

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Photochemical Formation of Phosgene¹BY LEWIS FOWLER² AND J. J. BEAVER

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The experimental study of the photochemical reaction $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ is extended by investigating the effect of a ten-fold variation in light intensity as well as pressure ratio changes. It is established that the true rate equation followed is $d(\text{COCl}_2)/dt = k'(\text{Cl}_2)(-1 + \sqrt{k''(\text{CO})I_{\text{abs}} + 1})$, and that use of this equation eliminates ambiguities in previously reported data. A convenient and precise method of calculating rate constants based on this equation is derived and applied. Quantum yields as functions of light intensity and reactant pressures are calculated, and found to be about 10^4 .

Introduction

The photochemical reaction $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$ has been the subject of a series of researches by Bodenstein and others.^{3,4} It has been postulated that the following rate steps describe the reactions

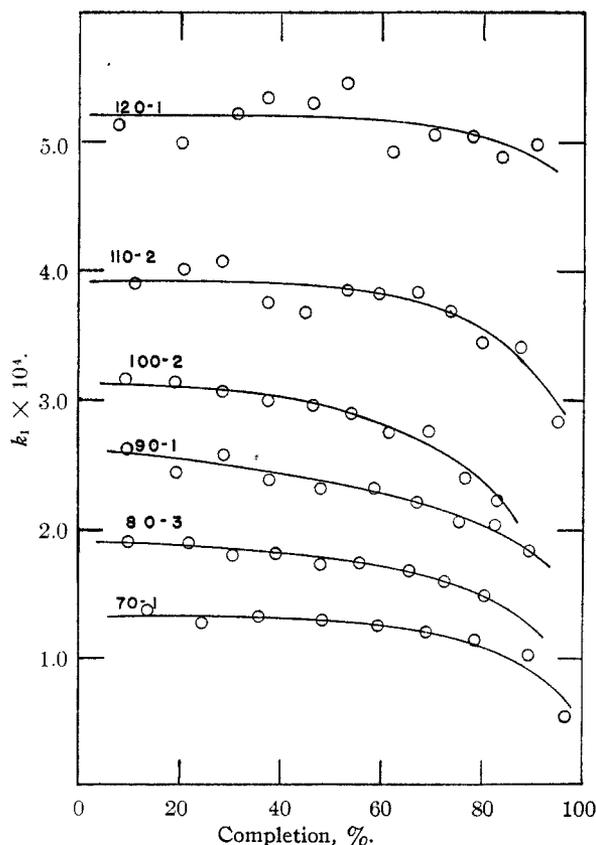
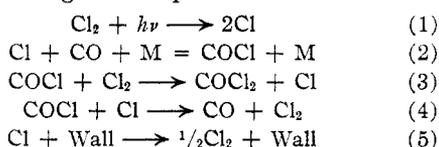


Fig. 1.

(1) This paper is based on a dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science in Columbia University.

(2) Monsanto Chemical Company, J. F. Queeny Plant, St. Louis, Mo.

(3) M. Bodenstein, S. Lenher and C. Wagner, *Z. physik. Chem.*, **B3**, 459 (1929); M. Bodenstein, W. Brenschede and H. J. Schumacher, *ibid.*, **B28**, 81 (1935); *ibid.*, **B40**, 121 (1938).

(4) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939; W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941; W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, **48**, 39 (1952).

In deriving the total rate expression, the chain-ending step (4) has been used to explain the results at total reactant pressures of 200 to 600 mm., while below 30 mm. it has been assumed that step (5) is controlling. Assuming a steady-state concentration of intermediates, rate expressions can be derived.

$$d(\text{COCl}_2)/dt = (k_2K_2^{1/2}/k_4^{1/2})(\text{Cl}_2)(\text{CO})^{1/2}I_{\text{abs}}^{1/2} \quad (\text{I})$$

$$d(\text{COCl}_2)/dt = \frac{(2k_3K_2)}{k_5}(\text{Cl}_2)(\text{CO})I_{\text{abs}} \quad (\text{II})$$

$$d(\text{COCl}_2)/dt = (k_3k_5/4k_4)(\text{Cl}_2)(-1 + \sqrt{(16K_2k_4/k_5^2)(\text{CO})I_{\text{abs}} + 1}) \quad (\text{III})$$

Equation (I) agrees with the experimental expression found at medium total reactant pressures of 200 to 600 mm., and equation (II) with that for low reactant pressures of 30 mm. or high surface/volume ratios. Equation (III) should be the general expression for the entire pressure range studied, including (I) and (II) as limiting cases. Correlating with this idea, attention has been variously called to the fact that equation (I), although generally used, is unsatisfactory, for constants ($k_{\text{exp}} = k_3K_2^{1/2}/k_4^{1/2}$) calculated by it always decline in value as the reaction nears completion (Fig. 1).

The possibility of extraneous reactions causing the decline in constants calculated by equation (I) has been ruled out by the definitive experiments of Weber⁵ and Manninen⁶ who have examined the inhibitory effects of various impurities including oxygen and by the work of Fye and Beaver⁷ who showed that induction and retarding effects could be eliminated by extreme purification of the reactants, especially the chlorine. It must be concluded, therefore, that the explanation of the decline in constants when equation (I) is used lies in an increasing importance of step (5), which is not used in the derivation of (I). This has been the usual explanation offered.^{3,4} No satisfactory quantitative treatment has, however, been suggested.

Experimental

The reactions are functions of both the reactant pressures and the incident light intensities, so equation (III) was tested by determining its applicability over a range of these variables. The experimental apparatus and procedure used was essentially that of Fye and Beaver,⁸ which is capable of giving results of good precision for this long-chain reaction. A ten-fold variation of light intensity was obtained by using 115-v. alternating current source for the lamps. This was regulated and adjusted by passage through a Raytheon constant-voltage transformer and a

(5) L. A. Weber, Columbia Dissertation, 1933.

(6) T. H. Manninen, Columbia Dissertation, 1938.

(7) P. M. Fye and J. J. Beaver, *This Journal*, **63**, 1268 (1941).

(8) P. M. Fye and J. J. Beaver, *ibid.*, **63**, 2395 (1941).

Powerstat variable transformer. These enabled the applied voltage to be adjusted to a chosen value and maintained constant within ± 0.2 v. for the duration of each experiment. Experiments were made at 70, 80, 90, 100, 110 and 120 v. The corresponding relative light intensities were measured with a General Electric barrier-layer cell and a set of glass filters covering the range of 4000 to 5000 Å. The resultant intensity values were corrected for the absorption of chlorine in this region, using the data of Halban and Seidentopf.⁹ The results expressed as ratios to the intensity at 100 v. are given in Table I, column 2. (Columns 3 and 4 will be discussed later.)

TABLE I
LIGHT INTENSITIES AT VARIOUS VOLTAGES AND RATE CONSTANTS FOUND

Voltage	I/I_{100}	$k'' \times 10^3$	$k^* \times 10^4$
70	0.29	0.6	1.49
80	.51	1.0	2.28
90	.75	1.5	2.90
100	1.00	2.0	3.53
110	1.5	3.0	4.31
120	3.1	6.2	5.58

The variation in intensity during the course of an experiment at any one voltage due to possible voltage fluctuations is not more than $\pm 0.3\%$. Combining this with the uncertainties due to pressure, temperature and time measurements gives a calculated over-all precision measure of $\pm 3\%$ in the rate constants.

Results

For purposes of calculating rate constants from the experimental data equations (I), (II) and (III) are written

$$dx/dt = k'k''^{1/2}(a-x)(b-x)^{1/2} \quad (\text{I})$$

$$dx/dt = (k'k''/2)(a-x)^2(b-x) \quad (\text{II})$$

$$dx/dt = k'(a-x)[-1 + \sqrt{k''(a-x)(b-x) + 1}] \quad (\text{III})$$

where $x = (\text{COCl}_2)$; $(a-x) = (\text{Cl}_2)$; $(b-x) = (\text{CO})$; $k' = k_3k_5/4k_4$; $k'' = 16K_2k_4/k_6^2\alpha I_0$. For the experimental conditions used $I_{\text{abs}} = (\text{Cl}_2)\alpha I_0$, α being the absorption coefficient. Concentrations are in mm. Hg.

The experimental rate constants ($k_1 = k'k''^{1/2}$), calculated by the point-to-point integration of equation (I), are shown in Fig. 1 for sample experiments at each of the six light intensities. These experiments covered total pressures of 250 to 550 mm. and (CO):(Cl₂) ratios of 1:3 to 2:1. The usual procedure has been to express the "best" value of k_1 as the mean of the values in the early part of the reaction. The uncertainty of this procedure is evidenced by the curvature of the graphs, which generally is greater with lower pressures and low light intensities. Presumably the ambiguity would be removed if equation (III) were used as noted above. It can be integrated by rearranging to read

$$k' \int_{t_1}^{t_2} dt = \frac{1}{k''} \int_{x_1}^{x_2} \frac{1 + [k''(a-x)(b-x) + 1]^{1/2} dx}{(a-x)^2(b-x)}$$

The result is

$$k'(t_2 - t_1) = \frac{1}{k''D} \left[R + \ln R + Q^{1/2} + \ln \left(\frac{Q^{1/2}}{R} + \frac{k''D^2 - 2}{2} \right) + \left(\frac{k''D^2 - 2}{2} \right) \ln \left(Q^{1/2} + R \right) + \left(\frac{k''D^2 - 2}{2} \right) \right]_{R_1}^{R_2}$$

(9) H. V. Halban and K. Seidentopf, *Z. physik. Chem.*, **B103**, 71 (1922).

where

$$R = (b-x)/(a-x)$$

$$Q = R^2 - (k''D^2 - 2)R + 1$$

$$D = (b-a)$$

This cannot be further simplified, and computations with it are arduous. The differential form (given above) can be used if the assumption is made that $dx/dt = \Delta x/\Delta t$, a less exact solution.

Both methods are sensitive to experimental errors. The values given in Table II are for the integrated form; simultaneous solutions give the values of k' and k'' to be used for $k_{\text{III}} = k'k''^{1/2}$. The differential form checks these within 1.5% so they are not given in the table. Even in this favorable case, the standard deviation of $\pm 7\%$ is considerably larger than the precision measure of $\pm 3\%$. We may note in passing that k^* , to be discussed later, shows a standard deviation of but $\pm 2\%$.

TABLE II
EXPERIMENT NO. 90-2, 90 VOLTS

t , min.	(Cl ₂)	(CO)	(COCl ₂)	$k_1 \times 10^4$	$k_{\text{III}} \times 10^4$	$k^* \times 10^4$
0	210.4	220.2	0
2	188.8	198.6	21.6	2.59	3.00	2.90
4	172.0	181.8	38.4	2.46	2.88	2.78
6.5	154.4	164.2	56.0	2.50	2.61	2.86
9.5	137.7	147.5	72.7	2.45	2.99	2.86
13.5	120.9	130.7	89.5	2.34	2.93	2.78
18.5	104.8	114.6	105.6	2.33	3.10	2.83
25.5	88.6	98.4	121.8	2.26	3.02	2.85
35.5	72.5	82.3	137.9	2.25	3.16	2.94
50.5	57.5	67.3	152.9	2.07	3.17	2.87
81.5	40.8	50.6	169.6	1.89	3.91	2.98
				Av.	3.07	2.87
				Standard dev.	± 0.21	± 0.05

In the region where $k''(a-x)(b-x)$ is larger numerically than one, the differential form of (III) can be expanded successively in binomial series to yield a final series expressible as

$$k'dt = \frac{dx}{(a-x)} \left([k''(a-x)(b-x)]^{-1} + [k''(a-x)(b-x)]^{-1/2} + \frac{1}{2}[k''(a-x)(b-x)]^{-3/2} + \dots \right)$$

These terms can be integrated and the results summed. Trials showed that no more than the first three terms are needed for experiments within the applicable region. The results are within $\pm 1\%$ of those found by using the correction procedure described below. This latter proves to be better than any of the preceding forms of equation (III) because it is simpler to use and it has no limits on its region of applicability.

By examining equations (I) and (III) it can be seen that (III) approaches (I) as the numerical value of $k''(a-x)(b-x)$ increases with respect to one. The unsuitability of (I) as a description of the reaction rate will then be a function of the numerical magnitude of the term denoted by

$$F = k''(a-x)(b-x)$$

In these terms

$$(dx/dt)_I = k'(a-x)F^{1/2} \quad (\text{I})$$

$$(dx/dt)_{\text{III}} = k'(a-x)(-1 + \sqrt{F+1}) \quad (\text{III})$$

and $(dx/dt)_I$ would be the rate during the entire reaction if equation (I) were always valid; while

$(dx/dt)_{III}$ is the actual rate for the entire reaction, assuming rate steps (4) and (5) both to be operative.

In defining the experimental rate constant, k_I , calculated using equation (I) the definition should read to be valid: $k_I = (dx/dt)_I / (a-x)^{1/2}(b-x)^{1/2}$. In practice, however, the experimental data provides the actual rate $(dx/dt)_{III}$ giving the expression: $k_I = (dx/dt)_{III} / (a-x)^{1/2}(b-x)^{1/2}$ which is invalid because the denominator and numerator refer to different total mechanisms. This accounts for the drift in the constants as usually calculated, as illustrated in Fig. 1. This latter equation can be converted to the valid form by multiplying by $(dx/dt)_I / (dx/dt)_{III}$, which is equivalent to $F^{1/2} / (-1 + \sqrt{F+1})$. Applying this multiplying correction, a new constant, k^* , is defined

$$k^* = \frac{(dx/dt)_{III} F^{1/2}}{(a-x)^{1/2}(b-x)^{1/2}(-1 + \sqrt{F+1})} \quad (IV)$$

$$k^* = k_I \frac{F^{1/2}}{(-1 + \sqrt{F+1})}$$

Hence $F^{1/2} / (-1 + \sqrt{F+1})$ is the function of F needed to correct the experimental constants as customarily determined into constants which allow for both steps (4) and (5) and should remain constant throughout the reaction. In other words, k^* should be a constant independent of the degree of completion of the reaction, if equation (III) contains the complete description of the reaction, and the constancy of k^* over a variety of conditions will verify the correctness of (III).

To calculate values of k^* , k_I is obtained by the usual methods of point-to-point integration of equation (I). F is computed for the interval by using the mean pressures of CO and Cl₂ and the value of k'' from Table I.¹⁰ The average values of k^* for the various light intensities are listed in Table I. The standard deviations of these values are $\pm 3\%$. The results of nineteen experiments under various conditions of light intensity and pressure are included.

Discussion

Consideration of these experimental results indicates that the hypothesis that equation (III) is the proper description of the reaction is a valid one within the experimental limits. As previously mentioned, the data offered by Fye and Beaver were also examined by the same procedure. In addition to the confirmation of the value of $k^* = 3.53 \times 10^{-4}$ at 100 v., their other data, with added wire gauze filter, and with unfiltered light, were examined. With a reasonable choice of k'' , values of k^* could be calculated whose standard deviation for any given condition was $\pm 3.5\%$. As a further trial of the procedure and conclusions presented in this research, the data assembled by Bodenstein³ were examined. He offers constants from "first

(10) The values of k'' given in Table I were computed by multiplying the value, 2×10^{-3} at 100 v, by the respective (I/I_{100}) ratios. 2×10^{-3} was found to be the value giving the "best" correction of the constants of the experiments at 100 v. Since Fye and Beaver give the data of several experiments in the same apparatus at 100 v. d.c., this value of k'' was also used in applying equation (IV) to their data. k^* thus determined for their data varied by no more than $\pm 3\%$ standard deviation, the same as found in this research.

and last intervals" of some 17 experiments performed at various times. The total pressure range he covered was 5 to 56 mm. The light intensity was about 4.3 times that at 100 v. in this work. The average k^* calculated was $7.4 \pm 1.3 \times 10^{-4}$. The calculated constants are erratic, but considering the widely varying experimental conditions and precision of measurement, this is not surprising. There are no definite trends. It appears that equation (III) is valid over a wide range of surface-volume ratios and under experimental conditions differing from those of the present research.

The chain-terminating reaction step (5), formulated as $Cl + Wall \rightarrow \frac{1}{2}Cl_2 + Wall$, has been shown to be a necessary part of the complete mechanism. It might be supposed that the kinetics would therefore be dependent on the total pressure as well as on the reactant pressures. This is not the case. It has been shown by Noyes^{11,12} that the explanation lies in the low recombination coefficient, 5×10^{-5} , of Cl atoms on the wall. It would be necessary to use total pressures much greater than any that have been tried to realize any measurable total pressure effect. Noyes¹² has also shown that only 7% of the chains terminate by step (5) under the experimental conditions of this work and reactant pressures of $(CO) = (Cl_2) = 300$ mm. Therefore, the explanation for the ability of previous experimenters to obtain useful data at reactant pressures of 200 to 600 mm. using only equation (I), $d(COCl_2)/dt = k_I I_{abs}^{1/2} (Cl_2)(CO)^{1/2}$, which ignores step (5), lies in the small magnitude of the wall effect at these pressures. Dainton,⁴ for example, whose experimental conditions are similar to those of this work, used the initial slope of the pressure vs. time curve in confirming equation (I), though he notes its inapplicability at lower reactant pressures and light intensities.

The quantum yield for the reaction is given by $\Phi = k'(Cl_2)(-1 + k''(CO)I_{abs} + 1) / I_{abs}$. Values of I_{abs} , k' and k'' are available from the data of Fye and Beaver,⁸ Halban and Seidentopf,⁹ and this research. Calculated results are shown in Table III. For convenience, values of Φ were computed assuming equal pressures of CO and Cl₂. It is seen that the values are in agreement with those of Bonhoeffer¹³ ($\Phi = 2.7 \times 10^3$), Bodenstein³ ($\Phi = 1.5 \times 10^3$), and Burns and Dainton⁴ ($\Phi = 6.2 \times 10^3$). The expected increase of Φ with decreasing light intensity and with increasing reactant pressures is shown.

TABLE III
QUANTUM YIELDS

I/I_{100}	$P_{CO} = P_{Cl_2}$, mm.	$\Phi \times 10^{-3}$	I/I_{100}	$P_{CO} = P_{Cl_2}$, mm.	$\Phi \times 10^{-3}$
3.1	200	4.4	1.0	50	1.3
1.5	200	6.0	0.75	200	8.2
1.0	300	11.2	.51	200	9.1
1.0	200	7.2	.29	200	12.8
1.0	100	3.1			

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- (11) R. M. Noyes, *THIS JOURNAL*, **73**, 3039 (1951).
 (12) R. M. Noyes and L. Fowler, *ibid.*, **73**, 3043 (1951).
 (13) K. F. Bonhoeffer, *J. Physik*, **13**, 94 (1923).