

694. *The Kinetics of Oxidation of Bromide Ion in Aqueous Nitric Acid.*

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The kinetics of oxidation of bromide ion in aqueous nitric acid (2.4–8.0M), and in sulphuric acid and perchloric acid containing some nitrous acid and some nitric acid, have been investigated. The order of the reaction is 1.5 with respect to "analytical" nitrous acid and unity with respect to bromide. The kinetic data indicate that the rate-determining step is the decomposition or rearrangement of a complex $[\text{N}_2\text{O}_3\text{BrH}]^+$.

LITTLE work has been reported on the oxidation of bromide by nitrous acid or nitrous oxides and apparently none on its oxidation by nitric acid. Merton-Bingham and Posner¹ investigated the catalytic effect of nitrogen dioxide on the autoxidation of hydrogen bromide and suggested that the slow step in this reaction is the interaction of nitrosyl bromide with an intermediate Z formed according to the equation $\text{HNO}_2 + \text{HBr} \rightleftharpoons \text{Z}$. Their experimental conditions differ widely from those discussed here: in particular they used large concentrations of nitrogen dioxide and studied a system in which the gaseous and the liquid phase were in equilibrium; in the present work the concentration of "analytical" nitrous acid is initially small and the liquid phase only has been investigated.

The kinetics of the oxidation of bromide ion by aqueous nitric acid were investigated by measuring the change in the concentration of "analytical" nitrous acid and, in some experiments, the formation of bromine during the reaction. ["Analytical" nitrous acid denotes all entities which behave as nitrous acid in diazotising amines, and is referred to subsequently as nitrous acid or HNO_2 and its concentration as (HNO_2)].

Preliminary experiments had shown that an appreciable quantity of nitrous acid escapes into the vapour phase under ordinary conditions; this difficulty was overcome by taking each sample in kinetic runs from a completely filled brown-glass stoppered bottle; thus the participation in the reaction of the vapour phase was excluded.

Kinetic experiments were carried out at 25° in 2.4–8.0M-nitric acid with 0.002–0.25M-potassium (or sodium) bromide and an initial concentration of nitrous acid approximately $5 \times 10^{-5}\text{M}$. The velocity of the reaction was also measured in media containing perchloric and nitric acid or sulphuric and nitric acid.

RESULTS

No reaction takes place in the absence of nitrous acid or of nitric acid. The concentration of nitrous acid increases during the oxidation, and the order of reaction is initially 1.5 with respect to nitrous acid and unity with respect to bromide ion. The rate of formation of nitrous acid decreases as the reaction proceeds, a stable equilibrium being reached, the position of which depends on the initial concentrations of nitrous acid and of bromide ion, and on the composition of the medium. The order of the reaction with respect to nitrous acid is illustrated by Fig. 1 in which $(\text{HNO}_2)^{-0.5}$ is plotted against time (t) for experiments in 4.8M-nitric acid; straight

TABLE I. *Reaction in 4.8M-nitric acid.*

$[\text{KBr}]$ (M)	0.01	0.008	0.006	0.004	0.002
k' ($1.0^{0.5}$ mole $^{-0.5}$ min. $^{-1}$)	0.86	0.596	0.50	0.31	0.17
k ($1.1^{1.5}$ mol. $^{-1.5}$ min. $^{-1}$)	86	75	83	78	85

lines are obtained initially (*i.e.*, in the region over which the percentage change in concentration of bromide is small); values of k' in $d(\text{HNO}_2)/dt = k'(\text{HNO}_2)^{1.5}$ can be obtained from the slopes of these lines and are given in Table I. The first order with respect to bromide is shown by the values of $k = k'/[\text{Br}^-]$.

¹ Merton-Bingham and Posner, *J. Amer. Chem. Soc.*, 1955, **77**, 3634.

Evaluation of the more accurate rate equation:

$$\frac{-2}{[\text{Br}^-]_0(\text{HNO}_2)^{0.5}} + \frac{4}{[\text{Br}^-]^{1.5}} \ln \frac{[\text{Br}^-]_0^{0.5} + (2\text{HNO}_2)^{0.5}}{[\text{Br}^-]_0^{0.5} - (2\text{HNO}_2)^{0.5}} = kt + \text{Constant}$$

(where $[\text{Br}^-]_0$ is the initial concentration of bromide) which is obtained by integration of $d(\text{HNO}_2)/dt = k(\text{HNO}_2)^{1.5}[\text{Br}^-]$ leads to virtually the same values for the velocity constant.

The value of k is independent of the initial concentration of nitrous acid, *e.g.* (in 5.6M-nitric acid):

[KBr] (M)	k' ($1.0^5 \text{ mole}^{-0.5} \text{ min.}^{-1}$)	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	Initial (HNO_2) (10^{-5}M)
0.006	2.08	362	12
0.006	2.30	383	1

The rate of the reaction is very strongly dependent on the concentration of nitric acid (Table 2). In greater than 5.6M-nitric acid the reaction takes place so rapidly—even when the concentration of bromide is reduced to 0.0002M—that it is not possible to obtain accurately the velocity constant at 25°, and the values for 6.4M- and 8.0M-nitric acid are included in the Table

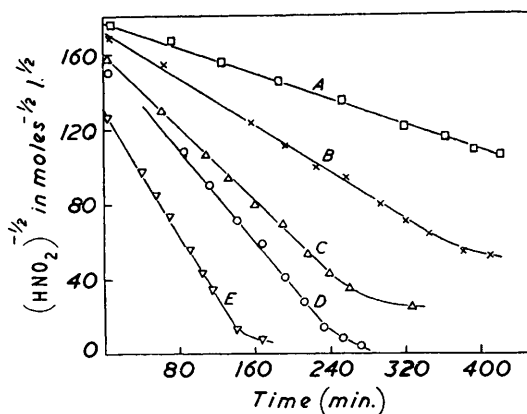


FIG. 1. Variation of $(\text{HNO}_2)^{-0.5}$ with time for reaction in 4.8M-nitric acid.

A, 0.002M-KBr. D, 0.008M-KBr.
B, 0.004M-KBr. E, 0.01M-KBr.
C, 0.006M-KBr.

only as indications of the order of magnitude. A plot of $\log k$ against $\log a_{\text{HNO}_3}$ gives approximately a straight line with slope 1.5, indicating that k is proportional to $(a_{\text{HNO}_3})^{1.5}$. The values of a_{HNO_3} given in Table 2 are obtained from the partial pressures of HNO_3 and H_2O above aqueous nitric acid at 25° given by Klemenc and Nagel² and from the activity coefficients of nitric acid measured by Abel, Redlich, and von Lengyel.³

TABLE 2.

$[\text{HNO}_3]$ (M)	[KBr] (M)	k' ($1.0^5 \text{ mole}^{-0.5} \text{ min.}^{-1}$)	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	a_{HNO_3}
2.4	0.25	0.66	2.6	5
3.2	0.02	0.15	7.5	10.5
4.8	0.002—0.01	—	80 (mean)	45
5.6	0.006	2.30	383	93
6.4	0.0002	0.230	1150	400
8.0	0.0002	5.16	25,800	2200

The range of validity of the order 1.5 with respect to nitrous acid and the equilibrium position also vary with the concentration of nitric acid, the conversion of bromide into bromine going almost to completion in 8.0M-nitric acid, to ~70% in 5.6M-nitric acid, to ~60% in 4.8M-nitric acid and to ~30% in 3.2M-nitric acid.

The reaction is accelerated by sodium nitrate and, to a greater extent, by sodium perchlorate (Table 3).

The effects of the concentrations of hydrogen and of nitrate ion on the rate of the reaction at constant ionic strength were investigated, the media for these experiments being prepared by mixing calculated quantities of nitric acid, perchloric acid, sodium nitrate, and sodium

² Klemenc and Nagel, *Z. anorg. Chem.*, 1928, **155**, 257.

³ Abel, Redlich, and von Lengyel, *Z. phys. Chem.*, 1928, **32**, 189.

perchlorate. The results of four sets of experiments in which the concentration of nitrate is varied at constant hydrogen-ion concentration ($[H^+] = 4.8, 3.2, 2.4,$ and $1.6M$ severally) and at constant ionic strength ($\mu = 4.8$) are summarised in Table 4. It can be seen that, at a given concentration of hydrogen ion, the rate of reaction increases as the concentration of nitrate is decreased from $4.8M$ to $1.0M$ and, moreover, that this trend increases with the acidity of the medium.

TABLE 3.

$[HNO_3]$ (M)	Added salt	$[KBr]$ (M)	k' ($1.0^5 \text{ mole}^{-0.5} \text{ min.}^{-1}$)	$k = k'/[Br^-]$ ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)
3.2	0	0.02	0.15	7.5
"	1.6M- $NaClO_4$	0.02	0.78	39
"	"	0.01	0.39	39
"	"	0.01	0.41	41
"	"	0.008	0.305	38
"	1.6M- $NaNO_3$	0.02	0.47	23.5
"	"	0.02	0.49	24.5
"	"	0.01	0.25	25
2.4	0	0.25	0.66	2.6
"	2.4M- $NaClO_4$	0.02	0.39	19.5
"	"	0.01	0.21	21
"	2.4M- $NaNO_3$	0.02	0.21	10.5
1.6	3.2M- $NaClO_4$	0.02	0.12	6
"	3.2M- $NaNO_3$	0.02	0.13	6.5

TABLE 4.

$[HNO_3]$ (M)	$[HClO_4]$ (M)	k' ($1.0^5 \text{ mole}^{-0.5} \text{ min.}^{-1}$)	$[KBr]$ (M)	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	$k/[NO_3^-]^{0.5}$ ($1.2 \text{ mole}^{-2} \text{ min.}^{-1}$)
$[H^+] = 4.8M$					
4.8	0	—	—	80 (mean value)	36.5
3.2	1.6	1.98	0.01	198	109
2.4	2.4	2.26	0.006	377	243
1.6	3.2	1.17	0.002	585	462
1.01	3.79	2.52	0.0025	1010	1010
0.74	4.06	2.87	0.0025	1150	1340
0.45	4.35	2.65	0.0025	1060	1580
0.1	4.7	2.04	0.0025	816	2580
0	4.8	0	0.002	0	—
$[H^+] = 3.2M$					
3.2	0	1.6	0	4.8	24
3.2	0	0	1.6	3.2	36
2.0	1.2	0	1.6	2.4	56
1.0	2.2	0	1.6	1.0	90
$[H^+] = 2.4M$					
2.4	0	2.4	0	4.8	10.5
2.4	0	0.8	1.6	3.2	16
2.4	0	0	2.4	2.4	20
1.0	1.4	2.4	0	1.0	25
$[H^+] = 1.6M$					
1.6	0	3.2	0	4.8	6.5
1.6	0	0	3.2	1.6	6
0.48	1.12	0	4.2	0.48	8.5

Experiments at $[H^+] = 4.8M$, $\mu = 4.8$, in which nitrate ion was progressively replaced by bisulphate ion, were also carried out (Table 5). The rate of the reaction again increases as the nitrate concentration is reduced, but the percentage increase is smaller.

The two sets of experiments in which the hydrogen-ion concentration is $4.8M$, $\mu = 4.8$, and the concentration of nitrate ion is progressively diminished (by replacement with either bisulphate ion or with perchlorate ion) were extended down to $[NO_3^-] = 0.1M$ (Tables 4 and 5). In both cases, the velocity constant passes through a maximum value. With the initial concentrations of bromide ion and of nitrous acid investigated, no increase in the concentration of nitrous acid and no formation of bromine take place when all the nitrate ion is replaced by

perchlorate ion or by bisulphate ion (*i.e.*, in 4.8M-perchloric or -sulphuric acid). Table 6 shows the effect on the rate of reaction of varying the hydrogen-ion concentration at constant ionic strength ($\mu = 4.8$) and at constant nitrate-ion concentration ($[\text{NO}_3^-] = 4.8, 3.2, 2.4,$ and 0.45M severally). The rate of the reaction increases with the hydrogen-ion concentration, the increase being greater the smaller the concentration of nitrate. Plots of $\log k$ against $\log [\text{H}^+]$ for these sets of experiments give approximately straight lines, the slopes of which vary from 2.5 to 4.5.

TABLE 5. *Experiments at* $[\text{H}^+] = 4.8\text{M}, \mu = 4.8$.

HNO_3 (M)	H_2SO_4 (M)	KBr (M)	k' ($1.0^5 \text{ mole}^{-0.5} \text{ min.}^{-1}$)	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	$k'' = k/[\text{NO}_3^-]^{0.5}$ ($1.2 \text{ mole}^{-2} \text{ min.}^{-1}$)
4.8	0	—	—	80	36.5
3.2	1.6	0.01	1.96	196	109
2.4	2.4	0.006	1.80	300	194
1.6	3.2	0.002	0.97	485	384
1.0	3.8	0.002	1.11	550	550
1.0	3.8	0.004	2.2	550	550
0.8	4.0	0.002	1.12	560	618
0.5	4.3	0.002	1.4	700	989
0.3	4.5	0.002	1.25	625	1140
0.2	4.6	0.002	1.11	550	1230
0.1	4.7	0.002	0.9	450	1430
0	4.8	0.002	0	0	—

Some experiments were carried out in which part of the water of the reaction mixture was replaced by acetic acid; the rate of the reaction increased with decrease in the concentration of water (Table 7).

TABLE 6.

$[\text{NO}_3^-] = 4.8\text{M}$	$[\text{HNO}_3]$ (M).....	1.6	2.4	3.2	4.8	} $d \log k/d \log [\text{H}^+] = 2.5$		
	$[\text{NaNO}_3]$ (M)	3.2	2.4	1.6	0			
	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	6.5	10.5	24	80			
$[\text{NO}_3^-] = 3.2\text{M}$	$[\text{NaNO}_3]$ (M)	0.8	0	0		} $d \log k/d \log [\text{H}^+] = 3.6$		
	$[\text{HNO}_3]$ (M).....	2.4	3.2	3.2				
	$[\text{NaClO}_4]$ (M)	1.6	1.6	0				
	$[\text{HClO}_4]$ (M)	0	0	1.6				
	$[\text{H}^+]$ (M)	2.4	3.2	4.8				
	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	16	36	196				
$[\text{NO}_3^-] = 2.4\text{M}$	$[\text{HNO}_3]$ (M)	2.4	2.4	2.4	2.4	2.4	2.4	} $\frac{d \log k}{d \log [\text{H}^+]} = 4.1$
	$[\text{HClO}_4]$ (M)	0	0.4	0.8	1.2	1.8	2.4	
	$[\text{NaClO}_4]$ (M)	2.4	2.0	1.6	1.2	0.6	0	
	$[\text{H}^+]$ (M)	2.4	2.8	3.2	3.6	4.2	4.8	
	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	20	39.5	53	90	200	346	
$[\text{NO}_3^-] = 0.45\text{M}$	$[\text{HNO}_3]$ (M)	0.45	0.45				} $d \log k/d \log [\text{H}^+] = 4.4$	
	$[\text{HClO}_4]$ (M)	1.15	4.35					
	$[\text{NaClO}_4]$ (M)	3.2	0					
	$[\text{H}^+]$ (M)	1.6	4.8					
	k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	8.5	1060					

TABLE 7. *Experiments in 4.8M-nitric acid.*

Acetic acid (M)	0	0.85	1.7	3.4	5.1
k ($1.1^5 \text{ mole}^{-1.5} \text{ min.}^{-1}$)	80	200	365	1330	6100

The stoichiometry of the reaction was determined by measurement of the rate of formation of bromine in some experiments. Considerable difficulty was experienced in finding a suitable method for the estimation of bromine, particularly as the total concentration formed in an experiment is small, but spectroscopic measurement of the concentration of bromine in a few runs showed that its rate of formation is equal to the rate of increase of concentration of nitrous acid (Table 8).

TABLE 8.

Time (min.)	(HNO ₂) (10 ⁻³ M) measured	(HNO ₂) (10 ⁻³ M) interpolated	[Br ₂] (10 ⁻³ M)	Time (min.)	(HNO ₂)(10 ⁻³ M) measured	(HNO ₂) (10 ⁻³ M) interpolated	[Br ₂] (10 ⁻³ M)
3	0.058	—	—	89	3.95	—	—
26	0.115	—	—	90	—	3.9	4.0
48	0.263	—	—	106	4.3	—	—
52	—	0.3	0.3	108	—	—	4.2
71	1.5	—	—	135	4.3	—	4.2
77	—	2.2	2.1				

TABLE 9.

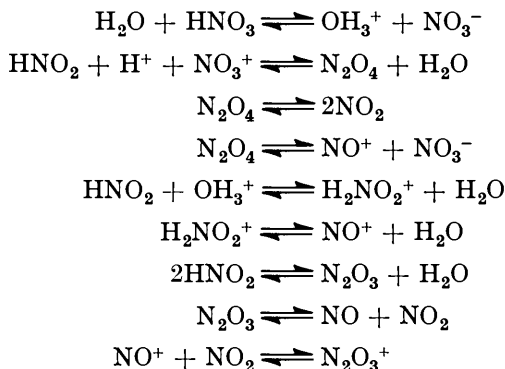
Temp.	[HNO ₃] (M)	[KBr] (M)	<i>k</i> ' (1.0 ⁻⁵ mole ^{-0.5} min. ⁻¹)	<i>k</i> = <i>k</i> '/[Br ⁻] (1.1 ⁻⁵ mole ^{-1.5} min. ⁻¹)
0°	8	0.002	1.55	775
„	6.4	0.01	0.71	71
„	6.4	0.01	0.65	65
„	5.6	0.024	0.48	20
„	5.6	0.024	0.36	15
15	5.6	0.01	1.062	106
„	4.8	0.04	1.11	27.8
35	5.6	0.0012	1.08	900
„	5.6	0.002	1.75	875
„	4.8	0.006	1.55	258

The results of experiments in 3.2, 4.8, and 5.4M-nitric acid at temperatures in the range 0—35° are summarised in Table 9. For each medium, log *k* is directly proportional to 1/*T*, and the activation energies are 23, 21.2, and 18.43 kcal. mole⁻¹ respectively.

DISCUSSION

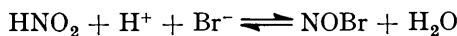
Bromide ion is not oxidised by nitric acid in the absence of nitrous acid and the orders of the reaction with respect to nitrous acid and bromide are respectively 1.5 and unity; therefore, entities derived from nitrous acid and bromide ion take part in the rate-determining step. Although replacing some of the nitric acid by perchloric or sulphuric acid markedly increases the velocity, no reaction takes place (in the concentration range investigated) in the absence of nitric acid. Since (HNO₂) increases during the reaction, one function of nitric acid must be to oxidise a product of the reaction between bromide ion and nitrous acid (probably nitric oxide) and thus to provide more nitrous acid for reaction. An entity derived from nitric acid in the presence of nitrous acid (but not in its absence) may also be directly involved.

The following equilibria (which are not all independent of each other) are known or assumed to exist in aqueous nitric acid containing analytical nitrous acid: ⁴



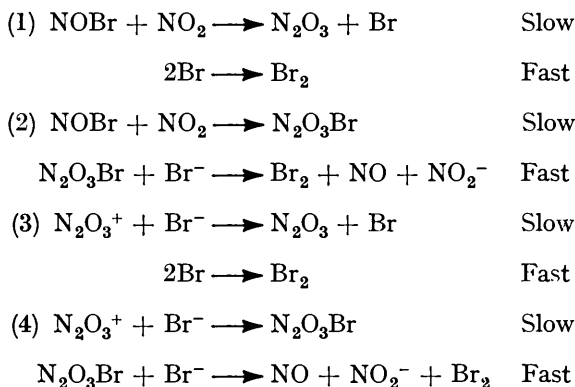
⁴ Abel, Schmid, and Stein, *Z. Elektrochem.*, 1930, **36**, 692; Goulden and Millen, *J.*, 1950, 2620; Hughes, Ingold, and Reed, *J.*, 1950, 2430.

In the presence of bromide ion, the following additional equilibrium exists :



In aqueous sulphuric acid, aqueous perchloric acid, and 2—8M-aqueous nitric acid (*i.e.*, in all the media used in the present work), the bulk of the " analytical " nitrous acid is present as molecular nitrous acid.⁵ The rate-determining step must therefore involve an entity or entities stoichiometrically related to $[\text{HNO}_2]$ in the ratio 1.5 : 1 and to $[\text{Br}^-]$ in the ratio 1 : 1 and very probably dependent in some way on nitric acid. The dependence on $[\text{HNO}_2]^{1.5}$ indicates very strongly that, in addition to an entity stoichiometrically related to (HNO_2) in the ratio 1 : 1, nitrogen dioxide takes part (either in the rate-determining step or in the formation of an entity involved in it), since nitrogen dioxide is the only entity proportional to $(\text{HNO}_2)^{0.5}$.

The following equations represent possible reaction schemes compatible with $k \propto (\text{HNO}_2)^{1.5}[\text{Br}^-]$:



Each of the rate-determining steps in the above schemes—and in fact any step involving one molecule of nitrogen dioxide—varies as $(a_{\text{HNO}_2})^{0.5}$. Experiments in aqueous nitric acid, however, show that k is proportional to $(a_{\text{HNO}_2})^{1.5}$. The very marked increase in rate when nitrate ion is partially replaced by perchlorate ion or bisulphate ion also points to the stronger dependence on acidity than occurs in the above schemes.

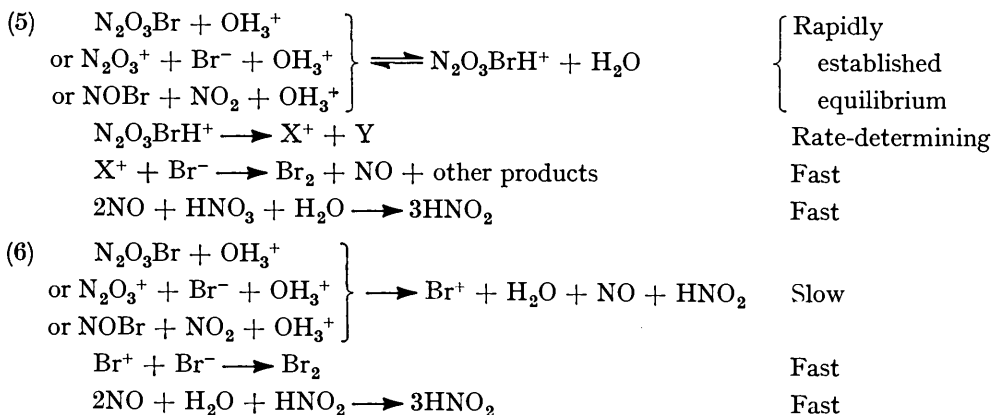
A rough estimate of the equilibrium concentration of bromine atoms (which is an upper limit for $[\text{Br}]$) can be made from thermodynamic data⁶ ($\text{Br}_2 \longrightarrow 2\text{Br}$; $2\text{Br}^- \longrightarrow 2\text{Br} + 2e$; $\text{NO}_2 + \text{H}^+ + e \longrightarrow \text{HNO}_2$) and is found to be so small that the rate of combination of bromine atoms with zero activation energy will not effectively compete with the rate of reaction of bromine atoms with nitrous acid unless the activation energy for the latter is of the order of 15 kcal. mole⁻¹. This is not likely. Reaction of bromine atoms with nitrous acid will therefore be fast compared with combination of 2 bromine atoms, so that schemes (1) and (3) would not be compatible with $k \propto (\text{HNO}_2)^{1.5}$. It is possible to calculate, fairly reliably, by using known activity coefficients and equilibrium constants^{4, 6} ($\text{HNO}_2 + \text{HNO}_3 \longrightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O}$; $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$; $\text{HNO}_2 + \text{HBr} \rightleftharpoons \text{NOBr} + \text{H}_2\text{O}$), the dependence of k upon a_{HNO_2} and $a_{\text{H}_2\text{O}}$ for mechanisms in which the rate-determining step involves reaction of nitrosyl bromide with nitrogen dioxide. The calculated variation of k with a_{HNO_2} differs very considerably from that obtained experimentally, providing additional evidence against schemes (1) and (2).

To account for the strong dependence of the rate of the reaction on acidity, it appears

⁵ Longstaff and Singer, *J.*, 1954, 2610; Singer and Vamplew, *J.*, 1955, 3971.

⁶ Latimer, "Oxidation Potentials," Prentice-Hall, New York, 1938.

to be necessary to introduce an additional hydroxonium ion into the mechanism; this can result in the formation of either a protonated entity or Br_2^+ as in the following equations:



The protonation of a neutral molecule is usually fast⁷ and not likely to be rate-determining. Therefore, if $\text{N}_2\text{O}_3\text{BrH}^+$ is involved in the reaction, the slow step might be

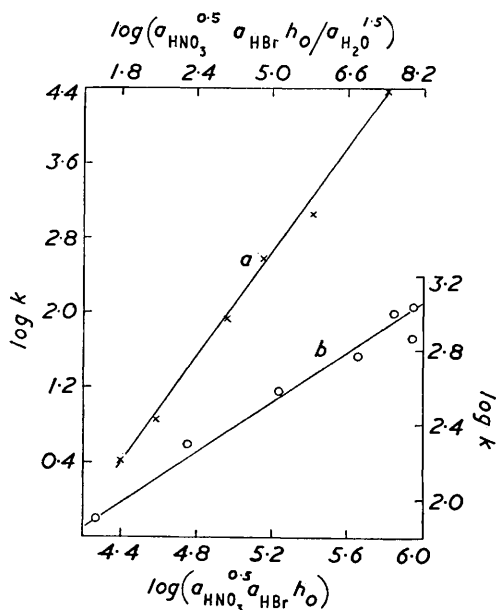
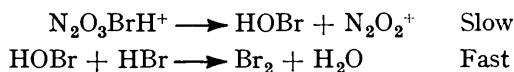


FIG. 2.

- (a) Relation of $\log k$ with $\log (a_{\text{HNO}_3}^{0.5} \cdot a_{\text{HBr}} \cdot h_o / a_{\text{H}_2\text{O}}^{1.5})$ for reaction in aqueous nitric acid (left hand and top scales).
- (b) Relation of $\log k$ with $\log (a_{\text{HNO}_3}^{0.5} \cdot a_{\text{HBr}} \cdot h_o)$ for reaction in nitric-perchloric acid (right hand and lower scales).

either the rearrangement of this protonated entity to form a less easily deprotonated complex or the formation of hypobromous acid:

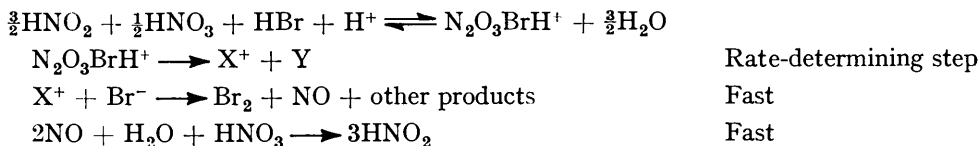


Although, at first sight, the introduction of a hydroxonium ion may appear rather implausible, the elimination of HNO_2 and NO from $\text{N}_2\text{O}_3\text{BrH}^+$ is thermodynamically more favourable than the elimination of NO and NO_2^- from $\text{N}_2\text{O}_3\text{Br}$ ($\text{HNO}_2 \longrightarrow \text{NO}_2^- + \text{H}^+$; $\Delta G = 4600$ cal.). Also, since NO_2 can associate with NO_2 , NO , and NO^+ , it is plausible that it can associate with NOBr to form $\text{N}_2\text{O}_3\text{Br}$. This entity should be more basic, and

⁷ Long and Paul, unpublished review on acidity functions.

therefore have a greater tendency to attract H^+ , than either N_2O_3 or N_2O_4 , since it contains two electron-attracting groups (NO_2 and Br) and since Br is more electron-attracting than NO_2 . The equilibrium concentration of Br^+ can be estimated from thermodynamic data ^{6, 8} ($Br^- + H_2O \longrightarrow 2e + Br^+ + H_2O$) and is so small that reaction between Br^+ and Br^- with zero energy of activation could not account for the observed rate of reaction. A rough estimate of the equilibrium concentration of $N_2O_3BrH^+$ can be made if it is assumed that the frequency factors for the bimolecular reactions involved are normal and that the activation energies are zero. The concentration of $N_2O_3BrH^+$ is such that its reaction with Br^- would lead to a velocity 10—100 times smaller than the observed velocity.

The proposed mechanism can therefore be summarised:



The overall reactions is:



which is consistent with the observed stoicheiometry of the reaction.

The velocity of a protonation in which a molecule of water is not present in the activated complex is known to be linearly correlated with the h_0 function of the medium.⁸ Hence for the above mechanism,

$$k = \text{Const.} a_{HNO_3}^{0.5} a_{HBr} h_0 / a_{H_2O}^{1.5}$$

h_0 data for aqueous nitric acid media are available⁹ and, if it is assumed that $f_{Br^-} = f_{NO_3^-}$, there is a linear relation between $\log k$ and $\log (a_{HNO_3}^{0.5} a_{HBr} h_0 / a_{H_2O}^{1.5})$ for the experiments in aqueous nitric acid (Fig. 2). The slope of the line is ≈ 0.7 instead of the theoretical unity, but in view of the approximation made this is not a serious discrepancy and these results are compatible with the above mechanism.

Any attempt to estimate the activities of chemical species in, and the h_0 function of, mixtures of perchloric and nitric acid is necessarily speculative. One might make the following additional assumptions:

(a) $H^0_{\text{medium}} = (M_1 H^0_p + M_2 H^0_n) / (M_2 + M_1)$ where H^0_p and H^0_n are respectively the values of the acidity function of perchloric acid and of nitric acid at molarity $M_1 + M_2$.

(b) $a_{HX} = a_{HNO_3} + a_{HClO_4} = m_p^2 \gamma_p^2 + m_n^2 \gamma_n^2$ where m_p is the molality corresponding to the concentration of perchloric acid in the medium and γ_p is the activity coefficient of perchloric acid in a $(m_p + m_n)$ -solution. γ_n and m_n are similarly defined for nitric acid.

Since $[HClO_4] + [HNO_3] = [HX] = \text{Constant}$

$$\gamma_{HX} = a_{HX} / [HX] = \text{Const.} a_{HX}$$

Hence

$$a_{HNO_3} = \text{Const.} [HNO_3] \cdot a_{HX}$$

$$a_{HBr} = \text{Const.} [HBr] \cdot a_{HX}$$

(c) $a_{H_2O} \approx \text{constant}$ in these media at constant ionic strength.

Again, a plot of $\log k$ against $\log (a_{HNO_3}^{0.5} a_{HBr} h_0)$ is approximately a straight line (Fig. 2) with slope ≈ 0.7 . No quantitative significance can be attached to this result but it indicates that the activities of the entities involved may well vary sufficiently, as nitric is replaced by perchloric acid, to account for the very marked increase in the velocity of reaction.

⁸ Bell and Gelles, *J.*, 1951, 2734.

⁹ Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

Data on the h_0 function of nitric acid in aqueous acetic acid are not available, but the h_0 functions of perchloric and sulphuric acid are known to be very greatly increased when water is replaced by acetic acid.⁸ Walker and Chadwick¹⁰ found that the velocity of decomposition of trioxan in a molar solution of sulphuric acid in acetic acid was 2000 times as great as in aqueous m-sulphuric acid and that the velocity was linearly correlated with the h_0 function of sulphuric acid in the two media. Hence the large increase (700-fold) in velocity constant obtained here in media containing 4.8M-nitric and 5.1M-acetic acid, compared with 4.8M-aqueous nitric acid, is probably explicable in terms of the increase of the h_0 function of the medium and would be expected from the suggested mechanism.

EXPERIMENTAL

Materials.—"AnalaR" sulphuric acid, perchloric acid, sodium nitrite, potassium bromide, sodium bromide, and sodium nitrate, and Hopkin and Williams's sodium perchlorate were used without further purification. Nitric acid was freed from nitrous acid by passage of a current of nitrogen for 30 min. in the dark—the concentration of nitrous acid is thus reduced to approx. $1 \times 10^{-6}M$.

Determination of Nitrite and of Bromine.—The concentration of analytical nitrous acid was determined by the colorimetric method described by Shinn¹¹ and modified by Kershaw and Chamberlin,¹² the colour being measured on a Unicam spectrophotometer S.P. 600 at 5460 Å. Nitrite concentrations in the range 1×10^{-5} to $7 \times 10^{-5}M$ can be estimated by this method: more concentrated solutions are determined after suitable dilution. The reagents are stable for several weeks; nitrate, perchlorate, and bromide do not interfere.

Bromine was determined by measurement of the absorption of the reactant solution in the region 4100—4200 Å. The control cell was filled with nitric acid of strength equal to that of the reaction medium. The extinction coefficient of bromine was found by adding 5 ml. of a standard solution of bromine (0.098M) to 495 ml. of nitric acid of suitable concentration and measuring the absorption of the solution. This solution was stable for more than 2 hr. In the region 4100—4200 Å, the absorption due to bromine is near its maximum and that due to nitrous acid (which is present in the reactant solution) is negligibly small.

Kinetic Experiments.—In order to prevent loss of gases and to exclude the effect of light, each sample in kinetic runs was taken from a completely filled brown-glass stoppered bottle. It is, of course, essential that the initial concentrations of all entities should be the same for all samples in one run, and since the required initial concentration of nitrous acid is very small (approx. $5 \times 10^{-6}N$) it is extremely difficult to ensure this if each sample is prepared separately. The reaction mixture was therefore prepared at 25° in a 250 ml. flask, by mixing calculated volumes of nitric acid, sodium or potassium bromide solution, and sodium nitrite solution, and diluting the whole to the mark with water. The reaction mixture was then poured quickly into small brown-glass stoppered bottles, completely filling each bottle. After suitable intervals 5 or 10 ml. samples were taken from the brown stoppered flasks and added to a slight excess of cooled sodium hydroxide solution, and the resultant solution was made up to a standard volume.

The colorimetric determination of nitrite was carried out on a suitable aliquot part of the solution.

In the experiments in which bromine was also measured, some of the reactant solution was poured into a stoppered cell and its absorption at 4100—4200 Å was measured immediately.

For the experiments in which $[NO_3^-]$ is varied at constant $[H^+]$ and constant ionic strength, and those in which $[H^+]$ is varied at constant $[NO_3^-]$ and constant ionic strength, the media were prepared by mixing calculated quantities of the appropriate acids and salts.

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¹⁰ Walker and Chadwick, *Ind. Eng. Chem.*, 1947, **39**, 974.

¹¹ Shinn, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 33.

¹² Kershaw and Chamberlin, *ibid.*, 1942, **14**, 312.