THE THERMAL AND PHOTOCHEMICAL SYNTHESIS
OF PHOSGENE

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Carbon monoxide and chlorine are able to combine, forming phosgene, as well under the influence of light as at slightly higher temperatures with an easily measurable velocity. This reaction has occupied our attention since 1914. The reason for such a long series of investigations is that this is a real chameleon; the law of its reaction velocity changes from dark to light, and for the photochemical reaction from temperature to temperature. So I beg leave to give a very brief account of the observations we have made in this direction.
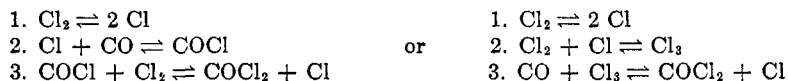
Let me begin with the reaction in the dark, which takes place with easily measurable velocity at 350–500°, and is accompanied by the reverse reaction, leading to an equilibrium. While this is of a perfectly normal kind given by

$$\frac{(COCl_2)}{(CO) \cdot (Cl_2)} = K,$$

the velocity with which it is established is not. This is given by

$$+\frac{d(COCl)}{dt} = k_1 \cdot (CO) \cdot (Cl_2) \cdot (Cl_2)^{\frac{1}{2}} - k_2 \cdot (COCl_2) \cdot (Cl_2)^{\frac{1}{2}}$$

This equation expresses the fact that each of the two reverse reactions is catalyzed by chlorine atoms, present in low concentration in equilibrium with the chlorine molecules. An interpretation of the mechanism was given by Christiansen, who published a short paper on the decomposition of phosgene while Plaut and I were occupied with the investigation of both reactions. He proposed two series of intermediate reactions:

1. $Cl_2 \rightleftharpoons 2\ Cl$		1. $Cl_2 \rightleftharpoons 2\ Cl$
2. $Cl + CO \rightleftharpoons COCl$	or	2. $Cl_2 + Cl \rightleftharpoons Cl_3$
3. $COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$		3. $CO + Cl_3 \rightleftharpoons COCl_2 + Cl$

In both cases reaction 3 is slow; the equilibria 1 and 2 are continually established,—a view which may easily be accepted because there is only a very slow production or consumption of the components. It is impossible to decide between these two possibilities. On the other hand, Plaut and I were able to show that all results as derived from both these schemes agree even quantitatively with the facts.

Oxygen has no influence whatever on this reaction in the dark. But if one investigates the photochemical reaction at room temperature, one finds that oxygen is a very remarkable inhibitor, and that it is used up, forming carbonic acid, in a reaction which at even very moderate concentrations of oxygen preponderates to the exclusion of the formation of phosgene. A mixture of oxygen-free carbon monoxide and chlorine reacts with a velocity given by

$$+\frac{d(COCl_2)}{dt} = k \cdot (I^*_{absorbed})^{\frac{1}{2}} \cdot (CO)^{\frac{1}{2}} \cdot (Cl_2)$$

* I = intensity of light.

the yield being of the order of magnitude of 3000 moles per Einstein, and changing of course with the concentration. If the absorbed energy is assumed to be proportional to the concentration of chlorine, a condition which is ordinarily permissible, this equation becomes

$$+\frac{d(COCl_2)}{dt} = k' \cdot (CO)^{\frac{1}{2}} \cdot (Cl_2)^{\frac{3}{2}}$$

Even then it is not in agreement with that governing the reaction in the dark where (CO) appears in the first power, and therefore a different mechanism is necessary to explain this fact. The knowledge acquired in recent years that a reaction like the combination of chlorine atoms to form molecules is not a simple one has forced us to seek another type of reaction by which the chlorine atoms may disappear and thus explain the breaking of the reaction chains. This reaction is:
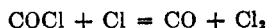
$$COCl + Cl = CO + Cl_2$$

and the whole scheme now adopted by us is:

1. $Cl_2 + E = 2\ Cl$
2. $CO + Cl = COCl$
3. $COCl = CO + Cl$ } equilibrium being established.
4. $CO + Cl_2 + Cl = COCl_2 + Cl$
5. $COCl + Cl = CO + Cl_2$

This series leads to the observed law of the reaction velocity and is in agreement with all facts. But it must be said, that reaction 4 is given only in a general form, because it is here, just as in the case of the reaction in the dark, impossible to decide which of the different possibilities included by it may be the best expression for the observed facts. These possibilities are:

$CO + Cl = COCl$ (Reactions 2 + 3)   or $Cl_2 + Cl = Cl_3$
$COCl + Cl_2 = COCl_2 + Cl$ $CO + Cl_3 = COCl_2 + Cl$
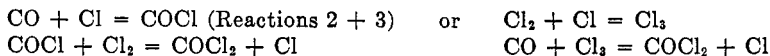
or even a three-body collision reaction, exactly like reaction 4 given above, which is not essentially different from the Cl_3 mechanism.

We are led somewhat further by observations of the photochemical reaction at higher temperatures in connection with measurements of the photosensitized formation of carbon dioxide. The latter takes place as soon as oxygen is present in the illuminated mixture of CO and Cl_2, and if the concentration of oxygen is higher than half that of chlorine, practically no more phosgene is formed, but only carbon dioxide. Its manner of formation must be through a chain reaction also, the yield being of the same order of magnitude as that of phosgene in the oxygen-free mixture.
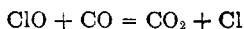
The checking of the formation of phosgene and the formation of carbon dioxide may be explained on the assumption that reaction 4

$$CO + Cl_2 + Cl = COCl_2 + CO$$

is replaced by

$$COCl + O_2 = CO_2 + ClO$$

followed by

$$ClO + CO = CO_2 + Cl$$
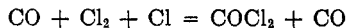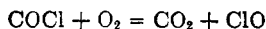
thus giving a chain.

The COCl was the substance which, reacting with Cl_2, terminated the chain in the oxygen-free reaction. If it is used up to a large extent it is no longer able to act in this way; the chains must be broken off by another reaction. The reaction $Cl + Cl = Cl_2$ is at least improbable; so the chlorine atoms must find another way to recombine, and that is by adsorption on the walls and a further recombination in the adsorbed state.

The consequence is that, for the photosensitized formation of carbon dioxide, the observed reaction velocity is no longer given by the square root of the absorbed energy, but by a power lying between the square root and the first power (to which the velocity of the diffusion of the atoms to the walls would be proportional) and changing with the form of the vessels, so that for larger ones the power is about one-half and for smaller ones practically one.

The power with which the absorbed energy enters into the law of the reaction velocity of the formation of phosgene changes in the same way if we change the temperature. Here several phenomena appear simultaneously: the photosensitized formation of carbonic acid ceases, together with the checking influence of oxygen; the power of the absorbed energy becomes exactly one, and this together with the fact that small amounts of impurity change the state of the walls and influence somewhat the reaction velocity. All these facts agree perfectly with the assumption that the equilibrium $CO + Cl \rightleftharpoons COCl$ is now changed so that only very low concentrations of COCl are available.

Since COCl is the substance leading to CO_2 formation, it is well understood that the formation of CO_2 ceases. But since COCl is also the substance which causes the consumption of Cl atoms, these now require another way of being consumed, i.e. by movement to the walls and by recombination on the walls. This is a diffusion process, and is therefore given by the first power of (Cl), thus leading to the first power of the absorbed energy in the equation for the velocity.

But this diffusion must depend upon the concentration of all gases and must be more rapid at low pressures. So we find the first power of the absorbed light already at somewhat lower temperature if the pressure is lower and if we go to pressures of a

few millimeters of mercury we can observe it even at room temperatures.

It should be possible, with the great number of measurements we have collected in a long series of investigations, to calculate in a somewhat quantitative manner all these rather complicated reactions. Perhaps that will happen in the near future, but today we are not able to do it in spite of our rich material. The greatest difficulty lies in the fact that the sensitized formation of carbon dioxide follows a law which we cannot yet interpret exactly. The velocity is given by

$$+ \frac{d(CO_2)}{dt} = k(I_{absorbed})^n (CO)^{\frac{1}{2}}$$

As long as the concentration of oxygen is not too low, it has not the slightest influence, while carbon monoxide occurs with its square root, and the absorbed energy with some power between the half and the first power as discussed above.

There is still a deep gap in our system. It is to be hoped that some one will have a good idea for filling it up and that then all these various reaction velocities may be reliably calculated, which will be of interest not only for the single question of the formation of phosgene but also for our general knowledge of chemical reactions.