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The Rate of Oxidation of Sulfite Ions by Oxygen

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Introduction

The oxidation of sulfite ions by oxygen has been shown[1] to be a chain reaction of unusual length for condensed systems and, as is frequently the situation in such cases, it is very sensitive to both positive and negative catalysts. This is a probable cause for the great variance in the experimental findings of the various workers and it seemed desirable to obtain more reliable data for a kinetic study of the system. In this paper results are reported for the rate of reaction in pure sulfite solutions as well as in the presence of typical positive and negative catalysts (copper and mannitol). The effect of the addition of acid is also reported.

Experimental

The essential parts of the apparatus are: (1) a 100 ml. quartz reaction vessel with a ground joint connection to a mercury seal through which a rotary stirrer operates, (2) a gas buret with an all-glass connection to the reaction vessel for the direct measurement of the rate of oxygen absorption at atmospheric pressure, (3) a thermostat for the entire apparatus. The sodium sulfite was weighed into the dry reaction vessel and to this was added 40 ml. of redistilled water at 25° (at which temperature all the runs were made). The vessel was set in place and the air displaced by passing oxygen for ten min. at 45 ml. per min. through the gas buret into the reaction vessel and out through the hollow stirrer shaft. The stirrer was set in motion after thermal equilibrium was established and readings were started thirty seconds thereafter when the mercury levels had stabilized. The amount of oxygen absorbed during a run, together with the iodine titer at the end, was used to calculate the sulfite concentration present at t_0.

The sodium sulfite used was recrystallized three times from redistilled water and dried at 110° in a platinum dish. Three different original samples were used during the investigation. The sulfuric acid was C. P. grade purified by distilling in an all-quartz apparatus. The mannitol was of C. P. grade and melted between 166 and 166.5°. Tank oxygen washed with concentrated sulfuric acid was passed through a quartz tube heated to a bright red color.

The purification of all water used in order to remove both positive and negative catalysts was very important. The procedure adopted was to distill the water from alkaline permanganate through a block tin condenser with 10% condensation and collecting the middle fraction. The product was stored in Nonsol bottles and used within three hours. Standing longer than this or purification in a Pyrex still gave considerable variations in the results. To make certain that no heavy metals came over a check was made by redistillation in an all-quartz system, collecting the middle fraction in this case with 20% condensation. This further step did not alter the results.

The reaction vessel was cleaned in a mixture of concentrated sulfuric acid and potassium dichromate for over an hour and after a final rinsing with redistilled water was dried in an oven.

If either positive or negative catalysts were present as impurities in the reagents, different amounts used in different runs would give rise to different catalyst concentrations in the solution, these in turn introducing large variations in the values of the velocity constants. No such differences were observed even though the amounts of sodium sulfite weighed out varied five-fold, the time of passing oxygen through the apparatus varied four-fold, and the amounts of sulfuric acid used varied five-fold. Furthermore, samples of sodium sulfite prepared from three different lots of the salt from two different manufacturers gave identical results within the limit of error of the values as reported in the following sections.

Results

Sodium Sulfite Solutions.—The results obtained for solutions of sodium sulfite with no addition of other substances were determined first and the data are given in Table I and Fig. 1. The constants shown in the last column were calculated from the simple first order relation. Since the concentration of dissolved oxygen remained constant, it is included in k_1. The initial concentrations taken were as high as 0.05 M but

TABLE I

SUMMARY OF CALCULATED FIRST ORDER SPECIFIC REACTION RATES

Sulfite sample[a]	Initial concn., M	Number of runs	Av. % completion	k_1 (sec.$^{-1}$) av.
A	0.01	2	80	0.014
A	.02	22	92	.014
B	.02	7	87	.012
C	.02	7	90	.013
A	.03	15	89	.014
A	.04	3	94	.012
A	.05	5	94	.013
				Av. = 0.013 ± 0.0015

[a] Samples A and B were prepared from different stocks of "Baker C. P. Sodium Sulfite." Sample C was prepared from "Reagent Sodium Sulfite Merck."

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[1] (a) Bigelow. *Z. physik. Chem.*, **26**, 493 (1898); (b) Titoff, *ibid.*, **45**, 641 (1903); (c) Lumière and Seyewetz, *Bull. soc. chim.*, [3] **33**, 444 (1905); (d) Milbauer and Pazourek, *Chem. Listy*, **15**, 34 (1921); (e) Reinders and Vlès, *Rec. trav. chim.*, **44**, 249 (1925); (f) Bäckström, THIS JOURNAL. **49**, 1460 (1927); (g) Vol'fkovich and Belopol'skii, *J. Applied Chem. U. S. S. R.*, **5**, 509, 529, 552 (1932); (h) Haber and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 103 (1932); (i) Briner and Biedermann, *Helv. Chim. Acta*, **16**, 548 (1933); (j) Reinders and Dingemans, *Rec. trav. chim.*, **53**, 231 (1934).

the curves of Fig. 1 show that the first order rate holds only below 0.015 *M*. Above this concentration the reaction is affected by the rate of solution of oxygen at our maximum practical stirrer speed of 1600 r. p. m. The constants were obtained then for the range of 0.015 *M* to the limit of the precision of the measurements, namely, 0.001 *M*. The values of k_1 given in the last column are an average for a number of runs at each concentration as indicated.

The results show clearly that the reaction is first order with respect to sulfite with no indication of the anomalies reported by other investigators. Bäckström[1f] found deviations from the first order law but his work was done with 0.6 *M* sulfite solutions and the value of k_1 obtained by extrapolating his data to zero concentration of inhibitor is 0.000343 instead of 0.013 as reported here. This low value would indicate the presence of negative catalysts from such sources as the rubber connections he used. Furthermore, it is not clear from his paper that the observed rate of reaction was not influenced by the rate of dissolution of oxygen. In the case of Reinders and Vlès[1e] the work cannot be considered reliable because no record of purification of reagents was given and rubber stoppers were used. This applies also to the investigations of Titoff,[1b] Lumière and Seyewetz,[1c] and Milbauer and Pazourek.[1d]

Inhibition by Mannitol.—The negative catalytic effect of mannitol is shown in Table II where the specific first order rate constant k_2 given in column 4 is seen to vary from 1.5×10^{-5} to 1.3×10^{-2} over a 10^5 fold range of mannitol concentration. Bäckström,[1f] using initial rates with 0.6 *M* sulfite solutions, found that a relation of the form

$$v = \frac{A}{B + m}$$

(where v is the velocity of absorption of oxygen, A and B are constants, and m is the concentration of mannitol) would fit his data over a range of m from 0.04 to 0.002 molar. However, at concentrations below 0.005 molar the difference between the observed and calculated values of v increases as the mannitol concentration decreases. The calculated rates are slower than those observed.

The following modified form of this relation is found to hold over a much wider range of mannitol concentration

$$\frac{-\mathrm{d}(\mathrm{SO_3^{=}})}{\mathrm{d}t} = \frac{A}{A + m} k_1(\mathrm{SO_3^{=}}) \quad \text{or} \quad \frac{-\mathrm{d}(\mathrm{SO_3^{=}})}{\mathrm{d}t} = k_2(\mathrm{SO_3^{=}}) \tag{1}$$

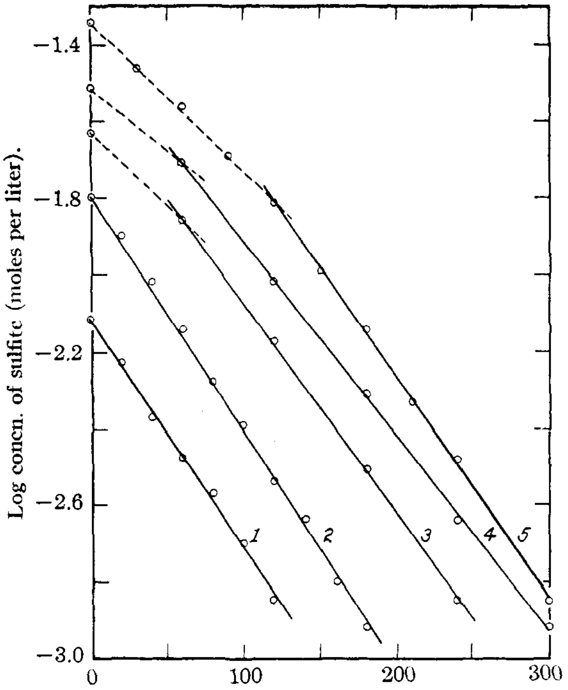

Fig. 1.—Effect of stirring on rate of reaction. The curves refer in order to sodium sulfite solutions having initial concentrations of 0.01, 0.02, 0.03, 0.04, 0.05 *M*.

where A is a constant and m is the concentration of mannitol. When A is taken as 10^{-5}, the values in Table II are found. At mannitol concentrations up to 10^{-2} molar, the agreement between k_2/k_1 and $A/(A + m)$ is fairly good. When the mannitol concentration falls below 10^{-7} molar, its inhibitory effect is no longer observable.

TABLE II

SUMMARY OF FIRST ORDER SPECIFIC REACTION RATES IN THE PRESENCE OF MANNITOL

Initial concn. of sulfite (mole/l.)	Concn. of mannitol (mole/l.)	% completion	k_2	k_2/k_1	$10^{-5}/(10^{-5} + m)$
0.08	3×10^{-2}	11	0.000015	0.001	0.003
.05	10^{-3}	7	.00027	.02	.01
.02	10^{-4}	38	.00080	.06	.09
.02	10^{-5}	82	.0085	.6	.5
.02	10^{-6}	88	.010	.8	.9
.02	10^{-7}	94	.013	1.0	1.0

Catalysis by Cupric Ion.—In the presence of cupric ion the reaction is so rapid that it seemed desirable to use a four-bladed impeller that would introduce oxygen faster than the two-bladed one employed in the previous investigations. It was found that the reaction followed the first order relation (with the same specific reaction rate as that reported for pure sulfite solutions) if the concentration of cupric ions added was not more than 10^{-9} *M*. Above this concentration the rate is no longer dependent on the sulfite alone as is shown by a four-fold increase in the first order specific reaction rate during a run. The curves in Fig. 2 show that there is a sharp increase (about 100%) in the initial rate when the cupric ion concentration is increased from 10^{-9} to 10^{-8} *M* and that no comparable rate increase takes place with further increases in cupric ion concentration up to 10^{-4} *M*. It was suspected that this result might be due to a stirring factor, *i. e.*, that the solutions more than 10^{-9} *M* in cupric ion might be capable of reacting faster than the stirrer could introduce the necessary oxygen.

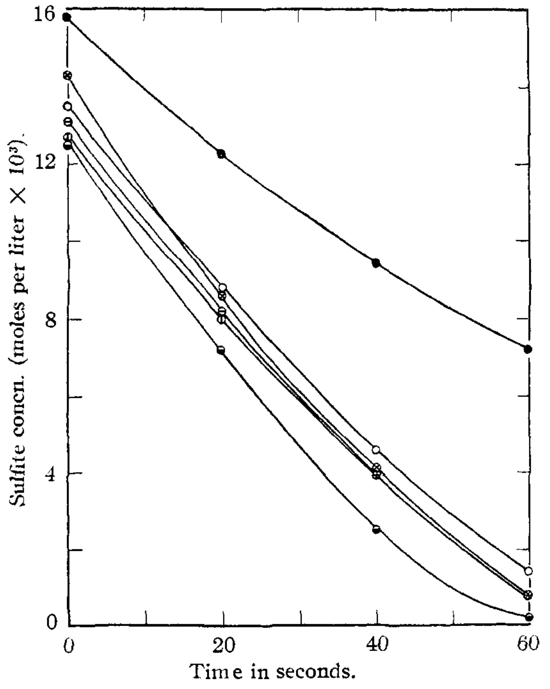

Fig. 2.—Effect of cupric ion, copper sulfate added (m./l.): ●, 10^{-9}; ⦶, 10^{-8}; ○, 10^{-7}; ⊖, 10^{-6}; ◒, 10^{-5}; ⊗, 10^{-4}.

To settle this question, the absolute rates of oxidation of sulfite given in Table III were compared to the rate obtained with a 0.05 *M* solution of sulfite alone, using the same stirrer speed and the same four-bladed impeller employed in the runs with cupric ion added. During the first twenty seconds sufficient oxygen was absorbed by this solution to convert 0.0078 mole per liter of sulfite to sulfate, an amount considerably greater than the 0.0057 mole per liter, which is the maximum conversion in twenty seconds observed with the solutions to which cupric ion had been added. This shows that the grouping of curves in Fig. 2 is not due to a stirring factor.

It is probable that cupric ion added in concentrations greater than of the order of 10^{-8} to 10^{-9} *M* is removed from solution by combining with the hydroxyl ion formed by the hydrolysis of the sulfite ion. At the beginning of each of the runs in Fig. 2 the *p*H is about 8.7, corresponding to a hydroxyl ion concentration of about 5×10^{-6}, based on the value 5×10^{-6} for the secondary ionization constant of sulfurous acid.[2] These figures lead to a calculated value of the order of 10^{-19} for the solubility product of cupric hydroxide. This is in agreement with the experimental values 1.0×10^{-19} and 0.56×10^{-19} given by Allmand[3] and by Latimer.[4]

As the sulfite ion is oxidized to sulfate, the solution becomes less basic and the solubility of the cupric hydroxide increases, resulting in more rapid oxidation rates. This increase accounts for the departure from the first order relation as the reaction proceeds. Since the autoxidation takes place in the absence of added copper, the cupric ion can be considered as a supplementary additive factor in the basic rate equation, thus

$$\frac{-\mathrm{d}(\mathrm{SO_3^=})}{\mathrm{d}t} = (k_1 + k_3(\mathrm{Cu^{++}}))(\mathrm{SO_3^=}) \qquad (2)$$

where k_3 is a constant and k_1 has the same significance as before. In the general case, $(\mathrm{Cu^{++}})$ is independent of $(\mathrm{SO_3^=})$. In the specific cases for which data are reported in this paper, $(\mathrm{Cu^{++}})$ is dependent on $(\mathrm{SO_3^=})$ because the latter determines the hydroxyl ion concentration which in turn determines the cupric ion concentration. If the solubility product of cupric hydroxide is taken as 10^{-19}, $(\mathrm{Cu^{++}}) = 5 \times 10^{-11}/(\mathrm{SO_3^=})$, and equation (2) becomes

$$-\mathrm{d}(\mathrm{SO_3^=})/\mathrm{d}t = k_1(\mathrm{SO_3^=}) + (5 \times 10^{-11})k_3 \qquad (3)$$

Integration of this equation gives

$$\log \frac{k_1(\mathrm{SO_3^=})_1 + (5 \times 10^{-11})k_3}{k_1(\mathrm{SO_3^=})_2 + (5 \times 10^{-11})k_3} = \frac{k_1(t_2 - t_1)}{2.3} \qquad (4)$$

When k_1 is 0.013 and $t_2 - t_1$ is taken as twenty seconds, the values of k_3 given in Table III are found.

The value of k_3 holds fairly well over sulfite and cupric ion concentration changes of about sixty-fold. This shows that the rate equation contains

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[2] "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1928, Vol. VII, p. 237.

[3] Allmand, *J. Chem. Soc.*, **95**, 2151 (1909).

[4] Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938, p. 174.

TABLE III

EFFECT OF CUPRIC ION

Cupric ion added, m./l.	Time, sec.	Sulfite ion concn., m./l.	Calcd. cupric ion concn. $\times 10^9$, m./l.	$k_3 \times 10^{-9}$ (l. m.$^{-1}$ sec.$^{-1}$)
10^{-4}	0	0.0143	3.5	2.7
	20	.0086	5.8	2.9
	40	.0041	12	2.7
	60	.0008	62	
10^{-5}	0	.0125	4.0	2.7
	20	.0072	6.9	3.5
	40	.0025	20	1.9
	60	.0002	250	
10^{-6}	0	.0131	3.8	2.1
	20	.0082	6.1	2.7
	40	.0039	13	2.5
	60	.0008	62	
10^{-7}	0	.0135	3.7	1.8
	20	.0088	5.7	2.6
	40	.0045	11	2.4
	60	.0014	36	
10^{-8}	0	.0127	3.9	2.0
	20	.0080	6.2	2.5
	40	.0039	13	
	60	.0016	31[a]	
			Av. =	2.5±0.33

[a] Since this calculated value exceeds considerably the concentration of cupric ion added, no value for k_3 can be calculated from this datum.

a catalytic constant that is additive to the thermal specific reaction rate. That k_3 is about 10^9 times as great as k_1 is a quantitative indication of the extreme sensitivity of the reaction to positive catalysts. When the cupric ion concentration is as low as 10^{-9}, the value of $k_3(\mathrm{Cu}^{++})$ is about 10^{-8} which is the limit of the observed precision of k_1. For this reason, the catalytic effect of copper is not observed when the cupric ion concentration is equal to or less than 10^{-9} M.

Effect of the Addition of Acid.—The results of the study of the effect of hydrogen ion are given in Fig. 3 and Table IV. The addition of sulfuric acid produces practically an equivalent amount of acid sulfite ions so that the sulfite ion concentration remaining (as given in column 4) is the total sulfite concentration less the concentration of hydrogen ion added. The hydrogen ion concentration after the conversion of the sulfite ions to acid sulfite ions is calculated from the ionization constant of acid sulfite ion and the concentrations of sulfite and acid sulfite ions given.

TABLE IV

EFFECT OF ACIDITY ON REACTION VELOCITY

Hydrogen ion added, m./l.	Time, sec.	Total sulfite concn., m./l.	Sulfite ion concn., m./l.	*p*H	k_4
0.0032	0	0.0164	0.0132	5.92	1.9[a]
	20	.0129	.0097	5.77	5.4
	40	.0096	.0064	5.60	5.9
	60	.0072	.0040	5.40	6.3
	80	.0055	.0023	5.15	
.0065	0	.0160	.0095	5.47	6.3
	20	.0121	.0056	5.24	7.0
	40	.0094	.0029	4.96	6.6
	60	.0078	.0013	4.60	6.9
	80	.0069	.0004	4.09	
.0097	0	.0145	.0048	5.00	6.8
	20	.0119	.0022	4.66	7.2
	40	.0104	.0007	4.16	
.0130	0	.0160	.0030	4.66	7.6
	20	.0139	.0009	4.14	6.9
	40	.0131	.0001	3.19	
.0162	0	.0174	.0012	4.17	6.1
	20	.0164	.0002	3.40	
				Av. =	6.6±0.47

[a] This figure was not used in calculating k_4 (average).

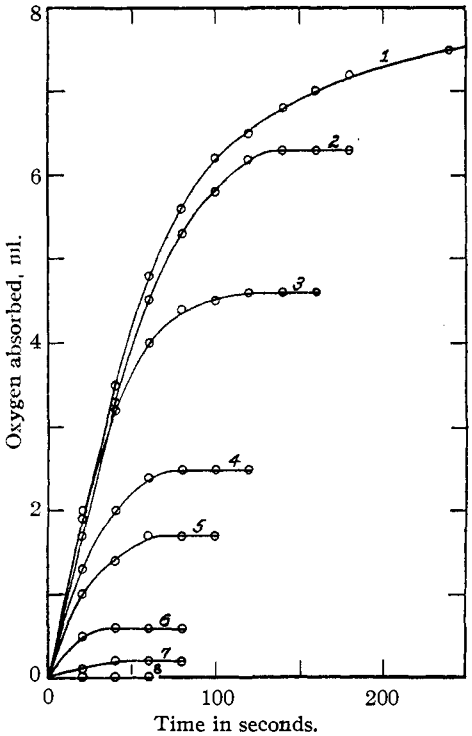

Fig. 3.—Effect of acidity. Curves 1 to 8 refer respectively to 0.02 molar solutions of sodium sulfite to which 0, 0.0032, 0.0065, 0.0097, 0.0130, 0.0162, 0.0195, and 0.0325 mole per liter of hydrogen ion have been added as sulfuric acid.

As found by previous investigators the observed effect is a marked decrease in the rate with decrease of *p*H. The greater part of the effect can be accounted for if we assume that the reaction is dependent only on the sulfite and independent of acid sulfite ion, both of which concentrations are calculable from the ionization constants of sulfurous acid. This assumption is based on Fig. 3 which shows that the addition of increasing amounts of acid to the same amount of sodium sulfite results in decreasing amounts of oxygen absorption. In each run, the reaction stops when the normal sulfite ion present is converted to sulfate. In run 8, practically all the normal sulfite ions had been converted to acid sulfite ions and no oxygen was absorbed. The first order rate constants calculated on the basis of the above assumption are not independent of the *p*H but are found (as a first approximation) to vary as the square root of the hydrogen ion concentration. However, with pure sulfite solutions (where the *p*H varied during a run from 8.8 to 8.2) it was found previously that the rate was first order throughout. These data can all be correlated quantitatively if we assume that the positive catalytic effect of the hydrogen ion is additive with respect to the reaction in the slightly alkaline range. These ideas are expressed in the equation

$$-\mathrm{d}(\mathrm{SO_3^=})/\mathrm{d}t = (k_1 + k_4(\mathrm{H^+})^{1/2})(\mathrm{SO_3^=}) \qquad (5)$$

where k_1 is the rate constant previously determined for the slightly alkaline range and k_4 is the catalytic constant of the hydrogen ion effect. Since the solutions were not buffered, $(\mathrm{H^+})$ depends on $(\mathrm{SO_3^=})$ and (5) takes the form

$$-\frac{\mathrm{d}(\mathrm{SO_3^=})}{\mathrm{d}t} = k_1(\mathrm{SO_3^=}) + k_4(5 \times 10^{-6})^{1/2}(\mathrm{HSO_3^-})^{1/2}(\mathrm{SO_3^=})^{1/2} \qquad (6)$$

Integration of this equation gives

$$\log \frac{k_1(\mathrm{SO_3^=})_1^{1/2} + k_4(5 \times 10^{-6})^{1/2}(\mathrm{HSO_3^-})^{1/2}}{k_1(\mathrm{SO_3^=})^{1/2} + k_4(5 \times 10^{-6})^{1/2}(\mathrm{HSO_3^-})^{1/2}} = \frac{k_1(t_2 - t_1)}{(2)(2.3)} \qquad (7)$$

The factor 5×10^{-6} is the second ionization constant of sulfurous acid.[5] When k_1 is 0.013 and $t_2 - t_1$ is taken as twenty seconds, the values of k_4 given in Table IV are found.

The rather good agreement among the values of k_4 indicates that the rate equation assumed is valid for a 500 fold change of hydrogen ion concentration (*p*H 3.19–5.92). The data reported cover most of the critical *p*H range within which the relative amounts of normal and acid sulfite ions change most rapidly (99% $\mathrm{HSO_3^-}$ at 3.19; 20% at 5.92). Furthermore, equation (5) is valid for solutions of sulfite alone which are slightly alkaline because of hydrolysis. In such solutions, the value of k_1 was found to be independent of the *p*H changes produced by sulfite ion concentration changes from 0.015 to 0.001 mole per liter. The hydrogen ion concentrations in these solutions varied from 1.8×10^{-9} to 7.1×10^{-9} or about four-fold. However, at these concentrations, the values for $k_4(\mathrm{H^+})^{1/2}$ are only 2.8×10^{-4} and 5.6×10^{-4}, respectively. These variations are within the precision of k_1 which was found to be 0.013 ± 0.0015 and hence no hydrogen ion catalysis is observed in solutions of sulfite to which no acid has been added.

Discussion

The oxidation of sulfite ions by oxygen exhibits the characteristics of a chain reaction and the kinetic data are to be interpreted from this point of view. It is possible to set up rather simple mechanisms that lead to equations (1) and (2). However, there needs to be some extension of the data to warrant the proposal of a detailed reaction scheme so that the discussion will be limited to certain general considerations.

In the first place the belief that the reaction always originates by a heavy metal catalysis does not seem to be borne out by the present data. In Fig. 1 results are shown for runs made with a five-fold variation in the original sulfite ion concentration. These changes would have given rise to similar changes in cupric ion concentration which in turn would have caused variations in k_1. Since no such variations were observed, it may be assumed that the sodium sulfite contained no significant amounts of soluble positive catalytic impurity. If such an impurity were only slightly soluble, the *p*H changes brought about by the oxidation of the basic sodium sulfite to the neutral sodium sulfate would have changed the solubility of the impurity and the value of k_1 would have increased as the solution became less alkaline (as was observed in the case of solutions to which cupric ion was added).

A brief calculation will illustrate this point. Since the sharp break in the rate of oxygen absorption by solutions to which copper sulfate had been added (see Fig. 2) comes between 10^{-9}

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(5) This is the value given in "International Critical Tables," Vol. VII, p. 237. Kolthoff (*Chem. Weekblad*, **16**, 1154 (1919)) reported a value of 1×10^{-7}. The use of this value would increase the calculated value of k_4 by a factor of about 7 but such a change would not alter the interpretation of the *p*H effect observed. The amount of sulfuric acid added is insufficient to form appreciable amounts of sulfurous acid so that only the normal sulfite and acid sulfite ions need to be considered here.

and 10^{-8} M cupric ion, the maximum possible value for the solubility of the cupric hydroxide must be 10^{-8} mole per liter. The concentration of hydroxyl ion at the beginning of the runs is about 5×10^{-6} M so the maximum value of the solubility product constant must be about 2.5×10^{-19}. Using this value, instead of 1×10^{19} as reported by Allmand,[3] would lead to a value of 1×10^6 for k_3. If k_1 represented copper catalysis, then the concentration of cupric ion present in the "pure" sulfite solutions could be calculated from $k_1 = k_3(\text{Cu}^{++})$, whence $(\text{Cu}^{++}) = 1.3 \times 10^{-8}$. In run 2 of Fig. 1 the hydroxyl ion concentration at t_0 is about 5.7×10^{-6}. The solubility of cupric hydroxide would then be 7.8×10^{-9} M. Since this is only about half the cupric ion concentration (1.3×10^{-8} M) calculated as necessary to account for the value of k_1, it is obvious that some primary process not involving cupric ion must be operative. Furthermore, the hydroxyl ion concentration at t_{60} in the same run is about 3.8×10^{-6} M. The solubility of cupric hydroxide would then be 1.7×10^{-8} M which is more than twice as great as at t_0. If the specific reaction rate at t_0 were due to copper present as impurity in the sodium sulfite, the rate at t_{60} would be more than twice as great. This is not the case and again it may be concluded that some primary process not involving cupric ion must be operative. The same conclusion is reached if Allmand's[3] and Latimer's[4] values for the solubility product constant for cupric hydroxide are used.

It might be thought that the sodium sulfite contained compensating amounts of both positive and negative catalysts. However, the decrease in pH during a run would have brought about an increase in the concentration of positive catalyst but would not have affected the concentration of the inhibitor and the specific reaction rate would have varied during the course of a run. Since the same specific reaction rate was found throughout the oxidation of pure sulfite solutions made up with initial concentrations from 0.01 to 0.05 M, it may be concluded that such compensating catalysts were not present. Thus if we wish to retain SO_3^- as the active radical we must assume that it originates from some reaction of sulfite and oxygen.

The effect of hydrogen ion on the rate of reaction is more complicated. The negative catalytic effect already has been explained by the observation that the acid sulfite ion does not react. The positive catalytic effect, which is proportional to the square root of the hydrogen ion concentration (equation (5)), may arise in more than one way. The hydrogen ion may be in equilibrium with a complex substance which acts as a positive catalyst just as cupric ion does. If the concentration of the complex is proportional to the square root of the hydrogen ion concentration, then the similarity of equations (2) and (5) would be explained. On the other hand, the hydrogen ion may give rise to an active radical different from that produced by the primary processes discussed previously, thus bringing into operation a new chain mechanism. If this new chain were broken by the removal of the new radical by a reaction which is second order with respect to the concentration of the radical, the kinetic expression derived on this basis would involve the square root of the hydrogen ion concentration. The parallel operation of the two chains would give rise to a kinetic expression like equation (5). It is impossible to choose between these two alternatives with the data at hand.

The unstable intermediates that are responsible for the development of chains may arise from the step-wise reduction of oxygen or oxidation of sulfite. Reduction of oxygen may produce HO_2 and H_2O_2 (or OH). The oxidation of sulfite may produce SO_3^-, $S_2O_6^=$, and SO_5^-. With the aid of these intermediates it is possible to set up reaction mechanisms which will account for the rates either in acid or in slightly alkaline solution. As yet, a mechanism that will hold for both types of solutions has not been found.

Summary

1. The reaction of sodium sulfite solutions saturated with oxygen at one atmosphere pressure has been found to be strictly first order with respect to sulfite ion concentration. The specific reaction rate is 0.013 sec.$^{-1}$ at 25°.

2. The rate is directly dependent upon the cupric ion concentration when this exceeds 10^{-9} M and the catalytic constant is 2.5×10^6 liters mole^{-1} sec.$^{-1}$ at 25°.

3. The inhibitory effect of mannitol has been found to be uniform over a 10^5-fold change of mannitol concentration.

4. The rate is independent of the pH between 8.8 and 8.2. It decreases in a complicated manner between 5.9 and 3.2. This may be accounted

for by assuming that the rate is dependent on the sulfite ion concentration and the square root of the hydrogen ion concentration, but is independent of the acid sulfite ion concentration.

5. The analysis of the effect of cupric ion indicates that there is a primary process independent of heavy metal ions.

6. The mechanism of the oxidation has been discussed in terms of the characteristics of chain reactions. The roles of positive catalysts in the primary process and of inhibitors in the chain breaking process have been interpreted in the light of the data available.

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The Energy of Isomerization of *cis*- and *trans*-Dichloroethylene

BY REUBEN E. WOOD AND D. P. STEVENSON*

Introduction

Several discussions of the relative stability of *cis*- and *trans*-dichloroethylene have appeared in the literature. Stuart[1] from the estimates of the dipole-dipole, induction, and dispersion forces concluded that the *cis* form was the more stable by about 1 kilocalorie per mole. The single gaseous equilibrium constant determined by Ebert and Büll[2] at 300° seemed to confirm Stuart's conclusion provided one assumed that the isomerization involved no change in entropy. Altar[3] disputed Stuart's conclusions and pointed out that Stuart's calculations ignored the steric repulsions. Altar's estimates of the steric interactions taken with Stuart's estimates of the other interactions led to the conclusion that the *trans* form is of slightly lower energy. A preponderance of the *cis* form in the equilibrium mixture was found by Ebert and Büll[2] and confirmed by Olson and Maroney.[4] Altar explained this by showing that the rotational entropy of the *cis* form is considerably greater than that of the *trans* form. He assumed that the vibrational entropy of the two forms is the same, the translational entropy of the two forms being equal, of course. Later experiments by Maroney[5] at higher temperatures seemed to indicate the *cis* form to be the lower energy form in agreement with the conclusions of Stuart.

In order to resolve these difficulties we have undertaken the analysis, with the aid of the entropy difference calculated by statistical methods, of new equilibrium data obtained at lower temperatures than the data of Olson and Maroney,[4] Maroney,[5] and Ebert and Büll.[2]

Equilibrium Measurements.—The preparation and storage of the dichloroethylenes has been described in a previous paper.[6] The iodine was twice sublimed from potassium iodide. The Pyrex reaction vessel has a volume of about 850 cc. It was heated in a tubular electric furnace controlled by a mercury temperature regulator. The temperature of the reactants was measured by a thermometer intruding into the vessel in a well.

The reactants, weighed and sealed into glass capsules, were introduced into the reaction vessel through a side arm. After the vessel had been evacuated and sealed off, the tips of these capsules were broken by shaking. The vessel was then put into the furnace and was maintained at the reaction temperature for the desired length of time.

After the heating period the vessel was removed from the thermostat and cooled rapidly. In the experiments at the highest temperatures cooling was hastened by the use of an electric fan and by the application of a wet towel to the flask. To condense out the dichloroethylene the side-arm of the reaction flask was immersed for about one-half hour in a dry ice–alcohol mixture. The side-arm was then broken off, a clean copper wire was quickly inserted into the condensed solution to remove iodine, and the tube was corked. After the solution had become colorless the extent of the isomerization was determined by a dielectric constant measurement. Care was taken during these operations to minimize the time the solutions were exposed to the air in order to prevent fractionation and water absorption. Table I presents the experimental data. It will be observed that at every temperature the equilibrium was approached from both sides. In the case of the first set of experiments at 185° it appears that the duration of the heating was too short to permit a close approach to equilibrium.[7] For this reason the results of

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[1] H. A. Stuart, "Molekülstruktur," Verlag Julius Springer, Berlin, 1934.

[2] Ebert and Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

[3] W. Altar, *J. Chem. Phys.*, **3**, 460 (1935).

[4] A. R. Olson and W. Maroney, THIS JOURNAL, **56**, 1322 (1934).

[5] W. Maroney, *ibid.*, **57**, 2397 (1935).

[6] R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 1581 (1939).

[7] Because of the fact that equilibrium was not attained in these first two experiments, it is possible to use them as very rough reaction-rate measurements. Although this research was not planned