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THE PHOTOCHEMICAL FORMATION OF PHOSGENE

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A photochemical reaction which has been the subject of considerable interest during the last few years is the formation of phosgene from carbon monoxide and chlorine. The principal investigations on this reaction have been carried out by Bodenstein and his co-workers.[2] They have shown that at room temperature the reaction rate is given by the expression

$$\frac{d(COCl_2)}{dt} = kI^{1/2}_{abs.}(Cl_2)\ (CO)^{1/2}$$

The quantum yield was found to be from 1000 to 3000 molecules of phosgene for every quantum of light absorbed by the chlorine. In the most recent paper cited above this is explained by a mechanism in which phosgene is formed by direct union of carbon monoxide and chlorine with chlorine atoms as a catalyst. It is the purpose of this paper to show that the observed rate law can be derived from a chain mechanism with fewer assumptions than were necessary in the previous case.

In the paper by Bodenstein, Lenher and Wagner the following set of reactions has been used in deriving the rate law

$$Cl_2 + h\nu = 2Cl \qquad (1)$$
$$CO + Cl = COCl \qquad (2)$$
$$COCl = Cl + CO \qquad (3)$$
$$CO + Cl_2 + Cl = COCl_2 + Cl \qquad (4)$$
$$COCl + Cl = CO + Cl_2 \qquad (5)$$

Reaction 3 is obviously the reverse of (2) and it is assumed that the rates are such that the three substances, CO, Cl and COCl, can be considered to be present in their equilibrium concentrations. In order to account for the inhibiting action of oxygen and the sensitized formation of carbon dioxide, the following reactions were used

$$COCl + O_2 = CO_2 + ClO \qquad (6)$$
$$ClO + CO = CO_2 + Cl \qquad (7)$$

The principal weakness in the above scheme is that it disregards the formation of phosgene by the action of chlorine on COCl. If the COCl reacts with oxygen as is indicated by (6), then it is certain to react with chlorine, which is a much more reactive substance than oxygen. The mechanism which we wish to present has the phosgene formed from COCl and chlorine at room temperature and retains the idea that the action of

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[2] (a) Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927); (b) Schumacher, *ibid.*, **129**, 241 (1927); (c) Bodenstein and Onoda, *ibid.*, **131**, 153 (1927); (d) Bodenstein, Lenher and Wagner, *ibid.*, **3B**, 459 (1929).

the oxygen is on the COCl but does not consider that the COCl is present in its equilibrium concentration at room temperature.

For the first step in our mechanism we must consider that the chlorine molecule is dissociated by light.[3] The second step is the formation of COCl, which occurs by a triple collision as indicated by the equation

$$CO + Cl + M = COCl + M^1$$

where M is a molecule which takes up energy in the form of vibrational, rotational or kinetic energy sufficient in amount to stabilize the COCl molecule. The latter molecule reacts with chlorine to form a phosgene molecule and a chlorine atom. The rate of formation of phosgene in this way is considered to be so fast compared to the rate of decomposition of COCl that it may be considered the determining factor in fixing the concentration of COCl. For a chain terminating reaction we shall use Reaction 5 of the mechanism proposed by Bodenstein, Lenher and Wagner. The complete mechanism is therefore

$$Cl_2 + h\nu = 2Cl \qquad \text{(I)}$$

$$CO + Cl + M = COCl + M^1 \qquad \text{(II)}$$

$$COCl + Cl_2 = COCl_2 + Cl \qquad \text{(III)}$$

$$COCl + Cl = CO + Cl_2 \qquad \text{(IV)}$$

From an inspection of the proposed scheme it is not obvious what rate law can be derived, hence we shall make a rather detailed calculation of the rate law. The assumption back of this derivation is that the intermediate compounds, COCl and Cl, are present in steady state concentrations which are controlling factors in determining the rate. In the usual way we can calculate the steady state concentrations as follows

$$\frac{d(Cl)}{dt} = k_1 I_{\text{abs.}} + k_3(COCl)(Cl_2)$$

$$-\frac{d(Cl)}{dt} = k_2(CO)(Cl)(M) + k_4(COCl)(Cl)$$

$$\frac{d(COCl)}{dt} = k_2(CO)(Cl)(M)$$

$$-\frac{d(COCl)}{dt} = k_3(COCl)(Cl_2) + k_4(COCl)(Cl)$$

$$(COCl) = \frac{k_2(CO)(Cl)(M)}{k_3(Cl_2) + k_4(Cl)}$$

In this case and in all others following where a term due to Reaction IV occurs in a sum with a term due to Reaction III, the principal chain reaction, we shall neglect the former. This is justified by the quantum yield, which shows that Reaction III occurs about one thousand times more frequently than Reaction IV. With this simplification, we obtain for the concentration of COCl

$$(COCl) = \frac{k_2(CO)(Cl)(M)}{k_3(Cl_2)}$$

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[3] The dissociation of molecules by light has been discussed by Franck, *Trans. Faraday Soc.*, **21**, 536 (1925), and Franck, Kuhn and Rollefson, *Z. Physik*, **43**, 155 (1927).

The concentration of chlorine atoms is obtained by equating $d(Cl)/dt$ and $-d(Cl)/dt$, substituting for COCl where it occurs.

$$k_1 I_{abs.} + k_2(CO)\ (Cl)\ (M) = k_2(CO)\ (Cl)\ (M) + k_4\,\frac{k_2(CO)\ (Cl)^2\ (M)}{k_3(Cl_2)}$$

$$k_1 I_{abs.} = k_4\,\frac{k_2(CO)\ (Cl)^2\ (M)}{k_3(Cl_2)}$$

$$(Cl)^2 = \frac{k_1k_3I_{abs.}(Cl_2)}{k_2k_4(CO)\ (M)}$$

$$(Cl) = \sqrt{\frac{k_1k_3I_{abs.}(Cl_2)}{k_2k_4(CO)\ (M)}}$$

Substituting the expression for (Cl) in the expression for COCl, we obtain

$$(COCl) = \frac{k_2}{k_3}\sqrt{\frac{k_1k_3I_{abs.}(CO)\ (M)}{k_2k_4(Cl_2)}}$$

The rate of formation of phosgene is

$$\frac{d(COCl_2)}{dt} = k_3(COCl)\ (Cl_2) = k_2\sqrt{\frac{k_1k_3I_{abs.}(CO)\ (M)\ (Cl_2)}{k_2k_4}}$$

$$\frac{d(COCl_2)}{dt} = k^1 I^{1/2}{}_{abs.}(Cl_2)^{1/2}\ (CO)^{1/2}\ (M)^{1/2}$$

where $k^1 = k_2\sqrt{k_1k_3/k_2k_4}$. Comparing this equation with the experimental one given by Bodenstein,[2] we see that if we set $(M) = (Cl_2)$ the two expressions are identical. Since M comes into the scheme in II as the substance which takes up the energy which the COCl must lose to become stable, the only condition which must be fulfilled for M to equal (Cl_2) is that chlorine should have a greater efficiency for such a process than carbon monoxide or phosgene. Such differences in efficiency in taking up energy are well known in the study of the extinction of fluorescence.[4]

Now that we write Equation II in our scheme as[5]

$$CO + Cl + Cl_2 = COCl + Cl_2^1$$

two questions arise, (a) why cannot $Cl + Cl_2$ in this reaction be written as Cl_3, and (b) why do we have COCl formed instead of phosgene as is the case in the mechanism proposed by Bodenstein, Lenher and Wagner? In regard to the first question, we can say that the experimental data available does not enable one to settle this question. If the Cl_3 can be considered to be present in its equilibrium concentration, then the two mechanisms are kinetically identical. Such an assumption must be considered improbable since the formation of the Cl_3 molecule must be through a triple collision and, therefore, the rate of formation probably is not very fast compared to the second order reactions which make up the following stages, hence the Cl_3 concentration would be below the equilibrium value. In such a case, the rate law would have to contain a factor corresponding to the

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[4] Geiger and Scheel, "Handbuch der Physik," Quanten XXIII, Julius Springer, Berlin, 1926.

[5] Cl_2^1 is an energy-rich chlorine molecule which dissipates its excess energy thermally.

third body involved in the triple collision. No evidence for such a factor has been obtained. Another possibility is that Cl_3 is formed as a quasi-molecule[6] which reacts with the carbon monoxide, thus greatly increasing the number of collisions in which COCl is formed over the number which would be calculated on a simple kinetic theory basis. Such a mechanism would account for an extremely specific action on the part of chlorine. We feel, however, that the latter case is adequately covered by writing the equation as a triple collision which involves chlorine specifically rather than to write equations involving such indefinite substances as quasi-molecules. At present, experiments are being carried out in the hope that the chlorine molecule may be replaced by some other molecule in this step.

Turning to the second question, we must consider the relative probabilities for the formation of COCl and phosgene in the triple collision. The formation of phosgene requires that the energy which must be removed from the phosgene molecule to stabilize the molecule must be converted into kinetic energy. The probability for the loss of energy of activation as kinetic energy is given by Frenkel and Semenoff as 10^{-4}.[7,8] If this figure is taken as applicable to energies of the magnitude we are concerned with, it means that the formation of phosgene would occur only once in ten thousand triple collisions of the kind we have. On the other hand, if we have COCl formed, the energy goes into both kinetic energy and energy of vibration and rotation of the chlorine molecule. Examining the data on the quenching of fluorescence by various gases we find that the diatomic gases are generally much more efficient than the monatomic gases.[9] A general quantitative comparison cannot be made because of various specific effects which are always present, but we can say that in a triple collision such as the one under consideration the most probable reaction is the one requiring a minimum amount of energy to be dissipated as kinetic energy, and in this case that is the formation of COCl. By this we do not mean to imply that no phosgene can be formed directly by such a triple collision but merely that at room temperature the amount of phosgene so formed is not sufficient to affect the rate law.

Bodenstein, Lenher and Wagner avoid any consideration of the mode of formation of COCl by assuming that it is present at its equilibrium concentration. In view of the fact that the formation process must be considered a triple collision, we can apply the same argument against COCl existing in its equilibrium concentration that we have already applied to the assumption of Cl_3.

[6] Born and Franck, *Z. Physik,* **31**, 411 (1925).

[7] Frenkel and Semenoff, *ibid.*, **48**, 216 (1928).

[8] Semenoff, *Z. physik. Chem.*, 2B, 161 (1929).

[9] Pringsheim, "Fluorescenz und Phosphorescenz," Springer, Berlin, **1928**, 3d ed., p. 126.

For the chain terminating reaction we have retained the one used by Bodenstein, Lenher and Wagner, *i. e.*

$$\mathrm{COCl} + \mathrm{Cl} = \mathrm{CO} + \mathrm{Cl_2}$$

Since this is a bimolecular reaction, it must be considered as more probable than any reaction involving a triple collision or diffusion to the walls of the reaction vessel. We also wish to carry over Reactions 6 and 7 for the action of oxygen on the system, so our complete scheme for the photochemical reaction at room temperature becomes as follows

$$\mathrm{Cl_2} + h\nu = 2\mathrm{Cl} \qquad \text{(I)}$$
$$\mathrm{CO} + \mathrm{Cl} + \mathrm{Cl_2} = \mathrm{COCl} + \mathrm{Cl_2}^1 \qquad \text{(II)}$$
$$\mathrm{COCl} + \mathrm{Cl_2} = \mathrm{COCl_2} + \mathrm{Cl} \qquad \text{(III)}$$
$$\mathrm{COCl} + \mathrm{Cl} = \mathrm{CO} + \mathrm{Cl_2} \qquad \text{(IV)}$$
$$\mathrm{COCl} + \mathrm{O_2} = \mathrm{CO_2} + \mathrm{ClO} \qquad \text{(V)}$$
$$\mathrm{ClO} + \mathrm{CO} = \mathrm{CO_2} + \mathrm{Cl} \qquad \text{(VI)}$$

Let us now summarize the advantages of this scheme over the one previously presented. We have eliminated the necessity for the following assumptions: (a) that COCl reacts with oxygen but not with chlorine; (b) that COCl or any other substance is present in its equilibrium concentration; (c) that the formation of phosgene depends on a triple collision of a type known to have a low probability. In order to accomplish this, the sole assumption needed is that chlorine molecules shall have a relatively high efficiency in causing the formation of COCl. We feel, therefore, that our scheme is preferable since it rests on fewer assumptions.

At temperatures around 300° or higher it has been found[2b] that the rate law becomes

$$\frac{\mathrm{d(COCl_2)}}{\mathrm{d}t} = kI_{\mathrm{abs.}}(\mathrm{Cl_2})\ (\mathrm{CO})$$

In order to account for this change it is considered that at high temperatures the rate of decomposition of COCl into carbon monoxide and atomic chlorine increases until it becomes fast compared with the other reactions involving COCl and, therefore, we can assume that under such conditions the COCl is present in its equilibrium concentration. We shall also assume that this equilibrium concentration is very small, thus accounting for the absence of $\mathrm{CO_2}$ formation at the higher temperature, since reducing the COCl concentration to a low value reduces the rates of V and VI to very low values. Such a reduction in the COCl concentration must necessarily also reduce the rates of III and IV and, therefore, we must seek some reaction other than III as the source of phosgene. The only one permitted by our mechanism is that phosgene is formed by the triple collision of chlorine atom, chlorine molecule and carbon monoxide. At room temperature this source of phosgene has been considered subordinate to the formation by way of COCl. With the latter reaction eliminated this triple collision becomes the sole source of phosgene. Now in order for the rate of formation of phosgene at the higher temperature to be of the same order of magnitude as the room temperature rate, it is necessary for the concentration of chlorine atoms to increase. That this must occur is seen from the elimination of IV, which is the principal cause of the destruction of chlorine atoms in the room temperature reaction. With IV eliminated, the rate of disappearance of chlorine atoms will be determined by such factors as the rate of recombination at the wall or by collisions in the gas phase. These processes are subordinate to IV in the room temperature reaction but at the higher concentrations of chlorine atoms such as we have with IV out, the rates may become quite large. The work of Bodenstein, Lenher and Wagner at low pressures indicates that recombination at the wall is not much slower than IV, even under the conditions prevailing at room temperature. It is possible, however, that these rates are slow enough so that the concentration of chlorine atoms at high temperature is ten or a hundred times as great as it is in the presence of COCl. Such being the case, the amount of phosgene formed by the triple collision would be ten to a hundred times as great as before. For example, suppose that at room temperature one out of a hundred of the triple collisions yields phosgene, the other ninety-nine giving COCl; on raising the temperature this ratio between the amounts of COCl and phosgene formed remains the same but the COCl immediately decomposes without entering into any other reaction, leaving the phosgene, which appears at a measurable rate due to the increased number of collisions of the kind mentioned.

According to what has just been said, we attribute the high temperature formation of phosgene to the reaction

$$\mathrm{CO} + \mathrm{Cl} + \mathrm{Cl_2} = \mathrm{COCl_2} + \mathrm{Cl}$$

The rate of this reaction is given by

$$\frac{\mathrm{d}(\mathrm{COCl_2})}{\mathrm{d}t} = k_1(\mathrm{Cl})\ (\mathrm{Cl_2})\ (\mathrm{CO})$$

A comparison of this equation with the empirically determined rate equation shows that the two are identical if we can show that the concentration of the chlorine atoms is proportional to the amount of light absorbed. To prove such a proportionality rigorously requires more knowledge concerning factors controlling the rate of recombination of chlorine atoms than we possess. It is possible, however, to prove the relation for a special case. Suppose that the rate of disappearance of chlorine atoms is proportional to the number of collisions between the atoms and the wall. According to the kinetic theory this will be proportional to the partial pressure of the chlorine atoms. Thus we may write

$$\frac{-\mathrm{d}(\mathrm{Cl})}{\mathrm{d}t} = k_2(\mathrm{Cl})$$

For the formation of the atoms we may write

$$\frac{d(\mathrm{Cl})}{dt} = k_3 I_{\mathrm{abs.}}$$

where k_3 is 2 if we give $I_{\mathrm{abs.}}$ in quanta and consider that one quantum of light breaks a molecule into two atoms. Equating, we have

$$k_3 I_{\mathrm{abs.}} = k_2(\mathrm{Cl})$$

or

$$(\mathrm{Cl}) = \frac{k_3}{k_2} I_{\mathrm{abs.}}$$

which is all we need to be able to write

$$\frac{d(\mathrm{COCl_2})}{dt} = kI_{\mathrm{abs.}}(\mathrm{CO})\ (\mathrm{Cl_2})$$

where

$$k = \frac{k_1 k_3}{k_2}$$

It is quite possible that other methods of destroying the chlorine atoms will lead to the same result but, since we have no information concerning the details of such mechanisms, it is useless to attempt to make quantitative calculations.

Summary

A mechanism has been proposed for the photochemical formation of phosgene at room temperature involving COCl as an intermediate step. This mechanism has been compared with one proposed by Bodenstein, Lenher and Wagner involving COCl in a side reaction, and the assumptions involved in the two mechanisms have been discussed. A possible mechanism for the reaction above 300° has been suggested and discussed briefly.

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