THE KINETICS OF SELECTED CHEMICAL REACTIONS

Thesis by

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THE KINETICS OF SELECTED CHEMICAL REACTIONS

Part I The Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst.

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THE KINETICS OF SELECTED CHEMICAL REACTIONS

Abstract

PART I

The Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst

The initial rate of the reaction was found to be directly proportional to the concentrations of cupric ion and ascorbic acid and inversely proportional to the square of the hydrogen ion concentration. These facts have been explained by the assumption that in the initial stages the ascorbate ion is oxidized by the cupric ion to an ion with a semiquinone-like structure which is rapidly oxidized by oxygen to dehydroascorbic acid. The cupric ion concentration is maintained constant through oxidation by oxygen of the cuprous ion formed. An observed increase in the specific reaction rate during the course of the reaction is attributed to the accumulation of hydrogen peroxide formed through oxidation of cuprous ion by oxygen.

It was found that in the absence of oxygen an equilibrium involving ascorbic acid and cupric ion as well as dehydroascorbic acid, cuprous ion, and hydrogen ion, is apparently attained. However, the results of some of the numerous experiments carried out in an attempt to measure the equilibrium cast some doubt on the reliability of the equilibrium constants determined.

PART II

The Photochemical Formation of Sulfuryl Chloride from Sulfur Dioxide and Chlorine

It was found that the photochemical formation of sulfuryl chloride from sulfur dioxide and chlorine proceeds at an immeasurably slow rate when the gases are dry. It was, however, found that if the vessel walls are wet with pure sulfuric acid the formation of sulfuryl chloride takes place at a slow but measurable rate. The effect of moisture on the rate, which had been observed by earlier workers, is explained in terms of the effect of the sulfuric acid produced by the reaction of water with chlorine and sulfur dioxide. Stationary states for the photochemical reaction are compared with the thermal equilibria.

PART III

The Thermal Isomerization of Dimethyl Maleate Catalyzed by Iodine

Rates of isomerization of dimethyl maleate in cyclohexane solution and employing iodine as a catalyst were measured. Although these rates fluctuated to a considerable extent, the kinetics appear to be compatible with an iodine atom catalysis plus a catalysis or inhibition due to some as yet undetermined factor.

Acknowledgements

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PART I

Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst

A. The Mechanism of the Reaction

Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst.

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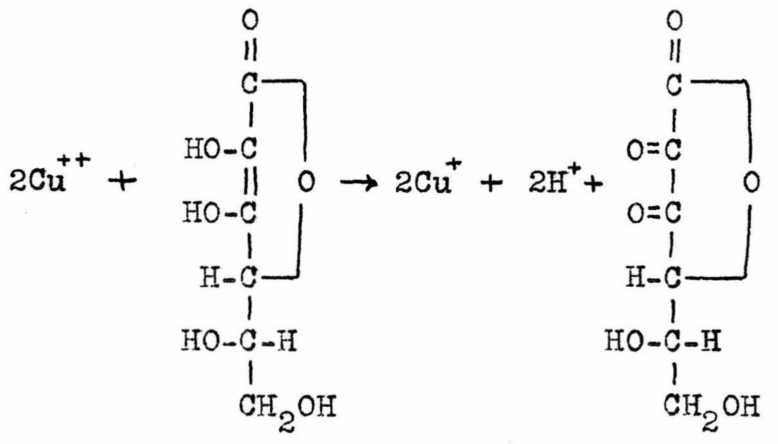
The Mechanism of the Reaction

By means of the Warburg respirometer Barron and co-workers[1] have investigated the rate of the reaction of ascorbic acid with oxygen in the presence and in the absence of cupric ion. They found that in the absence of cupric salts the oxidation of ascorbic acid proceeds at an immeasurably slow rate in acid solutions. The addition of small amounts of cupric chloride was found to increase the rate of oxidation tremendously. Their study of the effects of hydrogen cyanide and carbon monoxide on the rate of oxidation in solutions containing small amounts of cupric chloride indicated that cuprous ion was produced in the reaction and then rapidly oxidized to cupric copper by oxygen. On the basis of these experiments it was postulated that cupric ion oxidizes the ascorbic acid to dehydroascorbic acid, the cuprous ion thus formed being assumed to react rapidly with oxygen, regenerating the cupric ion and forming hydrogen peroxide. These reactions may be written in the following way:



(1)

$$2Cu^{+} + 2H^{+} + O_2 \longrightarrow 2Cu^{++} + H_2O_2 \qquad (2)$$

The peroxide was assumed to decompose rapidly in accord with the observation that one half mole of oxygen was absorbed for every mole of ascorbic acid oxidized.

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (3)$$

In some experiments the rate was found to be proportional to the partial pressure of oxygen above the solution. In further experiments made to determine the effect of the concentrations of cupric copper and hydrogen ion on the rate the results were inconclusive for it appears that no attempt was made to determine whether or not the concentration of oxygen was here, too, important in establishing the net rate of the reaction.

In a study of the effect of various acids on the rate of the copper-catalyzed oxidation of ascorbic acid[2] considerably larger amounts of oxygen were found to be consumed than were expected on the basis of the above assumptions. This was attributed to an accumulation of hydrogen peroxide due to slow (rather than fast) decomposition of the peroxide assumed to be formed during the reaction, and to corroborate this assumption the presence of hydrogen peroxide was demonstrated by means of qualitative tests.

The experiments described in this thesis were carried out for the purpose of obtaining more specific information concerning the nature of the copper-catalyzed oxidation of ascorbic acid. All of the experiments reported here were carried out under such conditions that steps involving oxygen as a reactant were not rate-determining. Furthermore, in order to avoid the possibility of cupric ion complexing with buffers no buffers were used, but instead the hydrogen ion concentration was maintained at an effectively constant value throughout the course of the reaction by the addition of a comparatively large amount of acid at the start.

Materials

Cupric Perchlorate - A good grade of basic cupric carbonate was added in slight excess to an aqueous solution of pure perchloric acid. The solution was shaken and heated until no more gas evolved. It was then cooled, filtered, and diluted with the proper amount of distilled water. The solution was standardized iodimetrically with standard sodium thiosulfate.

Indophenol - The salt was prepared according to the directions of Bessey and King[3] by coupling 2, 6-dichloroquinone chloroimide with phenol in the presence of sodium hydroxide. In stability in aqueous solution the purified product was superior to a purchased sample. The salt was extracted with boiling water, filtered, cooled, and diluted to the desired concentration. The solution was standardized by means of weighed ascorbic acid. It was found necessary to prepare a fresh solution of the indophenol about every three days.

Ascorbic Acid - Iodine titrations showed that each of the samples used contained more than 99.5% ascorbic acid on the assumption that the reduction of the iodine was all due to ascorbic acid. Consequently the material was used without further treatment. The ascorbic acid solutions were made up by weighing out the solid and dissolving it in ordinary distilled water immediately before each experiment. There was always a slow oxidation of the ascorbic acid in these solutions. This slow decomposition was followed by means of titrations with indophenol, and it was thus possible to calculate the ascorbic acid concentration in the stock solution at any time. The slow oxidation was expected to be unimportant in the readtion mixtures since in these the hydrogen ion concentration was always large and indeed it was not detectable in the blank experiments in which cupric ion was omitted.

Hydrogen Peroxide - Two samples were used. One was a 30% solution containing no preservative. The other was a U. S. P. grade containing a small quantity of acetanilide. Each was diluted to approximately the proper concentration and standardized by titrating with potassium permanganate. The two solutions gave identical results in rate experiments which were duplicates in all other respects.

The other solutions used in the experiments were prepared by dissolving the pure substance in distilled water. Where standardizations were required they were carried out by conventional methods.

Experimental Procedure

Portions of the proper stock solutions were pipetted into a flask which was then placed in the thermostat for half an hour. The ascorbic acid solution was also kept at the temperature of the thermostat. At an observed time a portion of the ascorbic acid solution was added to the flask, the contents were mixed well, and the flask was replaced in the thermostat. At suitable intervals portions of the reacting mixture were withdrawn, metaphosphoric acid was added to quench the reaction, and the samples were titrated with indophenol to determine the concentration of ascorbic acid, endpoint corrections being made with solutions to which no ascorbic acid had been added. Analyses by this method carried out on mixtures containing known amounts of ascorbic acid and cupric perchlorate showed that cupric ion does not interfere in the analysis. It was also found that although indophenol rapidly oxidizes cuprous ion the addition of the large excess of metaphosphoric acid used completely inhibited this oxidation.

Although the reaction by which oxidation is stopped when metaphosphoric acid is added is not known, it is presumed that the acid stops the reaction by forming a complex with the cupric ion and also by increasing the hydrogen ion concentration.

Blank rate experiments in which only cupric ion was omitted always showed a negligible decay of ascorbic acid.

Results of the Rate Measurements.

Preliminary experiments showed that although the rates of oxidation at constant cupric ion concentration were equal in nitric and perchloric acids of the same concentration the rates in hydrochloric acid were about fifty or a hundred times faster. Since nitrate ion and perchlorate ion do not show a tendency to form complexes to the extent that chloride ion does, it was decided to consider that hydrochloric acid exerts a specific effect and the remaining experiments were performed in perchloric acid solutions. It may be noted that the experiments in hydrochloric acid solution gave specific rate constants which were only about 25 to 75 percent greater than that calculated by us from the one experiment of Barron's which was carried out in hydrochloric acid solution. (See Appendix, page 47 for details of these calculations.)

In Table I are given the detailed results of representative experiments concerning the dependence of the rate of the reaction upon the concentrations of cupric perchlorate, ascorbic acid, and perchloric acid. All experiments were made at $24.89^{\circ} \pm 0.02^{\circ}$. The concentrations are expressed in formula weights per liter of solution and time is expressed in minutes. The values of the specific reaction rate <u>k</u> given in the last column were calculated on the assumption that the rate is directly proportional to the concentrations of cupric ion and ascorbic acid and inversely proportional to the square of the hydrogen ion concentration. That is

$$-\frac{d\,(H_2A)}{dt} = \frac{k\,(Cu^{++})\,(H_2A)}{(H^+)^2} \qquad (5)$$

and

$$k = 2.30\,\frac{(H^+)^2}{(Cu^{++})\ t} \qquad \log_{10}\frac{(H_2A)_o}{(H_2A)} \qquad (6)$$

Where $(H_2A)_o$ is the initial concentration of ascorbic acid and (H_2A) its concentration at the time <u>t</u>. The hydrogen ion concentration (H^+) and the cupric ion concentration (Cu^{++}) were assumed constant during the reaction.

Although there is a considerable drift in the rate constants with time, it is to be noted that the initial rate constants agree fairly well with one another in spite of the fact that: Experiments 2 and 4 differ from Experiments 1 and 3 by five-fold in cupric ion concentration; Experiments 3 and 4 differ by about fifty-fold in ascorbic acid concentration; Experiments 1 and 5 differ by two-fold in hydrogen ion concentration.

It should be noted that it was found to be necessary to bubble oxygen continuously through the solution during Experiment 4 in order to prevent slowing down of the reaction due to depletion of dissolved oxygen as a result of the large amount of ascorbic acid present. In other experiments in which smaller amounts of ascorbic acid were used, bubbling air or oxygen through the solutions had no effect upon the rate.

Further experiments were performed in which the hydrogen ion concentration was changed by the addition of varying amounts of a standard solution of sodium hydroxide. In Table II are summarized the results of these experiments. The two series were performed using two different samples of perchloric acid. It is to be noted that within each series _k_ is essentially a constant but that _k_ is different for each series in spite of the fact that they overlap in hydrogen ion concentration. Moreover, independent experiments upon the effect of ionic strength show that this large difference in rate is not to be attributed to ionic strength effect. Since reactions catalyzed by cupric ion are often promoted by iron salts,[4,5,6] experiments were carried out in which the acid of Series 1 was used and varying amounts of a ferric sulfate solution were added to the reaction mixture. It was found that the effect upon the rate was such that the presence of about 10^{-5} moles per liter of ferric ion in the reaction mixtures of Series 2 could account for the higher rates observed in this latter series. Rough colorimetric analysis of the two perchloric acid solutions by means of potassium ferrocyanide showed that the sample used in Series 2 contained ferric ion in approximately such quantity that the reaction mixtures prepared from it contained about 10^{-5} moles of ferric ion per liter. The iron in the perchloric acid used in Series 1 was evidently much less since it could not be detected by the method used. It thus appears probable that the discrepancies in Series 1 and 2 may be ascribed to impurities and that the rate of the reaction is inversely proportional to the second power of the hydrogen ion concentration.

In view of the fair agreement of the initial rates in the experiments in Table I it seems reasonable to assume that the differential equation (5) for the rate is essentially correct and that one of the products of the reaction is responsible for the drift of the rate constants with time. Since other investigators[2] have demonstrated that hydrogen peroxide is present in such solutions as these and since we also were able to show by means of the titanium sulfate test that hydrogen peroxide accumulated in our solutions during the reaction, it was decided to determine whether the addition of peroxide would cause an increase in the initial rate. Experiments 1 to 5 in Table III were carried out for this purpose. $(H_2O_2)_0$ represents the initial concentration of hydrogen peroxide. Plotting each k obtained in these five experiments against the corresponding $(H_2O_2)_0$ gives a straight line, as may be seen from an inspection of Figure 1. Rough colorimetric analysis made with the use of titanium sulfate indicated that the reaction mixture described in Experiment 2 in Table I contained (after most of the ascorbic acid had been consumed) about 10^{-5} to 10^{-4} moles of hydrogen peroxide per liter. This suggests that the hydrogen peroxide formed by the reaction is responsible for the trend in the rate constants calculated from equation (5). The situation is further complicated by the possibility that the cupric ion can catalyze the decomposition of the hydrogen peroxide.[7] Additional experiments were carried out in order to obtain more information concerning the manner in which the hydrogen peroxide concentration appears in the differential equation for the rate. The data for these experiments are shown in Table III. Experiments 6 to 10 represent a continuation of the first five experiments with the exception that the cupric ion and ascorbic acid concentrations have been altered. It is interesting to note that increasing the ascorbic acid concentration decreases the effect of the hydrogen peroxide upon k. This fact is also shown by the results of Experiments

11 to 17 in which higher concentrations of peroxide were used. The constants k' were calculated from the equation

$$-\frac{d\ (H_2A)}{dt} = 30 \times 10^{-4}\ \frac{(H_2A)(Cu^{++})}{(H^+)^2} + k'(Cu^{++})^{0.79}(H_2O_2) \qquad (7)$$

which is equation (5) with $k = 30 \times 10^{-4}$ and with an added empirical term $k'(Cu^{++})^{0.79}(H_2O_2)$. It should be mentioned that at the hydrogen ion concentrations employed in these experiments the rate of oxidation of ascorbic acid by hydrogen peroxide alone was found to be negligible.

To obtain additional information concerning the mechanism of the reaction, experiments were carried out in which the ionic strength was varied. The data are summarized in Table IV.. The reproducibility of the experiments is indicated by the results of Experiments 1(a) to 1(b). The lack of quantitative agreement with any Debye-Hückel limiting slope may be attributed in part to the previously mentioned increase of the reaction rate by very small smounts of iron salts. That is, the deviations may be a result of impurities in the salts used. The fact that two different samples of potassium nitrate differ as to the direction of the effect is in accord with this explanation. Furthermore, by means of potassium ferrocyanide spot tests iron was detected in Sample 2 but not in Sample 1. It appears then that there is at most a small negative salt effect; but this conclusion is somewhat uncertain.

TABLE I

SPECIFIC RATE CONSTANTS FOR THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID

Experiment 1

$Cu(ClO_4)_2 = 5.03 \times 10^{-4}$ f.

$HClO_4 = 0.01060$ f.

$(H_2A)_o = 2.92 \times 10^{-4}$ f.

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	2.92	....
25.8	2.15	26.3
43.8	1.64	29.4
68.7	1.09	32.0
89.2	0.750	34.0
104.0	0.572	34.9
122.0	0.421	35.4
145.4	0.276	36.2
163.1	0.186	37.6

Experiment 2

$Cu(ClO_4)_2 = 1.01 \times 10^{-4}$

$HClO_4 = 0.01060$

$(H_2A)_o = 2.83 \times 10^{-4}$

$NaClO_4 = 0.00121$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	2.83	....
62.4	2.39	30.3
124.6	1.98	31.8
181.7	1.65	33.0
241.4	1.34	34.5
304.8	1.04	36.4
368.4	0.790	38.4
430.8	0.589	40.4

TABLE I (Cont.)

Experiment 3

$Cu(ClO_4)_2 = 5.03 \times 10^{-4}$

$HClO_4 = 0.01060$

$(H_2A)_o = 1.46 \times 10^{-4}$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	1.46	....
17.2	1.15	31.0
33.5	0.884	33.4
49.7	0.655	36.0
66.1	0.485	37.2
82.1	0.328	40.6
102.1	0.223	41.0

Experiment 4

$Cu(ClO_4)_2 = 1.01 \times 10^{-4}$

$HClO_4 = 0.01060$

$(H_2A)_o = 7.62 \times 10^{-3}$

t, min.	$(H_2A) \times 10^3$	$k \times 10^4$
0	7.62	....
22.5	7.22	27.3
55.4	6.53	31.1
89.6	5.86	32.7
126.4	5.20	33.6

Experiment 5

$Cu(ClO_4)_2 = 5.29 \times 10^{-4}$

$HClO_4 = 0.00558$

$(H_2A)_o = 1.47 \times 10^{-4}$

$NaClO_4 = 0.00558$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	1.47	....
19.5	0.661	24.1
29.1	0.392	26.7
42.7	0.152	31.3

TABLE II

SPECIFIC RATE CONSTANTS FOR THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID.

	$(HClO_4)$	$(NaClO_4)$	$(Cu(ClO_4)_2)$	$(H_2A)_o \times 10^4$	t, min.	$(H_2A)/(H_2A)_o$	$k \times 10^4$
Series 1	0.0211 f.	0 f.	5.03×10^{-4} f.	3.51 f.	30.0	0.875	39.4
	0.0161	0.0050	"	3.50	30.0	0.793	39.8
	0.0111	0.0100	"	3.49	31.0	0.623	37.3
Series 2	0.0582	0	2.52×10^{-4}	2.84	609.4	0.718	73.0
	0.0482	0.0100	"	2.82	431.3	0.725	70.4
	0.0382	0.0200	"	2.81	257.1	0.715	75.5
	0.0182	0.0400	"	2.80	54.3	0.747	70.6
	0.0582	0	112.0×10^{-4}	2.84	33.6	0.466	68.8

TABLE III

THE EFFECT OF HYDROGEN PEROXIDE ON THE RATE OF THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID.

Ex.	$(HClO_4)$	$(Cu(ClO_4)_2)$	$(H_2A)_o \times 10^4$	$(H_2O_2)_o \times 10^4$	t, min.	$(H_2A)/(H_2A)_o$	k	k'
1	0.01056 f.	1.01×10^{-4} f.	2.84 f.	0.166 f.	60.0	0.840	32.2×10^{-4}	
2	"	"	2.83	0.332	60.0	0.821	36.3	
3	"	"	2.82	0.392	69.0	0.792	37.1	
4	"	"	2.82	0.453	55.7	0.817	40.1	
5	"	"	2.80	0.664	60.0	0.790	43.2	
6	"	"	5.46	0.166	60.0	0.872	25.2	
7	"	"	5.50	0.332	60.0	0.861	27.5	
8	"	5.03×10^{-4}	2.81	0.166	60.0	0.396	34.3	
9	"	"	2.82	0.332	60.0	0.379	35.8	
10	"	"	5.58	0.166	60.0	0.477	27.3	
11	"	1.01×10^{-4}	3.44	1.23	64.0	0.754	48.6	6.8
12	"	"	3.42	2.46	62.2	0.673	70.2	7.4
13	"	"	3.41	4.92	62.0	0.532	11 2.4	7.6
14	"	"	3.40	7.38	62.0	0.440	146.2	7.1
15	"	"	6.76	4.92	62.0	0.677	69.6	7.4
16	"	5.03×10^{-4}	3.45	1.23	62.0	0.293	43.9	7.8
17	"	"	3.46	2.46	62.0	0.198	57.9	7.2

Figure 1.

Effect of Hydrogen Peroxide
on the Rate.

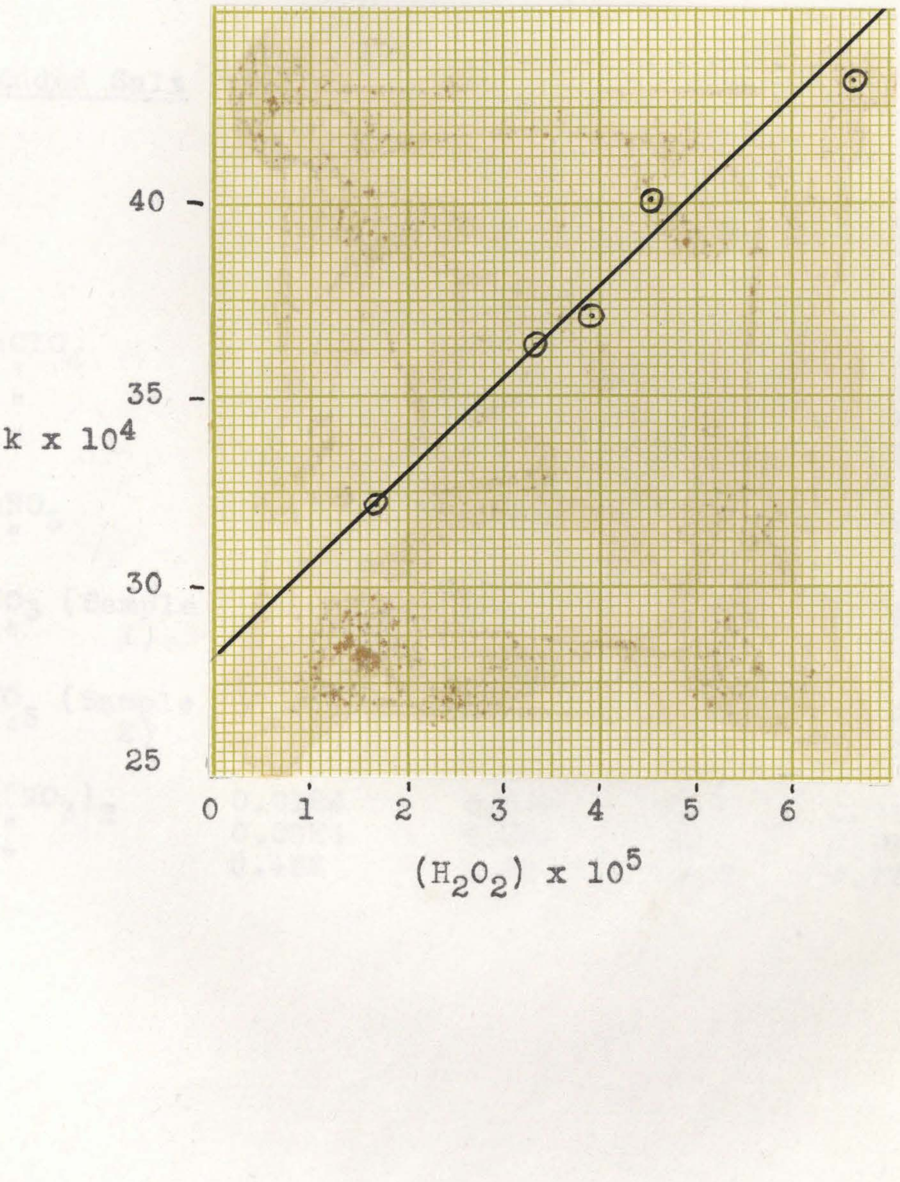


TABLE IV

EFFECT OF ADDED ELECTROLYTES UPON THE RATE

$(HClO_4) = 0.01056$ f.

$(Cu(ClO_4)_2) = 2.52 \times 10^{-4}$ f.

$(H_2A)_o = 2.80 \times 10^{-4}$ f. to 2.90×10^{-4} f.

Ex.	Added Salt	Conc. of Added Salt	Initial Ionic Strength	t,min.	$(H_2A)/(H_2A)_o$	$k \times 10^4$
1a			0.0116	51.1	0.737	26.5
b			0.0116	51.1	0.740	26.1
c			0.0116	51.3	0.729	27.2
d			0.0116	51.1	0.730	27.3
e			0.0116	51.0	0.733	26.9
2	$NaClO_4$	0.054 f.	0.067	51.3	0.749	24.9
3	"	0.058	0.070	51.2	0.765	23.2
4	"	0.161	0.173	51.3	0.754	24.3
5	"	0.323	0.334	51.3	0.754	24.3
6	$NaNO_3$	0.155	0.167	51.2	0.799	19.5
7	"	0.930	0.942	51.2	0.822	16.9
8	KNO_3 (Sample 1)	0.0707	0.083	50.1	0.791	20.7
9	"	0.424	0.436	51.2	0.815	17.7
10	KNO_3 (Sample 2)	0.135	0.147	51.0	0.692	31.9
11	"	0.270	0.282	51.0	0.603	43.9
12	$Ba(NO_3)_2$	0.0124	0.049	51.3	0.765	23.1
13	"	0.0824	0.259	51.0	0.794	20.0
14	"	0.462	1.40	51.2	0.771	22.5

Discussion

If we restrict ourselves at first to the main reaction, omitting consideration of the effect of the hydrogen peroxide produced, we have the problem of presenting a probable mechanism which would yield a dependence of the rate upon the first powers of the cupric ion and ascorbic acid concentrations and the inverse square of the hydrogen ion concentration. In addition, the mechanism postulated must provide a means for maintaining the cupric ion concentration essentially constant during the course of the reaction. One scheme which fulfills these requisites is the following:

$$H_2A \overset{K}{\rightleftharpoons} 2H^+ + A^= \tag{8}$$

$$Cu^{++} + A^= \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CuA \tag{9}$$

$$CuA \xrightarrow{k_3} Cu^+ + \text{Intermediate products} \tag{10}$$

$$\begin{matrix}\text{intermediate}\\ \text{products}\end{matrix} \longrightarrow \begin{matrix}\text{dehydroascorbic acid (series of}\\ \text{steps with high specific rate)}\end{matrix} \tag{11}$$

$$Cu^+ + H^+ + \tfrac{1}{2}O_2 \longrightarrow Cu^{++} + \tfrac{1}{2}H_2O_2 \text{ (high specific rate)} \tag{12}$$

Assuming $\frac{d\,(CuA)}{dt} = 0$, the differential equation for the rate of the reaction in dilute solutions would on the basis of the Brönsted-Bjerrum theory[8] be given by:

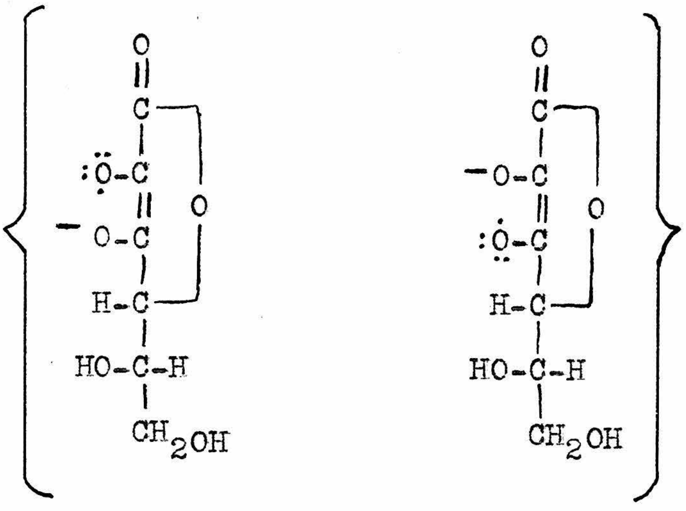
$$-\frac{d(H_2A)}{dt} = \frac{k_3 k_1 K\ (Cu^{++})(H_2A)}{(k_2 + k_3)\ (H^+)^2} \quad 10^{-\sqrt{\mu}} \qquad (13)$$

where μ is the ionic strength of the reaction mixture. It is probable that the negative ionic strength effect predicted on the basis of the above mechanism is masked in the data by the presence of catalysts in the form of impurities in the substances making up the reaction mixtures. The equilibrium constant for (8) as calculated from the dissociation constants for the first and second hydrogen atoms[9] is about 10^{-16}. Consequently, the concentration of the ascorbate ion, $A^=$, is very small in all solutions of ascorbic acid, not so small however as to preclude the probability of the mechanism suggested. It is only necessary to assume that the forward reaction of (9) takes place at approximately every collision and that $\underline{k_3}$ is much larger than $\underline{k_2}$, both reasonable assumptions.

A formally equivalent expression may be derived if it be assumed that the un-ionized ascorbic acid forms an unstable copper complex containing two hydroxyl ions. A rate expression equivalent to (13) may also be derived on the assumption that the un-ionized ascorbic acid and cupric ion are in equilibrium with cupric ascorbate, CuA, and hydrogen ion, the cupric ascorbate decomposing as already indicated.

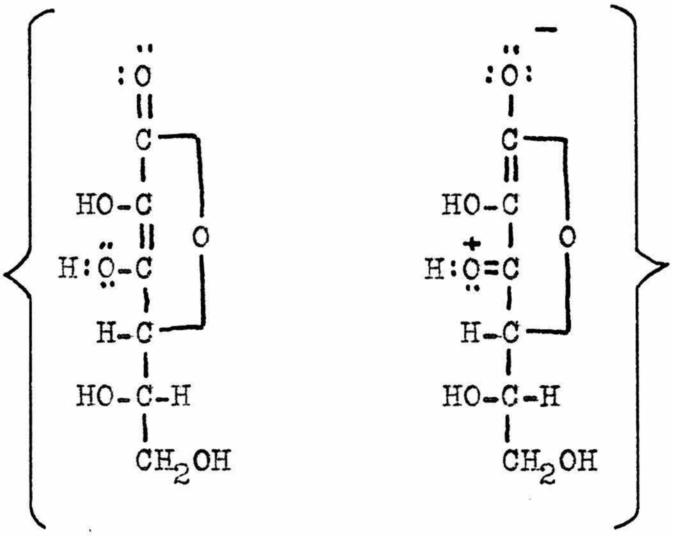
However, the mechanism involving the ionization of the ascorbic acid seems more probable. It may be remarked that on the basis of the assumption that copper held in combination with ascorbate ion is unable to act as a catalyst for the oxidation of other ascorbic acid molecules the kinetic data show that less than one percent of the copper present could have existed in combined form in any of the experiments.

Reasonable suggestions can also be made with reference to the constitution of the intermediate compound formed by the decomposition of the copper salt. Since it is necessary to remove two electrons from ascorbic acid to form dehydroascorbic acid, the product of the oxidation, and since the rate-determining step involves the first power only of the cupric ion concentration, it follows that the initial product of the decomposition or rearrangement of the copper salt must be a compound capable of reacting with an additional cupric ion or some other oxidizing agent such as oxygen to give dehydroascorbic acid. It is reasonable to suppose that the first product of the decomposition of the copper salt of ascorbic acid is an ion with the resonating structure



(I)

This ion would be expected to possess less stability in the acid solutions used than in basic solution, for the presence of a hydrogen atom on one of the oxygens involved in the resonance would destroy the equivalence of the two structures and decrease the resonance energy. Furthermore, the resonance (II) responsible for the acidic character of ascorbic acid competes with the semiquinone type resonance shown above and thus decreases the stability of the intermediate.



(II)

A few rate experiments were performed with the object of determining whether the presence of oxygen was necessary in order for the reaction to take place. To this end experiments were carried out in evacuated Thunberg tubes. In experiments for which the time was long equilibria seemed to be attained for which the experimentally determined equilibrium constants varied about two-fold and were within the limits calculated for the reaction

$$2Cu^{++} + H_2A \rightleftharpoons 2Cu^{+} + D + 2H^{+} \qquad (14)$$

where D represents dehydroascorbic acid. These experiments are described and discussed in detail on pages 31-46. In additional experiments similar to those in which equilibria were obtained but employing shorter times it was possible to determine the rate of oxidation of ascorbic acid in the absence of oxygen. It was noted that the rates of oxidation of the ascorbic acid were between fifty and seventy-five times smaller than the rates calculated from the expression for the rate of oxidation in air and the expression for the rate of the reverse reaction, the specific rate of the reverse reaction being calculated from the equilibrium constant for (14) and the value 30×10^{-4} for k in (5). This might indicate that in the rate experiments in the presence of air the oxygen was involved along with the intermediate (I) in the series of steps with high specific rates indicated by equation (11) while in the absence of air cupric ion is involved, the rate with cupric ion being assumed slow. Denoting the intermediate (I) by B^-, the equations for the above reactions might be written:

$$B^{-} + Cu^{++} \longrightarrow D + Cu^{+} \qquad (11)'$$

$$B^{-} + O_2 + H^{+} \longrightarrow D + HO_2 \qquad (11)''$$

Perhydroxyl, HO_2, is unstable in acid solution with respect to the decomposition[10]

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

so that a quantitative yield of hydrogen peroxide and oxygen is expected. Equation (12) should probably be written similarly:

$$Cu^+ + O_2 + H^+ \longrightarrow Cu^{++} + HO_2 \qquad (12)'$$

$$2HO_2 \longrightarrow H_2O_2 + O_2$$

Little can be said concerning the mechanism of the effect of hydrogen peroxide upon the rate. The guess might be made that since the ascorbic acid concentration does not appear in the second term on the right in equation (7), the supposed reaction between the cupric ion and hydrogen peroxide is slow and a product of this reaction, possible a complex $CuH_2O_2^{++}$, reacts rapidly with the ascorbate ion to produce the intermediate B^- which is rapidly oxidized to dehydroascorbic acid. Furthermore, since hydrogen peroxide accumulates in the solution, the mechanism must provide for the regeneration of hydrogen peroxide. The following reactions can account for the observations:

$$Cu^{++} + H_2O_2 \longrightarrow CuH_2O_2^{++} \qquad (16)$$

$$CuH_2O_2^{++} + A^{=} \longrightarrow Cu^{+} + H_2O_2 + B^{-} \qquad (17)$$

The fact that the cupric ion concentration in (7) appears to a power slightly less than one might be attributed to a decomposition of peroxide catalyzed by cupric ion[7].

Altogether then, the following reactions are possibly involved in the copper-catalyzed oxidation of ascorbic acid:

$$H_2A \rightleftharpoons 2H^{+} + A^{=} \qquad (8)$$

$$Cu^{++} + A^{=} \rightleftharpoons CuA \qquad (9)$$

$$CuA \longrightarrow Cu^{+} + B^{-} \qquad (10)$$

$$B^{-} + Cu^{++} \longrightarrow D + Cu^{+} \qquad (11)'$$

$$B^{-} + O_2 + H^{+} \longrightarrow D + HO_2 \qquad (11)''$$

$$Cu^{+} + O_2 + H^{+} \longrightarrow Cu^{++} + HO_2 \qquad (12)'$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

$$Cu^{++} + H_2O_2 \longrightarrow CuH_2O_2^{++} \qquad (16)$$

$$CuH_2O_2^{++} + A^{=} \longrightarrow Cu^{+} + H_2O_2 + B^{-} \qquad (17)$$

To the above series of equations might also be added those showing the catalytic decomposition of hydrogen peroxide by cupric ion.

Summary

The catalytic effect of cupric ion on the oxidation of ascorbic acid by oxygen has been studied. It was found that the initial rates were substantially directly proportional to the concentrations of cupric ion and ascorbic acid and inversely proportional to the square of the hydrogen ion concentration. In the initial stages the reaction mechanism is assumed to consist in the slow oxidation by cupric ion of the ascorbate ion to an ion with a semiquinone-like structure, followed by the rapid oxidation by oxygen of this semiquinone-like ion to dehydroascorbic acid. The cupric ion concentration is maintained constant through oxidation by oxygen of the cuprous ion formed. An observed increase in the specific reaction rate during the course of the reaction is attributed to the accumulation of hydrogen peroxide formed through the oxidation of cuprous ion by oxygen.

A marked increase of the rate of the reaction upon the addition of ferric ion was observed.

PART I

Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst

B. A Possible Equilibrium Involving Cupric Ion and Ascorbic Acid.

A Possible Equilibrium Involving Ascorbic Acid and Cupric Perchlorate

From the results of the work of Borsook <u>et</u>. <u>al</u>.[11] and of Ball[12] upon the oxidation-reduction potential of the system of which ascorbic acid is the reductant and from the measurements of Fenwick[13] of the cuprous ion—cupric ion potential, the equilibrium constant of the following reaction may be calculated.

$$2Cu^{++} + H_2A \rightleftharpoons 2Cu^{+} + D + 2H^{+} \qquad (18)$$

Using the following standard electrode potentials

$$Cu^{+} = Cu^{++} + E^{-} \qquad E^{\circ}_{298} = -0.167 \qquad (19)$$

$$H_2A = D + 2H^{+} + 2E^{-} \qquad E^{\circ}_{298} = -0.38 \pm 0.01 \qquad (20)$$

we obtain $E^{\circ}_{298} = -0.21 \pm 0.01$ for reaction (18) from which it follows that

$$\frac{(Cu^{+})^2(H)^2(D) \quad \gamma^2_{Cu^+}\gamma^2_{H^+}\gamma_{H_2O}}{(Cu^{++})^2(H_2A) \quad \gamma^2_{Cu^{++}}\gamma_{H_2A}} = K = \begin{matrix} 38 \times 10^{-9} \\ \text{to} \\ 180 \times 10^{-9} \end{matrix}$$

Thus it appears that the equilibrium should lie in such a position as to be measurable. The comparative rarity of measurable equilibria, the desire to improve the accuracy of the electrode potential for the ascorbic acid system, and the hope of shedding light upon the mechanism of the oxidation of ascorbic acid by cupric ion were the reasons for investigating this equilibrium.

Experimental Procedure

In carrying out the experiments a modification of the Thunberg tube was used in which bulbs were attached to the overhang tube in order to adapt their use to larger amounts of liquid. Into the overhang was first pipetted the perchloric acid solution used to maintain the hydrogen ion concentration essentially constant, followed by the ascorbic solution. The cupric perchlorate solution was placed in the main, lower compartment. The assembled and weighed tube was then placed in a dry-ice-alcohol slush and the contents frozen. Then the tube was connected with an oil pump and evacuated to a pressure of 2-4 mm. of mercury after which it was closed by rotating the overhang tube. The whole tube was thereupon warmed to room temperature and again pumped on for at least two minutes, then closed, weighed, placed in the thermostat, and shaken to mix the contents of the overhang and lower compartment when temperature equilibrium had been reached. The water removed during the pumping process was determined from the weight of the tube and its contents before and after evacuation. After remaining in the thermostat for a measured time, the tube was removed and opened, and 10 ml. of 10% metaphosphoric acid were added rapidly with immediate shaking in order to "freeze" the equilibrium. This presumably took place through the formation of inert complexes of both the cupric and cuprous copper with metaphosphoric acid. The contents of the tube were then titrated with indophenol in the usual manner, endpoint corrections being made by titrating similar solutions to which no ascorbic acid had been added. Blank equilibrium experiments in which cupric perchlorate was omitted showed a negligible amount of oxidation of the ascorbic acid.

It was necessary to insure that the air was sufficiently removed by the pumping operation, for it was calculated that the oxygen contained in 0.01 - 0.04 ml. of air would completely oxidize all the cuprous ion formed in the experiments. Calculations showed that the amount of water evaporated during the pumping was many times the amount necessary to wash out the oxygen to the extent that it would not interfere with the equilibrium measurements.

It was also necessary to guard against leaks in the joints of the Thunberg tubes. Occasionally an experiment gave a result quite different from the results of experiments which were run as duplicates of it. Because the rest of the duplicates agreed among each other and since on the other hand these occasional anomalous experiments not only disagreed with one another but also always corresponded to an increased oxidation of ascorbic acid, it was assumed that in these experiments air had leaked into the Thunberg tubes. These experiments are not reported.

Results of the Measurements and Discussion

Preliminary experiments showed that after three to six hours no more ascorbic acid was oxidized. Consequently in the experiments described here the time of equilibration was set at ten to twenty-five hours. In these preliminary experiments it was noted that the rate of oxidation of the ascorbic acid was between fifty and seventy-five times slower than the rate calculated from the rate of oxidation in air and the equilibrium data furnished by the electrode potentials. This might indicate that in the rate experiments in the presence of air the oxygen was involved in the steps with high specific rate indicated by equation (11) while in these rate experiments on the attainment of equilibrium (in the absence of oxygen) cupric ion is involved in the steps of (11), the rate with cupric ion being slow so that (11) now is rate-determining. Of course, whether oxygen or cupric ion is involved in (11) the rate of disappearance of ascorbic acid is presumably the same; it is the rate of formation of dehydroascorbic acid which is presumed to be different.

In Table V are listed the results of the equilibrium measurements, all of which were conducted at $24.89^\circ \pm 0.02^\circ$. The concentrations are expressed in formula weights per liter of solution. The equilibrium constant is given by the expression

$$\frac{(Cu^+)^2(H^+)^2(D)}{(Cu^{++})^2(H_2A)} = K \qquad (22)$$

where the cuprous ion concentration has been calculated from the amount of ascorbic acid decomposed. The hydrogen ion concentration is calculated from the perchloric acid originally added and the small contribution from the ionization of the ascorbic acid. The dehydroascorbic acid concentration is calculated from the amount originally present due to the slow oxidation of the stock solution and from the quantity formed by the oxidation of the ascorbic acid by cupric copper during the equilibration. The cupric ion concentration is equal to that originally present minus the cuprous ion formed. Thus we may write

$$K = \frac{4\left[(H_2A)_0 - (H_2A)\right]^2 \left[(H^+)_0 + \Delta\right]^2 \left\{(D)_0 + \left[(H_2A)_0 - (H_2A)\right]\right\}}{\left\{(Cu^{++})_0 - 2\left[(H_2A)_0 - (H_2A)\right]\right\}^2 \quad (H_2A)} \qquad (23)$$

where $(H_2A)_0$, $(H^+)_0$, $(D)_0$, $(Cu^{++})_0$ are the initial concentrations of ascorbic acid, hydrogen ion, dehydroascorbic acid, and cupric ion respectively, (H_2A) is the concentration of ascorbic acid at equilibrium, and Δ is the hydrogen ion formed by the ionization of ascorbic acid.

In Table V Experiments 1-5 are essentially duplicates of each other and by their agreement give evidence of the reproducibility of the experiments. Experiments 6-13 have been carried out with the hydrogen ion and cupric ion concentrations varying by a factor of two or more.

Experiments 14-20 were carried out with larger initial amounts of ascorbic acid and do not agree very well with the results of the first thirteen experiments. Experiments 21-27 were carried out using smaller initial quantities of ascorbic acid. Again the results do not agree with those of the first thirteen experiments. No explanation was found for the different results of these experiments.

Experiments 28-30 are tests of the reversibility of the supposed equilibrium. They were carried out in the following manner. Starting with the same initial concentrations as in Experiments 1-5, the tubes were left in the thermostat for 10 hours. They were then removed and various amounts of water were pumped off, the quantities removed being measured by weighing the tubes and their contents before and after pumping. The tubes were replaced in the thermostat and after ten hours removed and analyzed. At the end of the first ten hours equilibration the concentrations of the various species in these tubes were presumably very close to the final concentrations of the same species in Experiments 1-5 because both groups of experiments were carried out with reaction mixtures of almost identical initial compositions and both were given sufficient time for equilibrium to be reached. Now since pumping water off the solutions of Experiments 28-30 makes the solutions more concentrated it is evident that if the solutions are allowed to come to equilibrium again some of the dehydroascorbic acid formed in the first equilibration will be converted into ascorbic acid. This follows from a consideration of the effect of the change of concentration upon the rates of the two opposing reactions which make up the equilibrium. That the reaction actually was caused to proceed in this reverse direction by this treatment may be deduced from an inspection of the equilibrium constants or by a comparison of the ratios of ascorbic acid to dehydroascorbic acid in Experiments 1-5 and 28-30.

Experiments 31-39 were carried out at approximately the same initial cupric ion and hydrogen ion concentrations, and only the initial ascorbic acid concentration was varied. It should be noted that although K for this group of experiments is far from constant K' has a mean value of 4.5×10^{-3}, where

$$\frac{(H^+)^2(D)}{(Cu^{++})(H_2A)} = K' \qquad (24)$$

This fact might be explained upon the assumption that the equilibrium

$$2Cu^+ = Cu^{++} + Cu\ (s) \qquad (25)$$

is established in the solution. The equilibrium constant for this may be calculated from the experiments of Fenwick[13].

$$\frac{(Cu^{++})}{(Cu^{+})^2} = 1 \times 10^6 \qquad (26)$$

Substitution of this value in equation (21) yields

$$\frac{(H^{+})^2\,(D)}{(Cu^{++})(H_2A)} = 10^6\ K \qquad (27)$$

Therefore, neglecting the activity coefficients we have

$$K' = 10^6\ K$$

However, if we now substitute in this last equation the numerical values $K = 30 \times 10^{-9}$ and $K' = 4.5 \times 10^{-3}$ we find

$$4.5 \times 10^{-3} = 30 \times 10^{-3}$$

which is certainly not true! Let us then calculate what value $(Cu^{++})/(Cu^{+})^2$ must assume in order that $K' = \frac{(Cu^{++})}{(Cu^{+})^2} K$. This is $\frac{(Cu^{++})}{(Cu^{+})^2} = 1.5 \times 10^5$ which would correspond to the copper metal supposedly formed in experiments 31-39 having a higher free energy than the ordinary copper metal which appears in equation (25). This is indeed reasonable for it is easy to imagine that a colloidal precipitate of copper would be less stable than ordinary copper such as copper foil, wire, or lumps. It should be noted, however, that no metallic copper could ever be detected visually in these solutions.

About twenty experiments were carried out in which carefully cleaned copper wire was present. However, in these experiments the ascorbic acid oxidized was a function of the time and the amount of copper wire used, and no equilibrium was reached. Possibly some heterogeneous reaction took place on the surface of the wire. It is possible that oxygen adsorbed on the inserted wire reacted with the ascorbic acid.

Additional experiments in the absence of copper wire were performed in which the hydrogen ion concentration was increased ten times to 0.12 formal, the cupric ion concentration was increased to 0.07 formal, and the initial ascorbic acid was kept at about 3×10^{-4} formal. These gave equilibrium constants of 20×10^{-9} to 35×10^{-9} after about ten hours equilibration. However, when the equilibration time was increased to about twenty-five hours the equilibrium constant became about 50×10^{-9}. Increasing the equilibration time to forty hours changed the constant to almost 70×10^{-9}.

Experiments were also carried out in which dehydroascorbic acid (prepared by oxidizing ascorbic acid in the air using cupric perchlorate as a catalyst) was added to the initial reaction mixture. When the equilibration time was fifteen hours the resulting equilibrium constant was 13×10^{-9} to 35×10^{-9} and increased with the time of equilibration to 70×10^{-9} after forty hours.

Although the experiments described in the above two paragraphs display time drifts that are larger than those observed for the experiments in Table V, the results are nevertheless not radically different. The drift in the experiments at high hydrogen ion and cupric ion concentrations may be ascribed to the increased rate of side reactions due either to increased (H^+) and (Cu^{++}) or to increased concentrations of impurities present in the perchloric acid and cupric perchlorate. The drift in the experiments in which dehydroascorbic acid is added might be ascribed to the presence of hydrogen peroxide introduced by the preparation of the dehydroascorbic acid from ascorbic acid.

Although the discordant constants found in Experiments 30-39 have been plausibly accounted for it should be noted that the same explanation should apply to Experiments 17-20 but fails. Experiments 21-27, the results of which vary most markedly from those of other experiments, are also the experiments in which the concentrations of ascorbic and dehydroascorbic acids are lowest, and consequently the influence of disturbing factors would be expected to be manifested most strongly in these experiments.

TABLE V

EQUILIBRIUM MEASUREMENTS FOR THE REACTION $2Cu^{++} + H_2A \rightleftharpoons 2Cu^{+} + D + 2H^{+}$

No.	$(H_2A) \times 10^4$	$(D) \times 10^4$	$(H^+) \times 10^2$	$(Cu^{++}) \times 10^2$	$(Cu^+) \times 10^4$	t	$K \times 10^9$
1	0.404 f.	1.86 f.	0.833 f.	3.90 f.	3.58 f.	24 hrs.	26.9
2	0.366	1.86	0.829	3.94	3.57	"	28.6
3	0.331	1.90	0.828	3.94	3.58	"	31.8
4	0.353	1.88	0.832	3.95	3.52	"	29.3
5	0.431	1.89	0.829	3.93	3.71	19	26.9
6	1.485	1.58	1.090	2.05	2.93	10	25.8
7	1.430	1.63	1.095	2.07	2.98	"	28.4
8	0.875	2.19	0.552	2.06	3.97	"	28.4
9	0.811	2.24	0.549	2.05	3.90	"	30.2
10	0.663	2.25	1.090	5.19	4.18	24	26.1
11	0.791	2.20	1.086	5.17	4.30	33	22.7
12	0.983	2.32	0.610	2.27	4.38	"	32.8
13	1.997	1.87	2.29	4.30	3.53	19½	33.1
14	6.06	4.53	1.023	3.72	8.06	"	36.8
15	5.95	4.65	1.026	3.73	8.08	"	38.5
16	5.89	4.71	1.019	3.72	7.92	"	37.6
17	2.74	3.38	0.568	2.02	6.28	23½	38.4
18	2.76	3.33	0.567	2.02	6.08	"	35.1
19	2.62	3.47	0.564	2.02	6.22	"	40.0
20	2.61	3.49	0.564	2.02	6.14	"	39.4
21	0.113	0.893	1.090	2.08	1.55	19	52.0
22	0.114	0.890	1.088	2.08	1.49	"	47.5
23	0.289	0.731	1.089	1.025	1.38	17½	54.3
24	0.277	0.741	1.090	1.026	1.37	"	56.5
25	0.251	0.781	1.103	1.048	1.40	"	67.2

TABLE V (Cont.)

No.	$(H_2A) \times 10^4$	$(D) \times 10^4$	$(H^+) \times 10^2$	$(Cu^{++}) \times 10^2$	$(Cu^+) \times 10^4$	t	$K \times 10^9$
26	0.333 f.	0.694 f.	2.75 f.	2.11 f.	1.19 f.	17½ hrs.	50.0
27	0.336	0.700	2.77	2.12	1.15	"	47.1
28	1.11	2.60	1.320	6.29	5.06		26.7
29	1.51	3.09	1.675	7.82	5.96		33.3
30	1.53	3.38	1.775	8.36	6.40		41.0
31	3.43	2.40	1.105	2.05	4.44	16	40.3
32	3.41	2.40	1.102	2.05	4.28	"	37.3
33	3.29	2.48	1.094	2.03	4.26	"	39.7
34	3.22	2.59	1.099	2.04	4.30	"	43.1
35	3.21	2.58	1.099	2.04	4.12	"	39.5
36	3.26	2.55	1.105	2.05	4.18	24	39.7
37	4.03	2.91	1.099	2.03	5.28	17	59.1
38	4.11	2.87	1.103	2.04	5.08	"	52.8
39	8.47	6.16	1.134	2.01	9.40	29	205.

No.	$K' \times 10^3$
17	1.97
18	1.92
19	2.09
20	2.04
31	4.16
32	4.17
33	4.43
34	4.76
35	4.76
36	4.95
37	4.31
38	4.16
39	4.66

Summary

Apparent equilibrium constants experimentally determined for the reaction $2Cu^{++} + H_2A \rightleftharpoons 2Cu^{+} + D + 2H^{+}$ are of the order of magnitude predicted from electrode potential data. They show among themselves a variation equal to a factor of two while the concentrations of the various species have undergone larger variations. Experiments carried out to test the reversibility of the equilibrium show that the reaction can be made to proceed in both directions. Attempts to explain the various deviations in terms of complex formation failed. It appears probable that the equilibrium for which the constants were calculated does exist but that simultaneously a reaction (or perhaps more than one reaction) takes place which slowly consumes ascorbic acid. This makes it appear unwise to attach too much quantitative significance to the equilibrium constants. Nevertheless, the equilibrium experiments may be said to afford confirmatory evidence of the reliability of the determinations of the standard electrode potential of the ascorbic acid system.

APPENDIX

Table VI

Rate Experiments with HCl = 0.081 f.

$(H_2A)_o \times 10^4$f.	$(CuCl_2) \times 10^4$f.	t, min.	$(H_2A)/(H_2A)_o$	$k \times 10^2$
2.84	5.00	30.0	0.714	14.7
"	"	"	0.699	15.6
"	"	"	0.696	15.9
"	"	"	0.706	14.7
"	10.00	"	0.421	16.5
"	"	"	0.408	19.6
"	"	"	0.443	17.8
"	15.00	"	0.264	19.4
"	"	"	0.277	18.8
"	"	"	0.285	18.3
"	20.00	"	0.123	22.8
"	"	"	0.128	22.4
5.66	5.00	"	0.682	16.7
"	"	29.3	0.673	17.3
11.23	"	29.2	0.675	17.1
"	"	29.7	0.683	16.7

The <u>k</u> for each experiment has been calculated from equation (5) of the text. They may be compared with the following experiment of Barron and co-workers[1] which appears to be the only one carried out using hydrochloric acid (instead of a buffer) to maintain the hydrogen ion concentration.

$(H_2A)_o$	$CuCl_2$	HCl	Half-life	k
7.26×10^{-3}f.	7.27×10^{-5}f.	0.0675f.	367 min.	11.8×10^{-2}

Thus there is fair agreement in spite of the fact that the analytical methods differed, in one case the indophenol titration being used, in the other the measurement of oxygen consumption.

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PART II

The Photochemical Formation of Sulfuryl Chloride from Sulfur Dioxide and Chlorine

The Photochemical Formation of Sulfuryl Chloride from Sulfur Dioxide and Chlorine

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Using radiation absorbed only by chlorine, LeBlanc, Andrich, and Kangro[1] studied the photochemical formation of sulfuryl chloride from sulfur dioxide and chlorine. They determined no rate law but found that the rate was dependent upon the moisture in the sulfur dioxide and chlorine used, the velocity being greater in mixtures of the moist gases. Photochemical stationary states were found which were strongly dependent on the temperature and were not coincident with the dark equilibria as determined by Trautz[2]. The work of LeBlanc and co-workers, however, was carried out employing rather primitive techniques and cannot be considered accurate. In addition, Trautz's measurements of the dark equilibria cannot be considered definitive. Bonhoeffer[3] determined the quantum yield of the reaction and found it was of the order of magnitude of unity. Unfortunately he gives no details of his study. Tramm[4] determined the effect of careful drying of the gases upon the rate of the reaction and found that while the moist mixture reacted at a conveniently measurable rate, the dried gases reacted immeasurably slowly.

The low quantum yield reported by Bonhoeffer did not fit into the chain mechanism expected for the reaction on the basis of the analogy with the photochemical formation of phosgene from carbon monoxide and chlorine. Knowledge of the unconfirmed effect of moisture on the photochemical formation of hydrogen chloride from hydrogen and chlorine[5] led us to minimize the observation of Tramm, and experiments were therefore carried out for the purpose of finding more information concerning the mechanism of the photochemical formation of sulfuryl chloride.

Materials

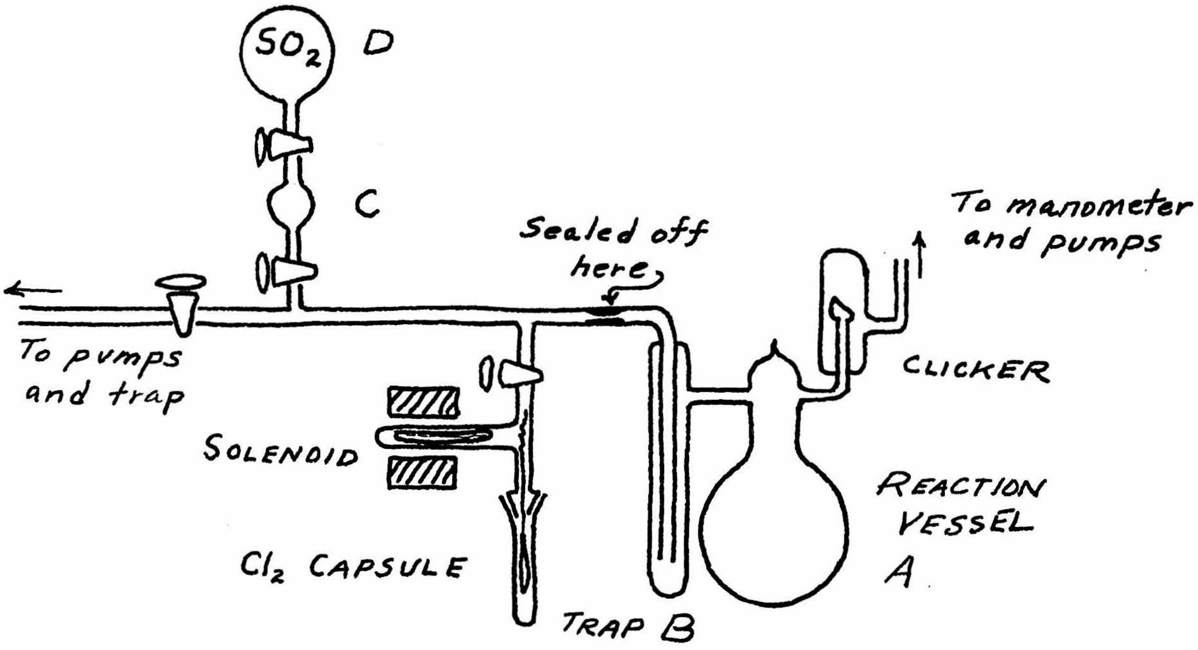
Sulfur Dioxide - Two preparations were used. Number 1 consisted of tank sulfur dioxide which was bubbled through concentrated sulfuric acid and was then led through a liter storage flask displacing air. Number 2 consisted of sulfur dioxide prepared by the action of concentrated sulfuric acid upon pure sodium sulfite and passed through a calcium chloride tube and a sulfuric acid wash bottle and finally through the storage flask. Liquid air was placed around a tit in the flask containing preparation Number 2 and the flask was pumped down to 10^{-3} mm. of mercury, the contents were melted and vaporized, the liquid air was replaced, and finally the flask was again pumped to 10^{-3} mm.

Chlorine - Tank chlorine was bubbled through potassium permanganate solution, passed through a calcium chloride tube, and bubbled through a sulfuric acid wash bottle, and then condensed into weighed capsules. A small length of rubber tubing was used to attach the capsule to the manifold. However, the capsules were connected flush against the glass tube of the manifold so that there was little opportunity for the chlorine to come in contact with the rubber. Consequently there was little chance of contaminating the chlorine since the rest of the apparatus was constructed of glass.

Apparatus and Experimental Procedure

The apparatus used is shown in Figure 1. The reaction vessel A of pyrex glass was heated and pumped down to a pressure of 10^{-5} mm. of mercury, proper precautions being taken to keep mercury vapor out of the system. Liquid air was placed around the trap B and the sulfur dioxide was introduced in small doses from D and C. The vessel was pumped down to 10^{-5} mm., the liquid air was removed, and a thermostat was placed around the trap and vessel. When equilibrium had been attained the pressure of the sulfur dioxide was determined with the click gauge. Liquid air was again placed around the trap and the chlorine was introduced by breaking the capsule with the solenoid and a glass-encased piece of steel. Again the vessel was pumped down to 10^{-5} mm., the flask was sealed off from the rest of the system, the liquid air was removed, the vessel was thermostated, and the pressure was determined. The rate of the reaction was followed by measuring the pressure at frequent intervals with the click gauge.

FIGURE 1.


SO_2
D
C
Sealed off here
To manometer and pumps
To pumps and trap
CLICKER
SOLENOID
REACTION VESSEL
A
Cl_2 CAPSULE
TRAP B

Results

No measurable dark reaction took place under any of the conditions employed. The room illumination at no time produced any measurable effect upon the rate of the reaction.

It was found that no reaction took place upon illuminating a mixture of the gases, chlorine and sulfur dioxide, either with the radiation from two 500-watt Mazda lamps or with the radiation from a mercury arc operated at 74 volts and 4 amperes. This was true for both preparations of sulfur dioxide.

To determine whether moisture was necessary for the reaction a capsule of water was heated and then opened in a side arm of the vessel A by means of a hammer operated by a solenoid. No pressure change was observed at the moment of breaking and no effect upon the rate of the reaction was found. The absence of a change of pressure was ascribed to the reaction

$$SO_2\ (g) + Cl_2\ (g) + 2H_2O\ (l) \rightarrow H_2SO_4\ (l) + 2HCl\ (g) \qquad (1)$$

in which two molecules of gas disappear but produce two molecules of gas.

Upon letting laboratory air into the reaction vessel at the end of the above-mentioned efforts to produce a reaction a fog was formed which was ascribed to reaction (1), the water being supplied by the air. The fog condensed on the walls of the vessel, and the other gases were removed by passing a current of air through the vessel. The vessel was then heated above 100° and pumped down, the liquid (presumably sulfuric acid) remaining on the walls. On the hunch that faulty technique on the part of some of the earlier experimenters might have caused this liquid to be left on the walls of their reaction vessels and that the presence of this liquid might be necessary for the reaction to proceed it was decided to attempt an experiment with the flask "dirtied" in the manner just described. Upon introducing sulfur dioxide and chlorine in the usual manner and illuminating with the mercury arc, a slow reaction indeed took place.

To determine whether the sulfuric acid presumed to be on the walls was responsible for the reaction the vessel was thoroughly cleaned and the walls were wet with pure concentrated sulfuric acid. It was found that when proceeding as usual, reaction took place upon illumination with the mercury arc. The reaction rate was slow and of the same order of magnitude as the rate observed when the walls were wet with the liquid from the fog produced by the laboratory air. Illumination with a

500-watt Mazda lamp also produced a decrease in pressure but the rate was much slower than that with the mercury arc.

It is concluded that the moisture itself probably is of no importance in determining the rate of the photochemical reaction, but that the sulfuric acid formed affects in some way the rate of the reaction. That the increased rate observed when the walls of the vessel were wet with sulfuric acid is not due to the extremely small pressure of water vapor in equilibrium with concentrated sulfuric acid may be concluded from the fact that the sulfur dioxide and chlorine used in all the experiments contained this same pressure of water vapor inasmuch as they had been bubbled through concentrated sulfuric acid before use. With respect to the function of the sulfuric acid it is possible that it either removes some inhibitor or chain-breaker or that it acts catalytically in some fashion. Of course it is also possible that the acid performs both of these functions.

The experiment in which a small amount of water was introduced into the system by means of a glass capsule broken by a magnetically operated hammer exhibited no measurable rate of reaction. This can probably be explained by the fact that it would be difficult for the sulfuric acid formed by the reaction of water with sulfur dioxide and chlorine to escape from the sidearm (in which the capsule was broken) into the main reaction flask where illumination took place.

Details of the rate experiments described above together with those of other experiments are given in graphical form in Figures 2 and 3, which represent the formation of sulfuryl chloride, and 4, which represents the decomposition of sulfuryl chloride. It can be seen from Figures 2 and 3, which are plots of total pressure against time, that the rate of the reaction between sulfur dioxide and chlorine is apparently independent of the concentrations of sulfur dioxide and chlorine in the initial stages. This may be deduced from the straight line relation between total pressure and time which holds for a considerable portion of each run. In addition, the plot of Experiment 4a shows that in agreement with the observation of Trautz[6] the temperature coefficient for the rate of the photochemical formation of sulfuryl chloride is very small.

It may also be concluded from the three figures that stationary states arise if illumination is continued long enough at 35°, 50°, and 100°. The stationary state of Experiment 4 seemed to be independent of the intensity of illumination, for when one, and then later two, 500-watt Mazda lamps were substituted for the mercury arc after the stationary state had been attained, no change in pressure could be detected.

Evidence of the occurence of some side reaction was found. Experiment 4b was carried out on the stationary state mixture resulting from Experiment 4a. After Experiment 4b was completed the reaction mixture was cooled down to 35° and illuminated. A stationary state was attained at a pressure of 16.02 cm. which does not agree with the value obtained in Experiment 4a on the same reaction mixture at the same temperature (but earlier in the history of this particular reaction mixture). Evidence of the formation of several mol-percent of a product other then sulfuryl chloride was found by LeBlanc and co-workers[1].

Stationary state "constants" have been calculated from the data of Experiments 3, 4a, and 4b and are compared in the table below with the thermal equilibrium data of Arii[7]. Not much significance can be attached to these calculations for the presence of side reaction and the fact that the reacting gases are all soluble to some extent in the sulfuric acid film have not been corrected for in the calculations. Moreover, extrapolations have been made to obtain the value of the total pressure at the stationary state. Furthermore, the fact that in Experiments 4a and 4b the final pressure of one of the reactants was very small means that the errors introduced by failing to correct for side reaction and solubility will have a very large effect on the value of the stationary state constants. These last were calculated simply from the equation

$$\frac{p_{SO_2Cl_2}}{p_{SO_2}\, p_{Cl_2}} = K$$

where the pressures are expressed in atmospheres partial pressure. The constants for the thermal equilibria calculated from the equation given by Arii are in the same units.

The extreme slowness of the reaction even when the reactants were exposed to the total radiation from the various lamps used discouraged further study of the reaction. Consequently it cannot be said whether the function of the sulfuric acid is to poison the walls and thus prevent them from breaking reaction chains involving free radicals, or whether the reaction itself takes place in the thin layer of sulfuric acid on the vessel walls, or whether the action of the radiation produces from the sulfuric acid and other substances present a catalyst which can operate in the gas phase.

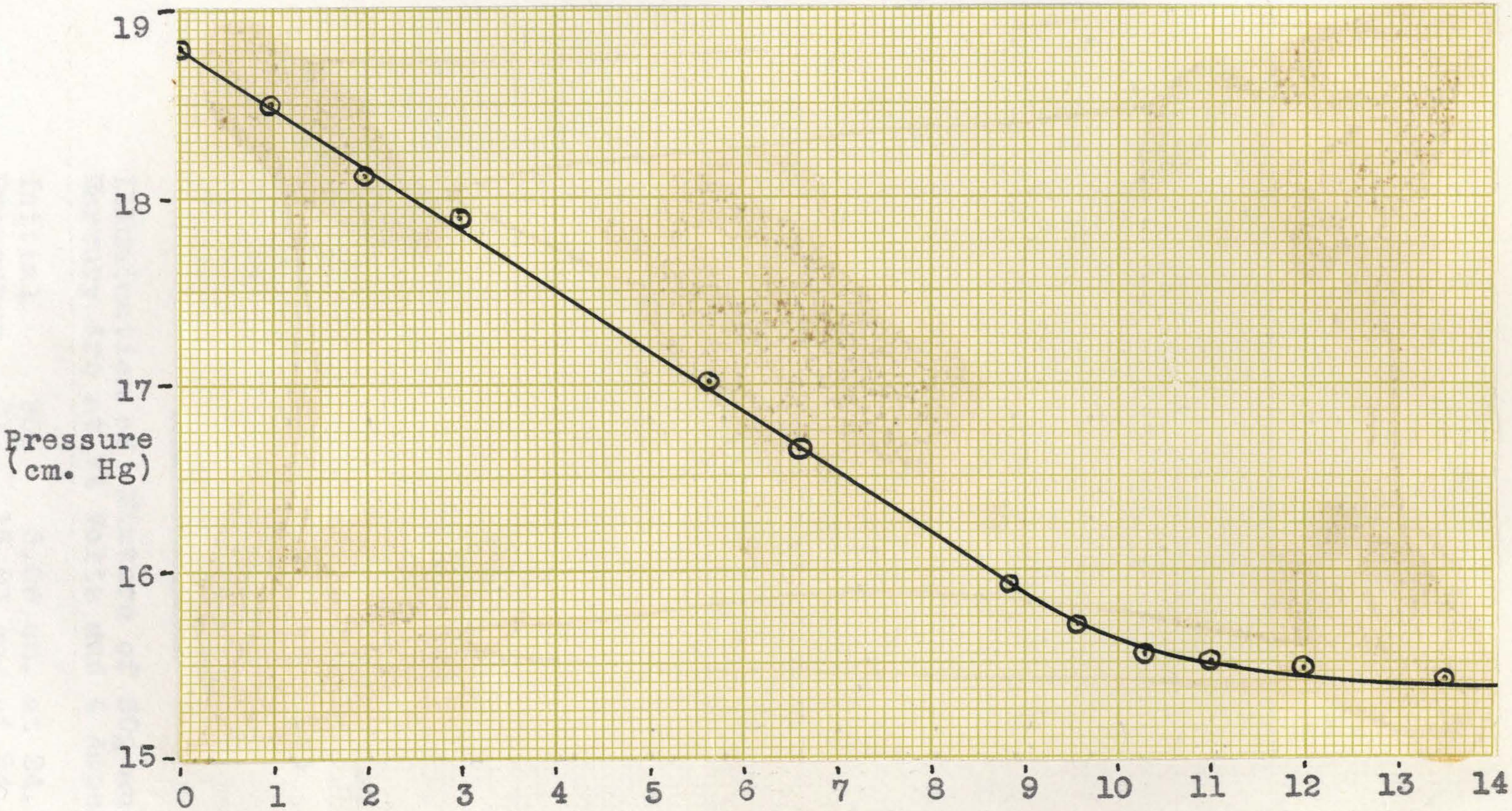
TABLE

Comparison of Photochemical Stationary States and Thermal Equilibria for the Reaction

$$SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$$

Temperature	Substance	Initial Pressure	Final Total Pressure	Final Pressure	K Photochem.	K Thermal
35°C.	SO_2	5.23 cm.		0.08 cm.		
(Exp't. 4a)	Cl_2	15.57		10.42		
	SO_2Cl_2	0		5.15		
			15.65 cm.		470	26.3
50°	SO_2	10.06		6.54		
(Exp't. 3)	Cl_2	8.76		5.24		
	SO_2Cl_2	0		3.52		
			15.30		7.8	12.0
99°	SO_2	6.32		4.37		
(Exp't 4b)	Cl_2	18.78		16.83		
	SO_2Cl_2	0		1.95		
			23.15		2.01	1.45

Figure 2.

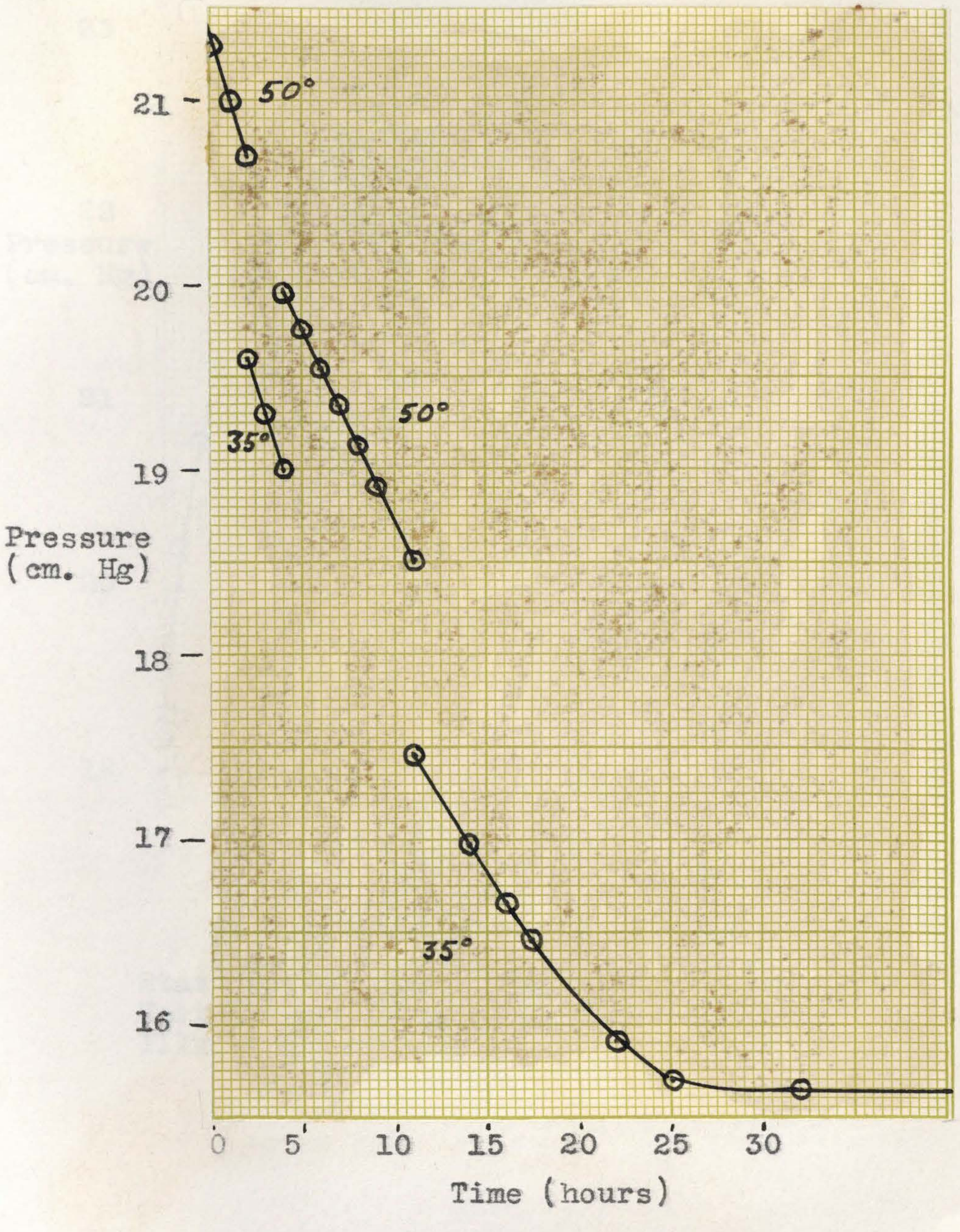


Experiment 3

Illumination of Mixture of SO_2 and Cl_2 at 50° with Mercury Arc at 74 Volts and 4 Amperes.

Initial Pressures	SO_2	9.21 cm. Hg at 23.0°
	Cl_2	8.04 cm. Hg at 23.0°

Figure 3.

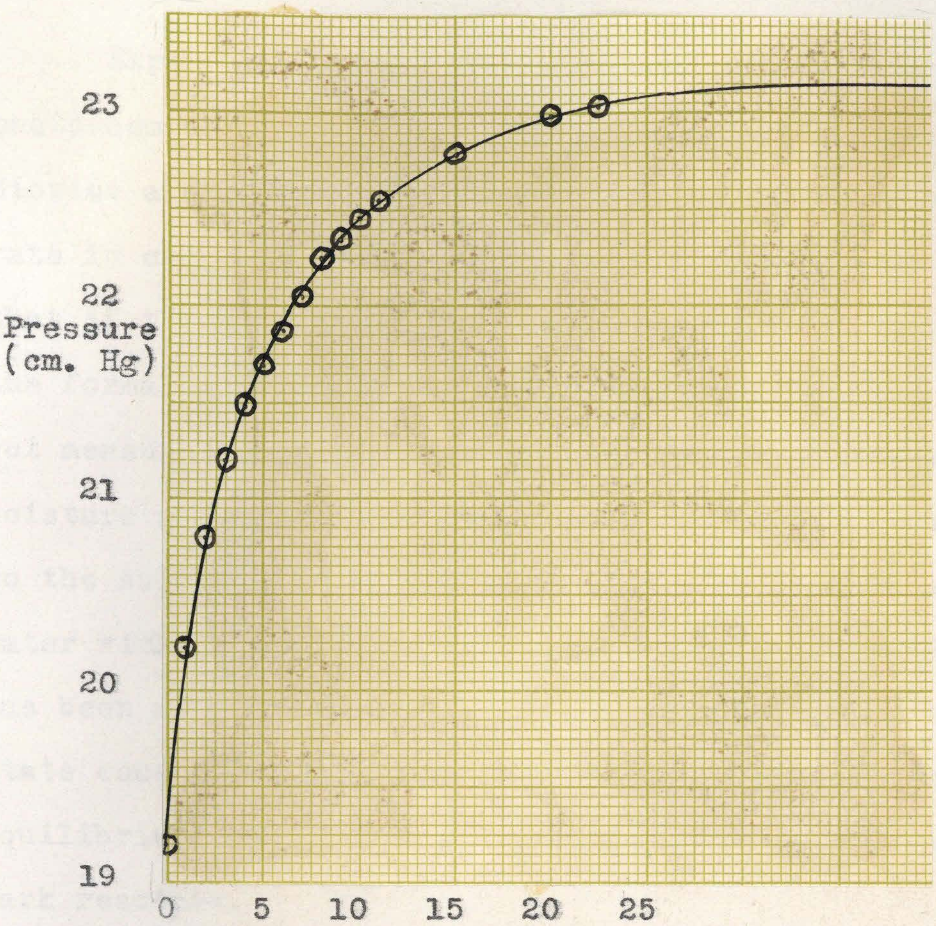


Experiment 4a

Illumination of Mixture of SO_2 and Cl_2 with Mercury Arc at 74 Volts and 4 Amperes.

Initial	SO_2	5.06 cm. at 24.5°
Pressures	Cl_2	15.03 cm. at 24.5°

Figure 4.



Experiment 4b

Stationary State Mixture from Experiment 4a
Heated from 35° to 99° in Dark and then
Illuminated at 99° with the Mercury Arc.

Summary

Experiments have been described which show that the photochemical formation of sulfuryl chloride from sulfur dioxide and chlorine proceeds at an immeasurably slow rate in case the gases are dry. It has also been shown that if the vessel walls are wet with pure sulfuric acid the formation of sulfuryl chloride takes place at a slow but measurable rate. The previously observed effect of moisture on the rate of the reaction has been attributed to the sulfuric acid produced by the reaction of the water with chlorine and sulfur dioxide. A comparison has been made of the approximate values of the stationary state constants found in these experiments with the equilibrium constants for the heterogeneously catalyzed dark reaction.

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PART III

The Thermal Isomerization of Dimethyl Maleate Catalyzed by Iodine

The Thermal Isomerization of Dimethyl Maleate Catalyzed by Iodine

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As part of a general investigation of the kinetics of *cis-trans* isomerizations catalyzed by iodine[1,2] it was decided to investigate the thermal isomerization of dimethyl maleate catalyzed by iodine. That iodine acts as a catalyst for the reaction involving diethyl maleate was observed very early and the analogous reaction for dimethyl maleate was confirmed by us. In preliminary experiments pure dimethyl fumarate prepared from fumaric acid and methyl alcohol underwent no decrease in melting point when mixed with the product obtained by heating dimethyl maleate with iodine in cyclohexane solution. This was also true for the products obtained by heating dimethyl maleate with iodine alone and with iodine in benzene solution. We have measured reaction rates for this thermal isomerization of dimethyl maleate catalyzed by iodine in cyclohexane solution.

Materials

Dimethyl Maleate - Maleic acid was esterified with methyl alcohol using the method of Corson, Adams, and Scott[4]. The ester was fractionally distilled at a pressure of 10 mm. of mercury, then dissolved in methyl alcohol and fractionally crystallized, when it was again fractionally distilled at 11 mm. At this pressure the material boiled at 88.0°. Its dielectric constant at 25° was 8.99.

Dimethyl Fumarate - Fumaric acid was esterified with methyl alcohol using the same method as was employed for maleic acid. The ester was twice recrystallized from ethyl alcohol and once from thiophene-free dry benzene. It melted at 101.5-102.0°.

Cyclohexane - Eastman "Practical" cyclohexane was stirred several hours with 110% fuming sulfuric acid, washed with sodium hydroxide once, washed three times with water, dried with calcium chloride and distilled. It boiled at 81.3°. At 25° its dielectric constant was 2.013.

Iodine - Pure Merck iodine was ground together with potassium iodide and sublimed. The product was resublimed and stored in a desiccator.

Analytical Method

Dielectric constant measurements were employed to determine the concentration of dimethyl maleate in cyclohexane solutions saturated with dimethyl fumarate. For this purpose the dielectric constants of a series of known solutions of dimethyl maleate in cyclohexane which was saturated with dimethyl fumarate were determined at 25°. The results are given in Table I.

TABLE I

DIELECTRIC CONSTANTS AT 25° OF SOLUTIONS OF DIMETHYL MALEATE IN CYCLOHEXANE SATURATED WITH DIMETHYL FUMARATE

$\frac{\text{grams of maleate}}{\text{grams of (maleate} + C_6H_{12})}$	0	0.0130	0.0333
Dielectric Constant	2.033	2.079	2.148

In practice, instead of using the dielectric constants, the corrected precision condenser readings corresponding to them were plotted against composition and a smooth curve (almost a straight line) was drawn through these points. Making use of this plot it was possible to read off directly the composition of a solution once its dielectric constant (or rather the corresponding precision condenser reading) had been determined. The apparatus and hook-up used are described by Wood[2,5].

In carrying out the dielectric constant determination it was necessary to correct the precision condenser reading for the effect produced by the dissolved iodine. This was done by adding the empirically found correction of -0.01 to the precision condenser reading for each centigram of iodine present in 14 grams of solution.

The accuracy and reliability of this method as applied to actual experiments were tested by analyzing by two different methods the contents of an ampoule with which a rate experiment had been made. First, the solution was analyzed by determining its dielectric constant. Then it was again analyzed by equilibrating at 25°, filtering off and weighing the solid fumarate, and adding to this weight the weight of fumarate calculated (from solubility measurements) to be dissolved in the cyclohexane and maleate mixture. The differences for each of the several reaction mixtures analyzed were not significant. That is, the amounts of fumarate found by the two methods agreed very well, and it was therefore concluded that the method of analysis was reliable in practice.

Experimental Procedure

Weighed amounts of dimethyl maleate, cyclohexane, and iodine were placed in a pyrex glass ampoule. The ampoule was placed in a dry-ice and alcohol slush and the contents frozen, the solution being protected from the access of moisture by means of a calcium chloride tube. The ampoule was then pumped down, sometimes with an oil pump and sometimes with a mercury vapor pump, suitable traps being used in each case. The tube was sealed off during the pumping and then placed for a measured period of time in the vapor in a light-tight thermostat containing a boiling liquid (chlorobenzene was used in some experiments and toluene in some others); in any one experiment the temperature range was less than 0.1°. The ampoule was then removed, cooled, and placed for a half hour in a shaking device in a thermostat at 25° in order to saturate the solution with the fumarate formed by the reaction. In case not enough fumarate had been formed to saturate the solution at 25° then sufficient fumarate was added to obtain a solid phase in equilibrium with the solution. The dielectric constant of the solution in the ampoule was then measured at 25°.

Blank experiments in which iodine was heated with cyclohexane in the absence of dimethyl maleate gave no change in the dielectric constant. Blank experiments in which iodine was omitted showed no isomerization of the maleate at the temperatures used.

Several experiments were made at 130° starting with dimethyl fumarate alone dissolved in cyclohexane. In no case did the measured dielectric constant change significantly; on the basis of these experiments it was concluded that the velocity of the reverse reaction of the *cis-trans* conversion could not be more than 1% as fast as the forward reaction. Consequently the reverse reaction has been regarded as negligible.

Experimental Results

In Table II are summarized the results of experiments carried out in order to determine the effect of various factors upon the rate of isomerization of dimethyl maleate. The numbers in the column with the heading k were calculated from the equation

$$k = \frac{1}{t\,(I_2)^{\frac{1}{2}}} \quad \ln \frac{(C)_0}{(C)}$$

where $(C)_0$ is the original concentration of dimethyl maleate and (C) its concentration after the time t. This equation is derived by integrating the equation

$$-\frac{d(C)}{dt} = k\,(C)(I_2)^{\frac{1}{2}}$$

the differential equation for the rate of disappearance of dimethyl maleate on the assumption that the kinetics are the same as for the iodine-catalyzed conversion of cis- into trans-cinnamic acid in benzene solution and for the iodine-catalyzed isomerizations of the cis- and trans-dichloroethylenes.

It is evident from an inspection of Table II that there is very little agreement among these k's. For example, Experiments 7-10 were run on the same reaction mixture divided among four different reaction vessels and heated to the same temperature for the same length of time. Nevertheless, <u>k</u> is different for each experiment in this group. Other groups of experiments of this type are Experiments 4 and 5; Experiments 12 and 13; Experiments 16 and 18; Experiments 27,28 and 29; Experiments 32 and 33.

In an attempt to determine the source of the irreproducibility of the rate experiments the technique of loading the reaction vessels was changed early in the course of the experiments. Instead of using an oil pump which was done in some of the work with the dichloroethylenes, first an oil pump with a trap was used, and then a mercury vapor pump with a trap all of the connections of which were of glass. No rubber was used. In using the mercury vapor pump the contents of a tube were frozen, pumped on, melted, refrozen, pumped on again, and then the tube was sealed off. No improvement in reproducibility was noted.

Experiments 11, 14, 17, and 23 in which various added materials were present during the reaction show the same variability as the "clean" experiments.

Experiment 26 was conducted in a reaction vessel in which had been placed enough pyrex rod to make the total surface in contact with the solution more than three times as large as in the other experiments. The <u>k</u> obtained, while lower than the average, is not strikingly low.

Blank experiments in which the reaction mixtures were exposed to sunlight and room light at room temperature in the presence and in the absence of oxygen showed no change in dielectric constant. Complete experiments were also carried out in a dark room in which all the operations requiring light were carried out with the aid of a shaded 5-watt Mazda lamp at least ten feet away. These are Experiments 27, 28, and 29 and they, too, exhibit the distressing variability.

Blank experiments were performed in which the dielectric constant of a reaction mixture was measured, the mixture loaded into a tube in the usual manner, the tube cooled, pumped down, and sealed off. Then without heating the tube was opened and analyzed. No change in dielectric constant was ever observed.

It is possible that the lack of reproducibility was due to a catalysis of the rearrangement by oxygen in the presence of iodine. That it could not be due to oxygen alone at the temperatures employed was demonstrated by blanks in which iodine was omitted. However, at higher pressures of the order of an atmosphere and at temperatures of 100°-150° oxygen is apparently capable of acting as a catalyst alone.[6] Certainly oxygen was not completely removed by the loading technique used in the experiments described in this thesis. In this connection it may be mentioned that the measures taken to remove oxygen are more extensive than those taken in the studies of the other two isomerizations of this type[1,2]. It is, however, possible that the fraction of a millimeter of mercury pressure of oxygen that was not removed could in some way act catalytically in the presence of iodine.

In spite of this irreproducibility of experiments it is possible to obtain some information from them. It should be noted that although the initial concentration of dimethyl maleate has been varied more than three-fold and the concentration of iodine thirteen-fold, there is no definite trend of $\underline{k}$ corresponding to these changes. The irreproducibility does not change with the concentrations of maleate and iodine. Perhaps it is then reasonable to assume that in the main the differential equation assumed for the rate is correct, and that the variations observed are due to a simultaneous catalysis by some unknown substance, or to some sort of inhibitory mechanism, or to both. The mean $\underline{k}$ for thirty-one experiments at temperatures of 130.5° to 131.4° is 0.695; this excludes those experiments in which $\underline{k}$'s greater than 1.00 were obtained. The two experiments performed at 110.2° are too widely divergent to warrant averaging the $\underline{k}$'s calculated from their results.

TABLE II

RATES FOR THE CONVERSION OF DIMETHYL MALEATE INTO DIMETHYL FUMARATE

No.	Temp.	Initial Conc. of Maleate mol/kg.	Conc. of Iodine mol/kg.	Duration hrs.	Final Conc. of Maleate mol/kg.	k mol$^{-\frac{1}{2}}$ kg.$^{\frac{1}{2}}$ hr.$^{-1}$
1	130.9°C.	0.428	0.0088	4.63	0.152	2.39
2	130.9	"	"	8.75	.241	0.700
3	130.9	"	"	25.0	.084	0.695
4	130.9	0.320	0.0126	5.01	.033	4.03
5	130.9	"	"	5.01	.187	0.957
6	130.9	"	"	5.20	.204	.772
7	131.4	0.339	0.0177	5.03	.177	.972
8	131.4	"	"	5.03	.211	.707
9	131.4	"	"	5.03	.218	.659
10	131.4	"	"	5.03	.244	.492
11 ★	131.4	"	"	5.03	.242	.506
12	131.4	0.344	0.0175	5.05	.215	.703
13	131.4	"	"	5.05	.179	.975
14 ✳	131.4	"	"	5.05	.200	.811
15	131.4	"	"	5.00	.196	.852
16	131.4	0.339	0.0144	5.03	.192	.945
17 ⊙	131.4	"	"	5.03	.211	.787
18	131.4	"	"	5.03	.247	.526
19	131.4	"	"	5.42	.224	.636
20	131.4	"	"	5.00	.229	.655
23 □	131.4	0.327	0.0155	5.03	.216	.662
25	131.2	0.327	0.0155	5.03	.154	1.203
26 †	131.2	0.325	0.0193	5.03	.233	0.477
27 △	131.2	"	"	5.00	.190	.773
28	131.2	"	"	5.00	.192	.758
29	131.2	"	"	5.00	.170	.933
30	131.1	0.341	0.00183	15.5	.250	.468
31	130.8	"	"	14.9	.261	.420
32	130.8	0.201	0.0243	5.05	.081	1.154
33	130.8	"	"	5.05	.125	0.603
34	130.8	"	"	9.87	.065	.733
35	130.8	0.656	0.0210	10.1	.325	.478
36	130.5	0.675	"	22.0	.067	.723
37	130.5	0.660	0.0211	22.0	.087	.633
38	130.8	0.654	"	10.1	.299	.533
39	110.2	0.380	0.118	8.97	.282	.097
40	110.2	"	"	25.0	.306	.025

★ 0.02 g. water present during run.
✳ few mg. sulfur " " ".
⊙ 1.0 g. dimethyl fumarate present during run.
□ few mg. benzoyl peroxide " " ".
† 400 cm^2 surface of pyrex rod " " ".
△ all operations under light of 5-watt Mazda lamp quite far away.

Discussion

Since the differential equation

$$-\frac{d(C)}{dt} = k\,(C)\,(I_2)^{\frac{1}{2}}$$

holds approximately for the isomerization of dimethyl maleate catalyzed by iodine, the mechanism of the catalysis may be assumed to consist partly of the following set of reactions, which apparently hold for the iodine-catalyzed isomerizations of _cis_-cinnamic acid and dichloroethylene;

$$I_2 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} 2I \tag{1}$$

$$I + C \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} AI \tag{2}$$

$$AI \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} BI \tag{3}$$

$$BI \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} T + I \tag{4}$$

where C and T represent respectively the _cis_- and _trans_-

compounds, dimethyl maleate and dimethyl fumarate in this case. On the assumption that I, AI, and BI remain at low concentration, the usual treatment leads to the rate expression

$$-\frac{d(C)}{dt} = \sqrt{\frac{k_1}{k_1'}(I_2)} \quad \frac{k_2k_3k_4(C) - k_2'k_3'k_4'(T)}{k_2'k_3' + k_2'k_4 + k_3k_4}$$

Since no isomerization was observed in experiments starting with dimethyl fumarate, the term in (T) may be dropped in discussing the present experiments, leaving

$$-\frac{d(C)}{dt} = \sqrt{\frac{k_1}{k_1'}} \quad \frac{k_2k_3k_4}{k_2'k_3' + k_2'k_4 + k_3k_4} (C)(I_2)^{\frac{1}{2}}$$

This is of the same form as the empirical equation which was found to represent the rate approximately.

An expression of this same form may be derived on the assumption that the catalyst consists of iodine ions in equilibrium with molecular iodine. That is

$$I_2 \longrightarrow I^+ + I^-$$

Wood and Dickinson, however, cite good evidence against an ionic catalysis in the case of dichloroethylene isomerization. Since in the case of the maleate experiments the oscillations in the dielectric constant apparatus were always strong and since the presence of an appreciable number of ions would bring about a quenching of the oscillations it is concluded that the number of iodine ions in solution was always small and that the ionic mechanism of iodine catalysis probably does not occur in the case of dimethyl maleate.

In the mechanism involving iodine atom catalysis it is assumed that the iodine atom ruptures the carbon-carbon double bond and attaches itself to one of the freed electron pairs of a carbon atom. This unstable iodine-dimethyl maleate complex, AI, therefore has a single carbon-carbon bond about which it is assumed rotation can take place resulting in the formation of an iodine-dimethyl fumarate complex, BI, which decomposes to form an iodine atom and dimethyl fumarate. In order for BI to be formed from AI according to this mechanism it is necessary either that an inversion take place during the rotation or that the tetrahedral configuration of the carbon atoms be lost during the rotation. I have not been able to find any experimental evidence concerning this point, nor have I been able to conceive of any experiments which might be performed to throw light on this problem of whether an inversion takes place or whether the carbon atoms being in an excited state during rotation no longer have their tetrahedral configurations.

It is still necessary to produce a plausible explanation of the lack of reproducibility of the experiments with dimethyl maleate. It has been suggested earlier in this thesis that the small and variable quantity of oxygen present might have been responsible for the fluctuations of the rate constants, and this suggestion is supported by the work of Tamamushi and Akiyama. The small pressures of oxygen present in the experiments described here together with the fact that in our experiments no isomerization occurred in the absence of iodine makes it appear necessary, however, to ascribe the fluctuations either to some other catalyst entirely or to ascribe some of the catalysis to the action of a free radical or some other substance formed from iodine and oxygen. The probability of oxygen inhibiting the catalysis cannot be excluded although it appears somewhat remote since no special precautions for excluding oxygen gas from the reactants were necessary in the case of the related reaction involving the dichloroethylenes.

Summary

Dielectric constants of solutions of dimethyl maleate in cyclohexane saturated with dimethyl fumarate have been measured. Rates of isomerization of dimethyl maleate in cyclohexane solution and employing iodine as a catalyst have been measured. Although these rates fluctuated to a considerable extent, they seem to indicate that the rate of the reaction is proportional to the concentration of the dimethyl maleate and to the square root of the iodine concentration, with some not yet identified catalyst or inhibitor or both producing variations in the rate. That is, the kinetics appear to be compatible with an iodine atom catalysis plus a catalysis or inhibition due to some as yet unidentified factor.

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PROPOSITIONS SUBMITTED

PROPOSITIONS SUBMITTED

1. As suggested by Stotz, Harrer, and King[1], the experimental evidence for the existence of ascorbic acid oxidase does not exclude an alternative interpretation of the observations, namely, one in which certain characteristics of the copper-catalyzed oxidation of ascorbic acid in the presence of protein are drawn upon.

2. The so-called mechanism postulated by Barron, De Meio, and Klemperer[2], for the copper-catalyzed oxidation of ascorbic acid by oxygen requires extensive revision.

3. The explanation of the kinetic origin of osmotic pressure and of the lowering of solvent vapor-pressure by solutes given by Eucken[3] is unsound.

4. The methods used for developing critical habits of thought in undergraduates at the California Institute of Technology can be improved.

5. Ernst Mach's formulation[4] of the laws of motion is representative of the form in which the laws of physics should be placed.

6. A probable value for the resonance energy of ascorbate ion in excess of that for ascorbic acid is 6 to 7 kcal. per mole.

7. The statement of Tramm[5] that the photochemical formation of sulfuryl chloride from sulfur dioxide and chlorine is dependent on the water-vapor content of the reacting mixture is not supported by the evidence[5,6].

8. The rates of the silver-ion-catalyzed reduction of peroxysulfate ion by (a) chromic ion[7], vanadyl ion[8], or manganous ion[9] and (b) by formic acid[10] imply that the mechanism of the reduction is different in the case of formic acid. It would be of interest to carry out a detailed study of the factors governing the rate of the reduction by formic acid.

9. The following constitute a reasonable set of objectives for a course in general chemistry in a liberal arts college:

   (a) To enable the student to acquire an elementary understanding of the principles of chemistry.

   (b) To give him practice in the application of these principles in the laboratory and to inform him of the applications of chemistry in the home, farm, and industry.

   (c) To give him an understanding of and practice in the method of science and the use of the method in fields other than science.

   (d) To give him an appreciation of the effect of science upon society.

   (e) To discover the student who possesses originality and to help him to develop it.

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