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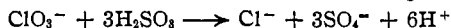
THE RATE OF REACTION BETWEEN CHLORATE AND SULFUR DIOXIDE IN ACID SOLUTION

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The rate of reaction between sulfurous acid and iodate has been the subject of extensive investigations.¹ At the suggestion of Professor William C. Bray, we undertook a study of the analogous reaction

**Experimental**

Rate determinations were made at three different acid concentrations, and the concentration of each reactant was varied four-fold at each acid strength. In all experiments the reaction mixture was kept at 0°.

All reagents used were standard c. p. chemicals. The potassium chlorate had been previously recrystallized to free it from all traces of bromate and iodate. The sulfurous acid solutions were made by diluting a saturated solution of sulfur dioxide. Different acid strengths were obtained by adding sulfuric acid.

The reaction was followed by pipetting samples at appropriate intervals into excess of 0.1 *N* iodine solution. The iodine stopped the reaction by removing sulfur dioxide, and the excess was titrated with 0.025 *N* thio-sulfate. In order to find the original concentration of sulfur dioxide, a blank determination was made concurrently with each run on a solution containing no chlorate but otherwise identical with the reaction mixture. Titrations made on the blanks at the beginning and end of each run indicate that the experimental error due to volatility of sulfur dioxide cannot amount to more than 0.5%. Chlorate concentrations were determined from end-point titrations in runs with excess sulfur dioxide. Preliminary experiments showed that ClO_3^- did not interfere with the thiosulfate titrations at the acid concentrations used.

Results and Discussion.—Values of *k* for the assumed rate law

$$-\frac{d(\text{ClO}_3^-)}{dt} = k(\text{H}_2\text{SO}_3)(\text{ClO}_3^-) \quad (1)$$

were obtained by the usual method of plotting against time the logarithm of the concentration of the reactant present in smaller amount. At any time the slope of this curve multiplied by 2.303 and divided by the concentration of the reactant in excess gave the value of *k*. For the plots of $\log \Sigma\text{SO}_2$ against time it was necessary further to divide the observed slope by 3 and to multiply by the ratio $\text{H}_2\text{SO}_3/\Sigma\text{SO}_2$. The concentrations of

¹ (a) Skrabal, *Z. Electrochem.*, **28**, 224 (1922); this reference contains a complete bibliography of previous work; (b) Skrabal, *ibid.*, **30**, 109 (1924); (c) Skrabal and Zakhorka, *ibid.*, **33**, 42 (1927).

sulfurous acid were calculated from the equilibrium constants of H_2SO_3 and HSO_4^- , which were found by interpolation from the data of Noyes and Sherrill.² A typical calculation for a single run is summarized in Table I, and in Table II the average k 's for all runs are tabulated. All values of k are given in liters per mole per minute.

TABLE I
MEASUREMENTS IN 0.2 N SULFURIC ACID AT $\mu = 0.165$

Time, min.	ΣSO_2 , M	ClO_3^- , M	$\text{H}_2\text{SO}_3/\Sigma\text{SO}_2$	Slope	k
0	0.01310	0.0160	0.878		
2	.00902	.0146	.880	0.056	2.59
3.5	.00735	.0141	.881	.054	2.59
5	.00600	.0136	.883	.0525	2.62
7.5	.00443	.0131	.882	.050	2.58
10	.00343	.0127	.882	.048	2.56
12.5	.00262	.0125	.881	.0465	2.51
15	.00200	.0123	.881	.046	2.53
17.5	.00151	.0121	.880	.0455	2.54
				Mean	2.57

TABLE II

ClO_3^- , M	ΣSO_2 , M	$\frac{(\text{HSO}_3^-(\text{H}^+))}{(\text{H}_2\text{SO}_3)}$	H_2SO_3 , M	$\frac{(\text{SO}_4^{--})(\text{H}^+)}{(\text{HSO}_4^-)}$	Mean μ	Mean k
0.0160	0.0135					2.73
.0160	.00673	0.017	0.25	0.04	0.033	2.82
.0040	.0505					2.89
.0160	.0131					2.57
		.017	.1	.03	.165	2.57
.0040	.0522					2.57
.0260	.0149					2.19
		.01604	2.23
.0065	.0595					2.23

$\Sigma\text{SO}_2 = \text{H}_2\text{SO}_3 + \text{HSO}_3^- = \text{total titratable SO}_2$.

The constancy of the k 's is ample evidence for the correctness of the above bimolecular rate law (equation 1): the largest deviation of any individual k from the average at the same ionic strength is 0.12.

The values of k obtained in the solutions containing sulfuric acid differ from the values obtained in the runs without acid by an amount greater than experimental error will account for. If the difference between the two higher values of k is assumed to be the variation with ionic strength which, according to Brönsted's theory, is allowable for reactions of this type, then extrapolation to zero ionic strength gives 2.5 ± 0.1 as the value of k . For the runs without acid an average value is 2.2 ± 0.1 . It appears impossible at present to decide between these two figures. The latter value could be raised to 2.5 by a 30% increase in the dissociation constant

² Noyes and Sherrill, THIS JOURNAL, 48, 1861 (1926).

of sulfurous acid; the former could be lowered either by the assumption of a third order side reaction involving H^+ or by the assumption of some specific effect of HSO_4^- , such as Livingston postulates in a recent paper.³

If the activity coefficient of sulfurous acid in these dilute solutions is assumed to be one, and if γ_{H^+} is assumed equal to $\gamma_{HSO_4^-}$, then

$$\frac{(H^+)(HSO_3^-)}{(H_2SO_3)} = K_0 = \frac{K_0\gamma^2}{\gamma^2} = \frac{K_0}{\gamma^2}$$

and the rate law (eq. 1) can be expressed

$$-\frac{d(ClO_3^-)}{dt} = \frac{\gamma^2 k}{K_0} (H^+)(HSO_3^-)(ClO_3^-) \quad (2)$$

This expression, which is experimentally indistinguishable from (1), is exactly similar to the rate law established by Skrabal and Zahorka^{1c} for the iodate reaction in acid solution

$$-\frac{d(IO_3^-)}{dt} = k_1(H^+)(HSO_3^-)(IO_3^-)$$

The value of k_1 at 25° and low values of μ is given as 0.53×10^6 . On the assumption of a normal increase of reaction rate with temperature, this indicates that the iodate reaction is about a thousand times as fast as the chlorate reaction. Skrabal and Zahorka noted that k_1 increases rapidly with ionic strength, and found a second independent reaction in alkaline solution.

Summary

The rate of the reaction between chlorate and sulfur dioxide in acid solution at 0° was found to follow the law

$$-\frac{d(ClO_3^-)}{dt} = 2.4 = 0.3(H_2SO_3)(ClO_3^-)$$

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³ Livingston, THIS JOURNAL, 54, 2393 (1932).