

The decomposition of dimethoxyborine is thus shown to be appreciably reversible. This reaction is not recommended as a means of preparation, even though the yields would be practically quantitative, for any attempts to increase the rate of reaction by heating would be likely to result in some formation of B_6H_{11} and B_4H_{10} , either of which would be very hard to remove from the product.

We are planning to study further the chemical properties of dimethoxyborine, as well as the reaction of a variety of alcohols with various boron hydrides. We have recently found that boron trimethyl, like boron trihalides and trimethyl borate, reacts with diborane. We hope in the near future to be able to report on some new derivatives of diborane, obtained by this method.

Summary

Dimethoxyborine, a compound of the new type HBX_2 , has been prepared by the reaction of diborane with methyl alcohol. A white, non-volatile, unstable solid which may be a complex polymer of monomethoxyborine, was obtained as a by-product.

Dimethoxyborine shows no tendency toward association, beyond that common to most volatile oxygen compounds. Its vapor tensions were measured with some care, and expressed by an equation of the Nernst approximation type.

The substance decomposes very easily to form diborane and trimethyl borate. This reaction is reversible to an appreciable extent.

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The Quantum Yields of the Photochemical Reactions of Phosgene

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In the previous work which has been reported¹ on the photochemical oxidation of phosgene, the phosgene-sensitized oxidation of carbon monoxide, and the photochemical reaction of phosgene with hydrogen, kinetic studies of the reactions have been carried out and an attempt has been made to arrive at well-correlated and self-consistent reaction mechanisms in the three cases. This program has been completely successful from the kinetic standpoint with one exception (for a discussion of this case see (1b).

Quantum Yields of the Phosgene Reaction

In order to gain further confirmation of the mechanisms already proposed, for certain photochemical reaction of phosgene it is still necessary

(1) (a) Rollefson and Montgomery, *THIS JOURNAL*, **55**, 142 (1933); (b) **55**, 4029 (1933); (c) **55**, 4036 (1933).

to show that the measured values for the quantum yields of the three reactions are in agreement with the values predicted from the reaction schemes.

As a preliminary step in order to facilitate the determination of the quantum yields by eliminating one of the necessary energy measurements, it was decided first to measure the absorption coefficients of gaseous phosgene in the ultraviolet region. Although the absorption spectrum has been fully studied, no available values of the integrated over-all absorption coefficients are recorded in the literature.

For this purpose a photographic method of spectrophotometry was employed. A cylindrical quartz absorption cell 19.9 cm. long and 3.0 cm. in diameter, having plane parallel ends, was filled with phosgene to the desired pressure; the pressure was then read on the manometer, the phosgene frozen out in a convenient quartz side tube, and the absorption cell then sealed off. Photographs were taken of the absorption spectrum by means of a Hilger E-3 quartz spectrograph, using the continuum from a quartz mercury discharge tube as the source. No lenses were used as the light from the discharge tube was sufficiently intense and parallel. A fairly wide slit was used on the spectrograph in order to cut down exposure time as well as to even out any trace of band absorption which might be obtained. "Speedway" plates were used and on each plate were recorded two photographs of the absorption spectrum, two photographs of the wave length scale (which was calibrated with a quartz mercury arc), and photographs of the discharge tube with a series of calibrated screens interposed (the quartz absorption cell being kept in place but the phosgene frozen out in the side tube). The plates were then photometered by means of a Zeiss microphotometer at various intervals throughout the absorption region. Values of I/I_0 were determined by comparison of the photometer curves for the absorption region with those for the arc with screens. The absorption coefficients were then calculated according to the equation $\epsilon = (1/pl) \log_{10} (I_0/I)$, where p is the pressure of phosgene in cm. and l is the length of the cell in cm.

The results are shown in Table I. Three different plates were taken; a pressure of 10 cm. of phosgene was used for I, 5 cm. for II, and 1 cm. for III. The results are also shown graphically in Fig. 1.

TABLE I

Å.....	2745	2696	2645	2594	2543	2491	2441	2391	2342
I, $\epsilon \times 10^2$	0.15	0.26	0.41	0.63					
II, $\epsilon \times 10^2$13	.26	.41	.64	1.00				
III, $\epsilon \times 10^2$28	.50	.85	1.13	1.42	1.78	1.99	2.04

For the quantum yield measurements, a Hilger quartz monochromator D-33 equipped with a Hilger F-83 thermopile was used. The area of the monochromator slit as used was 5.08 sq. mm. The thermopile, mounted in the monochromator slit

block, was calibrated against a standard lamp from the Bureau of Standards and found to have a sensitivity of 7.2×10^{-7} watt per mm. scale deflection with the galvanometer circuit.

The reaction vessel was similar to the cylindrical one used for the absorption coefficient determination. It was mounted flat in a cooling tank with one end about 3 mm. from a clear quartz window in the side of the tank. The transmissions of the quartz window and the plane parallel end of the reaction vessel were measured with the thermopile for the 2537 Å. line and the total transmission found to be 0.71; assuming 0.98 for the transmission of the narrow water layer between reaction vessel and window gave a total transmission for the system of about 0.70. The volume of the reaction vessel and manometer arm was measured and found to be 110 cc.

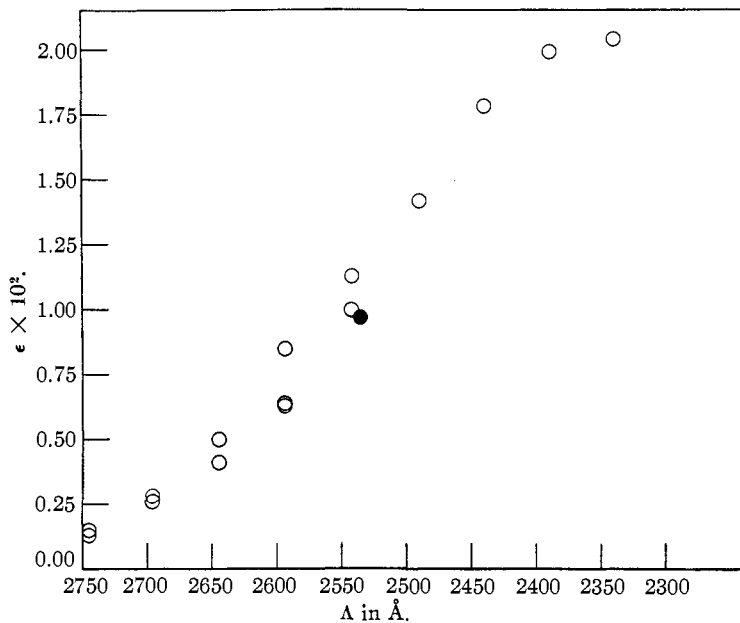


Fig. 1.

The experimental procedure was as follows. The monochromator was set on three or four prominent mercury lines visually and then turned to the 2537 region. Final setting on the line was accomplished by means of the thermopile galvanometer readings. The monochromator was then placed so that the slit was flush against the cooling tank window, directly in line with the reaction vessel. After the mercury arc had warmed up, several thermopile readings were taken. The gases were then introduced into the reaction vessel and the cooling water temperature noted. The thermopile was removed from the monochromator slit finally and illumination begun. The period of illumination varied, of course, with the reaction, sometimes being carried out for two days. At intervals during this time, thermopile readings were taken so that an average value of the rate of energy input might be obtained. Finally the manometer was read with as nearly as possible the same temperature of water in the tank as at the start (usually $\pm 0.5^\circ$).

In order to check the value of the absorption coefficient as measured by the photographic method, a more direct measurement was made. This was done by means of the

monochromator and thermopile for the 2537 Å. Hg line and gave the result $\epsilon = 0.0097$. This value is somewhat lower than the average value from Fig. 1 but is in fair agreement with the point on the curve taken from plate II. The points from plate III thus appear to be too high, and the thermopile value for ϵ has accordingly been used in the calculations. From the average rate of energy supply and the absorption coefficient of phosgene for $\lambda = 2537$ Å. ($\epsilon = 0.0097$) the amount of absorbed energy could be calculated and the number of molecules reacting was calculated, of course, from the pressure change.

I. The Photochemical Oxidation of Phosgene.—As an example of the data, the following determination is given

$$\begin{aligned}
 P_{\text{COCl}_2} &= 6.26 \text{ cm. Hg, } P_{\text{O}_2} = 6.82 \text{ cm. Hg} \\
 \text{Total no. of quanta absorbed} &= 4.4 \times 10^{18} \\
 \text{COCl}_2 \text{ reacting} &= 16.0 \text{ mm.} = 7.84 \times 10^{18} \text{ molecules} \\
 \gamma &= (7.84 \times 10^{18}) / (4.4 \times 10^{18}) = 1.78
 \end{aligned}$$

Three similar experiments gave values for γ of 1.87, 1.73 and 1.83, the average of all four being 1.80.

II. The Phosgene-Sensitized Oxidation of Carbon Monoxide.—The quantum yield of the sensitized oxidation of carbon monoxide might be expected to vary as the ratio $(\text{CO})^{1/2} / I_{\text{abs}}^{1/2}$ at high pressures of oxygen and as $(\text{CO})^{1/2} (\text{O}_2)^{1/2} / I_{\text{abs}}^{1/2}$ at low oxygen pressures. This point was not investigated, however, as the principal object was merely to get some idea of the order of magnitude of the chain length.

Two direct measurements of the quantum yield gave $\gamma = 87$ and 95 for reaction mixtures in which the pressure of each gas (COCl_2 , CO and O_2) was approximately 30 cm. of sulfuric acid.

An independent check on these values of γ was made by means of a comparison of the rate with the direct phosgene oxidation. Assuming 1.8 for the quantum yield of the latter reaction, γ for any other reaction in which phosgene is the absorbing substance may easily be found by comparing the rates of the two reactions, provided P_{COCl_2} and the light intensity is the same for both reactions. Several rate comparisons on the above reaction mixture were made, the rate being found to be 50–60 times as fast as the direct oxidation. This indicates a value for γ of 90–110, in good agreement with the directly measured values.

III. The Photochemical Reaction of Phosgene with Hydrogen.—No direct measurements of the quantum yield of the phosgene–hydrogen reaction were made but an idea of the value of γ can be had from a comparison of the rates of the oxidation and reduction. The following initial rate results are an example of the values obtained by comparison of rates.

	$P_{\text{COCl}_2} = P_{\text{H}_2} = 40.0 \text{ cm. H}_2\text{SO}_4$				
t , minutes.....	2	4	6	8	10
γ	3.8	2.8	2.6	2.4	2.4

Discussion

In general, the results of the quantum yield determinations confirm the conclusions of the kinetic studies and the mechanisms proposed for the

reactions. While the quantum yield of the oxidation is slightly lower than the value 2 predicted by the reaction mechanism, this is not a serious or unusual situation in photochemical work. Much more serious would be an experimental value greater than that predicted. There may be various factors which tend to lower the yield in this case. Although the determination of γ was made with an excess of oxygen present and the reaction was not carried out very far toward completion, still it is possible that the chlorine-oxygen ratio may be a contributing factor in lowering the rate. Furthermore, if CO_3Cl is postulated, this intermediate may take part in some side reaction which might effectively lower the rate of reaction between CO_3Cl and COCl_2 .

The quantum yield of the phosgene-sensitized oxidation indicates that the reaction involves a long chain of the same magnitude as that of the chlorine-sensitized oxidation and further confirms the similarity of the two reactions. (For a fuller discussion of this point see (2).)

In the case of the hydrogen reaction, the relatively larger value of γ at the start of the reaction is in agreement with the proposed mechanism and rate law. As will be shown later,^{1c} this higher initial rate of reaction is probably due to the second term in the rate law

$$\frac{d(\text{CO})}{dt} = I_{\text{abs.}} \left[1 + \frac{k(\text{H}_2)}{(\text{CO})(\text{M})} \right]$$

which makes a large contribution to the rate at the start of the reaction, then rapidly diminishes. If it were possible to measure the quantum yield at a very short time interval after the reaction started, it is to be expected that even larger values of γ would be found. The lower limiting value of γ as shown by the first term of the above rate law should be 1.

THE PHOTOCHEMICAL REACTION OF PHOSGENE WITH HYDROGEN

Bredig and von Goldberger² investigated the photochemical reaction of phosgene with hydrogen. They made no attempt to study the kinetics of the reaction but were concerned solely with the stoichiometry and the question of the existence or non-existence of formaldehyde as one of the reaction products. They found that the predominant reaction (they followed it to 95-98% completion in some cases) could be represented by the equation $\text{COCl}_2 + \text{H}_2 \longrightarrow \text{CO} + 2\text{HCl}$, and, further, that formaldehyde was present "only in traces at 10°," and at 80° was not detectable. They concluded that if formaldehyde were formed in some primary process, it was probably immediately decomposed photochemically.

A study of the reaction kinetics has been made in order to determine whether a reaction mechanism could be formulated in essential agreement with those of other phosgene reactions. In the event that formaldehyde

(2) Bredig and v. Goldberger, *Z. physik. Chem.*, **110**, 521 (1924).

appeared to be one of the products it was thought likely that such a study might yield an insight into some new partial reactions involving the intermediate (COCl).

Experimental

The apparatus used was the same as that previously described for the other phosgene reactions.^{1a} Phosgene was purified in the same manner as before. Hydrogen was prepared electrolytically, purified by passing over hot copper, and dried in a storage bulb containing magnesium perchlorate. Carbon monoxide was prepared and purified as before and the carbon dioxide used in the inert gas experiments was taken, without purification, from a cylinder and dried by passing through magnesium perchlorate.

In order to test the stoichiometry of the reaction, several preliminary experiments were made in which from time to time during the course of the reaction the reaction vessel was immersed in liquid oxygen and the manometer readings taken with the condensable gases (COCl_2 and HCl) frozen out. It was found that these liquid oxygen pressure readings remained constant throughout each experiment. It was concluded, therefore, that the above equation holds for the over-all phosgene reduction since it indicates that there should be no pressure change at liquid oxygen temperature. If formaldehyde were formed during the reaction, it might be expected that the liquid oxygen pressure readings would gradually decrease as the reaction proceeded. The constancy of the low temperature pressure readings must therefore be interpreted as substantiation of the conclusions of Bredig and von Goldberger that little if any formaldehyde is formed and that their equation holds for the over-all reaction. Furthermore, on the basis of the volume change in their equation, the reaction proceeded quite smoothly and in some experiments was carried out to 90–95% completion.

Results

The experimental results fall into two classes: those results which led to the elucidation of the initial rate law, and the results of further experiments designed to indicate how this initial law might be modified in order to be applicable over the entire course of the reaction.

The effect on the initial rate of varying the hydrogen pressure is shown by the results in Table II.

TABLE II

H_2 , cm. H_2SO_4	4.93	15.07	25.20	50.00
Rate, cm. H_2SO_4 /min.....	0.560	0.573	0.600	0.617

Although the hydrogen pressure was varied ten-fold, there is but little change in the initial rate. There is unquestionably a trend, however, toward higher initial rate as the hydrogen pressure increases, but the rate, at most, appears rather insensitive to variations in the hydrogen pressure.

Table III shows the results of a series of experiments in which the effect of varying the phosgene pressure was investigated. Pressures are expressed in cm. and initial rates in cm./min.

From the rates and the phosgene pressures alone, it is impossible to decide how (COCl_2) enters the rate law. The rate has an upward trend but appears to approach a limiting value at high phosgene pressures. This apparent independence of the rate on the phosgene pressure is easily

TABLE III

COCl ₂	d(CO)/dt	Absorption, %	COCl ₂	d(CO)/dt	Absorption, %
2.90	0.060	20.0	23.74	0.211	83.5
5.73	.096	35.5	26.75	.233	86.9
8.74	.124	48.5	29.82	.220	89.6
11.80	.156	59.2	32.65	.240	91.6
14.70	.175	67.3	35.80	.250	93.4
20.68	.211	79.2			

explained as follows. From the exponential character of Beer's law it is known that strict proportionality between the amount of light absorbed and the concentration of the absorbing substance exists only for low absorption, *i. e.*, low concentrations. When the amount of absorption is large, this proportionality breaks down, the amount of absorption increasing more and more slowly as the concentration increases. Hence photochemical reactions which are first order with respect to the amount of light absorbed tend to become zero order with respect to the absorbing substance at high concentrations where absorption becomes large. This is exactly the case here. In connection with the work on the quantum yields of the phosgene reactions, the absorption coefficients of phosgene were measured in the predissociation region. Thus it is possible to calculate the percentage absorption, which, unlike the phosgene pressure, should be proportional to the initial rate. This has been done in column 3 of Table III, assuming a value of the absorption coefficient $\epsilon = 0.011$, where ϵ is defined by the equation $\log(I_0/I) = pl\epsilon$, the units of p being in cm. and l in cm. ($l = 3.0$). From this equation the percentage absorption can be calculated by Percentage Absorption = $[(I_0/I) - 1]/(I_0/I)$. The value taken for ϵ is that corresponding to $\lambda = 2537 \text{ \AA.}$, the most intense Hg line beyond the predissociation limit.

If the initial rates of Table III are plotted against the corresponding percentage absorption calculated in the above manner, a straight line is obtained, clearly indicating that the rate is a function of the first power of the light absorbed.

In Table IV are summarized the results of a series of experiments in which the effect of variation of the incident light intensity, by means of a set of calibrated screens, was investigated.

TABLE IV

Transmission, %.....	100.0	69.5	48.6	38.0	29.7	15.6
Rate.....	0.080	0.057	0.038	0.029	0.027	0.013
Δ	-.002	.000	-.002	-.003	+.003	+.002

The third column of the Table shows the deviations from linearity (*i. e.*, from the best straight line through the points). As might have been predicted from the phosgene results, the rate is a linear function of the incident intensity.

From the above results it appears that the rate is much more sensitive to the amount of light absorbed than to the hydrogen pressure. If $d(\text{CO})/dt = kI_{\text{abs.}} = kI_0(\text{COCl}_2)$, we may write $d(\text{CO})/dt = -d(\text{COCl}_2)/dt = kI_0(\text{COCl}_2)$, or, $-d \log (\text{COCl}_2)/dt = k'$. If, therefore, the rate law were the simple first order expression above, the change in the logarithm of the (COCl_2) per unit time might be expected to remain constant. That this is not so is shown by the results of Table V. δ is the rate of change of the $\log (\text{COCl}_2)$.

TABLE V

Time, minutes.....	3	6	10	15	20	25	30	35
δ	0.015	0.013	0.013	0.011	0.009	0.009	0.009	0.007
Time, minutes.....			45	55	65	75	85	100
δ			0.007	0.005	0.005	0.004	0.003	0.003
								(71% completion)

In order to investigate the cause of this deviation from the first order law, further series of experiments were undertaken. In Table VI are shown the results of some experiments in which the effect of total pressure was investigated. (COCl_2) , (H_2) , and the incident light intensity were kept constant and total pressure varied by the addition of (CO_2) .

TABLE VI

CO_2 , cm.....	0.0	10.0	15.0	20.0	25.1	40.1	45.2
Relative rate.....	1.000	0.909	0.871	0.841	0.775	0.630	0.594
Δ	0.000	-.005	.000	+.015	-.005	-.015	-.005

The rate appears to be inversely proportional or at least involves a term which is inversely proportional to the first power of the total pressure. A series of experiments in which nitrogen was the added gas yielded quite similar results.

Next, a series of experiments was made in which carbon monoxide was added to the reaction gases in varying amounts. The results appear in Table VII.

TABLE VII

CO , cm. H_2SO_4	0.00	10.09	15.07	21.35	34.91
Relative rate.....	1.000	0.757	0.722	0.666	0.595

It is evident that the inverse effect on the rate is much more pronounced with carbon monoxide than with carbon dioxide (or nitrogen). Furthermore, when the relative rate is plotted against the carbon monoxide pressure, a distinct curvature is observed so that the curve resembles the graph of an inverse square function. This must be interpreted as due to the fact that carbon monoxide, apart from its total pressure effect, has a specific effect as well in lowering the rate. This means that carbon monoxide probably enters the rate law explicitly.

In the following table the values of δ have been tabulated for a series of three experiments. Expt. A was a "control" reaction showing the usual

falling off of δ . In Expt. B hydrogen was added during the reaction and in Expt. C there was a large excess of carbon monoxide present. In other respects the conditions were identical in the three experiments ($P_{H_2} = P_{COCl_2} = 10$ cm. H_2SO_4).

TABLE VIII

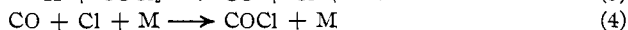
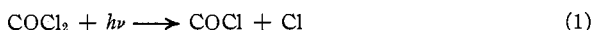
A		B		C	
<i>t</i> , mins.	δ	<i>t</i> , mins.	δ	<i>t</i> , mins.	δ
15	0.082	10	0.077	10	0.038
25	.069	20	.067	20	.038
35	.066	30	.061	30	.036
45	.063	40	.063 ^a	40	.042
55	.058	50	.064	60	.041
65	.057	60	.075 ^b	80	.038
75	.052	70	.081	100	.039
85	.047				

^a 5 Cm. H_2SO_4 of H_2 added. ^b 27 Cm. H_2SO_4 of H_2 added.

The above experiments and other similar ones seem to indicate that the amount of deviation from first order may depend upon the value of the ratio $H_2/(CO)(M)$. By alternate additions of hydrogen and carbon monoxide, it was found possible to vary the deviation almost at will. It is further evident that fairly constant values of δ may be obtained by maintaining an excess of hydrogen as in "B" or by adding a large excess of carbon monoxide as in "C."

Discussion

It has been possible to derive a rate law in formal agreement with the above experimental facts from the following reaction mechanism



The rate of reaction according to this reaction scheme is given by

$$d(CO)/dt = k_3(H)(COCl_2) + k_5(COCl)^2 - k_4(CO)(Cl)(M)$$

Assuming that the rates of change of $(COCl)$, (Cl) , and (H) are negligibly small compared to their rates of formation and disappearance, we may write

$$d(COCl)/dt = I_{abs.} + k_4(CO)(Cl)(M) - k_5(COCl)^2 = 0 \quad (I)$$

$$d(Cl)/dt = I_{abs.} - k_2(Cl)(H_2) + k_3(H)(COCl_2) - k_4(CO)(Cl)(M) = 0 \quad (II)$$

$$d(H)/dt = k_2(Cl)(H_2) - k_3(H)(COCl_2) = 0 \quad (III)$$

$$I + II + III = 0 = 2I_{abs.} - k_5(COCl)^2$$

$$\text{or, } k_5(COCl)^2 = 2I_{abs.} \quad (IV)$$

From II we obtain

$$k_3(H)(COCl_2) - k_4(CO)(Cl)(M) = k_2(Cl)(H_2) - I_{abs.}$$

Substituting the right-hand member in the expression for the rate of reaction we have

$$d(CO)/dt = k_2(Cl)(H_2) - I_{abs.} + k_5(COCl)^2 \quad (V)$$

According to IV this becomes

$$d(\text{CO})/dt = k_2(\text{Cl})(\text{H}_2) + I_{\text{abs.}} \quad (\text{VI})$$

From I we obtain

$$\begin{aligned} k_4(\text{CO})(\text{Cl})(\text{M}) &= I_{\text{abs.}}, \text{ or} \\ (\text{Cl}) &= I_{\text{abs.}}/k_4(\text{CO})(\text{M}) \end{aligned} \quad (\text{VII})$$

Substitution of VII in VI gives

$$\begin{aligned} d(\text{CO})/dt &= I_{\text{abs.}} + k_2 I_{\text{abs.}}(\text{H}_2)/k_4(\text{CO})(\text{M}) \\ &= I_{\text{abs.}} \left[1 + \frac{k_2(\text{H}_2)}{k_4(\text{CO})(\text{M})} \right] \end{aligned} \quad (\text{VIII})$$

Since in most of the experimental work the total absorption was small we may make the substitution $I_{\text{abs.}} = I_0(\text{COCl}_2)$, which reduces VIII to

$$d(\text{CO})/dt = I_0(\text{COCl}_2) \left[1 + \frac{k_2(\text{H}_2)}{k_4(\text{CO})(\text{M})} \right]$$

an equation in formal agreement with and capable of explaining the experimental facts.

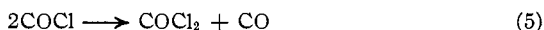
It may be remarked that a rate law of this form indicates an infinite initial rate of reaction (since carbon monoxide is one of the reaction products). This, of course, is not observed. In every case, however, where carbon monoxide is not added before the start of the reaction, the first two or three values of δ are invariably noticeably larger than succeeding values. The second term thus makes its largest contribution to the rate at the start of the reaction. The fact that the ratio $\text{H}_2/(\text{CO})(\text{M})$ decreases so rapidly as reaction proceeds explains the rapid falling off of the δ values.

Special notice should be taken of the manner in which (M) enters the rate law, as any molecule which is capable of taking up the excess energy of, and so stabilizing, the intermediate COCl . In the case of the photochemical formation of phosgene, Lenher and Rollefson³ identified (M) with (Cl_2) and this was later confirmed on theoretical grounds by Rollefson and Eyring.⁴ The possibility of Cl_3 molecules (such as they postulated) reacting with CO to form COCl is indeed remote in the phosgene-hydrogen reaction since no Cl_2 is present. Hence it is difficult to identify (M) with any particular molecular species in our present case. Furthermore, it is undoubtedly incorrect to assume that all the kinds of molecules present are equally capable of stabilizing COCl and thus tacitly to assume the identity of (M) and the total pressure. It is well known from the study of the extinction of fluorescence that molecules differ greatly in their efficiency in taking up energy. In confirmation of this, carbon monoxide was found to have a more pronounced "total pressure" effect than nitrogen. For this reason, (M) should probably be written $(\text{M}) = a(\text{COCl}_2) + b(\text{H}_2) + c(\text{CO}) + d(\text{HCl})$, where the coefficients are "stabilizing efficiencies." It is this indeterminate character of (M) which makes a more rigorous analytical test of the rate law impossible.

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

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

In the reaction mechanism, no reaction has been postulated between COCl and H_2 to form, possibly, COH , since there was no evidence of formaldehyde formation, which might be supposed to take place through this latter intermediate. As a consequence COCl may be supposed to build up sufficient concentration to bring about the chain terminating step



This step is thus fairly consistent with the other partial reactions of the mechanism.

Summary

The quantum yields have been measured for the photochemical oxidation of phosgene, the phosgene-sensitized oxidation of carbon monoxide, and the photochemical reaction of phosgene with hydrogen. The results confirm the rate mechanisms proposed for these three reactions.

The photochemical reaction between phosgene and hydrogen: $\text{COCl}_2 + \text{H}_2 \longrightarrow \text{CO} + 2\text{HCl}$, has been studied. The rate of the reaction has been investigated and a mechanism devised from which the theoretical rate law

$$\frac{d(\text{CO})}{dt} = kI_0(\text{COCl}_2) \left[1 + \frac{k_2(\text{H}_2)}{(\text{CO})(\text{M})} \right]$$

may be derived. It has been shown that this expression is in essential accord with the experimental facts. The reaction rate has been discussed from the standpoint of this rate law and various experimental points explained. The absence of formaldehyde formation, it has been pointed out, is probably due to the non-reactivity of COCl toward H_2 . This non-reactivity in turn is believed to cause an increase in the concentration of COCl so that $2\text{COCl} \longrightarrow \text{COCl}_2 + \text{CO}$ becomes the chain terminating process.

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