81. *Decomposition of Chromic Acid in Sulphuric Acid. The First-order Thermal Reaction.*

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The thermal decomposition of chromic acid in sulphuric acid between 140° and 170° has been studied. In concentrated solution the reaction is complex, but in 81·5% sulphuric acid and with concentrations of solute <0·05N. a reaction of first order with respect to chromic acid occurs with an activation energy of 10·3 ± 0·5 kcals. At high acid concentrations chromic sulphate inhibits the decomposition, but its effect decreases as the sulphuric acid concentration falls and disappears in about 82% sulphuric acid. In more dilute acid chromic sulphate slightly catalyses the decomposition of chromic acid. The effect of stirring on the reaction has been examined.

The stability of chromic acid in hot sulphuric acid is of interest because these solutions are used in the determination of such oxidisable vapours as ether (*e.g.*, Schaffer and Ronzoni, *J. Biol. Chem., Baltimore*, 1923, **57**, 741). Snethlage's work (*Rec. Trav. chim.*, 1936, **55**, 712, 874) with unstirred (*vide infra*) sulphuric acid at 138°, and fuming acid at 100°, was believed to show that two reactions occur (in the main simultaneously): (i) a reaction of first order with respect to chromic acid, with a velocity coefficient rising with increasing sulphuric acid concentration up to 99% and thereafter much more rapidly, and (ii) a reaction of second order with respect to chromic acid, with a velocity coefficient rising with the sulphuric acid content up to a concentration of 81% and then falling as the concentration rose to 99%. Chromic sulphate, prepared by reducing chromic acid in sulphuric acid with mannitol or salicylic acid, was found to catalyse the decomposition of chromic acid, the effect decreasing as the concentration of the sulphuric acid was increased and becoming negative in sulphuric acid stronger than 95%.

The speed of decomposition at 138°, even in the most favourable concentrations of acid is not high. Snethlage followed the quickest reaction only to 50% and the slower reactions to less than about 15%. In the present work, with 0·010—0·702N-chromic acid, higher temperatures (140—170°) were employed, thus enabling the reaction to be followed nearly to completion.

EXPERIMENTAL.

Solutions were prepared by shaking the solid with sulphuric acid, setting the mixtures aside for 24 hours, and filtering them through sintered glass. 25-Ml. portions were heated in a 100-ml., Hysil, round-bottomed flask closed with a hollow stopper carrying a 6″ glass stem through which passed a glass stirrer. Precaution was taken to prevent access of dust or other contaminants, and it was shown that there was no appreciable change in the moisture content during the heating which was by a large bath of liquid paraffin maintained within ±0·2° of the desired temperature. For a determination the flask was cooled in boiling water, followed by cold water, and its contents washed into excess of water and titrated with standard ferrous and permanganate solutions.

Table I establishes that equivalent solutions of potassium dichromate, ammonium dichromate, and chromic acid in sulphuric acid behave identically, presumably as a complex involving chromic acid, and since pure potassium dichromate is readily available it was used throughout. Potassium sulphate is without measurable influence : an excess of 50 molecular parts increased the hourly decomposition of 0·06N-potassium dichromate in 99·05% sulphuric acid by only 1·6%.

TABLE I.

Percentage losses in one hour in 99·15% H_2SO_4 *at* 160°.

Normality of solution.	$K_2Cr_2O_7$.	$(NH_4)_2Cr_2O_7$.	CrO_3.
0·010	18·0	17·8	17·9
0·025	17·7	17·9	18·1
0·100	17·9	18·0	18·3
0·150	17·5	18·2	18·5
0·250	18·0	18·5	18·8
0·400	18·6	18·9	19·1

An effect on the course of the reaction which has not previously been observed is that of stirring. In solutions of lower concentrations the rate of decomposition may be increased as much as 27% by this means, but in concentrated solutions (about 0·7N.) the rates in stirred and in unstirred solutions are identical. Both conditions yielded reproducible results. Since precautions were always taken to see that a solution was at the required temperature before timing a run, the difference cannot be a result of the unstirred mixtures not being at the temperatures of the paraffin bath, the low thermal conductivity, or the lack of convection in the system. The acceleration is not affected by oxygen because, when the solution is agitated by a stream of preheated oxygen, admittedly less effectively than by the stirrer, a 20·1% increase was recorded in a 0·15N-solution of potassium dichromate in 99% sulphuric acid. This suggests that the reaction is not reversed by molecular oxygen. Nor was it due to increased contact with the surface since a 20-fold increase in the glass surface was without influence on the reaction, which is presumed homogeneous. Snethlage used unstirred solutions; the results reported in this work were obtained in stirred solutions.

FIG. 1.

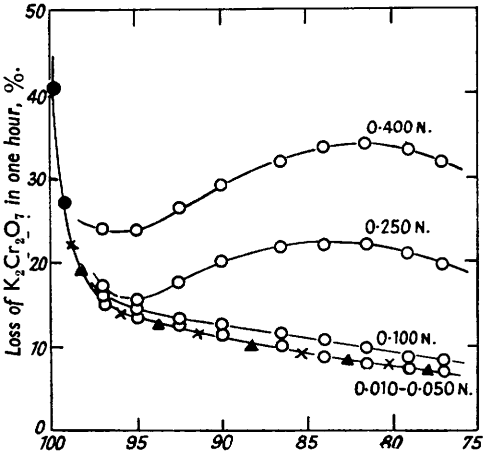
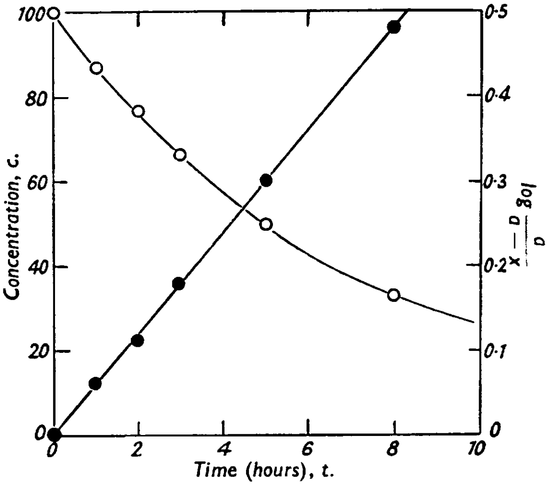


FIG. 2.



0·05N-CrO_3 *in* 81·5% H_2SO_4 *at* 170°.

Figure 1 shows the initial percentage losses, per hour, of chromic acid in sulphuric acid of different strengths at 160°, for six concentrations of solute. Clearly in more concentrated solutions of chromic acid the reaction is complex and reaches a maximum speed in 81·5% sulphuric acid. At a solute concentration of <0·1N., the initial speed falls steadily with decreasing sulphuric acid concentration and at concentrations less than 0·05N. the initial percentage losses per hour are almost identical in all acid concentrations. In acid solutions stronger than 99% there is a rapid increase in speed and the initial percentage losses are identical for all concentrations of solute. However, in fuming acid the decomposition is so rapid that accurate measurement is difficult.

Table II shows that in 99·15% sulphuric acid at 160° there is a fall in the reaction rate as the heating proceeds, shown by the decreasing values of k calculated from the first-order equation $k = (2{\cdot}303/t) \log_{10} 100/(100 - x)$ (t = time of heating in seconds, and x = the percentage loss of chromic acid in time t).

TABLE II.

Heating periods (160°) in hours. Values of $k \times 10^5$. 99·15% H_2SO_4.

Normality.	1 hr.	2 hr.	4 hr.	8 hr.	16 hr.	Normality.	1 hr.	2 hr.	4 hr.	8 hr.	16 hr.
0·025	5·41	4·96	3·95	3·51	2·98	0·150	5·28	4·53	3·63	3·15	2·84
0·050	5·51	4·80	3·78	3·46	—	0·400	5·72	4·86	4·17	3·47	—
0·075	5·44	4·70	3·72	3·23	—	0·702	6·24	5·67	4·86	4·32	—
0·100	5·48	4·45	3·56	3·13	—						

This fall in speed is due to chromic sulphate which is a by-product of the reaction, and comparable results can be obtained by using added chromic sulphate. Table III gives (*a*) the percentage losses observed in the first hour at 160° in a 0·025N-chromic acid solution in 99·15% sulphuric acid to which different amounts of chromic sulphate (prepared by reducing chromic—sulphuric acid solutions with sulphur dioxide) were added and, for comparison, (*b*) the calculated percentage losses in solutions containing the decomposition product $Cr_2(SO_4)_3$ equal in concentration to that added in (*a*).

TABLE III.

r = ratio $Cr_2(SO_4)_3/CrO_3$. 0·025N-CrO_3 in 99·15% H_2SO_4 at 160°.

r = 0.	r = 0·5.		r = 0·6.		r = 0·8.		r = 1·0.		r = 2·3.	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
17·7	13·9	13·0	12·6	12·0	9·7	9·4	9·3	9·2	9·1	9·0

The results indicate that the poisoning effect is due to chromic sulphate and that there is a concentration limit to this effect, *viz.*, $1Cr_2(SO_4)_3 : 1CrO_3$. The poisoning effect falls as the sulphuric acid concentration falls and it disappears in about 82% acid. Below this acid concentration, chromic sulphate has a slight catalytic effect. Thus, at 160° in a 0·06N-CrO_3–80% H_2SO_4 solution with r = 4, a 10% increase in the decomposition in one hour was observed.

Working with 81·5% acid and using concentrations of solute <0·05N. it was shown that within these narrow limits the reaction obeys reasonably well a kinetic equation of the first order with respect to dichromate, as is shown by (i) the constant values of k at all temperatures (Table IV), (ii) Fig. 2 which shows a typical set of these results plotted as (*a*) concentration against time and (*b*) log $[a/(a - x)]$ against time, and (iii) Table V which gives the times of one-fifth conversion for the same set of results.

TABLE IV.

Values of k × 10^5 *in* 81·5% H_2SO_4.

		Heating periods in hours.				
Temp.	Normality of solution.	1.	2.	3.	5.	8.
170°	0·050	3·9	3·6	3·8	3·9	3·9
	0·025	3·8	3·7	3·7	3·6	3·7
	0·010	3·7	4·0	3·6	3·5	3·8
165	0·050	2·9	2·8	2·9	2·8	2·6
	0·025	2·8	2·8	3·0	2·9	2·7
	0·010	3·0	2·9	3·0	2·7	2·7
160	0·050	2·1	2·2	2·2	2·1	2·0
	0·025	2·3	2·3	2·3	2·0	2·1
	0·010	2·2	2·2	2·1	2·2	2·0
155	0·050	1·6	1·7	1·6	1·6	1·5
	0·025	1·7	1·6	1·5	1·7	1·6
	0·010	1·6	1·6	1·5	1·6	1·5
150	0·050	1·2	1·2	1·2	1·0	1·1
	0·025	1·1	1·3	1·2	1·3	1·2
	0·010	1·0	1·1	1·3	1·2	1·3

TABLE V.

Concn., %	100	80	60	50	40
$t_{\frac{1}{5}}$ (hours)	1·7	1·6	1·5	1·5	1·7

From these results the plots of $\log_{10} k$ against $1/T$ gives a straight line from which an Arrhenius activation energy of 10·3 ± 0·5 kcals. is obtained.

Analysis of the results shows that the thermal decomposition of chromic acid in sulphuric acid is complex in all solutions (except those within the narrow concentration limits of 81·5% sulphuric acid and solute concentration less than 0·05N. where a reaction of the first order prevails) and cannot be adequately accounted for by assuming a second-order reaction to be superimposed on a first-order reaction. Moreover, chromic sulphate is found to poison the reaction down to 82% sulphuric acid and thereafter to act as a mild catalyst. These results are not in agreement with those of Snethlage who found chromic sulphate to be a poison down to 95% H_2SO_4 and in more dilute sulphuric acid solutions to be a powerful catalyst.

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