produced by substitution on the energy of activation of quinone. The second is ascribed to a "steric hindrance" affecting the probability of reaction of the activated molecule.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SENSITIZED PHOTOSYNTHESIS OF CARBON DIOXIDE AT LOW CHLORINE PRESSURES

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In studying the photosynthesis of phosgene, Chapman and Gee[1] found that oxygen had an inhibiting effect on the reaction. Later Bodenstein[2] showed that the concentration of the oxygen did not remain constant during the reaction, but decreased, due to the formation of carbon dioxide. Schumacher,[3] in a more extensive investigation, found that at high oxygen pressures the phosgene formation was so small that it could be neglected for chlorine pressures below 50 mm. In this case the oxygen and carbon monoxide reacted to form carbon dioxide, the rate law being

$$\frac{d(CO_2)}{dt} = kI_{abs.}^{0.71}\ (CO)^{1/2}$$

or for small absorption of light

$$\frac{d(CO_2)}{dt} = kI_0^{0.71}\ (Cl_2)^{0.71}\ (CO)^{1/2}$$

where I_0 is the intensity of the incident light. The exponent, 0.71, for the light absorbed suggests at once that the conditions were probably such that two parallel reactions were involved, one being proportional to the first power of the light absorbed, the other to the square root. A case of this type was shown to exist in the photosynthesis of hydrobromic acid.[4,5] That reaction followed the square root law at high pressures and the first power at low pressures. It seemed not unreasonable to think that in the sensitized formation of carbon dioxide a similar behavior should be found so that at high pressures of chlorine the square root of the light absorbed would appear in the rate law and at low pressures the first power. In both reactions the explanation of this behavior would be the same, *i. e.*, the destruction of the halogen atoms by first order reactions such as collisions with the walls of the reaction vessel or with impurities predominates at low pressures, whereas the recombination in the gas phase is of greater importance at high pressures.

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[1] Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).

[2] Bodenstein, *Sitzb. preuss. Akad. Wiss.*, **13**, 104 (1926).

[3] Schumacher, *Z. physik. Chem.*, **129**, 241 (1927).

[4] Briers and Chapman, *J. Chem. Soc.*, **130**, 1802 (1928).

[5] Jost and Jung, *Z. physik. Chem.*, **B3**, 83 (1929).

Experimental

From Schumacher's results it seemed that the first power law must hold at pressures of chlorine below two centimeters of mercury; therefore the apparatus used in these experiments was designed for work in that range. The reaction vessel was made of pyrex, cylindrical in form with a plane window at one end and the inlet for the gases at the other. The length of the vessel was 18 cm. and the diameter 6 cm. Uniform illumination was obtained by rendering the light from a 500-watt tungsten filament lamp approximately parallel and passing it through a solution of quinine sulfate to remove rays of wave length less than 4050 Å. It is readily shown that under such conditions the change in intensity of the effective light in passing through the reaction vessel is never more than 10% if the pressure of chlorine is less than 2 cm. of mercury. Furthermore, the deviation from strict proportionality between the amount of light absorbed and the chlorine pressure is less than 5%.

The chlorine was prepared by heating anhydrous cupric chloride in a small side tube sealed onto the tube leading into the reaction vessel. The gas prepared in this manner has been tested previously and found thoroughly satisfactory.[6] The carbon monoxide was prepared by the decomposition of formic acid in sulfuric acid, washed with strong sodium hydroxide solution and finally dried with concentrated sulfuric acid. The gas was stored in a three-liter bulb from which it could be admitted to the reaction vessel as needed. The oxygen was prepared by the electrolysis of potassium hydroxide solution, was freed from hydrogen by passing over hot copper oxide, and was stored in a three-liter bulb containing some anhydrous calcium chloride which served as a drying agent.

The reaction was followed by observing the change in pressure with time. Due to the marked heating which occurs during the reaction, all readings were taken after turning off the light and allowing the system to stand until the pressure became constant. The manometer liquid was sulfuric acid of specific gravity 1.84. As the total pressure used in these experiments was of the order of half an atmosphere, a special form of manometer had to be devised in order to keep the length of the column to be measured within reasonable dimensions. The form finally adopted consisted of a vertical section of glass tubing, internal diameter 3 mm., the upper end of which was connected to the reaction vessel by means of a capillary tube and the lower end was ring-sealed into a flask of one-liter capacity in such a manner that the end dipped into thirty cubic centimeters of sulfuric acid in the bottom of the flask. Another tube leading out of the flask permitted either the simultaneous evacuation of both sides of the manometer or the admission of air into the flask to any desired pressure. Thus the manometer read the difference in pressure between the reaction vessel and the other side. For any one setting the range was approximately 50 cm. of sulfuric acid or 6.75 cm. of mercury. Pressure changes beyond this range were read by resetting the manometer as many times as necessary.

The procedure followed in making a run was to introduce chlorine into the reaction vessel up to a pressure 8–10 cm. of sulfuric acid above that to be used in sensitizing the carbon dioxide formation. Next the carbon monoxide was admitted from the reservoir bulb. These two gases were illuminated with resultant phosgene formation until the chlorine pressure had been reduced to the value desired for the run. This procedure was considered necessary by Schumacher in order to destroy inhibitors which would otherwise cause an induction period in the carbon dioxide formation. Some preliminary tests with the materials used in these experiments showed that frequently this procedure was unnecessary in order to obtain results free from an induction period but the number of

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[6] Rollefson, THIS JOURNAL, 51, 770 (1929).

cases in which the induction period appeared was sufficient so that it was deemed expedient to carry out the reaction as recommended by Schumacher. After this preliminary formation of phosgene, the oxygen was admitted to a pressure 80–100 cm. of sulfuric acid in excess of the amount required for complete oxidaton of the carbon monoxide. A period of from one to three hours was allowed for the gases to mix before starting the reaction. In following the reaction readings were taken at intervals of from one-half to five minutes depending on the speed of the reaction.

Results

The data obtained are summarized in graphical form. Under the conditions of the experiments the amount of phosgene formed should be negligible and the rate independent of the oxygen pressure so that at a given chlorine pressure the observed law should be

$$-\frac{d(\mathrm{CO})}{dt} = k(\mathrm{CO})^{1/2}$$

Integrating this expression

$$(\mathrm{CO})^{1/2} = kt + a$$

where a is the constant of integration. Hence if we plot the square root of the carbon monoxide pressure against the time, the resulting curve should

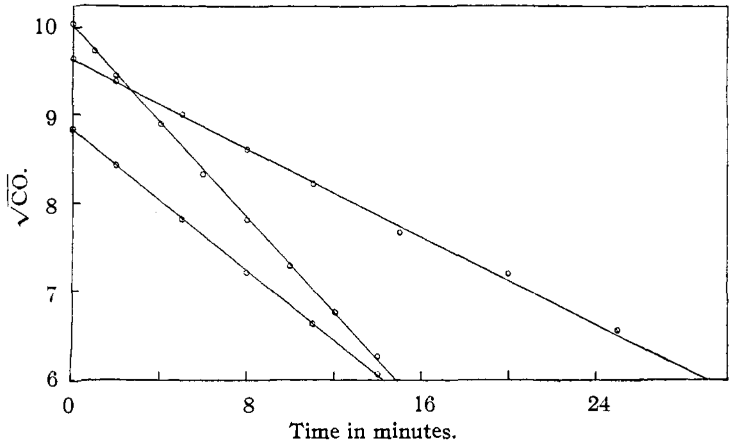

Fig. 1.

be a straight line. Figure 1 shows the curves obtained at three different chlorine pressures. In each case the straightness of the line[7] shows that the assumptions of constancy of the chlorine pressure during the run and independence of the rate from the oxygen pressure are valid.

The effect on the rate of varying the chlorine pressure is obtained by plotting the values of k obtained above against the chlorine pressure raised to such a power that a straight line is obtained. Figure 2 shows the plot using the first power of the chlorine pressure and it is obvious that this law holds well within the limits of error of the experiments.

[7] In these plots the pressures have been left in terms of cm. of sulfuric acid.

It remains to show the effect of varying the intensity of the incident light. The procedure followed was to illuminate a given reaction mixture for three-minute intervals, using various screens to reduce the light intensity. The screens were of black cloth and had been calibrated with a thermopile and tested for neutrality. In Fig. 3 the observed rates are plotted against the light intensity, the intensity with no screen being taken as one. The circles were obtained with one reaction mixture and the crosses with another. The point on the abscissa axis represents the amount of reaction produced by light reflected from the walls of the room and surrounding objects. Another source of error which would be of consequence at low light intensities, but could not be corrected for, is the variation in light intensity due to imperfections in the filters. The graph shows that the rate of reaction is proportional to the first power of the light intensity.

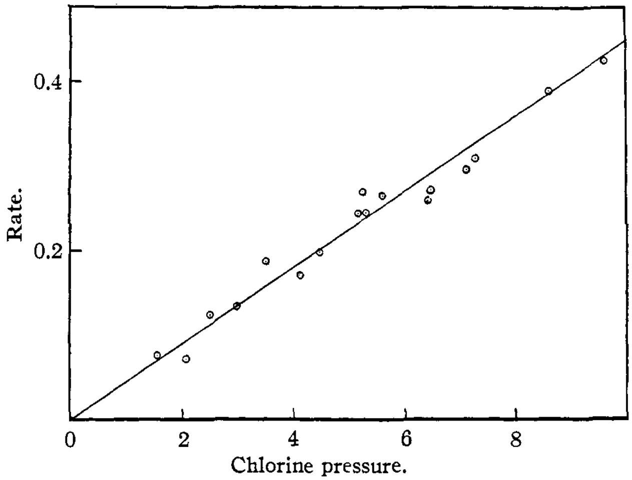

Fig. 2.

Discussion

From the data which have been presented, we see that at low pressures of chlorine the rate of formation of carbon dioxide is given by the expression

$$\frac{d(CO_2)}{dt} = kI_{abs.}\,(CO)^{1/2} = kI_0(Cl_2)(CO)^{1/2}$$

where the substitution of $I_0(Cl_2)$ for $I_{abs.}$ is justified by the fact that the total amount of light absorbed is small. This result confirms the view expressed at the beginning of this paper, to the effect that the exponent 0.71, found by Schumacher, is due to a mixture of reactions. The extension of the measurements to cover the pressure range studied by Schumacher has been delayed pending the construction of an apparatus which will permit the simultaneous observation of the carbon dioxide formation and the phosgene formation which is always present at high chlorine pressures. It may be that the deviation from the first power of the chlorine pressure at high pressures is due to the formation of phosgene, causing a break in the chain of reactions giving carbon dioxide, which would result in the observed yield being less than it would be if the phosgene formation remained negligible. This possibility is to be investigated.

Turning to a consideration of the possible mechanisms for the carbon dioxide formation, we find that the equations given by Bodenstein, Lenher and Wagner[8] and by Lenher and Rollefson[9] agree in that both have the carbon dioxide formed by the action of oxygen on an intermediate compound COCl. No detailed calculations concerning the formation of carbon dioxide were made in either paper as both were primarily concerned with the formation of phosgene. Some attempts have been made to calculate the rate law obtained in this paper from those mechanisms, but they have been unsuccessful, as the derived equations either showed a dependence of the rate on the oxygen pressure, or else gave the wrong exponents for the factors involved. These difficulties may be due to using the wrong chain-terminating reaction, although several different ones were tried. It is, however, possible to draw some conclusions concerning the nature of the

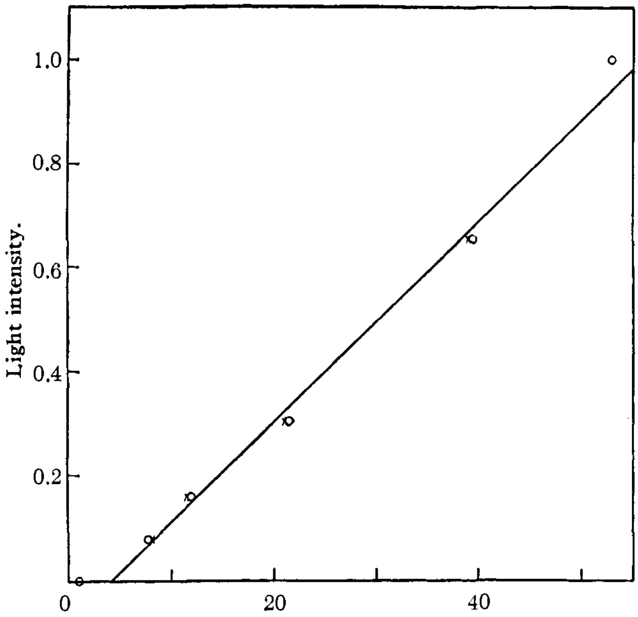

Fig. 3.

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[8] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, B3, 459 (1929).

[9] Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

reaction. In the first place the fact that the rate of the reaction is independent of the oxygen pressure at moderate pressures of oxygen, but not at lower pressures, indicates that in the higher range the step involving oxygen is too fast to be one of the rate-determining steps; therefore, on the basis of both the mechanisms referred to above, the rate of formation of carbon dioxide is essentially the rate of formation of COCl. Now it is an experimental fact that the rate of oxidation of carbon monoxide at a given chlorine pressure is comparable with the rate of formation of phosgene, at the same chlorine pressure, in the absence of oxygen. On the basis of the mechanism of Bodenstein, Lenher and Wagner, this would mean that their Reactions 2 and 4, namely

$$CO + Cl = COCl, \text{ and}$$
$$CO + Cl_2 + Cl = COCl_2 + Cl$$

have comparable rates. Such being the case, it is difficult to see how it would be possible for the phosgene formation to be negligible at any moderate pressure, as is found to be the case. This difficulty does not exist in the mechanism of Lenher and Rollefson, as COCl is a step in the formation of phosgene in that mechanism so that if the COCl is removed rapidly by oxygen, the rate of formation of phosgene will drop to a low value. At high temperatures the rate of dissociation of COCl becomes faster than the rate of reaction with oxygen, and therefore the carbon dioxide formation ceases at such temperatures. From this viewpoint the sensitized photosynthesis of carbon dioxide supports the views of Lenher and Rollefson concerning the formation of phosgene. Further discussion of this system will be postponed until more data are available.

Summary

The chlorine-sensitized photosynthesis of carbon dioxide has been studied for pressures of chlorine ranging from 2 to 13 mm. of mercury. In this range the rate law has been shown to be

$$\frac{d(CO_2)}{dt} = kI_0(Cl_2)(CO)^{1/2}$$

The results have been discussed briefly from the standpoint of the mechanisms which have been proposed by Bodenstein, Lenher and Wagner, and by Lenher and Rollefson.

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