that only the $^2P_{\frac{1}{2}}$ state reacts with hydrogen is therefore not required by the evidence.

Eyring[13] has calculated the heat of activation of reaction (I) from wave mechanics and obtains a value for E_0 between 14,000 and 25,000 calories according to the assumptions. The agreement is perhaps as good as is to be anticipated.

The authors wish to express their appreciation to Professor Bodenstein for his courtesy in communicating to them his recent experimental results.

Summary

The technique of preparing chlorine atoms has been developed. The conditions favoring recombination of chlorine atoms are not the same as for hydrogen atoms.

When chlorine atoms are introduced into a hydrogen–chlorine mixture at low pressure a chain reaction is started which will run, under favorable conditions, until one of the gases is used up. Oxygen and water are without effect on this reaction and the simple mechanism proposed by Nernst is adequate to account for it.

The reaction probability for the reaction $Cl + H_2 = HCl + H$ (I) has been estimated to be 1.4×10^{-5} per collision at 0° and 3.3×10^{-5} at 25°. From the temperature coefficient a heat of activation of 6100 ± 1000 calories is estimated.

[13] Eyring, THIS JOURNAL, **53**, 2537 (1931).

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The Photochemical Oxidation of Phosgene

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The direct photochemical oxidation of phosgene has never been reported in the literature. It was thought possible that the reaction might take place upon insolation with light of $\lambda < 2700$ Å., since Henri[1] had found evidence of predissociation of phosgene beginning in this region. The primary act of absorption is believed[2,3] to lead to the process

$$COCl_2 + h\nu \longrightarrow COCl + Cl$$

in which the intermediate compound COCl is formed. This same intermediate has been postulated in the mechanisms of Bodenstein, Lenher and Wagner[4] and Lenher and Rollefson[5] for the photochemical formation of phosgene.

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[1] Henri, *Proc. Roy. Soc.*, (London) **A128**, 178 (1930).

[2] Almasy and Wagner-Jauregg, *Naturwissenschaften*, **19**, 270 (1931).

[3] Herzberg, *Ergebnisse exakt. Naturwiss.*, **10**, 207 (1931).

[4] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **3B**, 459 (1929).

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

The direct oxidation has been found to take place upon irradiation with ultraviolet light. Since there can be but little question as to the direct formation of COCl in the primary process, a study of the reaction must be chiefly concerned with the subsequent processes involving the intermediate. Thus an entirely new point of attack on the mechanism of phosgene photochemical reactions is afforded.

Experimental

The reaction vessels employed were of clear fused quartz, one a spherical bulb of about 200 cc. volume, the other a cylindrical absorption cell 20 cm. long and 2 cm. in diameter. The cylindrical vessel was mounted on end and illuminated from a source parallel to the longitudinal axis. The source of illumination was the full light of the quartz mercury arc. Two Cooper–Hewitt quartz arcs were used, the earlier work being done with a 110-volt arc while later a 220-volt arc giving greater intensity in the ultraviolet was used. As the arc was run quite close to the reaction vessel, it was found necessary to cool the latter during the work at room temperature. This was done by allowing water to flow smoothly over the surface of the vessel. The temperature of the water never varied more than 2° over a run. For the work at 90 and 200°, a small electric oven having a long narrow quartz window was used. Temperature was kept constant at 90 ± 2° and 200 ± 3° by varying a slide wire resistance in series with the oven.

The phosgene (Kahlbaum) was distilled directly into the line from a glass bomb after freezing the liquid by means of liquid air. The phosgene was then distilled through three reservoir traps in the line, the gas being allowed to bubble through the liquid. Finally, approximately the first and last thirds were pumped off, the middle third being collected in a reservoir trap which was always kept immersed in a Dewar filled with ice water. The liquid phosgene remained perfectly clear, showing no trace of discoloration. When the gas was needed, the liquid in the reservoir was allowed to vaporize into a three-liter bulb from which small amounts could be drawn. The chlorine was prepared by heating anhydrous cupric chloride in the manner previously described.[6,7] Oxygen was prepared electrolytically from potassium hydroxide solution, freed from hydrogen by passing over hot copper oxide, and dried in a storage tube containing magnesium perchlorate.

The course of the reaction was followed by measuring the pressure increase with time. For the low pressure work a sulfuric acid (sp. gr. 1.84) manometer was used and later, with higher pressures, mercury was used as the manometer liquid, protected by 3 or 4 cm. of sulfuric acid. Readings were taken with the arc off at intervals of fifteen to sixty minutes depending on the speed of the reaction. In several of the runs, in order to check the pressure readings, the oxygen was measured by freezing out the other gases (phosgene, carbon dioxide and chlorine) with liquid air.

Results

In Fig. 1 log ($COCl_2$) is plotted against time for several runs. The straight lines obtained indicate that the rate of reaction is proportional to the first power of the phosgene concentration.

The effect of incident light intensity was investigated by using various wire screens which had been previously calibrated by means of a thermopile. The results summarized in Fig. 2 show that the rate is proportional

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(6) Rollefson, THIS JOURNAL, **51**, 770 (1929).

(7) Loeb, *Phys. Rev.*, **35**, 184 (1930).

to the first power of the incident intensity. The intensity with no screen is taken as unity.

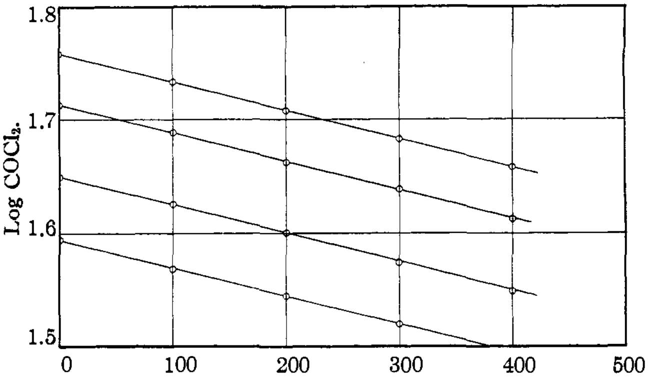

Fig. 1.

At higher oxygen pressures, the rate was found to be independent of the oxygen concentration, while at lower pressures, the rate gradually fell off with decreasing oxygen. This suggested that the rate of reaction might be a function of the chlorine-oxygen ratio rather than of the oxygen concentration itself. In Fig. 3 the rate is plotted against the function $1/(1 + k'(Cl_2/O_2))$ for the temperature, 90°. In each case such a value of k' was taken as would yield a straight line through the origin.

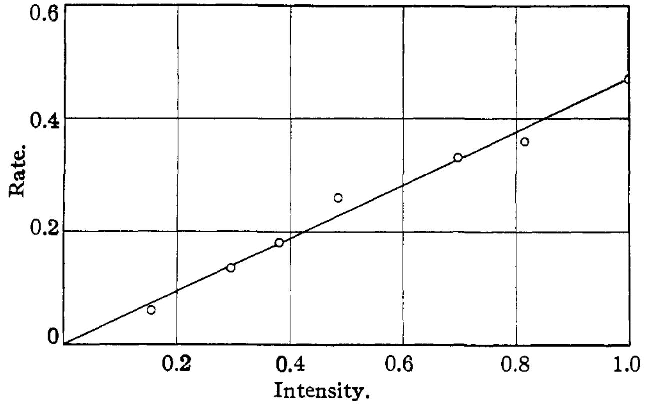

Fig. 2.

As has been pointed out[8] k' should be a definite function of the temperature. The reaction was therefore studied at three temperatures: 20, 90 and 200°. The values of K' found corresponding to these temperatures are as follows

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[8] Rollefson, THIS JOURNAL, **55**, 148 (1933).

Temp., °C.	20	90	200
K'	0.17	0.38	1.00

As an example of the data, the following values of the rate and the Cl_2/O_2 ratio may be given. These points are those obtained at 90° and are represented graphically in Fig. 3.

Rate	0.545	0.475	0.389	0.335	0.139
Cl_2/O_2	0.134	0.565	1.28	2.18	9.89
$1/[1 + 0.4(Cl_2/O_2)]$	0.95	0.81	0.66	0.53	0.22

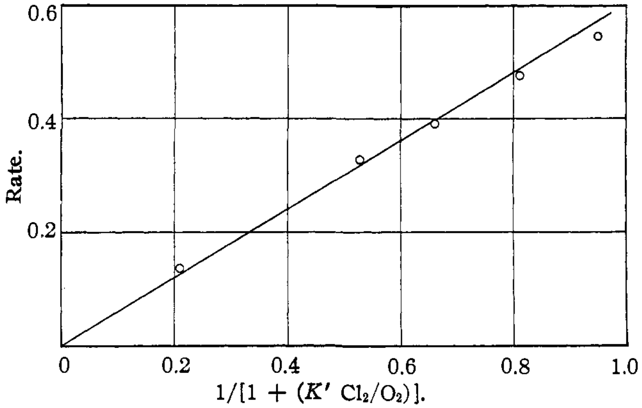

Fig. 3.

Discussion

The data presented above indicate that the rate law for the oxidation of phosgene may be expressed by the equation

$$\frac{d\,(CO_2)}{d\,t} = \frac{k\,I_0\,(COCl_2)\,(O_2)}{(O_2) + k'\,(Cl_2)}$$

or, showing more clearly the dependence on the chlorine–oxygen ratio

$$\frac{d\,(CO_2)}{d\,t} = \frac{k\,I_0\,(COCl_2)}{1 + k'\left(\frac{Cl_2}{O_2}\right)}$$

This rate law may be very simply derived from the following rate mechanism

$$\begin{array}{lll} COCl_2 + h\nu & \longrightarrow COCl + Cl & (1) \\ COCl + O_2 & \longrightarrow CO_2 + ClO & (2) \\ COCl_2 + ClO & \longrightarrow CO_2 + Cl_2 + Cl & (3) \\ COCl + Cl_2 & \longrightarrow COCl_2 + Cl & (4) \\ \left\{\begin{array}{l} Cl + W \\ Cl + Cl \end{array}\right. & \left.\begin{array}{l} \longrightarrow {}^1/_2Cl_2 + W \\ \longrightarrow Cl_2 \end{array}\right\} & \begin{array}{l} (5a) \\ (5b) \end{array} \end{array}$$

Assuming that the rate of change of (COCl) and (ClO) is negligibly small compared to their rates of formation and reaction, we may write

$$\frac{\mathrm{d}\,(\mathrm{COCl})}{\mathrm{d}\,t} = I_{\mathrm{abs.}} - k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) - k_4\,(\mathrm{COCl})\,(\mathrm{Cl_2}) = 0 \qquad \text{(I)}$$

$$\frac{\mathrm{d}\,(\mathrm{ClO})}{\mathrm{d}\,t} = k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) - k_3\,(\mathrm{ClO})\,(\mathrm{COCl_2}) = 0 \qquad \text{(II)}$$

The rate of oxidation is given by

$$\frac{\mathrm{d}\,(\mathrm{CO_2})}{\mathrm{d}\,t} = k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) + k_3\,(\mathrm{ClO})\,(\mathrm{COCl_2}) \qquad \text{(III)}$$

According to II we may write

$$k_3\,(\mathrm{ClO})\,(\mathrm{COCl_2}) = k_2\,(\mathrm{COCl})(\mathrm{O_2})$$

Substituting this expression in III, we obtain

$$\frac{\mathrm{d}\,(\mathrm{CO_2})}{\mathrm{d}\,t} = 2\,k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) \qquad \text{(IV)}$$

From I we have

$$\begin{aligned} k_2\,(\mathrm{COCl})\,(\mathrm{O_2}) + k_4\,(\mathrm{COCl})\,(\mathrm{Cl_2}) &= I_{\mathrm{abs.}} \\ \mathrm{COCl}\,(k_2\mathrm{O_2} + k_4\mathrm{Cl_2}) &= I_{\mathrm{abs.}} \\ (\mathrm{COCl}) &= \frac{I_{\mathrm{abs.}}}{k_2\mathrm{O_2} + k_4\mathrm{Cl_2}} \qquad \text{(V)} \end{aligned}$$

Substituting V in IV gives us

$$\frac{\mathrm{d}\,(\mathrm{CO_2})}{\mathrm{d}\,t} = \frac{2\,k_2\,(\mathrm{O_2})\,I_{\mathrm{abs.}}}{k_2\mathrm{O_2} + k_4\mathrm{Cl_2}} \qquad \text{(VI)}$$

Since the total amount of light absorbed is small, we may write

$$I_{\mathrm{abs.}} = I_0\,(\mathrm{COCl_2})$$

which reduces VI to the expression already obtained experimentally

$$\frac{\mathrm{d}\,(\mathrm{CO_2})}{\mathrm{d}\,t} = \frac{2\,I_0\,(\mathrm{COCl_2})\,(\mathrm{O_2})}{(\mathrm{O_2}) + (k_4/k_2)\,(\mathrm{Cl_2})} = \frac{kI_0\,(\mathrm{COCl_2})\,(\mathrm{O_2})}{(\mathrm{O_2}) + k'\,(\mathrm{Cl_2})}$$

As (Cl) does not enter the derivation explicitly, it is immaterial which process (5a or b) leads to recombination. The rate mechanism is seen to lead to a quantum yield of 2, a point which is to be tested experimentally in the near future.[9]

The manner in which oxygen and chlorine enter the rate law brings out once more the close analogy between a purely chemical process in which two reactants ($\mathrm{Cl_2}$ and $\mathrm{O_2}$) are in competition for a chemical intermediate (COCl) and the process of quenching of fluorescence. This similarity which holds even to the form of the mathematical expressions involved may be seen clearly in this case. Here, although we do not have fluorescence, we may say that the COCl molecule has a definite life period with respect to its reaction with chlorine. If, however, we start with a definite chlorine pressure and vary the oxygen pressure, the number of COCl molecules formed which react with chlorine will decrease as the oxygen pressure

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(9) Experimental evidence obtained from a comparison with the phosgene sensitized formation of carbon dioxide which is very similar to the chlorine sensitized reaction indicates that the quantum yield cannot be greater than 10 and is probably of the order of magnitude of 2 or 3. This phosgene sensitized reaction is being investigated in this Laboratory and the results will be published in the near future.

increases in much the same manner that the intensity of fluorescence decreases with increasing amount of foreign gas present.

k' has been shown to be equal to the ratio k_4/k_2 and may thus be interpreted as a measure of the relative reactivity of chlorine and oxygen with COCl. These two reactions (2 and 4) also appear in the mechanism proposed by Lenher and Rollefson.[5] In some recent work, Rollefson[8] has studied the relative amounts of carbon dioxide and phosgene produced by these two processes in the chlorine sensitized oxidation of carbon monoxide. In both this reaction and the direct oxidation, the same intermediate COCl is reached, though by entirely different processes. Likewise, in both reactions, COCl is believed to react in the same manner with oxygen and chlorine. This parallelism between the two systems is emphasized by the plot in Fig. 2 of Rollefson's paper which shows that the relative efficiencies of oxygen and chlorine are the same for both reactions at all temperatures. While it is possible that different intermediates might give the same ratio at one temperature, it is extremely improbable that the temperature coefficients would also be the same. Therefore we believe that the experiments presented here constitute a definite proof of the existence of COCl as an intermediate in the reactions discussed.

Summary

The direct photochemical oxidation of phosgene has been studied and the following rate law has been determined for the reaction

$$\frac{\mathrm{d}\,(\mathrm{CO_2})}{\mathrm{d}\,t} = \frac{k\, I_0\, (\mathrm{COCl_2})\, (\mathrm{O_2})}{(\mathrm{O_2}) + k'\, (\mathrm{Cl_2})}$$

A mechanism has been suggested for the reaction and the results have been correlated with the work of Lenher and Rollefson on the photochemical formation of phosgene and the chlorine sensitized oxidation of carbon monoxide.

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