[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE REACTION BETWEEN CARBON MONOXIDE AND IODIC ACID IN AQUEOUS SULFURIC ACID

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It was found in the course of war-time investigations that a mixture of iodine pentoxide and fuming sulfuric acid incorporated with granular pumice, or shredded asbestos, not only removes carbon monoxide rapidly from a current of air, but also undergoes a marked color change which can be utilized as a sensitive test for that gas.[1] Up to the present little or nothing appears to be known as to the mechanism of this reaction. We have, therefore, as a beginning, studied the velocity of this reaction in relatively dilute solutions of sulfuric acid, varying the concentrations of the several factors, in the hope of elucidating the roles which each of them plays.

Orienting Experiments.—Solutions of iodic acid, or iodine pentoxide in 90%, and particularly in fuming sulfuric acid, react instantly with carbon monoxide at room temperature, while pure aqueous solutions of iodic acid are without action. In order to obtain orienting quantitative data on this accelerating effect of sulfuric acid, we measured the velocity of the reaction in 3.74 *M* (30.0%), 2.98 *M* (24.8%), and 2.28 *M* (19.66%) sulfuric acid.

For these measurements 0.01 *M* solutions of iodic acid in the sulfuric acids of the three concentrations were prepared, and 50cc. portions were shaken with pure carbon monoxide at atmospheric pressure in carefully stoppered and sealed 250cc. Erlenmeyer flasks submerged in a thermostat at 24.77 ± 0.01°. The approximately 200 cc. of carbon monoxide in each flask afforded a nearly 12 times excess, as compared with the iodic acid. After suitable intervals the flasks were removed, and to arrest the reaction their contents were poured into a large excess of ice-cold water, and analyzed for free iodine.

The shaking was performed in a machine which gave four shakes per second with an amplitude of 5 cm. This thoroughly "atomized" the contents of the flasks. The analysis was accomplished by careful extraction of the ice-cold solution with carbon tetrachloride, washing with water, and titration of the iodine with 0.02 *N* sodium thiosulfate solution after the addition of potassium iodide, using starch as an indicator.

The carbon monoxide was prepared from formic acid, and had been carefully freed from acidic impurities. The iodine pentoxide had been prepared by the chloric acid method[2] and was very pure. The solutions of sulfuric acid were made up by weight from a carefully standardized and carefully protected stock supply.

From two to four measurements were made at each time interval. The mean values obtained in these measurements are shown in Fig. 1. Their average deviation was only ± 0.00002 equivalent of iodine, or about ± 2%.

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[1] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12,** 213 (1920). Hoover, *ibid.*, **13,** 720 (1921).

[2] Lamb, Bray and Geldard, THIS JOURNAL, **42,** 1636 (1920).

In spite of the violent agitation maintained during these experiments, there was still the possibility that the carbon monoxide diffused so slowly into the solution that its reaction with the iodic acid was thereby retarded, and that the observed velocities were fictitiously low on that account. To test this point, we repeated a number of the above mentioned measurements, except that the flasks were rotated rather slowly (once in two seconds) end-over-end, instead of being violently shaken. Very little dispersion of the solution into fine drops took place, and the areas of the liquid-gas boundaries must have been small as compared with those secured in the previous measurements. The values obtained in this way are marked with an R in the figure. It can be seen that in the most dilute acid there is no appreciable lag, in the intermediate acid there is a slight, and only in the most concentrated acid is there a decided lag of the rotated behind the shaken samples. Since the great increase in the rapidity of diffusion secured by shaking, as compared with rotation, produced so slight an effect, at least in the more dilute acids, it is reasonable to conclude that a further increase in the rapidity of diffusion would have been without material effect; or, in other words, that slowness of diffusion must have played only a negligible role in these cases. Any effect it may have had in the most concentrated acid, when corrected for, would have indicated an even more marked accelerating effect of the sulfuric acid.

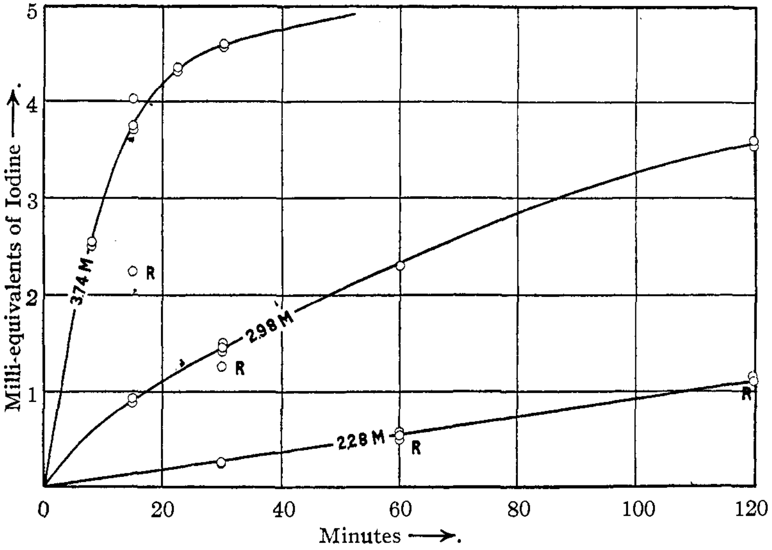

Fig. 1.

Velocity constants were computed from these data on the assumption of a unimolecular reaction $\left(k = 2.30\ 1/t \log \frac{a}{a-x}\right)$ between the iodic acid and carbon monoxide at nearly constant concentration. The constants obtained for each concentration showed an average deviation from the mean of only ± 6%, and this indicates that in the presence of an excess of carbon monoxide, under these conditions, the reaction is indeed unimolecular. The mean constants were, respectively, at concentrations of sulfuric acid of 2.28, 2.98 and 3.74 *M*, 1.96 ± 0.12, 11.4 ± 0.9 and 90 ± 5 $\times 10^{-3}$. The marked increase of these constants and of the slopes of the curves in Fig. 1 with increasing concentration of the sulfuric acid shows the great accelerating effect of this substance.

The Role of the Iodic Acid.—The above experiments indicated that the iodic acid in the presence of a large excess of carbon monoxide reacts unimolecularly. To establish this point more conclusively, we have measured the amounts of iodine present after an interval of 30 minutes in 50cc. samples of sulfuric acid of the same concentration, but containing iodic acid of widely varying concentrations. The results are collected in Table I.

TABLE I

EFFECT OF CONCENTRATION OF IODIC ACID ON THE VELOCITY

H_2SO_4 = 24.4% Time = 30 min. Temp. = 24.77°

I HIO_3 Milli-moles	II Iodine formed Milli-equivalents per liter Obs.	III Mean	IV $\frac{III}{I}$
5.00	1.69 1.68	1.68	0.34
10.00	2.90 2.88 2.96	2.91	0.29
20.00	6.00 6.28 6.72	6.33	0.32
50.00	13.7 15.4	14.5	0.29

The values given in the last column of Table I, representing the ratio between the equivalents per liter of iodine formed and the concentration of the iodic acid, are substantially constant, and show that the velocity of the reaction is directly proportional to the first power of the concentration of the iodic acid, and that this substance, therefore, does indeed react unimolecularly under these conditions.

The Role of the Carbon Monoxide.—Preliminary experiments where equal volumes of 0.010 and 0.005 *M* solutions of iodic acid in 25% sulfuric acid were each shaken with an excess, first of pure carbon monoxide, and then of a 1:1 mixture of carbon monoxide and air gave, respectively, identical amounts of liberated iodine after a 60-minute interval. This indicated that the concentration of the carbon monoxide was without noticeable influence on the velocity of the reaction.

To verify this surprising observation, we have carried out an extended series of velocity measurements with a considerably improved technique. We have, namely, eliminated the uncertainty regarding diffusion by using only *solutions* of carbon monoxide in sulfuric acid. These solutions were of necessity extremely dilute, and this obliged us to adopt all possible refinements of analytical procedure. Our general method has been to prepare a nearly saturated solution of carbon monoxide, divide it among 5 to 10 separate reaction flasks, add to each a large excess of iodine pentoxide dissolved in 10 cc. of the same sulfuric acid, mix the contents of the completely filled and tightly stoppered flasks by means of weighted "floats," after an appropriate interval pour them into a large excess of ice-cold water, extract the free iodine, and titrate this with thiosulfate solution. The details of the apparatus, and the precautions necessary to secure the requisite accuracy are as follows.

Apparatus and Procedure.—The sample of sulfuric acid was shaken with carbon monoxide in a large bottle provided with a delivery tube reaching almost to the bottom. The nearly saturated acid could thus be transferred to the reaction flasks without suffering any change in composition, for the bottle was large enough so that a generous portion of the surface acid, which might have gained or lost some carbon monoxide, could be rejected.

The reaction flasks were of the Erlenmeyer type, of about 250cc. capacity with heavy walls, and were fitted with ground-glass stoppers to which were attached long handles. Glass collars, 10 cm. high, were sealed on to the necks of the flasks, so that when the stoppers were inserted into the filled flasks, the overflowing liquid was caught. In this way the flasks could be completely filled, and all gas bubbles eliminated. This was necessary, since otherwise some of the carbon monoxide would have entered the liquid phase, and then only slowly have redissolved as the reaction progressed. The loaded glass "float" with which each flask was provided so that the contents of the full and stoppered flasks could be stirred, had a volume of about 15 cc. The net volume of each flask was ascertained in advance.

When a series of measurements was to be made, five or ten reaction flasks were quickly filled in the fashion described above with a solution of carbon monoxide in sulfuric acid. The stoppers were quickly inserted, and the flasks were placed in the thermostat. After a half-hour one of the flasks was removed, the excess acid drawn off by suction from the overflow collar and 10 cc. of the iodic acid solution was introduced by means of a pipet with its tip close to the bottom of the flask. The pipet was emptied to within one or two millimeters of its tip by means of controlled air pressure, care being exercised to avoid introducing any bubbles of air into the surrounding liquid. The pipet was then quickly withdrawn, the stopper inserted, the overflow acid again removed, and the contents thoroughly mixed by a careful rotation and manipulation of the flask with its submerged float. This was all done with the greatest possible dispatch and the flask replaced in the thermostat. The time interval was reckoned from the moment of the complete introduction of the iodic acid solution.

Analysis.—The total amount of carbon monoxide gas in the 250cc.

samples to be analyzed was only 2 to 3 cc., and the accurate titration of the minute amount of iodine produced by it required the use of very dilute solutions of thiosulfate. For this purpose, a large volume of approximately 0.001 N sodium thiosulfate solution was filtered and then stored in a light-tight container. Air was removed from the solution and the flask by bubbling pure hydrogen through it, a little chloroform was added, and access of carbon dioxide and dust was prevented by a wash bottle half filled with potassium hydroxide, and attached to the inlet tube. This thiosulfate solution was standardized by means of a copper sulfate solution at weekly intervals during the investigation, and the following results were obtained: 0.825; 0.825; 0.819; 0.805; 0.781 and 0.764 millinormal. These values show that during the first three weeks the decomposition was very slow, and that at no time was it too rapid to prevent an accurate estimate of the concentration of the solution.

After the reaction thus started had progressed for an appropriate interval, the reaction flask was removed from the thermostat and its contents poured into 500 cc. of ice-cold water. The dilution of the sulfuric acid on the one hand, and the low temperature on the other, halted the reaction sharply, and the moment of dilution was taken as the end of the time interval.

The 750 cc. of solution was then carefully extracted with eight or ten 10cc. portions of carbon tetrachloride, with vigorous shaking. In every case the last few extracts were colorless. The combined extracts were washed with four successive 25cc. portions of water to remove all of the iodic acid, for evidently the minutest amount of this substance would, with the potassium iodide used in the iodine titration, produce serious inaccuracies. This aqueous solution was then in turn extracted similarly with a small additional amount of carbon tetrachloride.

A little water was added to the combined solutions of iodine in a separatory funnel, the thiosulfate solution was run in from a buret until the carbon tetrachloride solution became colorless, and then about a.1cc. excess was added. This was indeed about as closely as the color change could be detected. The aqueous solution was then extracted, and with two 10cc. portions of wash water placed in a 100cc. test-tube. An equal volume of water which had also been shaken with carbon tetrachloride was placed in another similar test-tube of the *same glass*, and 2 cc. of fresh starch solution was added to each test-tube. Enough of a 0.001 N iodine solution was then added to the sample to produce a faint color, and the solution was again made colorless by the addition of thiosulfate solution. With practice, and with care in securing identical illumination, a change in color was discernible to within two drops on either side of the end-point. We found this procedure preferable to that of Washburn, who recommends the use of an artificial color standard.[3]

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[3] Washburn, THIS JOURNAL, **30**, 42 (1908).

The accuracy of our end-point was attested by the concordance obtained in our comparisons of the standard thiosulfate and iodine solutions, both approximately millinormal. In 14 consecutive series of comparisons the average deviation from the mean of the four duplicate titrations was ± 0.13 cc. This corresponds to an uncertainty of about 1×10^{-7} g. atoms of iodine, or to 0.006 cc. of carbon monoxide measured under standard conditions. This was sufficiently precise, even for our requirements.

To test as well the accuracy of the extraction and the titration, four 25cc. samples of a solution of iodine in 3.20 M sulfuric acid were extracted and analyzed; 9.63, 9.35, 9.17 and 9.45 cc., or a mean volume of 9.45 cc. of thiosulfate solution, with an average deviation from the mean of ± 0.18 cc., were required. This is as concordant as could be expected.

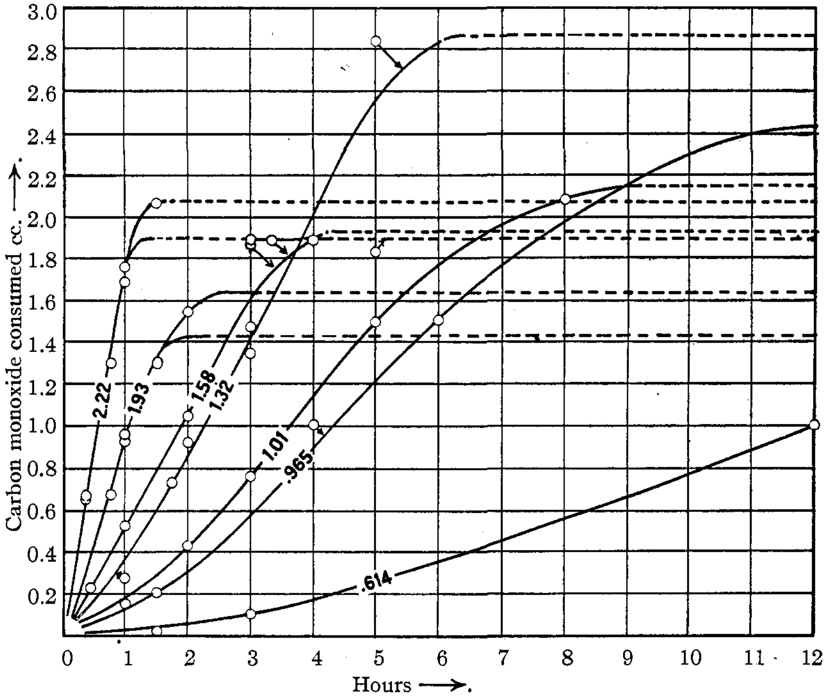

Fig. 2.

Similar samples heated to 70° for an hour required 8.85 and 8.27 cc. of thiosulfate solution, indicating a slight loss of iodine. On the other hand, 25cc. samples of a 1% solution of iodic acid in 3.2 M sulfuric acid, heated for the same time, required 1.23 and 1.10 cc. of thiosulfate solution, indicating a minute decomposition under these conditions. Heat was not, therefore, resorted to as a means of carrying the reaction to completion.

Results.—We carried out ten series of measurements in sulfuric acid of eight different concentrations at 25° and one series in 2.5 *M* acid at 0°. The initial concentration of the carbon monoxide varied from about 4.8 to 12 cc. per liter, corresponding to molar concentrations of 0.00021 and 0.00054. The concentration of the iodic acid was 0.012 *M*, and this substance was therefore present in 50 to 150 times excess. The condensed results of all these measurements are collected in Table II, and have been plotted in Fig. 2.

It can be seen from these results, and with particular clarity from Fig. 2, that the reaction in every case progresses with nearly constant speed until it is almost complete. In other words, in the presence of a large excess of iodic acid, the velocity of this reaction, at least during the major part of its course, is nearly independent of the concentration of the carbon monoxide. This is in agreement with the indications of the preliminary experiments.

TABLE II

VOLUME OF CARBON MONOXIDE CONSUMED AT SUCCESSIVE INTERVALS OF TIME IN SULFURIC ACID OF VARIOUS CONCENTRATIONS

Temperature = 24.77° Concn. HIO_3 = 0.0120 *M* Vol. of solution = 250 cc.

	2.22 *M*			2.22 *M*			1.93 *M*	
	CO			CO			CO	
Time Min.	Obs. Cc.	Calcd. Cc.	Time Min.	Obs. Cc.	Calcd. Cc.	Time Min.	Obs. Cc.	Calcd. Cc.
20	0.65	0.65	20	0.67	0.70	25	0.23	0.33
45	1.31	1.52	60	1.77	1.70	45	.68	.72
60	1.69	1.79	180	1.86	1.90	60	.93	.97
90	2.07	2.01	∞	1.90	(1.90)	90	1.30	1.31
180	2.05	2.08				120	1.54	1.49
∞	2.03	(2.08)				∞	1.64	(1.64)
	1.93 *M*			1.58 *M*			1.32 *M*	
60	0.97	0.94	60	0.53	0.60	60	0.29	0.34
90	1.31	1.21	120	1.05	1.33	105	.74	.81
180	1.35	1.40	180	1.89	1.68	120	.93	.95
∞	1.41	(1.41)	210	1.88	1.75	180	1.58	1.53
			300	1.83	1.89	300	2.84	2.30
			∞	1.93	(1.93)	∞	2.88	(2.88)
	1.01 *M*			0.965 *M*			0.614 *M*	
60	0.16	0.12	90	0.21	0.22	90	0.03	0.03
120	.43	.42	120	.44	.38	180	.11	.11
180	.77	.77	240	1.01	.98	720	1.01	.77
300	1.50	1.30	360	1.51	1.55	∞	1.44	(1.50)
∞	2.16	(2.16)	480	2.09	1.94			
			∞	2.54	(2.54)			

Temperature = 0° Concn. HIO_3 = 0.0120 *M* Concn. H_2SO_4 = 2.37 *M*

Time, min.	30	60	180	540	∞
CO, cc.	0.25	0.58	1.60	2.16	2.16

An explanation of this striking relationship evidently would be that the carbon monoxide takes part in two successive reactions of not very different speeds. Successive reactions of this type are known to give approximately linear curves for the formation of the end product, similar to those observed here.[4] The mathematical treatment of the kinetics of such reactions is not simple, at least if one wishes to use the integral forms of the equations. Moreover, since two constants are involved there is considerably flexibility in these equations, and the invariance of the constants calculated from the various data cannot always be taken as conclusive evidence of the correctness of the assumptions on which the equations are based.

However, to show that such an explanation at least does not conflict with our experimental results, we have computed constants on the assumption of two successive unimolecular reactions. The integral equation applying to such a combined reaction is

$$z = a\left[\frac{k_1e^{-k_2t} - k_2e^{-k_1t}}{k_2 - k_1}\right] + a$$

where k_1 and k_2 represent the velocity constants of the first and second partial reactions, z the number of moles of the final product, a the initial number of moles of the reacting substance, and t the time.[5]

A graphical examination of this equation and our curves indicated that at least approximate agreement would be secured, provided the ratio of k_2 over k_1 were 0.9. On this basis, using a graphical method followed by one of successive approximations, values of k_1 and k_2 were obtained which, in turn, yielded calculated values of z, that is, amounts of carbon dioxide formed, in satisfactory agreement with the observed amounts of carbon monoxide consumed. This of course involves the assumption that there is no reduction, that is, no liberation of iodine except in the second of the two successive reactions. To permit a comparison of these calculated and observed values we have placed them in adjoining columns in Table II.

It is not claimed that this satisfactory agreement *demonstrates* that the reaction progresses as two successive unimolecular reactions, or granting this, that the constants are the best possible ones to fit the observed data. It does show that the assumption of two successive unimolecular reactions is not in conflict with the experimental results.

The Role of the Sulfuric Acid.—In any case, these partial velocity constants furnish a convenient means of studying more carefully than could be done in the orienting experiments the variation of the speed of the reaction with the concentration of the sulfuric acid. For this purpose the values of the velocity constant k_1 and the corresponding concentration of sulfuric acid have been collected in the fifth and first columns, respectively, of Table III.

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[4] Mellor, "Chemical Statics and Dynamics," Longmans, Green and Co., **1904**, p. 96.

[5] It should be noted that there is a mistake in sign in the corresponding equation given by Mellor, Ref. 4, p. 98.

TABLE III

CORRELATION OF VELOCITY CONSTANTS WITH ACTIVITIES

Concn. H_2SO_4 M	Activity coeffi-cient	Mean activity ions $\alpha_{\pm}$	Activity H_2SO_4 α_2	k_1 obs. $\times 1000$	$\frac{k_1}{c}$	$\frac{k_1}{\alpha_{\pm}}$	$\frac{k_1}{\alpha_2}$
0.614	0.169	0.164	0.0044	2.5	0.0041	0.015	0.56
0.965	.151	.231	.0123	6.0	.0062	.026	.49
1.01	.149	.239	.0137	7.2	.0072	.030	.53
1.32	.146	.327	.0350	10.6	.0080	.032	.30
1.58	.146	.366	.0490	21.0	.0133	.057	.43
1.93	.148	.453	.093	37.5	.0195	.083	.40
2.22	.152	.535	.153	60.0	.0267	.112	.39
2.37	.155	.583	.198	..	....	...	..
							.44
							± .07

It can be seen at once that the velocity constant (k_1) increases much more rapidly than does the concentration, the ratio $\frac{k_1}{c}$, given in the sixth column, increasing markedly at higher concentrations. However, over the range of concentrations which we have studied, neither the activity of the sulfuric acid nor the mean activity of its ions is by any means proportional to the total concentration, and hence a strict proportionality between it and the velocity constant k_1 could hardly be expected.

To see whether there is proportionality between k_1 and either the activity of the sulfuric acid or the mean activity of its ions, we have computed these quantities from the values of the activity coefficients of sulfuric acid given by Lewis and Randall,[6] based on a critical discussion of all the pertinent data. By interpolation we have obtained the activity coefficients given in Col. 2 of Table III, corresponding to the total concentrations of our solutions of sulfuric acid. From these we have computed the mean activities of the ions, $\alpha_{\pm}$, given in Col. 3. The ratio of these values and the corresponding velocity constants, $\frac{k_1}{\alpha_{\pm}}$, given in Col. 7, is evidently no more constant than the previous ratio involving the total concentrations. From the mean activities of the ions we have computed the activities of the undissociated sulfuric acid (α_2) by the relation $\alpha_2 = \sqrt[1/3]{\alpha_{\pm}}$. These values are given in Col. 4, and those of the ratio $\frac{k_1}{\alpha_2}$ are given in Col. 8. It can be seen that these values are substantially constant. This indicates that the velocities of both partial reactions which determine the velocity of the total reaction are proportional to the activity of the sulfuric acid molecule.

Interpretation.—The above experiments have shown, first, that the

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 357.

iodic acid, or more probably the iodate ion, and dissolved carbon monoxide both react unimolecularly and presumably in two relatively slow successive reactions of approximately the same speed; and, second, that these speeds are directly proportional to the activity of the sulfuric acid molecule.

A particular mechanism which would operate in accordance with these findings would be represented by the following hypothetical equations.

$$H^+ + H_2SO_4IO_3^- + CO \xrightarrow{(a)} H^+ + (H_2SO_4IO_3CO^-) \xrightarrow{(b)} H^+ + H_2SO_4IO_2^- + CO_2$$

$$H^+ + H_2SO_4IO_2^- + 3/2CO \xrightarrow{(c)} 1/2H_2O + H_2SO_4 + 1/2I_2 + 3/2CO_2$$

Reactions (a) and (b) are the slow successive reactions which determine the speed of the reaction as a whole. Reaction (c) is rapid, and is the only one which yields free iodine. The concentrations of the reactive complexes in Reactions (a) and (b) would evidently be directly proportional to the concentration of the sulfuric acid molecule. It would, of course, be equally compatible with our results to assume that a complex between the sulfuric acid and the carbon monoxide, or some dehydrated product of the iodic acid, whose concentration was proportional to the concentration of the sulfuric acid molecule, was the active reagent in the slow reaction.

Summary

1. The velocity of the reaction between carbon monoxide and iodic acid in 0.6–2.5 *M* sulfuric acid has been measured by extracting the iodine liberated at successive intervals of time, and titrating.

2. It has been found (a) that in sulfuric acid of constant concentration, and in the presence of an excess of carbon monoxide, the velocity is proportional to the concentration of the iodic acid; (b) that in sulfuric acid of a given concentration, and in the presence of iodic acid, the velocity of the reaction is approximately constant until the carbon monoxide is nearly all consumed; and (c) that over the range of concentrations of sulfuric acid used, the velocity under these conditions is nearly proportional to the activity of the undissociated sulfuric acid.

3. These findings have been interpreted as indicating, first, that the iodic acid, or more probably the iodate ion, and the carbon monoxide interact unimolecularly, presumably in two successive reactions of approximately the same speed; second, that the active reagent in both of these reactions is a complex or a reaction product whose concentration is proportional to the activity of the sulfuric acid molecule; and third, that the final slow reaction is followed by a rapid reaction setting free the iodine.

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