278. *The Oxidation of Hydrobromic Acid by Chromic Acid in the Presence of Manganous Sulphate.*

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The rate of oxidation of hydrobromic acid by chromic acid in sulphuric acid solutions, both with and without manganous sulphate as catalyst, was measured by determining the amount of bromine oxidised. As the method involved expulsion of the bromine from the reaction vessel, it necessitated a correction in the usual formulæ of reaction orders for the time lag caused by this expulsion. The corrected equation for a zero-order reaction (k_0 = catalytic constant) is (2). The corrected equation for a first-order reaction where one of the reagents is in large excess is (3).

For both types of reaction the logarithm of the reaction rate varies linearly with the concentration of sulphuric acid (from 4 to 10N). The temperature coefficients are also identical.

It is concluded that the rate-determining step for the catalytic reaction is $Cr^{VI} + Mn^{II} \rightleftharpoons Cr^{V} + Mn^{III}$.

THE oxidation of hydrobromic acid by chromic acid has been studied by Bobtelsky and Rosenberg (*Z. anorg. Chem.*, 1928, **177**, 137; 1929, **182**, 93). Their results promised to be of interest especially in the study of reaction rates in concentrated electrolyte solutions. The object of this study was to follow more closely the influence of sulphuric acid on the velocity of the above reaction, and the catalytic effect of manganous sulphate.

EXPERIMENTAL.

The solutions and the analytical methods were similar to those employed in the previous work. The reaction vessel was blown from a "Pyrex" glass tube. It had the form of a large test-tube with a bulb at the upper half. A concentric inner tube which almost reached the bottom of the vessel served for the introduction of the solutions and of carbon dioxide. The exit tube for the gases branched off from the upper bulb and led to a three-way stop-cock which directed the evolved gases to one or other of the absorption vessels. These consisted of ten bulbs in a row, inclined upwards at a constant angle, and filled with potassium iodide solution. The stop-cock was turned at fixed intervals, and the iodine set free in the absorption vessels titrated with N/10-thiosulphate from a micro-burette. The carbon dioxide was obtained from a bomb with double valves. It was washed with potassium permanganate and then passed a flow-meter before entering the reaction vessel. In this work a constant current of 1 l. of carbon dioxide per 3 minutes was employed.

Calculations.—Measurements made by driving out the free halogen from the reaction vessel will give a fairly good picture of the rate and order of a reaction as long as this proceeds at a far lower rate than the expulsion of the halogen. Should these two rates become close to each other, then the time taken to drive out the halogen from the reaction vessel has to be taken into consideration. To overcome this objection the velocity of transfer of bromine was ascertained in a number of blanks. It was found that under standard conditions, if the solution contained only one halogen (bromine or chlorine), the velocity of expulsion was proportional to the free bromine in the solution, and independent of the viscosity of the solution, *i.e.*, its content of sulphuric acid or other sulphate, but varied greatly with temperature. Accordingly, the expulsion rate can be represented by the first-order equation

$$dx/dt = k(x_0 - x) \qquad \text{. . . . .} \quad (1)$$

where x_0 is the total amount of free halogen and x the amount transferred to the absorption vessels after the time t; k was ascertained at 10° and 20° for the standard current of carbon dioxide (above) and was found to be 0·392 at 10° and 0·540 at 20° (both ± 1%).

In a full experiment we may regard the amounts of bromine collected in the absorbing vessels as the result of two successive reactions, the first of which is the reaction studied. For the purpose of this work two cases had to be considered.

(i) The oxidation of the bromide is catalytic, *i.e.*, $k_0 = x_0/t$, where x_0 is the total amount of free bromine (formed by oxidation) after the time t in minutes. On combining this with (1), we obtain:

$$dx/dt = k(x_0 - x) = k(k_0 t - x)$$

which on integration and rearrangement gives

$$k_0 = x/[(t - 1/k) + e^{-kt}/k] \qquad \text{. . . . .} \quad (2)$$

and the catalytic constant k_0 may be calculated from the measured amounts of x, namely, the number of c.c. of thiosulphate necessary for the titration of the iodine in the absorption vessels.

(ii) The oxidation of the bromide is of the first order, *i.e.*, $k_1 = (1/t) \log a/(a - x_0)$, where a is the amount of the halide introduced into the reaction vessel and x_0 is as defined above. On substituting in (1) and integrating, we obtain

$$(k - k_1)(a - x)/a = ke^{-k_1 t} - k_1 e^{-kt} \qquad \text{. . . . . . .} \quad (3)$$

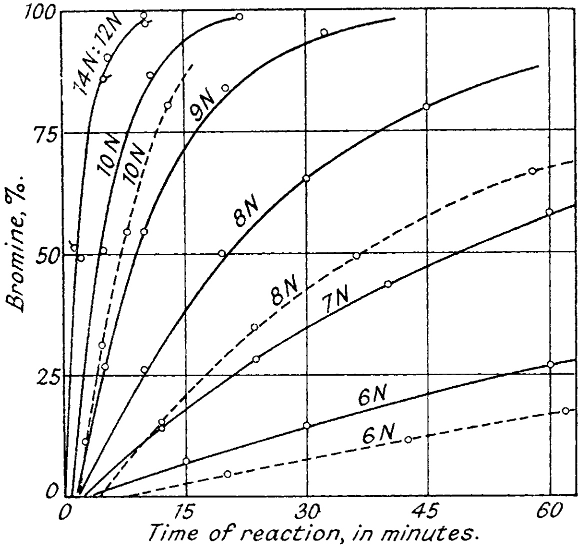
In equation (3), k_1 is implicit, but if x and k are known it can be obtained easily by a graphic method.

Results.—The velocity of oxidation in solutions of sulphuric acid of various concentrations. The amounts of bromine absorbed in the potassium iodide solutions, t minutes after the start of the experiment, from a series of solutions having the general composition 5 c.c. of 0·333M-K_2CrO_4 + 5 c.c. of 0·200M-KBr + Y c.c. of 15N-H_2SO_4 + (20 − Y) c.c. of H_2O are plotted in Fig. 1. Most experiments were made at 20° (± 0·1°); those at 10° are shown in broken lines. The final concentration of the sulphuric acid in the reaction mixture is indicated on each curve. In preparing the solutions containing 12N-sulphuric acid and above, 95% acid was used, and the amount of water to be introduced was calculated from tables to give after contraction a final volume of 30 c.c.

The reaction rate below 5N-sulphuric acid is immeasurably slow. It increases greatly on increasing the concentration of acid up to a maximum, so that between 12 and 14N-sulphuric acid no appreciable difference can be observed. It is clear that this limit is set by the velocity of expulsion of the bromine, which also causes a time lag in the absorption of the bromine so that the curves do not start at the origin.

It was proved that under the conditions employed no measurable quantities of hydrobromic acid were oxidised by the sulphuric acid alone.

FIG. 1.



Reaction between chromic acid and hydrobromic acid in sulphuric acid solutions at 10° (*broken lines*) *and* 20°.

Bobtelsky and Rosenberg (*loc. cit.*) have shown that the studied reaction is bimolecular, the velocity of the oxidation being proportional to the concentration of each of the reactants. As in our experiments a five-fold excess of chromic acid was used, the evolution of bromine should coincide with a first-order equation, and equation (3) is applicable. In Table I are given two typical runs, and the validity of equation (3) is demonstrated by the observed and the calculated values of $(a - x)/a$, the values of k_1 obtained graphically being used.

Table II shows the values of k_1 obtained at 20° in various concentrations of sulphuric acid. In the same table are given also the times of half reaction ($t_{1/2}$) as read from Fig. 1 and also those ($t^*_{1/2}$)

TABLE I.

$T = 20°$; $a = 9·50$ c.c. of $0·10525$N-$Na_2S_2O_3$.

No. 14.		7N-H_2SO_4.		No. 15.		9N-H_2SO_4.	
		$(a - x)/a$,				$(a - x)/a$,	
t, mins.	x, c.c.	obs.	calc.	t, mins.	x, c.c.	obs.	calc.
12	1·33	0·860	0·860	5	2·58	0·728	0·731
24	2·70	0·716	0·718	10	5·22	0·451	0·451
40	4·14	0·564	0·565	20	7·93	0·165	0·166
60	5·47	0·424	0·419	32	9·05	0·047	0·050

TABLE II.

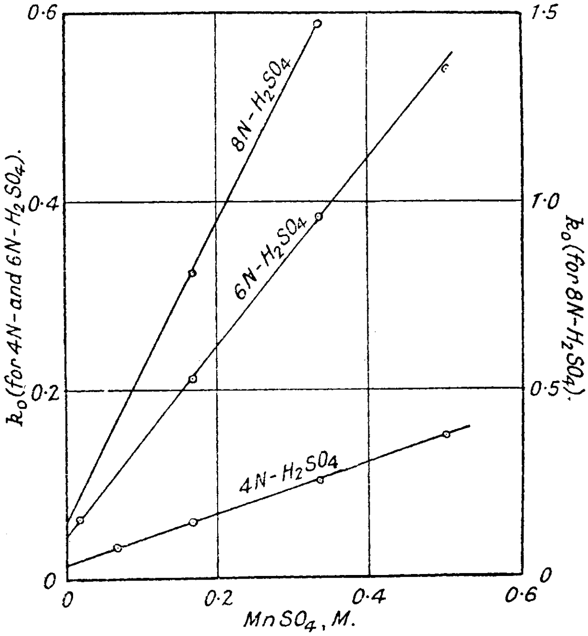
Influence of sulphuric acid on rate of direct oxidation.

H_2SO_4, N.	k_1.	$t_{1/2}$, mins.	$t^*_{1/2}$, mins.	H_2SO_4, N.	k_1.	$t_{1/2}$, mins.	$t^*_{1/2}$, mins.
6	0·006	—	115·5	10	0·240	5·0	2·9
7	0·015	48·5	46·2	12	—	2·0	—
8	0·038	20·25	18·2	14	—	2·0	—
9	0·100	9·0	6·9				

calculated from the k_1 values by the well-known equation $t^*_{1/2} = 0·693/k_1$. It is seen that for slow reactions there is not much difference between the apparent and the corrected half-time values, but for the faster reaction the apparent values would not give a good idea of the relative velocities of the reactions.

The velocity of oxidation in the presence of manganous sulphate. Three series of runs were made with varying amounts of manganous sulphate, in 4, 6, and 8N-sulphuric acid solution. The concentrations of potassium bromide and potassium chromate were, as in the previous experiments, M/30 and M/18, respectively. Although, in the absence of manganese, it did not matter which of the reagents was added last, identical results being obtained in either case, yet in the presence of manganese salts the potassium chromate was always the last reagent added to the reaction vessel. Otherwise, an intense red colouration developed in the solution, the bromide was almost wholly oxidised immediately on addition, and the results were inconsistent. In the calculation of the reaction rates equation (2) was applied, yielding a good constancy of k_0 for each run. The k_0 values thus obtained were plotted in Fig. 2.

FIG. 2.



The influence of manganous sulphate on the rate of oxidation, at 20°, in 4, 6, and 8N-H_2SO_4.

It is seen that the increase in reaction rate is linear with the increase in manganese-ion concentration : the empirical equation $k_0 = A + B[Mn^{++}]$, where A and B are constants, is valid for all the three series of solutions. The respective values of these constants are given below :

	A.	*B.*		*A.*	*B.*		*A.*	*B.*
4N-H_2SO_4 ...	0·0153	0·270	6N-H_2SO_4 ...	0·0477	0·984	8N-H_2SO_4 ...	0·156	3·942

To obtain further knowledge of the mechanism of the catalytic reaction, concentrations of potassium bromide and potassium chromate were varied independently. The concentration of manganese sulphate in all these solutions was 0·333M, and measurements were made at 20°. The results in the form of k_0 are plotted in Fig. 3. It is seen that, although the variation of the concentration of chromate is followed by a proportional change in the k_0 values, yet this constant seems to be almost independent of the concentration of bromide.

Temperature coefficient. In the following table are compared some reaction constants at 20° and at 10°. (All the solutions contained M/18-chromate and M/30-bromide.) The constancy of the temperature coefficient for the uncatalysed and the catalysed reaction is noteworthy.

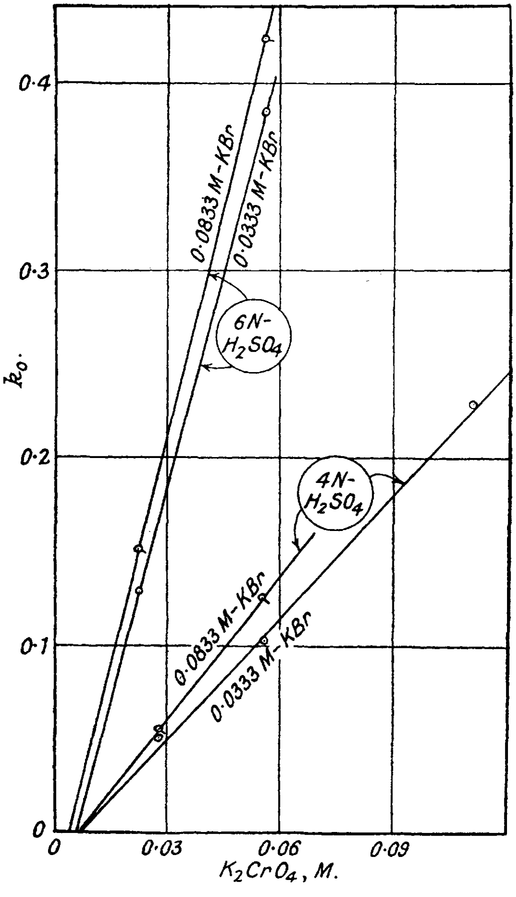
Influence of temperature on reaction rates.

H_2SO_4, N.	$MnSO_4$, M.	$k_1^{10°}$.	$k_1^{20°}$.	$k_0^{10°}$.	$k_0^{20°}$.	$k^{20°}/k^{10°}$
4	0·333	—	—	0·0534	0·1027	1·92
6	0·000	0·003	0·006	—	—	2·00
6	0·333	—	—	0·191	0·384	2·00
8	0·000	0·020	0·038	—	—	1·90
8	0·333	—	—	0·768	0·147	1·92
					Mean	1·95

DISCUSSION.

The usefulness of the modified equations (2) and (3) has been amply demonstrated by the foregoing results. For both the simple and the catalytic oxidation of the bromide, a regular increase in the reaction rate with the increase of the concentration of the sulphuric acid is observed; for each unit increase in the normality of the sulphuric acid, the reaction velocity is increased by a constant factor (2·5-fold for k_1, and 1·95-fold for k_0). Similar regularities for the influence of concentrated electrolytes on reaction velocities were observed by us for the velocity of oxidation of arsenious acid by vanadic acid in sulphuric acid and in hydrochloric acid solutions (*J. Amer. Chem. Soc.*, 1942, **64**, 1463), and by others (Grube and Schmid, *Z. physikal. Chem.*, 1926, **119**, 19; von Kiss, *ibid.*, 1928, **134**, 26). This regularity cannot be adequately discussed until further relevant data are collected. The purpose of the present discussion is to elucidate the catalytic oxidation by manganese ions.

FIG. 3.



The influence of the concentration of the reactants on the catalytic constants, at 20°, in 4N- *and* 6N-H_2SO_4.

The development of a characteristic cherry red-colour on mixing the chromate and manganous solutions in sulphuric acid and the prompt oxidation of bromide by this mixture indicate that the manganic ion Mn^{+++} is responsible for the catalytic oxidation. Hence it may be assumed that in a catalytic run the manganic ion is reduced by the bromide as soon as it is formed, so that the concentration of the manganous ions does not change during the whole course of a run : $Mn^{+++} + Br^- \longrightarrow Mn^{++} + Br$ (very rapid). This assumption is confirmed by the applicability of equation (2), as well as the slight dependence of the reaction rates on the concentration of potassium bromide (Fig. 3). Accordingly the constants A and B should represent the direct and the catalytic oxidation respectively.

The proportionality of the reaction rate to the concentration of the manganous salt (see Fig. 2) and to that of the chromate (see Fig. 3) shows that the determining rate is a bimolecular reaction between these two reagents. Evidently this reaction leads to the temporary formation of a quinquevalent chromium compound and a manganic salt. The data are rather scanty for a complete equation, but it may be added that the regular increase of the reaction constants with the increase of the sulphuric acid in the solution, together with the smooth bimolecular results, point to a non-ionic reaction (see also Hinshelwood, *J.*, 1947, 698).

For the existence and the identity of the manganic compound much evidence might be cited (*e.g.*, Grube and Huberich, *Z. Elektrochem.*, 1923, **29**, 8). Also, the temporary existence of a quinquevalent chromium compound is supported by many papers (Wagner and Peiss, *Z. anorg. Chem.*, 1928, **168**, 265; Wagner, *ibid.*, p. 279; Bobtelsky and Rosowskaja-Rossienskaja, *ibid.*, 1931, **197**, 158; Dhar, *J.*, 1917, **111**, 707). How the quinquevalent chromium is further reduced is not clear; it may oxidise the bromide forthwith, or through the manganic ion intermediary, or by both processes (see also Fales and Roller, *J. Amer. Chem. Soc.*, 1929, **51**, 345): in any case these successive reactions should be very fast.

The activation energy calculated from the average temperature coefficient is 11,000 cals., and it is the same for the direct and the catalytic oxidation. It is also independent of the concentration of the sulphuric acid. This would point to the possibility that in both reactions the activation of the sexavalent chromium is the decisive factor. That the activation energy of the catalysed reaction is not lower than that of the direct oxidation of the bromide is not surprising, since the manganous sulphate is active only if it is present in large excess. The constant concentration of this salt during a run is also an accelerating factor.

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