHARD C. THOMPSON*[2]

Received February 20, 1979

A kinetic study of the cerium(IV)–bromous acid reaction in acid sulfate solution using stopped-flow techniques is reported. The empirical rate expression is $-d[Ce(IV)]/dt = k_{HBrO_2}[Ce(IV)][HBrO_2]$. The values of k_{HBrO_2} are very sensitive to the distribution of cerium(IV) among various sulfato complexes; $Ce(SO_4)_3^{2-}$, the predominant species in 1.5 M H_2SO_4, appears to be unreactive relative to disproportionation of bromous acid. The implications of this study for the Belousov–Zhabotinskii oscillating reaction are discussed. The results of a brief kinetic investigation of the cerium(IV)–chlorous acid reaction are summarized.

Introduction

Considerable effort has been devoted to the elucidation of the mechanism of the Belousov–Zhabotinskii oscillating reaction. An elegant reaction scheme was proposed by Noyes and co-workers[3] and has been refined to the extent that computer simulations of the reaction and various component processes have been reported.[3b,4] These computer analyses appear to be quite successful. However, as Edelson, Field, and Noyes have stated:[3b] "The values of the rate constants for the reactions of cerium(III) and cerium(IV) with the various oxybromine compounds involve considerable speculation". The current scheme for this component process is[4] given in eq 1–7.

$$2H^+ + Br^- + BrO_3^- \rightleftarrows HOBr + HBrO_2 \tag{1}$$

$$k_1 = 2.1\ M^{-3}\ s^{-1},\ k_{-1} = 10^4\ M^{-1}\ s^{-1}$$

$$H^+ + Br^- + HBrO_2 \rightleftarrows 2HOBr \tag{2}$$

$$k_2 = 2 \times 10^9\ M^{-2}\ s^{-1},\ k_{-2} = 5 \times 10^{-5}\ M^{-1}\ s^{-1}$$

$$H^+ + Br^- + HOBr \rightleftarrows Br_2 + H_2O \tag{3}$$

$$k_3 = 8 \times 10^9\ M^{-2}\ s^{-1},\ k_{-3} = 110\ s^{-1}$$

$$H^+ + HBrO_2 + BrO_3^- \rightleftarrows 2BrO_2 + H_2O \tag{4}$$

$$k_4 = 10^4\ M^{-2}\ s^{-1},\ k_{-4} = 2 \times 10^7\ M^{-1}\ s^{-1}$$

$$H^+ + BrO_2 + Ce^{3+} \rightleftarrows Ce^{4+} + HBrO_2 \tag{5}$$

$$k_5 = 6.5 \times 10^5\ M^{-2}\ s^{-1},\ k_{-5} = 2.4 \times 10^7\ M^{-1}\ s^{-1}$$

$$Ce^{4+} + BrO_2 + H_2O \rightleftarrows 2H^+ + BrO_3^- + Ce^{3+} \tag{6}$$

$$k_6 = 9.6\ M^{-1}\ s^{-1},\ k_{-6} = 1.3 \times 10^{-4}\ M^{-3}\ s^{-1}$$

$$2HBrO_2 \rightleftarrows H^+ + HOBr + BrO_3^- \tag{7}$$

$$k_7 = 4 \times 10^7\ M^{-1}\ s^{-1},\ k_{-7} = 2 \times 10^{-10}\ M^{-2}\ s^{-1}$$

The main features of the oxidation of cerous ions by bromate ions in sulfuric acid medium are indeed consistent with this scheme. However, the large number of parameters that are required and the uncertainty in the values of many of the rate constants justify efforts to determine directly those rate constants amenable to investigation.

In this communication we summarize the results of a kinetic study of the oxidation of bromous acid by cerium(IV) in acid sulfate media. The value determined for k_{-5} is in serious disagreement with the estimated value. We conclude that this reaction plays a negligible role under the experimental conditions for the oscillating reaction.

Experimental Section

Preparation and Analysis of Barium Bromite. The synthesis and stability of bromite salts and solutions have been reported.[5] The details of the preparations are scant, and claims of the stability of the solid samples and solutions are conflicting. This situation is in part due to the proprietary nature of bromite, which has extensive commercial applications, and the difficulty in analyzing mixtures of bromate, bromite, hypobromite, and bromide. In our hands, the direct synthesis of pure barium bromite was unsuccessful. Commercial sources of

0020-1669/79/1318-2375$01.00/0