

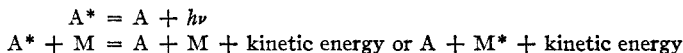
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemistry of Mixtures of Chlorine, Oxygen and Carbon Monoxide

By G. K. ROLLEFSON

When mixtures of carbon monoxide, chlorine, and oxygen are illuminated with light which is absorbed by the chlorine, part of the carbon monoxide is changed to phosgene and part to carbon dioxide. At relatively high pressures of oxygen, carbon dioxide formation occurs almost exclusively, whereas at low oxygen pressures the phosgene formation is predominant. The action of oxygen in this system has been attributed to a reaction with the intermediate COCl .^{1,2} According to the mechanism of Lenher and Rollefson the COCl molecule may react either with chlorine or oxygen, the relative amounts of the two being determined by the specific rate constants for the reactions and the relative pressures of the two gases. In the original mechanism of Bodenstein, Lenher and Wagner it was postulated that only the oxygen reacted with the COCl and the latter compound was assumed to be in equilibrium with carbon monoxide and chlorine in the absence of oxygen but not in the presence of oxygen. Recent work from Bodenstein's laboratory³ indicates that they now accept the view held by Lenher and Rollefson that COCl reacts with both oxygen and chlorine, but they still retain the assumption of equilibrium in the absence of oxygen and a non-equilibrium state in the presence of oxygen. In order to have such conditions it is necessary that the rates of formation and decomposition of COCl be fast compared to the rate of reaction of COCl with chlorine and comparable with the rate of oxidation of COCl . It is the purpose of this paper to present experimental results which show that the specific rates for the reactions of COCl with chlorine and oxygen are of the same order of magnitude and therefore the postulates of Bodenstein and his students are invalid.

The experimental procedure for determining the relative efficiency of reaction of chlorine and oxygen with COCl is suggested by a comparison with the most simple system of this type which we can find, namely, the quenching of fluorescence by the addition of gases. In that case we may represent the processes involved by the equations



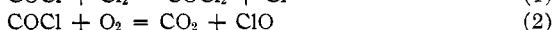
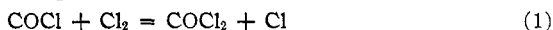
That is, we have the activated molecules, A, returning to the normal state with the emission of light or being deactivated by collision with some molecule M. The relative amounts of these two processes are well known from

(1) Lenher and Rollefson, *THIS JOURNAL*, **52**, 500 (1930).

(2) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929).

(3) Schumacher and Stieger, *ibid.*, **B13**, 157 (1931).

results in the literature. In the present case we do not have any fluorescence, but we may speak of the COCl molecule as having a certain life period with respect to its reaction with chlorine. Now if we take a definite pressure of chlorine and vary the pressure of the oxygen, the fraction of the total number of COCl molecules formed that react with chlorine will decrease as the oxygen pressure increases, much as the intensity of fluorescence is decreased by the addition of a foreign gas. To express this behavior in terms of chemical equations, let us consider the reactions



The rates of these reactions are given by

$$-\frac{d(\text{Cl}_2)}{dt} = k_1 (\text{COCl}) (\text{Cl}_2)$$

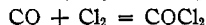
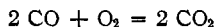
$$-\frac{d(\text{O}_2)}{dt} = k_2 (\text{COCl}) (\text{O}_2)$$

The fraction of the phosgene molecules reacting with oxygen is

$$\frac{\frac{d(\text{O}_2)}{dt}}{\frac{d(\text{O}_2)}{dt} + \frac{d(\text{Cl}_2)}{dt}} = \frac{k_2 (\text{COCl}) (\text{O}_2)}{k_1 (\text{COCl}) (\text{Cl}_2) + k_2 (\text{COCl}) (\text{O}_2)} = \frac{1}{1 + \frac{k_1 (\text{Cl}_2)}{k_2 (\text{O}_2)}}$$

According to this equation the number of moles of oxygen reacting according to (2) will be equal to the number of moles of chlorine reacting according to (1) when $k_1(\text{Cl}_2)$ is equal to $k_2(\text{O}_2)$. Therefore if we determine the ratio of the pressures of chlorine and oxygen for which equal numbers of moles of these two gases react, we will have the ratio of the rate constants.

The experimental technique involved is extremely simple, consisting of illuminating mixtures of chlorine, oxygen and carbon monoxide and determining the extent of the two reactions from the pressure change at room temperature and also after freezing out the condensable gases with liquid air. In order to show how this is done, consider the two reactions



Let Δp_1 be the pressure change due to the first reaction and Δp_2 be that due to the second. The total pressure change is $\Delta p = \Delta p_1 + \Delta p_2$. One other equation involving Δp_1 and Δp_2 will suffice for the determination of these two quantities. To obtain this consider the changes in the sum of the carbon monoxide and O_2 pressures which we shall represent by $\Delta(\text{CO} + \text{O}_2)$.

$$\Delta(\text{CO} + \text{O}_2) = 3\Delta p_1 + \Delta p_2$$

Combining this with our previous equation

$$\Delta p_1 = \frac{1}{2} [\Delta(\text{CO} + \text{O}_2) - \Delta p]$$

$$\Delta p_2 = \Delta p - \Delta p_1$$

Since carbon dioxide, chlorine and phosgene all have very low vapor pressures at liquid air temperatures the pressure measured when the reaction

vessel is immersed in liquid air is that of the carbon monoxide and oxygen. The value of $\Delta(\text{CO} + \text{O}_2)$ may be obtained by immersing the reaction vessel in liquid air before and after a period of illumination, reading the change in pressure, and calculating the value of $\Delta(\text{CO} + \text{O}_2)$ at room temperature by means of an experimentally determined factor. This factor varies slightly with temperature of the liquid air but was usually about 3.2.

In Fig. 1 the values of $\Delta\text{O}_2/(\Delta\text{O}_2 + \Delta\text{Cl}_2)$ obtained at 20° are plotted against the values of Cl_2/O_2 . From this curve we find that the number of moles of chlorine and oxygen reacting are equal when the chlorine pressure is 5.0 times that of the oxygen. In order to be certain that the relative amounts of the two reactions are a function solely of Cl_2/O_2 , the partial pressures of the reactants were varied between the following limits (pressures in cm. of sulfuric acid): carbon monoxide from 10 to 25, chlorine

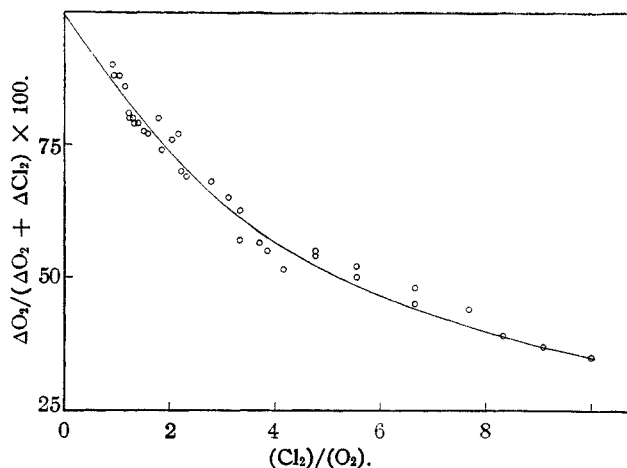


Fig. 1.

from 18 to 57, oxygen from 2.7 to 42. Regardless of the pressures used the points fall on the curve within the limits shown by the graph, thereby justifying the assumption that the relative amounts of chlorine and oxygen reacting are a function solely of the ratio of these two gases.

If we carry out experiments of the same type at different temperatures the division between reactions (1) and (2) should vary, as the heats of activation for the two reactions would normally be expected to be different. Such experiments have been carried out at 89 and 130° . The results fall on the same type of curve as those at 20° but the values of Cl_2/O_2 for which the rates of (1) and (2) are equal are 2.0 and 1.25, respectively. Such a trend shows that reaction (1) has a higher temperature coefficient and therefore a higher heat of activation than reaction (2). The difference between the heats of activation may be calculated from a consideration of the relationship existing between the rate constant and temperature,

$k = se^{-Q/RT}$, where s is a factor involving the number of collisions and possibly some steric factor, and Q is the heat of activation. If we let the subscripts 1 and 2 refer to the reactions (1) and (2) we have

$$\frac{k_1}{k_2} = \frac{s_1}{s_2} e^{-(Q_1 - Q_2)/RT}$$

Taking the logarithms of both sides

$$\ln \frac{k_1}{k_2} = \ln \frac{s_1}{s_2} - \frac{Q_1 - Q_2}{RT}$$

Therefore if we plot the logarithms of the experimentally determined values for k_1/k_2 against the reciprocal of the absolute temperature a straight line should be obtained. The slope of this line is $-(Q_1 - Q_2)/R$ and the intercept on the $\ln(k_1/k_2)$ axis is $\ln(s_1/s_2)$. Figure 2 shows such a plot of the

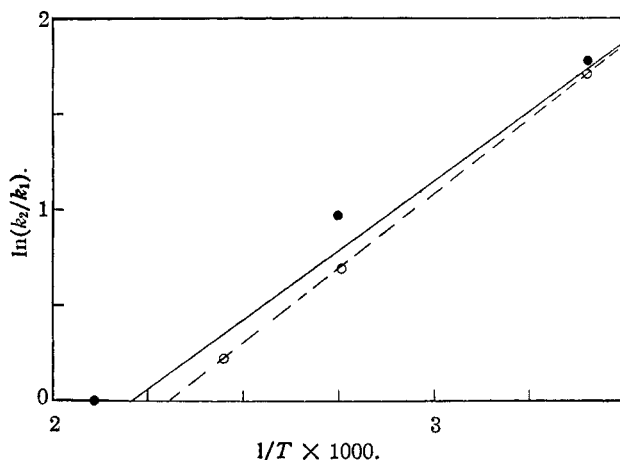


Fig. 2.

data reported in this paper combined with that obtained by Rollefson and Montgomery⁴ using phosgene as a source of COCl . From the graph we find that $Q_1 - Q_2 = 2880$ cal. and $\ln(s_1/s_2) = 3.16$ or $s_1/s_2 = 24$. These figures are taken from the line which represents the combined results of the two researches; if the line is drawn through the points obtained by the method reported in this paper a slightly higher result, 3200 cal., is obtained for $Q_1 - Q_2$ and 38 for s_1/s_2 . Due to the approximate methods of calculation used in obtaining k_1/k_2 in the work of Rollefson and Montgomery the higher values given above are favored. Probably the best values are 3000 ± 200 cal. for $Q_1 - Q_2$ and 30 ± 5 for s_1/s_2 .

The interpretation of the difference in the two heats of activation must await an explanation of the nature of such activation. The s values, however, have been interpreted as collision numbers modified by a "steric" factor. In the case we are concerned with the difference in the number of

(4) Rollefson and Montgomery, *THIS JOURNAL*, **55**, 142 (1933).

collisions of COCl with oxygen and with chlorine cannot be very great. Using the data for molecular diameters obtained from viscosity measurements it may be calculated that if the same pressures of the two gases were used there would be 1.45 times as many collisions with chlorine as with oxygen. After allowing for this effect we have a factor of approximately twenty for the so-called "steric" effects. This does not mean that there are twenty times as many geometrical arrangements of COCl and Cl₂ which lead to reaction as there are of COCl and O₂, but rather the probability of a rearrangement to give the products is twenty times as great in the former case as in the latter. This difference in probabilities may be due in part to geometrical considerations but must depend also on such factors as changes in electron spins and electron distribution.

From the facts which have been presented we have a definite mechanism to account for the diminishing effect of oxygen as the temperature is raised. That COCl is an intermediate step in the formation both of carbon dioxide and phosgene seems very definitely established by the identity of the ratio of the rate constants obtained by the two methods of attack. Furthermore, the results indicate that CO₂ formation should not disappear entirely as the temperature is raised but should be small except in the presence of relatively high pressures of oxygen. From the magnitude of the ratios observed we see that at equal pressures of oxygen and chlorine the rates of reaction with COCl never differ by more than a factor of approximately five in the temperature range from 20 to 200°. This means that we can never consider either reaction as negligible compared to the other under comparable conditions and therefore Bodenstein's postulate that COCl is present in its equilibrium concentration in the phosgene reaction and not in the sensitized carbon dioxide formation must be considered extremely questionable. A more quantitative discussion of the magnitude of the rates of the individual steps in the mechanism must await the development of the mechanism for the chlorine sensitized photochemical formation of carbon dioxide.

Summary

An experimental investigation has been made of the relative amounts of carbon dioxide and phosgene formed when mixtures of carbon monoxide, chlorine and oxygen are illuminated with light absorbed by the chlorine. It has been shown that the relative amount of the two reactions is a function solely of the ratio of chlorine to oxygen provided the temperature is kept constant. If the temperature is varied the logarithm of the ratio is a linear function of the reciprocal of the absolute temperature. These facts have been shown to be in accord with the assumption that the carbon dioxide and phosgene are formed by the reaction of an intermediate compound COCl with oxygen and chlorine, respectively.

BERKELEY, CALIFORNIA

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