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Nitrogen Peroxide as a Catalyst for the Autoxidation of Hydrobromic Acid

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The kinetics of a reaction in which NO_2 acts as an O_2 carrier for the autoxidation of HBr in a closed system, is described. It is suggested that the slow step occurs in the liquid phase by way of reaction between two intermediates, one soluble and the other slightly soluble. Direct and spectroscopic evidence is given as to the nature of the intermediates. The reaction rate is proportional to the square of the [NO] introduced into the system, and a more complex function of $[O_2]$ and [HBr]. It is suggested that the ion pair HBr plays an important role in the reaction. The effect of temperature is described and a reaction mechanism given. Below an O_2 partial pressure of 0.2 atm., deactivation of the catalyst occurs. It may be reactivated by raising the O_2 partial pressure.

The use of NO_2 as an oxygen carrier in the gas phase is well known in the case of the Chamber Process for the manufacture of H_2SO_4. Although this reaction has been extensively studied, its mechanism is still in some doubt.

Some semi-quantitative work on the use of nitrite as a catalyst for the autoxidation of aqueous HI was carried out by Lombard.[2] He came to the conclusion that the active species was N_2O_3 formed in the gas phase.

The use of NO_2 for the production of bromine was proposed in 1872[3] whilst a patent using HNO_3 as an intermediate was taken out by Grebe, Bauman and Robinson.[4]

The present work was initiated after an observation that a strongly acid HBr solution containing a trace of nitrate is oxidized to Br_2 when left in contact with O_2. A preliminary study of this reaction showed that it was autocatalytic.

Nitrites were more effective than nitrates in promoting the reaction. It was concluded that at least part of the catalyst was a gaseous species formed from the nitrite or nitrate.

Experiments were then carried out using a closed system and introducing a known amount of NO into the oxygen containing gas phase; a rapid reaction ensued with the liberation of Br_2 and consumption of O_2. The following is an account of the results obtained in a study of this reaction.

Experimental

The kinetics could not be conveniently studied by sampling since the reaction was thought to take place in the gas phase. A separate run was therefore carried out for each point on the kinetic curves. The $[Br_2]$ was estimated by titration.

The reaction vessel, which could be isolated from the rest of the system by a tap A, was a 293-cc. round-bottomed Pyrex flask attached to a vertical shaker. The flask was connected to an Hg manometer, O_2 reservoir and pumping line by a cone, socket and polyvinyl chloride tubing. All taps were greased with Silicone grease.

The whole apparatus was immersed in a water thermostat maintained constant to ±0.1°.

The system was pumped out, gas (O_2, or O_2 and N_2) let in up to the required pressure (total pressure = atmospheric) and a known volume of solution and NO introduced *via* a side-arm and tap on the flask. The run was timed from the commencement of shaking.

From time to time tap A was opened and O_2 introduced from the reservoir in order to maintain the total pressure at atmospheric ±0.5 cm. Variations in partial pressure of O_2 due to the increase in partial pressure of Br_2 vapor would not be greater than 4% at the highest $[Br_2]$.

At the end of the run the solution was transferred to a volumetric flask, the reaction vessel washed with dilute HBr and the washings transferred to the flask. The Br_2 was estimated by titrating the I_2 liberated on addition of KI with standard $Na_2S_2O_3$.

In several runs duplicate titrations using sodium arsenite were carried out. Complete agreement was obtained. Any nitrite and nitrate present did not interfere, therefore, with the $Na_2S_2O_3$ titrations.[5]

The Continuous Flow Apparatus.—Fresh solution was run continuously into the reaction vessel (6 cm. diam., 30 cm. length) at a constant rate, on to a sintered glass disc (3 cm. diam.) rotated externally by a magnet. The solution was thrown on to the ground glass walls of the reaction cell and fell as a thin film. The inlet and outlet flow of solution was the same so that no accumulation of solution occurred in the reaction vessel.

A constant pressure was maintained in the apparatus by restoring the O_2 pressure as fast as it fell. A solution seal on the outlet prevented escape or contamination of the gas phase. The apparatus was immersed in a water thermostat at 50 ± 0.1°.

Absorption spectra were obtained by using a Beckman DU quartz spectrophotometer.

The chemicals used were of A.R. Quality. The NO was prepared by the reaction between $FeSO_4$, H_2SO_4 and $NaNO_2$ in the apparatus as described by Blanchard.[6]

The pure O_2 used was scrubbed with acidified $KMnO_4$.

Results and Discussion

1. **Shaking Speed.**—Up to 100 cycles/min. the rate of Br_2 formation was independent of the shaking speed. But at 200 cycles/min. where the surface of the liquid was slightly broken, the rate increased rapidly becoming independent of shaking speed above 270 cycles/min. Subsequent experiments were carried out at speeds greater than 600 cycles/min.

2. **The Effect of Varying [HBr].**—The result of plotting the $[Br_2]$ against time for various initial [HBr] is shown in Fig. 1. There is effectively no reaction below 1.0 *N*. At the higher initial $[HBr]_i$ the initial rate of Br_2 formation is independent of [HBr]. The curves are initially linear and the time at which they deviate from linearity decreases with decreasing initial [HBr].

3. **Partial Pressure of O_2.**—Figure 2 shows the effect of varying the $[O_2]$ on the kinetic curves. It shows that the initial rate of Br_2 formation is independent of the O_2 partial pressure. Down to 0.20 atm. relatively small deviations from the kinetic curve at 1 atm. occur as the reaction proceeds. At partial pressures lower than 0.20 atm. deviations are much more marked.

In the partial pressure range 1–0.20 atm. a second sample of HBr solution was introduced toward

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[1] County Laboratories, Stanmore, Middlesex, England.

[2] M. Lombard, *Bull. soc. chim. France*, **31**, 161 (1922).

[3] A. Morris, Brit. Patent 3448.

[4] J. J. Grebe, W. C. Bauman and H. A. Robinson, U. S. Patent 2,371,886.

[5] R. O. Griffith and R. Irving, *Trans. Faraday Soc.*, **45**, 305 (1949).

[6] A. A. Blanchard, "Inorganic Syntheses," Vol. II, Editor W. C. Fernelius, McGraw-Hill Book Co., New York, N. Y., 1946, p. 126.

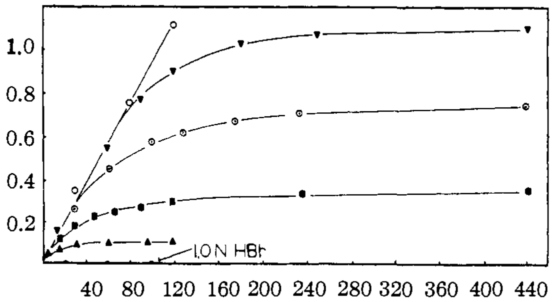

Fig. 1.—The relationship between [Br_2] formed after a given time for various initial [HBr] (50°, 76 cm., 20 cc. soln. 273 cc. O_2, [NO] = 9.1 cc. (18°)/273 cc. O_2): ○, 5 *N* HBr; ▼, 3.0 *N* HBr; ⊙, 2.5 *N* HBr; ■, 1.92 *N* HBr; ▲, 1.5 *N* HBr; ▴, 1.0 *N* HBr.

the end of the reaction, and the reaction allowed to proceed for a further length of time. The [Br_2] at the end of this time agreed with the value calculated from the original kinetic curve on the assumption that no catalyst was spent (Table I, A, Biii.).

TABLE I

	Part. press. O_2 (atm.)	Addn, time of 20 cc. soln. (mins.)	Total time (min.)	[Br_2]N immed. after addn.	Calcd.	[Br_2]N. Obsd.
A	50° [NO] = 11.5 cc./273 cc.			20 cc. 1.92 *N* HBr		2.7 *N* HCl soln./273 cc.
	1.0	150	255	0.65	0.98	1.04
		50°, 9.2 cc. NO/273 cc.			20 cc. 3 *N* HBr sln./273 cc.	
B(i)	0.1	110	262	.20	.35	0.19 complete deactivn.
(ii)	.15	242	332	.37	.52	.45 incomplete deactivn.
(iii)	.20	242	322	.47	.63	.62
C	Time of O_2 part. press. increase					no deactivn.
	.1	120	180	.4	.7	.73 complete reactivn.

Below an O_2 partial pressure of 0.15 atm. the fall in rate was much faster than that indicated by the kinetic curves at the higher [O_2] (Fig. 2D,G.). This suggested that the catalyst was deactivated. Confirmation was obtained when no further reaction occurred on introducing a further sample of HBr solution (Table I, Bi).

At partial pressures between 0.20 and 0.15 atm. only partial deactivation had taken place.

The activity of the catalyst was restored by increasing the O_2 pressure to 0.20 atm. or above (Table IC).

4. $[NO]_I$ ([NO] Introduced into System).—When the slope of the initial linear portion of the kinetic curve is plotted against $[NO]_I^{\frac{1}{2}}$, a linear relationship is obtained (Fig. 3).

5. Location of the Slow Step.—The NO introduced into the system is rapidly converted to NO_2 but it is apparent from the results that the reaction is by no means simple. It is not at all clear in which phase the slow step of the reaction occurs. The following discussion examines this problem in some detail.

(A) The Effect of Surface Area.—An experiment using a reaction vessel containing glass beads but the same gas volume (293 cc.), as before showed that increase in surface area had little effect on the reaction.

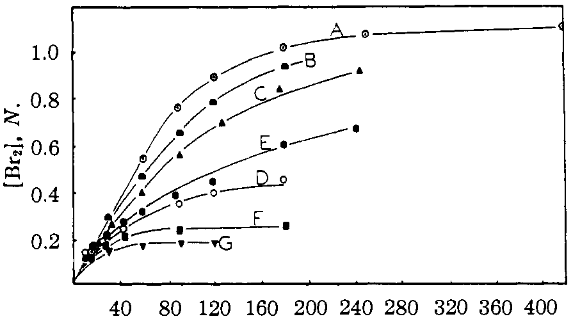

Fig. 2.—[Br_2] as a function of time for various [O_2] and temperatures (20 cc. 3 *N* HBr, 9.1 cc. NO (18°)/273 cc. O_2, 76 cm.): A, [O_2] = 1.0 atm.; B, [O_2] = 0.5 atm.; C, [O_2] = 0.2 atm.; D, [O_2] = 0.1 atm., 50°; E, [O_2] = 0.1 atm., 40°; F, [O_2] = 0.1 atm., 60°; G, [O_2] = 0.05 atm., 50°. Curves A, B and E, no deactivation at 50°; E, partial deactivation; D, F and G, complete deactivation.

A similar result was obtained by the addition of glass powder and the use of a double surfaced reaction vessel. The surface of the reaction vessel does not therefore, initiate or take part in the reaction.

(B).—The importance of the gas phase was clearly shown by quickly transferring the reactant solution to a reaction vessel containing O_2 only. The [Br_2] at the end corresponded to the [Br_2] at the time of transfer (Table I). The slight decrease was due to the Br_2 left in the gas phase of the first reaction vessel.

TABLE II

50°, [NO] = 9.1 cc./273 cc. O_2 at 18°, 76 cm., 20 cc. of 1.92 *N* HBr, 2.7 *N* HCl.

[Br_2] at time of transfer (30 min.)	= 0.30 *N*
[Br_2] 60 min. after transfer	= .24 *N*
[Br_2] at time of transfer (60 min.)	= .52 *N*
[Br_2] 90 min. after transfer	= .47 *N*

It may be concluded from these experiments that the gas phase intermediate has a low solubility in the solutions used, otherwise further reaction might have been expected on transfer.

(C).—Some experiments using the continuous flow apparatus (see above) were carried out. Figure 4 shows the result of plotting [Br_2] against time at constant flow rate, the [Br_2] falls off very rapidly. At the point where velocity had fallen by more than 90%, the ratio [NO]/total solution used, was still greater than that used in the static systems. This fall in velocity could not therefore be due to removal of the slightly soluble gas phase intermediate. A soluble intermediate must therefore also be present.

Reaction occurred without fall in velocity when the same sample of solution was continuously cycled through the apparatus.

As a result of the experiments given under sections 3 and 5A,B,C, it is suggested that the slow step of the reaction occurs *via* two intermediates, (i) a slightly soluble intermediate and (ii) a soluble intermediate which could be in equilibrium with the gas phase. It is difficult to decide whether the

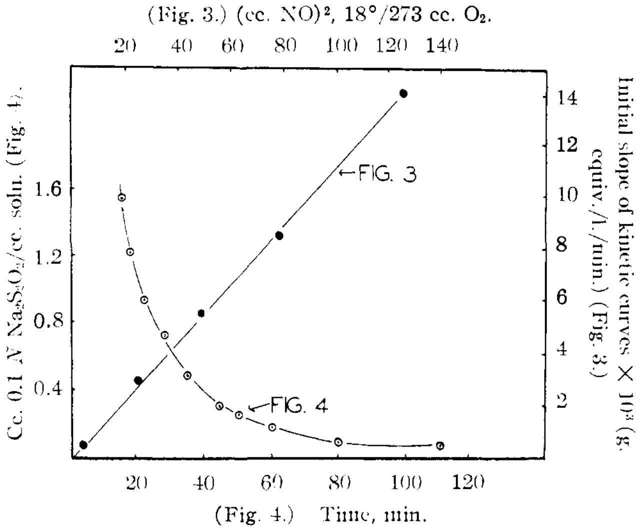

Fig. 3.—The linear relationship between the initial slope of the kinetic curves and $[NO]^2$ (20 cc. soln./273 cc. O_2) (for both Figs. 3 and 4, 1.92 *N* HBr, 3.0 *N* HCl, 50°, 76 cm.).

Fig. 4.—$[Br_2]$ plotted against time for the continuous flow system (flow rate = 6 cc./min., 150 cc. NO (18°) in 900 cc. O_2).

slow step actually takes place in the gas or solution phase or both. The further examination of these phases is described below.

(D) Examination of the Gas Phase.—Analysis showed that at the end of a run in which 150 cc. of NO and 170 cc. of solution (1.92 *N* HBr, 2.7 *N* HCl giving 1.2 *N* Br_2 at the end) were used, no elemental nitrogen was produced.

Solution of the soluble portion of the gas phase in KOH, followed by a Devarda analysis, showed that 8% of the nitrogen introduced into the system as NO remained in the gas phase.

In a similar experiment the gas phase was passed through a liquid air trap. An orange-brown solid condensed out. Most of it could be distilled from ice giving a reddish brown gas, the residue being pure bromine. The solid collected after distillation gave a brown liquid which boiled just below the melting point of ice.

The molecular weight of this intermediate, determined by measuring the vapor density, was about 120 whilst rational analysis showed that it contained 12% N_2 and 75% Br_2 which corresponds to nitrosyl bromide. The intermediate in the gas phase is thus nitrosyl bromide.

The amount of NOBr at the beginning and end of the run was found to correspond to 8% of nitrogen introduced as NO and was independent of the O_2 pressure. It thus seems clear that the relatively insoluble intermediate is NOBr. These results suggest that the NOBr and solution intermediate are formed by independent reactions, the rate of formation of the latter being 11–12 times the former.

(E) Examination of the Solution Phase.—The absorption spectrum of a solution, prepared by treating 20 cc. of 3 *N* HBr with 50 cc. of NO in a 293-cc. flask containing O_2 and shaking for 20 sec. at 18°, is shown in Fig. 5A. The shaking time did not influence the shape of the curve, so the equilibrium between the solution and gas is reached very rapidly. The spectrum of a Br_2 solution containing six times the $[Br_2]$ present in Fig. 5A is shown in Fig. 5B. There is a plateau at 620–660 mμ in curve A not exhibited by curve B. This suggests that the soluble intermediate is responsible for the plateau.

The initial optical density (O.D.) of the solution complex was found to be independent of $[O_2]$. This agrees with the fact that the initial reaction rate is independent of the $[O_2]$ and indicates that the formation of the solution intermediate is rapid.

A plot of O.D. against [HBr] is given in Fig. 6; above 1.0 *N* the concentration of the complex increases rapidly, becoming constant above about 2.5 *N*.

The linear relationship between the [NO] introduced into the system and O.D. (Fig. 7) is explained by the fact that the experiments were carried out in the limiting region of Fig. 6.

The initial velocities of the reaction at the various initial [HBr], follow the pattern of Fig. 6 very closely. Thus there is effectively no reaction below 1.0 *N*, the velocity rising rapidly above this concentration, becoming constant at about 2.5 *N*.

Each Br_2 formed in the reaction will effectively reduce the $[Br^-]$ by forming Br_3^-, under the conditions used[7]

$$\left(17 = \frac{[Br_3^-]}{[Br^-][Br_2]}\right)^6$$

Taking this into account, Table III shows the [HBr] at which the reaction effectively stops for the experiments given in Fig. 1. As to be expected from Fig. 6 these values are reasonably constant. They

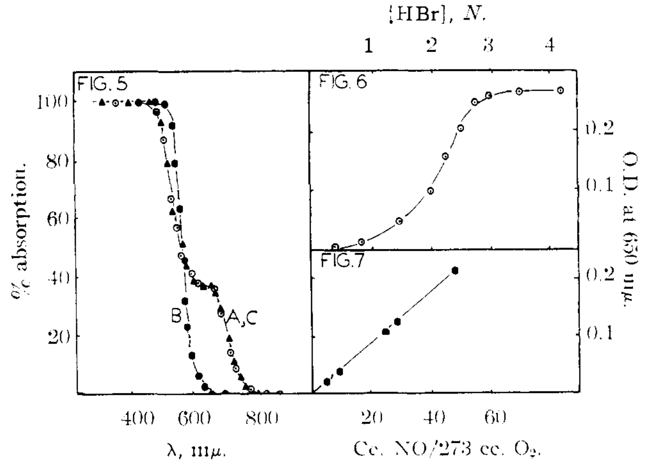

Fig. 5.—The absorption spectra of various solutions (at 18°, 76 cm.): (A), 50 cc. NO/273 cc. O_2, gas phase, 20 cc. 3 *N* HBr; (B), Br_2 in 3 *N* HBr, $[Br_2]$ six times that in (A); (C), 20 cc. 3 *N* HBr containing HNO_2 equivalent to the NO in (A).

Fig. 6.—The relationship between optical density and [HBr] (20 cc. soln., 50 cc. NO/273 cc. O_2, 18°, 76 cm.).

Fig. 7.—The optical density plotted against [NO] (20 cc. 2.5 *N* HBr, 18°, 76 cm.).

(7) R. D. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

are somewhat higher than expected (~1.0 *N*), probably because the results in Table III were obtained at 50°, whereas Fig. 6 was determined at 18°. (The spectrophotometer could not be used at 50°.)

TABLE III

$[HBr]_0$, *N*	3.00	2.50	1.92	1.50
$[HBr]_\infty$, *N*	1.30	1.36	1.39	1.34

The rapid rise in reaction velocity between 1.0 and 1.5 *N* HBr (Fig. 1) and the shape of Fig. 6 is reminiscent of the sudden and rapid rise in the autoxidation of Fe^{2+} in concentrated HCl (>4 *N*).[8] In the latter study it was concluded that associated HCl played an important role in the latter reaction. In the present case it is suggested that the reaction proceeds *via* a similar association of the HBr.

Figure 6 is very characteristic of a Mass Action Equilibrium depicting the formation of a complex. It is suggested that in the solution there are the equilibria

$$H^+ + Br^- \rightleftharpoons HBr$$ (this is probably ion pair formation rather than a true association)

$$HBr + X \rightleftharpoons HBrX$$

where X is a soluble nitrogen containing species formed rapidly on the introduction of the NO. Unfortunately it is not possible to test the application of the Law of Mass Action to Fig. 6 because activity data are lacking in the region required.

In order to identify X, the absorption spectra of standard solutions containing HBr and HNO_3 or HNO_2 corresponding to the previously determined distribution (see Section D) of the NO used, were examined. The solution containing the HNO_3 showed no spectrum corresponding to X, whilst the spectrum of the solution containing the HNO_2 (Fig. 5C) was identical with the corresponding solution prepared from NO (Fig. 5A). This result indicates that X is HNO_2 (in these strongly acid solutions there will be little NO_2^- present) and that the NO introduced into the system goes rapidly and exclusively to NOBr and HNO_2 rather than to NOBr, HNO_2 and HNO_3.

The active intermediate in solution thus seems to be formed *via* an equilibrium between HBr and HNO_2. However because of the uncertainty involved, this intermediate will be denoted by Z.

$$HNO_2 + HBr \rightleftharpoons Z$$

NOBr already has been shown to be the slightly soluble intermediate. It seems unlikely that the partial pressure of any other complex in solution formed by the interaction of HNO_2 and HBr will be significant. The slow step of the reaction probably occurs, therefore, in the solution phase.

6. The Kinetic Equation.—It is clear from the kinetic curves (Fig. 1) that the equation is not of a simple type. As a result of the previous discussion it is suggested that the slow step is the interaction of NOBr and Z, in which case the kinetic equation may be written as

$$-dc/dt = K[NOBr][Z]$$

where *c* is the analytical [HBr].

[NOBr] appears to be constant throughout the reaction (see Section D), whilst Z varies in a manner suggested by Fig. 6. At all the initial [HBr] ($[HBr]_0$) the NO introduced into the system ($[NO]_I$) is rapidly and completely converted into NOBr and HNO_2 by what appear to be independent reactions (see Section D). At the higher $[HBr]_0$, the HNO_2 will be rapidly and completely converted into Z, consequently [Z] and [NOBr] will each be proportional to $[NO]_I$. The initial rate at the higher activities will therefore vary as $[NO]_I^2$ (Fig. 3). As the reaction proceeds [Z], and therefore the rate, decreases in a manner depicted by Fig. 6 due to a change in the equilibrium

$$HNO_2 + HBr \rightleftharpoons Z$$

Although Fig. 6 was obtained at 18°, it is reasonable to suppose that the variation in [Z] (O.D.) with [HBr] will be similar at 50°. With its aid, the integration of the above differential equation was carried out graphically. A function $F \propto \int_c^{c_0} dc/[Z]$ was obtained, which when plotted against *t* gives a straight line through the origin for 3.0, 2.5 and 1.92 *N* HBr (Fig. 8). This seems to confirm the general validity of the equation over the whole of the run. At times greater than 200 min. the errors became very large due to the flattening of the kinetic curves.

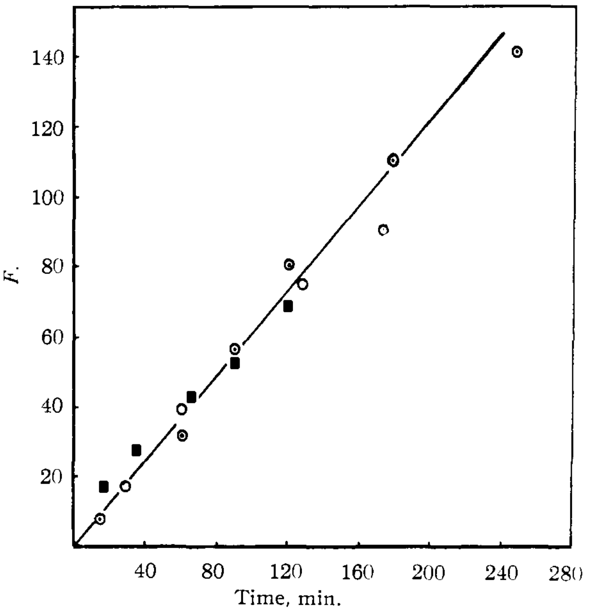

Fig. 8.—The linear relationship between *F* and time (20 cc. soln., 9.1 cc. NO (18°)/273 cc. O_2, 76 cm., 50°): ⊙, 3 *N* HBr; □, 2.5 *N*; ■, 1.92 *N* HBr.

Consider a solution whose [HBr] is just below that required for the autoxidation to occur. Then if the associated HBr is playing the part suggested above, the addition of salts and acids should give rise to the autoxidation by way of primary and secondary salt effects.

Figures 9 and 10 show the effect of adding varying amounts of LiCl, LiBr, $LiClO_4$, LiBr and Li_2SO_4. All except the latter have a marked effect in increasing the velocity of Br_2 formation. At the concentrations used, the salts which promote the reaction have activity coefficients >1 and would there-

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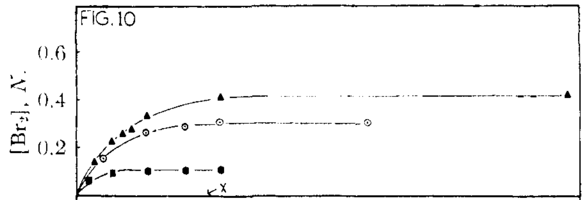
[8] A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

fore be expected to increase the activity of the HBr. The activity coefficient of the Li_2SO_4 at the concentrations used (up to 3.7 *N*) is $\ll 1$, consequently the activity of the HBr will be reduced. At high $[H_2SO_4]$ (>14 *N*) both primary and secondary salt effects promote the reaction. HCl promotes the reaction in a similar manner.



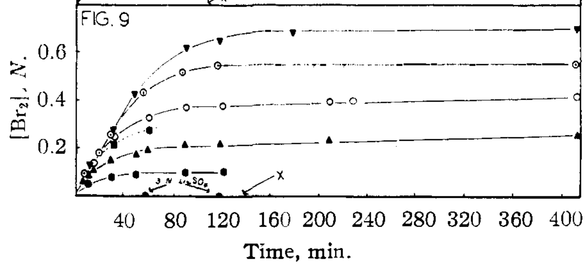


Fig. 9.—The effect of LiCl, $LiClO_4$ and Li_2SO_4 on the reaction rate (20 cc. *N* HBr, 9.1 cc. NO (18°)/273 cc. O_2) 50°, 76 cm.): ▼, 6 *N* LiCl; ⊙, 5 *N* LiCl; O, 4 *N* LiCl; ■, 3 *N* $LiClO_4$; ▲, 3 *N* LiCl; ●, 2 *N* LiCl; ▲, 3 *N* Li_2SO_4; X, no added salt.

Fig. 10.—The variation of $[Br_2]$ with time for various HBr/LiBr mixtures (20 cc. soln., 9.1 cc. NO (18°)/273 cc. O_2, 50°, 76 cm.): ▲, 0.7 *N* LiBr and 2.8 *N* HBr; ⊙, 0.5 *N* LiBr and 3.0 *N* HBr; ■, 0.2 *N* LiBr and 3.3 *N* HBr; X, no added LiBr.

7. **A Suggested Reaction Scheme.**—The following scheme is proposed which is based on the previous discussion

$$HNO_2 + HBr \rightleftarrows Z$$

$$Z + NOBr \xrightarrow{k_1} 2NO + Br_2 + (xH_2O) \quad (1)$$

$$2NO + O_2 \xrightarrow{k_2} 2NO_2$$

$$NO_2 + HBr \xrightarrow{k_3} NOBr + OH$$

$$OH + HBr \xrightarrow{k_4} H_2O + Br$$

$$NO_2 + HBr \xrightarrow{k_5} HNO_2 + Br$$

(1) is the suggested slow step; by comparison the others are likely to be rapid.

This scheme gives the equation

$$-\frac{dc}{dt} = 4k_1[Z][NOBr]$$

which is identical with the experimentally determined expression.

8. **The Effect of Temperature.**—The effect of temperature on the slope (*K*) of the initial linear portion of the kinetic curve at $[O_2]$ = 1 atm., was examined. Since the true concentrations of the intermediate complexes were not known, it was impossible to calculate k_1. However, from the slope of the linear relationship between log *K* and 1/temperature (Fig. 11) the activation energy of the reaction was found to be 10.7 kcal./mole.

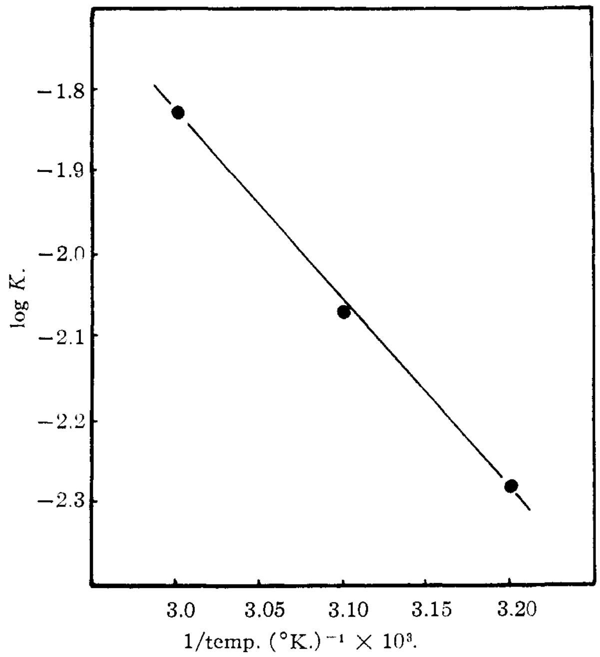


Fig. 11.—Log *K* plotted against 1/temperature (20 cc. 2.5 *N* HBr, 9.1 cc. NO (18°)/273 cc. O_2, 76 cm.).

9. **The Effect of Varying the O_2 Partial Pressure.**—In the initial region of the kinetic curves, the $[O_2]$ has little or no effect on the rate or [Z]. As the reaction proceeds, deviations from the initial linear relationship occur which depend on the $[O_2]$. In the region 0.2–1.0 atm. the deviations are small, but increase rapidly below this. When the $[Br_2]$ reaches certain values at $[O_2] < 0.2$ atm., the catalyst no longer oxidizes the HBr, but it may be reactivated by increasing the $[O_2]$.

Since the [NOBr] does not vary with $[O_2]$ or during a run, the deviations were thought to be due to the Br_2 and solution intermediate being in a reversible equilibrium with an inactive species and O_2.

The apparent irreversibility of the catalyst with respect to HBr at the lower $[O_2]$ (<0.2 atm. at 50°) may be due to a slowness of the reactivation process at the lower pressures. The activation energy for the reactivation process is certainly larger than that for the deactivation since the $[Br_2]$ at which deactivation is complete increases with decreasing temperature (Fig. 2 D,E,F).

The absorption spectrum of some reactant solutions at points corresponding to complete deactivation still showed a plateau at 650 mμ, but the extinction coefficient was halved. This indicates some change in the solution intermediate.

We should like to thank Professor Sir Eric Rideal for his continuous help and advice. The above follows part of a research program that is being sponsored by the British Electricity Authority, to whom due acknowledgment is made.

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