Kinetics of Oxidation of Hydrobromic Acid by Nitric Acid in the Presence of Nitrous Acid

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The rate of formation of bromine on treating nitric acid with hydrobromic acid has been investigated at 2, 25, and 50 °C. The order of reaction is 1·5 with respect to nitrous acid and between 1 and 2 with respect to bromide ion. The rate is strongly dependent on acid and neutral salt concentrations, but the influence of nitrate-ion concentration is small. A proposed mechanism, in accord with the data, is based on fast equilibria forming an intermediate which reacts further in a slow step. The equilibria are reversed by high water concentrations; cations, by hydration, reduce the water concentration and increase the rate. Hydration numbers of salts can be calculated from this increase in rate.

ONE of the oldest catalytic processes in the chemical industry is the lead-chamber oxidation of sulphur dioxide to sulphuric acid. The oxidation of bromide to bromine in the presence of nitric acid is a similar process which has never been used in practice (a plant producing chlorine is in operation [1]), although patents for the manufacture of bromine by this route have been issued.[2,3] It was thought worthwhile to reinvestigate

$$2HBr + HNO_3 \longrightarrow Br_2 + H_2O + HNO_2 \quad (1)$$

this reaction [equation (1)] which has some interesting theoretical features, being both autocatalytic (the nitrous acid produced increases the rate) and having a negative order with respect to one of the reactants over a wide range of concentration. It is known [4] that the reaction does not proceed when the nitric acid is pure and when the nitrous acid produced is destroyed, the reaction ceases. This provided a relatively easy method for following the reaction.

EXPERIMENTAL

A mixture of nitrous and hydrobromic acids was added to outgassed nitric acid and the reaction was allowed to

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[1] H. F. Johnstone, *Chem. Eng. Progr.*, 1948, **44**, 657.

[2] J. Kenat and Dead Sea Works Ltd., Israel P. 23,817/1965.

[3] J. Kenat, U.S.P. 3,437,444/1969.

[4] J. V. L. Longstaff, *J. Chem. Soc.*, 1957, 3488.

proceed for the desired time. It was then quenched by injection of an excess of sulphamic acid, equation (2).

$$HNO_2 + NH_2SO_3H \longrightarrow N_2 + H_2SO_4 + H_2O \quad (2)$$

This reaction is instantaneous, elementary bromine does not interfere, and the product solution can be titrated with thiosulphate for bromine, or the nitrogen evolved measured. Experiments were carried out at 2, 25, and 50 °C. The nitric and hydrobromic acid concentrations used were sufficiently high to ensure virtual constancy during a run. The volume of the gas phase was kept at less than one tenth of that of the liquid.

RESULTS

It was found that the rate of production of bromine was proportional to nitrous acid concentration (order 1·5),

$$d[Br_2]/dt = k[HNO_2]^{\frac{3}{2}} \quad (3)$$

confirming previous work[4] carried out by another method. This is illustrated by Figures 1—3 which present integral kinetic curves for runs at different temperatures. The dependence of the rate on bromide-ion concentration was linear at high acidity as reported previously,[4] but at low acid concentration became second order (Table 1). This change in the order was not due to varying Na^+ concentrations as can be seen from some experiments with added NaCl.

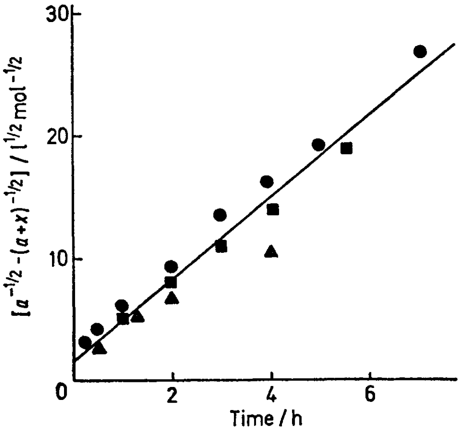

FIGURE 1 Integral rate relation for formation of bromine at 2 °C. Initial concentration of nitrous acid (10^6a/M): (●), 240·4; (▲), 480·8; (■), 961·6. Concentration of bromine produced (x); $[HNO_3]$ = 3·87M; $[Br^-]$ = 0·023N

Table 2 shows the effect of acid concentration. It may be seen that at low acid concentrations the order of reaction with respect to $[H^+]$ is 2, but rises above 6 at high concentrations. When the logarithm of the initial rate is plotted against the Hammett acidity function $-H_0$, the slope of the straight line obtained by least squares is 2·25 at 2, 2·04 at 25, and 2·29 at 50 °C, *i.e. ca.* 2·2. The Hammett functions for this calculation were obtained from the weighted average of the function for hydrochloric and nitric acids as reported by Long and Paul.[5]

When different chloride salts were added the rate of formation of bromine was increased considerably. On varying the cation at constant $[Cl^-]$ it was apparent that this effect was due to the cation rather than to the chloride ion. Working under standard conditions, the addition of chloride salts (0·59N) increased the rate by 7, 38, 79, 61, and 118% for K^+, Na^+, Li^+, Ca^{2+}, and Mg^{2+} respectively.

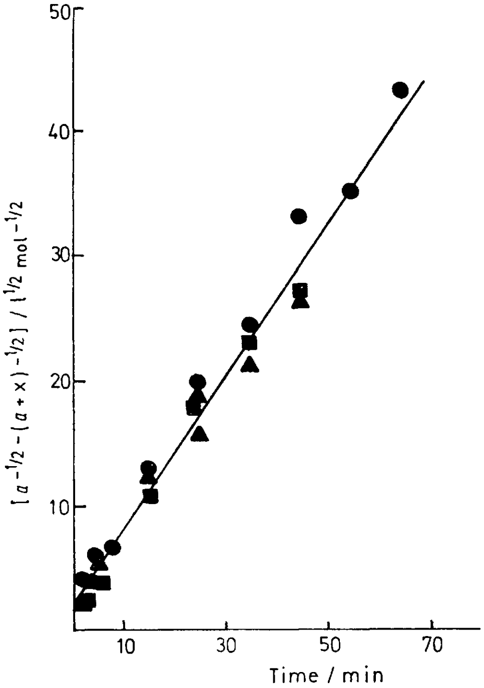

FIGURE 2 Integral rate relation for formation of bromine at 25 °C. For relevant concentrations see Figure 1

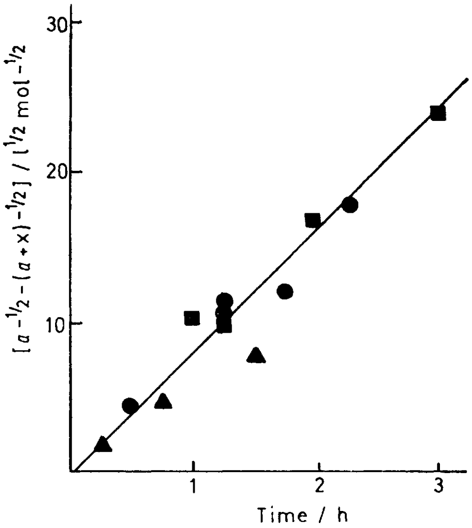

FIGURE 3 Integral rate relation for formation of bromine at 50 °C. Initial concentration of nitrous acid (10^6a/M): (■), 120·2; (●), 240·4; (▲), 480·8. Concentration of bromine produced (x); $[HNO_3]$ = 1·0M; $[Br^-]$ = 0·1M

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[5] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

TABLE 1

Influence of bromide concentration on the rate of reaction

t/°C	[HNO$_3$] M	[NaBr] M	10^6[HNO$_2$]$_0$ M	[NaCl] M	Initial rate micromol l^{-1} h^{-1}	Partial order in [Br$^-$]
2	2·0	0·0348	480	0·035	3·2	1·6
	2·0	0·070	480		10·1	
	4·0	0·035	480	0·035	272	0·9
	4·0	0·070	480		488	
25	1·0	0·200	480	0·200	48·3	1·3
	1·0	0·400	480		117·4	
	2·0	0·100	480	0·300	279	1·2
	2·0	0·400	480		1532	
	2·0	0·017	240	0·017	8·6	1·2
	2·0	0·035	240		21·0	
	4·0	0·009	240		295	1·1
	4·0	0·017	240		583	
	4·0	0·035	240		1394	1·1
	4·0	0·017	240	0·017	647	
50	0·5	0·100	960	[a]	75	2·2
	0·5	0·200	960	[a]	348	
	0·5	0·237	480	0·237 [b]	216	1·8
	0·5	0·474	480	[b]	751	
	1·0	0·095	480	0·142	158	1·9
	1·0	0·237	480		920	
	1·0	0·237	480		920	1·8
	1·0	0·095	480		172	
	2·0	0·050	480		913	1·2
	2·0	0·100	480		2184	

[a] [NaNO$_3$] = 1·0M. [b] [NaNO$_3$] = 0·5M.

TABLE 2

Influence of acidity on the rate of reaction

t/°C	[H$^+$] M	[NO$_3^-$] M	[NaBr] M	10^6[HNO$_2$]$_0$ M	[Cl$^-$] M	Initial rate micromol l^{-1} h^{-1}	Partial order in [H$^+$]
2	3·27	3·87	0·023	240		10·4	
	3·87	3·87	0·023	240		25·3	5·6
	4·47	3·87	0·023	240	0·6	76·8	7·3
	5·07	3·87	0·023	240	1·2	155·8	5·6
25	2·00	2·00	0·023	240		10	
	3·00	2·00	0·023	240	1·0	76	5·0
	4·00	2·00	0·023	240	2·0	348	5·3
	5·00	2·00	0·023	240	3·0	1200	5·6
50	0·25	1·00	0·474	480		279	2·0
	0·50	1·00	0·474	480		1068	
	0·50	1·00	0·237	480		200	2·2
	1·00	1·00	0·237	480		920	
	1·00	1·00	0·100	120		30	3·2
	2·00	2·00	0·100	120		272	
	3·00	1·00	0·0035	240	2·0	186	6·2
	4·00	1·00	0·0035	240	3·0	1116	

The rate is, therefore, mainly dependent on the concentrations of H$^+$, HNO$_2$, Br$^-$, and added metal cation. The influence of nitrate-ion concentration was surprisingly small; indeed, addition of sodium nitrate (1·84M) increased the initial rate of reaction from 25 to 83 micromol l^{-1} h^{-1}, whilst an equivalent amount of sodium chloride increased the rate from 25 to 91 micromol l^{-1} h^{-1}. Similar effects were also observed by Longstaff [4] using sodium perchlorate and nitrate respectively.

When the reaction was carried out under an atmosphere of oxygen the rate was increased by 10%. Added bromine also increased the rate for the forward reaction somewhat.

DISCUSSION

The results show three features of particular interest: the accelerating effect of the reaction products on the forward rate of reaction, that of neutral salts, and the very high dependence on the acidity. Since water is produced in the reaction, it seems reasonable to trace the effect of the cation to its influence on the water concentration; the cations tested are known to be hydrated and the more they are hydrated the smaller the concentration of free water. Indeed, the acceleration of rate increased from K$^+$ through Na$^+$, Li$^+$,

Ca^{2+} to Mg^{2+}, for the same cation concentration, as would be expected from the known hydration behaviour which increases in the same order.[6] The H^+ would then be doubly effective in accelerating the reaction, as a reactant and as a water acceptor causing the equilibria preceding the rate-determining step to shift to the right.

Considering the major factors influencing the rate, the following mechanism for the reaction can be proposed:

$$HNO_2 + HBr \xrightleftharpoons{K_1} NOBr + H_2O \tag{4}$$

$$HNO_2 + HNO_3 \xrightleftharpoons{K_2} N_2O_4 + H_2O \tag{5}$$

$$N_2O_4 \xrightleftharpoons{K_3} 2NO_2 \tag{6}$$

$$NO_2 + NOBr \xrightleftharpoons{K_4} N_2O_3Br \tag{7}$$

$$N_2O_3Br + H^+ \xrightarrow[k_5]{\text{slow}} HNO_2 + NO + Br^+ \tag{8}$$

$$Br^+ + Br^- \xrightarrow[k_6]{\text{fast}} Br_2 \tag{9}$$

$$N_2O_3Br + Br^- \xrightarrow[k_7]{\text{slow}} Br_2 + NO + NO_2^- \tag{10}$$

The compound N_2O_3Br has been suggested previously[4] as an intermediate in the reaction sequence. It has, to the best of our knowledge, not been isolated, but its existence is not unreasonable. Alternatively, in reaction (7) nitryl bromide may be formed as in equation (11). In spite of many attempts, nitryl bromide has

$$NO_2 + NOBr \rightleftharpoons NO_2Br + NO \tag{11}$$

never been prepared, though the analogous chloride is well known. If step (11) is correct, the steady-state concentration of nitryl bromide will be determined by the rate of reoxidation of nitric oxide and it is difficult to envisage this being dependent on the bromide concentration. Of course, the nitric oxide must be reoxidized for the process to be autocatalytic but, as this occurs with a high rate constant[7] after steps (8) and (10) with low rate constants, the reoxidation need not be rate determining. Reaction (5) has been formulated here as giving the dimer N_2O_4; as regards the kinetics of the reaction it is immaterial whether the monomer or the dimer is formed, providing equilibrium is reached.

From measurements on the hydrolysis of nitrosyl bromide, carried out in connection with another study, we know that equilibrium (4) lies mainly to the left. This is also confirmed from the equilibrium constant of this reaction, as determined by Schmid, Pinz, and Ruess.[8] At 0 °C, $1/K_1 = ([HNO_2]/[NOBr])(a_{H^+}a_{Br^-}/a_{H_2O}) = 44{\cdot}6$ mol^2 l^{-2} and the ratio $[HNO_2]:[NOBr]$ *ca.* 200 under the conditions of the present work. If, initially, it is assumed that under experimental conditions equilibria (4)—(6) lie mainly to the left, the concentrations of NOBr and NO_2 in solution will be given by equations (12) and (13), and, therefore, the steady-state concentration of the stipulated intermediate N_2O_3Br by (14). If the first term in the denominator

$$[NOBr] = K_1[HNO_2][H^+,nH_2O][Br^-][H_2O]^{-(n+1)} \tag{12}$$

$$[NO_2]^2 = K_2K_3[HNO_2][H^+,nH_2O][NO_3^-][H_2O]^{-(n+1)} \tag{13}$$

$$[N_2O_3Br] = \frac{k_4K_1(K_2K_3)^{\frac{1}{2}}[HNO_2]^{\frac{3}{2}}[H^+,nH_2O]^{\frac{3}{2}}[Br^-][NO_3]^{\frac{1}{2}}[H_2O]^{-\frac{3}{2}(n+1)}}{k_{-4} + k_5[H^+,nH_2O] + k_7[Br^-]} \tag{14}$$

of equation (14) is much greater than the second and third terms, the steady-state concentration of N_2O_3Br will be at its equilibrium value and the rate of reaction according to the above mechanism will become:

$$\text{Rate} = K_1(K_2K_3)^{\frac{1}{2}}K_4[HNO_2]^{\frac{3}{2}}[NO_3^-]^{\frac{1}{2}}[H_2O]^{\frac{3}{2}(n+1)} [H,^+nH_2O]^{\frac{3}{2}}[Br^-](k_5[H^+,nH_2O] + k_7[Br^-]) \tag{15}$$

This relation fits the experimental facts in so far as it calls for a partial order of 1·5 with respect to HNO_2, some high negative order with respect to water, an order between 1·5 and 2·5 with respect to H^+, and from 2 to 1 with respect to Br^-, the former value being approached at high $[Br^-]$ and low $[H^+]$ and the latter at low $[Br^-]$ and high $[H^+]$.

The hydration number of the H^+ ion has been investigated to a considerable extent and is now generally accepted to be 4.[9] At high acidity the dependence of the initial rate on the H^+ concentration (all other factors being kept constant) should then be given by equation (16). The total concentration of water c_w was

$$\text{Initial rate} = \alpha[H^+,4H_2O]^{\frac{5}{2}}[H_2O]^{\frac{15}{2}} \tag{16}$$

$$\text{where } \alpha = K_1(K_2K_3)^{\frac{1}{2}}K_4k_5[HNO_2]^{\frac{3}{2}}[NO_3^-]^{\frac{1}{2}}[Br^-]$$

calculated from the experimentally determined weight of solution (1 l) and the concentration of free water is given by equation (17), where n is the hydration number

$$c_f = c_w - 4[H^+] - n[\text{Salt}] \tag{17}$$

of the salt. The initial rate is then expressed by (18).

$$\text{Initial rate} = \alpha[H^+]^{\frac{5}{2}}[c_f]^{-\frac{15}{2}} \tag{18}$$

As seen from Figure 4, the initial rate is indeed pro-

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[6] R. H. Stokes and R. A. Robinson, 'Electrolytic Solutions,' Butterworths, London, 1959.

[7] G. Schmid and G. Bähr, *Z. phys. Chem.* (*Frankfurt*), 1964, **41**, 8.

[8] H. Schmid and M. G. Fouad, *Monatsh.*, 1957, **88**, 631.

[9] E. Wicke, M. Eigen, and T. Ackermann, *Z. phys. Chem.* (*Frankfurt*), 1954, **1**, 340.

portional to this expression up to $[H^+]^{\frac{5}{2}}c_f^{-\frac{15}{2}} = 3 \times 10^{-10}$ which corresponds to $[H^+] = 4{\cdot}5\text{M}$ and $c_f = 30\text{M}$. The temperature dependence is given by an Arrhenius expression setting A *ca.* 20 kcal mol^{-1}.

Results dealing with the influence of the free-water concentration on the initial rate of formation of bromine at 2 °C are summarized in Table 3. In column 6, data obtained from equation (16) are tabulated for $K_1(K_2K_3)^{\frac{1}{2}}K_4k_5 = 1{\cdot}45 \times 10^{12}$. Except for the numbers in italics the calculated results are in good agreement with the experimental data. This is particularly satisfying since only one free parameter has been adjusted for the experiments without salt addition and for those with added salt the second parameter, the hydration number n of the salt, is reasonable when compared with data obtained by other authors from measurements of activities.[6,10,11] At low free-water concentrations, however, the experimental rates were lower than would be expected. The deviation may be due to equilibria (5) and (6) being shifted markedly to the right at low free-water concentrations. This approach received additional support through the odd behaviour on addition of nitrate ion. The latter would be expected to increase the rate of reaction according to a half-order law. In fact, its effect was negligible or even negative over a wide range of concentration though, of course, in the complete absence of nitrate ion, the reaction did not proceed. From the proposed mechanism it is to be expected that the addition of nitrate ion will increase the concentrations of NO_2 and N_2O_4 and reduce those of HNO_2 and NOBr, possibly to such an extent that the resultant rate, depending on the product $[NO_2][NOBr]$, is not only not increased but even reduced. The three simultaneous equations for fulfilling equilibria (4)—(6) can be solved and thence, for high $[H^+]$, the initial rate $k_5K_4[H^+][NO_2][NOBr]$ calculated. In column 7 of Table 3 results are listed setting $K_1K_4k_5 = 0{\cdot}97 \times 10^{12}$, $K_2 = 4 \times 10^5$, and $K_3 = 10^{-5}$.

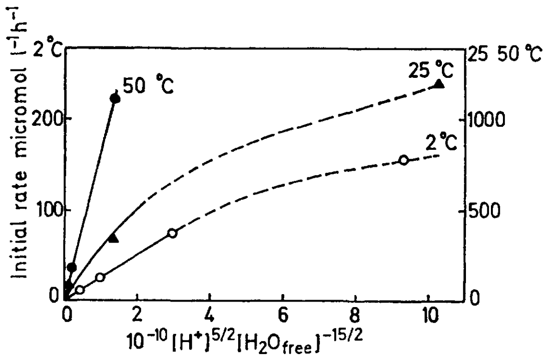

FIGURE 4 Plot of initial rate of reaction against $[H^+]^{\frac{5}{2}}$ $[H_2O]^{-\frac{15}{2}}$ for different temperatures. Initial concentration of $HNO_2 = 240{\cdot}4 \times 10^{-6}\text{M}$; bromide-ion concentration = 0·023M (at 2 and 25 °C), 0·0035M (at 50 °C); nitrate-ion concentration = 3·87M (at 2 °C), 2·0M (at 25 and 50 °C)

The calculations are not sensitive to changes in K_3; setting $K_3 = 10^{-7}$ with the appropriate change in $K_1K_4k_5$ gives no worse fit. The constant K_3 has actually been measured in chloroform solution at 8·2 °C to be $1{\cdot}56 \times 10^{-5}$ mol l^{-1}.[12] The use of one more free parameter accounts for the shift of equilibrium (5) to the right due to the changes in water, proton, and nitrate-ion concentrations. It may be seen that this refinement explains the deviations previously observed at low free-water concentrations. Since the activities of the various substances are no doubt influenced by the high concentrations of the constituents as well as by the binding of water, the proposed mechanism is able to describe the experimental data with a remarkable degree of accuracy.

TABLE 3

Measured and calculated initial rates of reaction. $[HNO_2]_0 = 240{\cdot}4 \times 10^{-6}\text{M}$, $[H^+] = 3{\cdot}87\text{M}$ unless otherwise stated

Salt	[Salt] / M	n	c_f / M	Initial rate / micromol l^{-1} h^{-1} Measured	Calculated [f]	
a			35·65	10·4	10·8	12·3
			33·67	25·3	25·4	26·6
b			30·65	76·8	73·6	65·5
c			27·49	155·8	*228·0*	152·4
d			33·67	76·9	71·9	76·3
e			33·67	217·6	202·9	218·2
$MgCl_2$	0·197	10	31·24	47·0	44·5	42·6
$MgCl_2$	0·295	10	30·06	56·3	59·4	53·6
$MgCl_2$	0·495	10	27·70	84·2	*109·6*	85·0
$MgCl_2$	2·014	6	18·18	359·3	*2579·1*	376·6
$CaCl_2$	0·195	6	32·28	35·3	34·8	34·8
$CaCl_2$	0·295	6	31·57	41·3	41·3	39·9
LiCl	0·390	4	31·72	40·7	39·7	38·6
LiCl	0·580	4	30·70	45·7	50·7	47·3
NaCl	0·390	2·5	32·33	35·5	34·4	34·4
NaCl	0·580	2·5	31·67	35·5	40·1	39·1
NaCl	1·84	2·5	27·13	91·4	*128·1*	94·8
KCl	0·380	0	33·08	27·6	29·0	29·8
KCl	0·570	0	32·79	27·6	30·9	31·5
$NaNO_3$	1·84	2·5	27·13	82·7	*155·5*	93·8

[a] $[H^+] = 3{\cdot}27\text{M}$. [b] $[H^+] = 4{\cdot}47\text{M}$. [c] $[H^+] = 5{\cdot}07\text{M}$. [d] $[HNO_2]_0 = 480{\cdot}8 \times 10^{-6}\text{M}$. [e] $[HNO_2]_0 = 961{\cdot}6 \times 10^{-6}\text{M}$. [f] Values in the first column are calculated from equation (16), in the second from $k_5K_4[H^+][NO_2][NOBr]$ (see text).

If, instead of the H^+ concentration, the Hammett acidity function h_0 is considered, it must be borne in mind that this function includes the hydration effect of the acid. The Hammett type equilibrium will now be (19), whereupon $a_{H^+} \propto h_0(a_{H_2O})^4$ is obtained. Moreover, if the main effect on the activity coefficient of water is due to the decrease of free water concentration, then $\alpha_{H_2O} = c_f/[H_2O]_{pure}$ and $a_{H^+} \propto h_0c_f^4$. Substituting a_{H^+} for $[H^+]$ in equation (18), the initial rate must therefore be proportional to $(h_0c_f)^{\frac{5}{2}}$ to be consistent, as

$$H^+,4H_2O + B \rightleftharpoons BH^+ + 4H_2O \qquad (19)$$

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[10] J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1971, **71**, 627.

[11] E. Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

[12] J. T. Cundall, *J. Chem. Soc.*, 1891, **59**, 1076.

indeed it is. The use of $[H^+]$ instead of h_0 is therefore justified.

There remain a few finer points to be explained. The presence of oxygen causes a slight increase in the reaction rate under certain experimental conditions. It may be noted that in reactions (8) and (10) nitric oxide is produced which is reoxidized by nitrogen dioxide; in the presence of oxygen an additional route for oxidation is possible, and the steady-state concentration of nitric oxide decreases. Apparently, reaction (8) is somewhat reversible, and the slight back reaction is still further retarded, resulting in a small increase in the rate of production of bromine. If this is the case, addition of bromine might be expected to increase the back reaction and to decrease the rate of formation of bromine. While this is true for the addition of large amounts of bromine where the equilibrium of the overall reaction is approached, small amounts appear to react with nitric oxide to form nitrosyl bromide, increasing the rate of formation of bromine slightly.

It is interesting to compare the present results with those for the oxidation of thiocyanate by nitric acid.[13] Superficially the two reactions are similar, both being autocatalytic because of the formation of nitrous acid. However the rate laws are different; in the case of thiocyanate the rate is first order with respect to both nitrous acid and nitrate, suggesting that the oxidizing species is dinitrogen tetroxide. In terms of the present system, the rate-determining step for formation of bromine would be the production of HOBr from N_2O_4 and HBr.

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[2/847 *Received, 17th April, 1972*]

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[13] M. N. Hughes, E. D. Phillips, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.* (*A*), 1969, 1148.