When sufficient ozone has been formed, the residual oxygen is pumped off after shutting off the transformer, the liquid air removed, and the ozone condensed with liquid air into that part of the system in which it is to be used. This is done while the ozonizer is warming up from the lower temperature, thus keeping the vapor pressure fairly low, and serves three purposes: there is less danger of explosion on vaporization, less decomposition while going through any stopcocks in the line and by closing the stopcock next to the ozonizer before the last bit of liquid ozone has evaporated, impurities such as traces of water or nitrogen pentoxide are retained in the ozonizer (to be thoroughly pumped out later).

Repeated distillation is unnecessary to obtain quite pure ozone, for any oxygen formed may be pumped off before vaporization in the system where it is to be used. It should be strongly emphasized that the essential precaution in avoiding explosions in handling liquid ozone is to prevent any mechanical agitation and bubble formation during vaporization. This is done by always keeping the pressure low, so that vaporization takes place principally from the surface. It has been observed by several workers that the greatest danger of explosion is incurred when the liquid reaches its boiling point and bubbles form in the body of the liquid. If a few per cent. of oxygen, due to decomposition while going through greased stopcocks in the line, are permissible, a convenient method is to vaporize the liquid into an evacuated bulb of such size that the pressure never becomes greater than about a half atmosphere. It can then be transferred to the rest of the system as needed, and the oxygen pumped off as before.

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

The Photochemical Decomposition of Phosgene

BY C. W. MONTGOMERY AND G. K. ROLLEFSON

At the beginning of the present program of work on the photochemical reactions of phosgene, it was thought likely that a knowledge of the kinetics of the phosgene decomposition reaction would be necessary for interpreting completely the results of the other reactions. Furthermore, it was believed that the decomposition might enter as a primary reaction, in the oxidation, the reaction with hydrogen and in the phosgene-sensitized oxidation of carbon monoxide. The results already published[1,2,3] indicate, however, that, in the case of these latter three reactions, the decomposition may be considered negligible in so far as we are concerned with the stoichiometry and mechanisms of these reactions. The results of the present research, therefore, do not alter any of the conclusions or explanations arrived at in the preceding work, but rather constitute additional confirmatory evidence for the correctness of the mechanisms already postulated.

Experimental

Most of the experimental details have already been described. The reaction vessel, a clear fused quartz spherical bulb of approximately 200-cc. capacity, was mounted in a small tank having a clear fused quartz window. This tank was filled with water and, before recording pressure measurements, the water temperature was always adjusted to 20°. A 200-volt quartz mercury arc was used in conjunction with a short focal length cylindrical quartz lens. For part of the work, a quartz chlorine–bromine light filter was used. This was made from a cell about 6 cm. thick with detachable plane parallel end plates and was filled with chlorine bubbled through liquid bromine at a total pressure somewhat greater than atmospheric. Photographs of the mercury arc spectrum showed that the transmission of the filter for the prominent lines in the region of the chlorine absorption maximum (3300–3400 Å.) was negligibly small. A sulfuric acid (sp. gr. 1.84) manometer was used to follow the course of the reaction.

Results

In Table I are recorded the results of a series of initial rate experiments in which the phosgene

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[1] G. K. Rollefson and C. W. Montgomery, THIS JOURNAL, **55**, 142 (1933).

[2] C. W. Montgomery and G. K. Rollefson, *ibid.*, **55**, 4025 (1933).

[3] G. K. Rollefson and C. W. Montgomery, *ibid.*, **55**, 4036 (1933).

pressure was varied, other factors being kept constant. Throughout this paper pressures are expressed in terms of cm. of sulfuric acid and rates in terms of cm. of sulfuric acid per unit time.[4]

TABLE I

($COCl_2$)	Absorption, %	Rate	Rate/% absorption
22.5	37	0.42	1.14
30.8	47	.55	1.17
50.2	64	.79	1.23
65.6	74	.84	1.14
70.3	76	.90	1.18
79.8	80	1.02	1.28
90.3	84	1.11	1.32
101.1	87	1.00	1.15
			Av. 1.20

The percentage absorption given in the second column is calculated from the average length of light path through the reaction vessel (5.9 cm.) and the values of the absorption coefficients already measured.[2] The values given in the last column indicate that the initial rate is simply proportional to the light absorbed, or

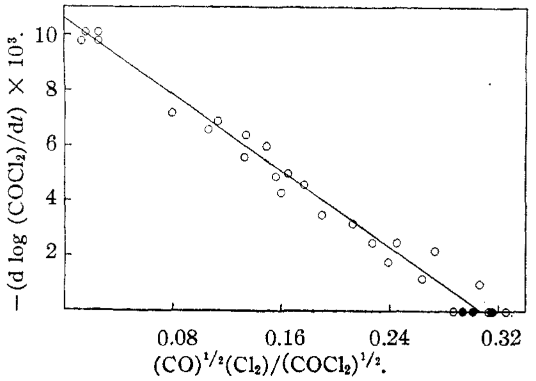

Fig. 1.

$$-\mathrm{d}(COCl_2)/\mathrm{d}t = kI_{\text{abs.}}$$

At low pressures of phosgene where the light absorption is weak we may consequently write

$$-\mathrm{d}(COCl_2)/\mathrm{d}t = kI_0(COCl_2)$$

In accordance with the above equation it was found that, with low pressures of phosgene, a plot of log ($COCl_2$) against time gave a straight line which, however, rapidly curved off as the reaction proceeded. This departure from linearity is due to the rapid long-chain back reaction which effectively stops the decomposition and causes a photostationary state.

In order to investigate the later stages of the reaction it was decided to dispense with the chlorine-bromine filter. Although such a filter ensures purity of light, by decreasing the intensity in the near ultraviolet, it also slows down the reaction inconveniently. A comparison of the data on the absorption of chlorine (I. C. T., Vol. VI) with our own data on phosgene absorption showed that it would be possible to study the whole course of the reaction without a filter under such conditions that light absorption by phosgene should be approximately ten times greater than that absorbed by chlorine. This procedure was followed in the later work and the results obtained indicate that chlorine absorption may be neglected.

Since it had been found that the reaction is initially first order, and since the departure from first order was believed to be due to the back reaction, it was thought likely that some function involving the CO and Cl_2 pressures might be found against which to plot d log ($COCl_2$)/dt to yield a straight line. After trying several expressions which gave "lines" of definite curvature, it was found that the empirical function $(CO)^{1/2}(Cl_2)/(COCl_2)^{1/2}$ was suitable. This function is related to the rate law for the photochemical formation of phosgene, $\mathrm{d}(COCl_2)/\mathrm{d}t = kI^{1/2}_{\text{abs.}}(CO)^{1/2}(Cl_2)$ in a simple manner. Divide both sides of this equation by $I_{\text{abs.}}$ and substitute $k'I_0(COCl_2)$ for $I_{\text{abs.}}$ since phosgene is the absorbing substance in this case and we see that d log ($COCl_2$)/dt should be a linear function of $(CO)^{1/2}(Cl_2)/(COCl_2)^{1/2}$. The data are shown graphically in Fig. 1. The points are taken from a number of experiments in some of which only $COCl_2$ (20–35 cm. H_2SO_4) was present initially, while in others CO (0–6 cm. H_2SO_4) and Cl_2 (0–3 cm. H_2SO_4) either together or separately were added.

The points with zero ordinate are especially interesting as they represent the photostationary state reached after four to six hours illumination. The circles are data taken from *decomposition* experiments while the solid points are from experiments in which *formation* of phosgene took place. The function $(CO)^{1/2}(Cl_2)/(COCl_2)^{1/2}$ thus seems to be valid for the photostationary state as approached from either side, *i. e.*, decomposition or formation. No other expression tried gave this same result. There appears to be no systematic deviation in the points. The scattering is most probably due to variations in the arc intensity. The complete rate law may be written

$$-\mathrm{d}(COCl_2)/\mathrm{d}t = kI_{\text{abs.}} - k'I^{1/2}_{\text{abs.}}(CO)^{1/2}(Cl_2)$$

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(4) In Table I, the unit time is taken as one hour. For the results shown in Fig. 1, the unit time is fifteen minutes.

or for small light absorption

$$-\frac{\mathrm{d}\log(\mathrm{COCl_2})}{\mathrm{d}t} = a - \frac{\mathrm{b}(\mathrm{CO})^{1/2}(\mathrm{Cl_2})}{(\mathrm{COCl_2})^{1/2}}$$

Within the limit of accuracy of the pressure measurements, several experiments, in which a comparison of the initial rates of the decomposition and the oxidation of phosgene was made, indicate that the initial rates of pressure change of both reactions are equal. From the equations of the reactions

$$\mathrm{COCl_2 = CO + Cl_2}, \text{ and}$$
$$\mathrm{2COCl_2 + O_2 = 2CO_2 + 2Cl_2}$$

and the known value, 1.8, for the quantum yield of the oxidation,[2] a value of 0.9 may be deduced for the quantum yield of the decomposition. Since there is some reason to believe, however, that the quantum yield of the oxidation may be (2.0),[1,2] the value for the decomposition may well be 1.0.

Discussion

It has been possible to set up the following mechanism from which may be derived a rate law in accord with the salient experimental facts:

$$\mathrm{COCl_2} + h\nu = \mathrm{COCl + Cl} \quad (1)$$
$$\mathrm{COCl + Cl = CO + Cl_2} \quad (2)$$
$$\mathrm{COCl + Cl_2 = COCl_2 + Cl} \quad (3)$$
$$\mathrm{CO + Cl + Cl_2 = COCl + Cl_2} \quad (4)$$

Applying the usual methods of calculation, this mechanism gives

$$\frac{-\mathrm{d}(\mathrm{COCl_2})}{\mathrm{d}t} = I_{\mathrm{abs.}} - (\mathrm{Cl_2})\sqrt{\frac{k_3k_4}{k_2}I_{\mathrm{abs.}}(\mathrm{CO})}$$

or substituting $I_{\mathrm{abs.}} = k_1I_0(\mathrm{COCl_2})$ and dividing both sides by $(\mathrm{COCl_2})$ we have

$$\frac{-\mathrm{d}\log(\mathrm{COCl_2})}{\mathrm{d}t} = a - b\,\frac{(\mathrm{CO})^{1/2}(\mathrm{Cl_2})}{(\mathrm{COCl_2})^{1/2}}$$

which is the experimental law. The constants a and b depend upon the individual rate constants of the reactions in the mechanism and I_0. At the start of the reaction, the second term in the right-hand member is zero and the reaction consequently appears to be first order. As the reaction proceeds, however, the second term increases, the rate falls off and finally the second term becomes equal to the first at the photostationary state. This mechanism predicts a limiting value of unity for the quantum yield at the start of the reaction, as was indicated by the comparative rate experiments.

The mechanism is in perfect agreement with the preceding work on phosgene reactions and is also, in fact, identical with the mechanism of Lenher and Rollefson[5] for the formation of phosgene, with the necessary exception that the initial reaction involves absorption by $\mathrm{COCl_2}$ rather than $\mathrm{Cl_2}$. We may again interpret reaction (4) and the implied specific action of $\mathrm{Cl_2}$ in stabilizing the formation of COCl as, perhaps, a reaction between CO and the quasi-molecule $\mathrm{Cl_3}$.[6] In this respect the system differs from the phosgene–hydrogen reaction (2) in which $\mathrm{Cl_3}$ could not be postulated as no $\mathrm{Cl_2}$ was present. The terminating reaction COCl + Cl has been used not only in the mechanism of Lenher and Rollefson, but also in various mechanisms of Bodenstein.[7]

In the mechanism which has been presented the action of the light in the primary process is represented as dissociating the phosgene molecule. According to the work of Henri and Howell[8] the absorption spectrum of phosgene shows a band structure beginning at 3050 Å. and becoming diffuse at 2700 Å., the diffuseness increasing gradually to the limit of the band system at 2380 Å. Henri ascribed the diffuseness to predissociation and consequent shortening of the life of the molecule in the excited state. As the life period of this excited molecule is less than the time between collisions in gas mixtures at ordinary pressures we may as well write the dissociation as occurring in one step.

Recently Almasy and Wagner-Jauregg[9] have shown that a definite, though small, amount of phosgene decomposition results on illumination with light of longer wave length than 2700 Å., the supposed predissociation limit. The fact that this "long wave length decomposition" has a zero temperature coefficient does not necessarily exclude a mechanism involving collisions of excited phosgene molecules since, as Mecke[10] has pointed out, temperature coefficients in such cases depend on the spacing of vibrational levels and the relative slopes of the potential energy curves corresponding to the normal and excited molecules. There are, however, two facts which indicate that the decomposition in the region of the bands proceeds according to the mechanism we have given. In the first place, Almasy and

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

(6) Rollefson and Eyring, *ibid.*, **54**, 170 (1932).

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

(8) Henri and Howell, *Proc. Roy. Soc.* (London), **A128**, 178 (1930).

(9) Almasy and Wagner-Jauregg, *Z. physik. Chem.*, **B19**, 405 (1932).

(10) Mecke, *Trans. Faraday Soc.*, [8] **27**, 504 (1931).

Wagner-Jauregg reported that they could not detect any trace of a fluorescence spectrum of phosgene exciting with mercury lines in the region of the sharp bands. Now Herzberg[11] and others have shown that the absence of fluoresence is probably the best criterion of predissociation. Therefore it is very probable that predissociation is occurring at longer wave lengths than the limit of 2700 Å. given by Henri. The second fact that points to this same conclusion is that the sharp bands are superimposed on a continuous absorption and some measurements by Kuhn and Martin[12] at $\lambda = 2816$ Å. attribute 76% of the absorption at that wave length to the continuum which undoubtedly results in dissociation. On the basis of these observations we feel justified in saying that our mechanism applies to the decomposition at all wave lengths absorbed by phosgene.

Summary

The photochemical decomposition of phosgene has been studied kinetically and a reaction mechanism has been proposed from which the rate law

$$-\mathrm{d}(\mathrm{COCl_2})/\mathrm{d}t = kI_{\mathrm{abs.}} - k'I_{\mathrm{abs.}}^{1/2}\,(\mathrm{CO})^{1/2}(\mathrm{Cl_2})$$

may be derived. It has been shown that this rate law represents the experimental facts and that the mechanism is in accord with the previous work on phosgene photochemical reactions. The work of Almasy and Wagner-Jauregg has been discussed and a possible explanation presented.

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[11] Herzberg, *Ergebnis der exakt. Naturwiss.*, **10**, 207 (1931).

[12] Kuhn and Martin, *Z. physik. Chem.*, **B21**, 93 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

New Indicators for Oxidimetry: Some Phenanthroline and Diphenylamine Derivatives[1]

BY LOUIS P. HAMMETT, GEORGE H. WALDEN, JR., AND SYLVAN M. EDMONDS

The ability to titrate to or from a visual end-point representing any one of a series of definite oxidation potentials which differ by moderate intervals should be of advantage in the use of oxidimetry in analytical chemistry. Toward the goal of developing the necessary series of mobile, reversible oxidation indicators the present article offers some progress. The starting points were the already known phenanthroline ferrous[2] and diphenylamine[3] indicators.

Phenanthroline Derivatives

The intense color of the phenanthroline ferrous complex is entirely lacking in the known complexes of phenanthroline with nickel, cobaltous, cupric, zinc and cadmium ions.[4] Nor have we found it possible to oxidize or to reduce these complexes to intensely colored products. The addition of phenanthroline to a solution of chromous acetate produces a red solution which undergoes a sharp and reversible change to reddish-violet with oxidants in acid solution, presumably because of oxidation to a chromic compound. From the behavior of the oxidized compound with ferrous ion it appears that the potential of this system is not very different from the ferric–ferrous potential. The shift of some three-quarters of a volt upward which the chromic–chromous system undergoes when complex formation with phenanthroline takes place is of theoretical interest, but the compounds have no value as indicators, because the color intensity is not high and color contrast at the end-point is not great.[5]

Nitrophenanthroline Ferrous Ion.—We have obtained a hitherto unknown nitrophenanthroline by the following procedure. One gram of *o*-phenanthroline was dissolved in 10 cc. of concentrated nitric acid, and the solution was added to 20 cc. of 95% sulfuric acid. After one hour at 115–120°, the product was precipitated by dilution with water and addition of sodium hydroxide. It was recrystallized from water: melting point

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[1] This article is based mainly upon part of a dissertation submitted by Sylvan M. Edmonds to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933.

[2] (a) Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931); **55**, 2649 (1933); (b) Walden, Hammett and Edmonds, *ibid.*, **56**, 57 (1934); (c) Walden, Hammett and Edmonds, *ibid.*, **56**, 350 (1934).

[3] (a) Knop, *ibid.*, **46**, 263 (1924); (b) Willard and Young, *Ind. Eng. Chem.*, **20**, 764 (1928); (c) Willard and Young, THIS JOURNAL, **50**, 1334 (1928); (d) Sarver and Kolthoff, *ibid.*, **53**, 2902 (1931).

[4] Blau, *Monatsh.*, **10**, 372 (1889); **19**, 647 (1898).

[5] Barbieri and Tettamanzi, *Atti Accad. Lincei*, **15**, 877 (1932), have reported recently on the chromous dipyridyl complex, but the phenanthroline complex seems not to have been observed previously.