limited, it is not possible to study quantitatively the data from the point of view of the Arrhenius equation.

An approximation of the change in the factors of the Arrhenius equation may be obtained by plotting the values of the energies of activation, E, against log k at 30°. This relationship is shown in Fig. 1. The broken line having a slope of $2.303RT$ is included since the acids would lie on a line of this slope if their velocity constants were entirely dependent on E. From the data given it is apparent that the factor P varies since the solid lines do not have a slope of $2.303RT$.

Further investigation of the kinetics of esterification of polysubstituted benzoic acids is being conducted.

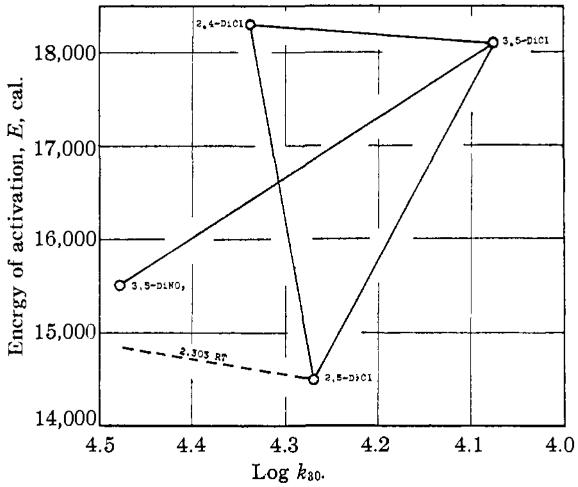

Fig. 1.—Relationship between reaction velocity and activation energy.

Summary

The velocity constants and energies of activation of 2,4-dichlorobenzoic acid, 2,5-dichlorobenzoic acid, 3,5-dichlorobenzoic acid and 3,5-dinitrobenzoic acid have been determined.

The velocity of esterification is apparently affected by both the P factor of the Arrhenius equation and E, the energy of activation.

BLOOMINGTON, INDIANA RECEIVED APRIL 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Kinetics of the Photochemical Formation of Phosgene

BY PAUL M. FYE AND J. J. BEAVER[1]

Introduction

The various investigations concerning the photochemical formation of phosgene from carbon monoxide and chlorine have included the development of possible mechanisms explaining the accumulated data. At present there are two mechanisms—both of which on final analysis give the observed over-all rate equation—which must be given consideration. First that originating with Bodenstein[2] and his co-workers for room temperature and total pressures ranging from 200 to 600 mm. of mercury is given as

$$Cl_2 + h\nu \longrightarrow 2Cl \quad (1)$$
$$Cl + CO + M \longrightarrow COCl + M \quad (2)$$
$$COCl + M \longrightarrow CO + Cl + M \quad (2a)$$
$$COCl + Cl_2 \longrightarrow COCl_2 + Cl \quad (3)$$
$$COCl + Cl \longrightarrow CO + Cl_2 \quad (4)$$

It is assumed that an equilibrium concentration of the free radical (COCl) is established and maintained by equations (2) and (2a) and that reactions (3) and (4) are too slow to prevent the maintenance of this equilibrium. If it is also supposed in the customary manner that a fixed concentration of chlorine atoms is maintained, the following empirical rate equation may be derived

$$\frac{d(COCl_2)}{dt} = \frac{k_3 K_{COCl}^{1/2}}{k_4^{1/2}} I_a^{1/2}(Cl_2)(CO)^{1/2} \quad (I)$$

k_3 and k_4 are the specific reaction rate constants for (3) and (4), K_{COCl}, the equilibrium constant for $CO + Cl \rightleftarrows COCl$, equals k_2/k_{2a}, and I_a is the light absorbed by the reacting gases.

The chain-breaking process above is reaction (4); however, at total pressures below 20 mm. of mercury it is assumed to be

$$Cl \longrightarrow \text{wall} = {}^1/_2Cl_2 \quad (5)$$

When (5) has completely replaced (4) the rate equation becomes

$$\frac{d(COCl_2)}{dt} = \frac{2k_3K_{COCl}}{k_5} I_a(Cl_2)(CO) \quad (II)$$

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[1] Excerpt from the thesis submitted by Paul M. Fye to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1939.

[2] Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929); Bodenstein, *Helv. Chim. Acta*, **18**, 743 (1935); Bodenstein, *Naturwissenschaften*, **23**, 10 (1935).

Lenher and Rollefson[3] have objected to this mechanism largely on the grounds that the three-body equilibrium of equations (2) and (2a) could not be maintained and have offered in its place a mechanism consisting of reactions (1), (2), (3) and (4) as given above. Following the customary assumptions concerning stationary-state concentrations of Cl and COCl the following equation is derivable

$$\frac{\mathrm{d}(\mathrm{COCl_2})}{\mathrm{d}t} = \left[\frac{k_2k_3}{k_4}\right]^{1/2} I_a{}^{1/2}(\mathrm{Cl_2})^{1/2}(\mathrm{CO})^{1/2}(\mathrm{M})^{1/2} \quad \text{(III)}$$

which, it may be seen, is the same as the experimental rate equation (I) if (Cl_2) is substituted for (M), the third-body necessary to stabilize reaction (2).

The principal proof offered by Bodenstein[4] for his mechanism is a series of involved calculations, containing several doubtful assumptions, by which are obtained values for each of the individual constants. It is claimed that these check within 20% of experimental values. These assumptions would also permit the calculation of corresponding constants for another mechanism.[5]

The recent work of Manninen[6] in this Laboratory showed that when pure gases are used, the over-all temperature coefficient of the reaction is equal to zero within the experimental error (± 5%) from 0 to 40°. This fact casts considerable doubt on the desirability of including a temperature sensitive equilibrium in the mechanism as outlined by Bodenstein and indicates that further work is necessary before complete reconciliation of experiment and theory is possible.

As reported from other laboratories, the rate of phosgene formation characteristically showed a marked induction period and a typical falling off at the end. The work of Weber[7] has shown that with sufficient purification of reactant gases the induction period could be eliminated. This we have confirmed and have reported the present method of purification in a previous article.[8]

In addition to further standardization of experimental procedures, it has been the purpose of this investigation to study the possibility of "third-body" effects as suggested by the Rollefson rate equation (III above) and to study systematically the decrease in the rate constants toward the end of the reaction, as well as offer an explanation for this latter phenomenon. The apparatus and method used throughout was essentially as described by Weber,[7] Manninen[6] and Fye and Beaver.[8]

All constants were calculated by means of the integrated form of the rate equation[7] with constants given in the experimentally observed units—*i. e.*, millimeters of mercury and minutes. The dimensions are $(\mathrm{mm.})^{-1}$ $(\mathrm{min.})^{-1}$.

In these experiments the largest error is that arising from the error made in the measurement of the pressure change for a definite interval of time. The precision of a single measurement of pressure is ±0.2 mm. Using the customary rules of precision this results in a 3.1% error in k for the case where the pressure of chlorine is 300 mm., the pressure of carbon monoxide 200 mm., and the pressure change is 10 mm.

Third-Body Effects

Experimental Results and Discussion.—Inspection of the rate equation as derived from the Lenher–Rollefson[3] mechanism (III) shows that any third-body (M) which will stabilize the formation of COCl should increase the rate of reaction an amount proportional to the square root of the concentration of (M). The assumption that only chlorine can stabilize this reaction has been justified[3] by the fact that specific third-body effects have been found in the quenching of fluorescence and by the possibility of the existence of the Cl_3 molecule as indicated by the calculations of Rollefson and Eyring.[9] In general when the function of a third body is merely to absorb energy and thus stabilize the molecule formed by collision, the efficiency of such action increases with size, *i. e.*, effective cross section, and the complexity of the molecule.[10] Furthermore, specific third-body effects have been found in general to follow a principle first postulated by Franck,[11] that the highest probability of energy transfer between excited states occurs when the resultant kinetic energy is at a minimum. Hence, the requirements for the stabilization of the COCl molecule are: first, a third body of sufficient size and complexity

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(3) Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930); Rollefson, *ibid.*, **56**, 579 (1934); Rollefson, *Z. physik. Chem.*, **B37**, 472 (1937).

(4) Bodenstein, Schumacher and Brenshede, *Z. physik. Chem.*, **B40**, 121 (1938).

(5) *Cf.* Rollefson and Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 319.

(6) Manninen, Columbia Dissertation, 1938.

(7) Weber, Columbia Dissertation, 1933.

(8) Fye and Beaver, THIS JOURNAL, **63**, 1268 (1941).

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

(10) *Cf.* Gershinowitz, *J. Chem. Phys.*, **5**, 54 (1937); Rabinowitch and Wood, *Trans. Faraday Soc.*, **32**, 907 (1936); Hilferding and Steiner, *Z. physik. Chem.*, **B30**, 399 (1935).

(11) Franck, *Naturwissenschaften*, **14**, 211 (1926).

to absorb the necessary energy; second, one with vibrational levels sufficiently close to the vibrational levels of the carbon–chlorine bond in COCl that its efficiency may be high; and, finally, a molecule which is non-reactive with all the gases present. The molecule CCl_2F_2[12] is quite ideal for the first and third requirements and better than the Cl_2 molecule in regard to the second.

The essential data for two typical experiments with dichlorodifluoromethane are given in Table I where $(P_{CO})_0$ and $(P_{Cl_2})_0$ indicate initial pressures and K_{av} is the mean value of K for the first half of the reaction. The decrease in the rate constants toward the end of the reaction is discussed below.

The results of these experiments as shown in Fig. 1 indicate that there is no measurable change in the rate of the reaction when CCl_2F_2 is added to the reaction mixture in amounts as large as 300 mm. In each case the third-body gas was added to the reaction mixture after at least two determinations of the value of the rate constant had been made and in no case was there a deviation in the constants. It may be noted that the initial pressure of CCl_2F_2 is about half that of chlorine in no. 113 and more than twice the pressure of chlorine in no. 118. Of course, after the reaction has proceeded for some time and some of the chlorine consumed the concentration of CCl_2F_2 is several times that of either reactant. The data of experiments no. 115 and no. 117 are also plotted to show the normal rate of reaction without the addition of any foreign substance.

TABLE I

Expt.	$(P_{CO})_0$	$(P_{Cl_2})_0$	CCl_2F_2	k_{av}
113	137.5	144.6	77.7	3.30 ± 0.08
115	103.4	165.6	0.0	3.15 ± .05
117	161.0	152.6	0.0	3.22 ± .08
118	221.0	146.0	295.0	3.20 ± .07

The data for Experiment 113 are typical experimental results.

EXPERIMENT NO. 113

71.7 mm. CCl_2F_2 added to reaction mixture (total energy input = 1.86×10^{-2} watt)

Time min.	P_{CO}, mm.	P_{Cl_2}, mm.	P_{COCl_2}, mm.	$k \times 10^4$	Av.
0.0	137.5	144.6	0.0	...	
1.0	131.0	138.1	6.5	3.35	
2.0	125.4	132.5	12.1	3.16	
71.7 mm. CCl_2F_2 added					
3.5	117.2	124.3	20.3	3.42	
5.5	107.9	115.0	29.6	3.37	
8.0	98.1	105.2	39.4	3.34	
11.0	88.7	95.8	48.8	3.23	
16.0	76.2	83.3	61.3	3.26	3.30 ± 0.08
21.0	67.1	74.2	70.4	3.09	
27.0	59.0	66.1	78.5	2.90	
35.0	50.4	57.5	87.1	3.01	
45.0	43.7	50.8	93.8	2.46	
60.0	36.3	43.4	101.2	2.43	

These results must eliminate the possibility that the function of the third body in reaction (2) is solely one of stabilization of COCl formed by collision of CO and Cl unless the equilibrium of Bodenstein is accepted. For, in accordance with the principle of microscopic reversibility, the addition of a third body—regardless of its effectiveness—cannot shift the equilibrium $CO + Cl + M \rightleftarrows COCl + M$. They do not, however, preclude the possibility of the specificity of Cl_2 being explained by some complex such as Cl_3—the only one so far postulated.[13]

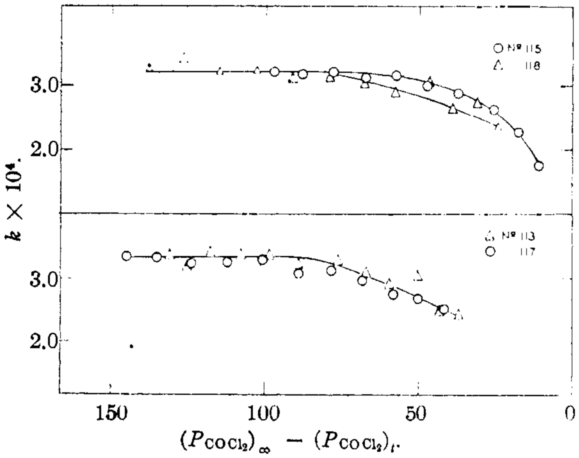

Fig. 1.

Inclusion of the Cl_3 radical as a stable molecule raises a further objection that has not previously been mentioned or considered. This requires that the mechanism contain the chain-breaking process $Cl_3 + Cl_3 \rightleftarrows 3Cl_2$ unless the reaction of CO and Cl_3 is so rapid as to keep the concentration of Cl_3 negligibly small in comparison with the concentration of COCl. However, the experimental rate cannot be derived if $Cl_3 + Cl_3 \rightleftarrows 3\,Cl_2$ is the chain breaking process.

Decrease in Rate Constants at the End of the Reaction.—The decrease in rate constants as the

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(12) The dichlorodifluoromethane ("Freon-12") was furnished through the courtesy of the Kinetic Chemicals, Inc., Wilmington, Delaware.

(13) This is further confirmed by the fact that building up large pressures (400 mm.) of phosgene—a molecule the vibrational levels of which should be close to those of COCl—as well as N_2, had no effect on the rate (Hurka and Beaver, private communication).

reaction nears completion has not been explained. Bodenstein's[14] suggestion that it may be due to the interdiffusion of impurities into the reaction cell cannot be correct, since neither permitting the reactant gases to stand in the cell in the dark for twenty-four hours before the reaction was started nor the interruption of the reaction for several hours resulted in a lowering of the reaction rate when pure chlorine[8] was used.

This deviation from constancy near the end of the reaction indicates that there is a change in the mechanism of the reaction as it nears completion. It has been assumed by both Bodenstein[2] and Rollefson[3] that this decrease in the constant occurs when the chain breaking process (5) becomes significant in comparison to the normal chain breaking reaction (4). Since (5) is sufficient to explain the breaking of the chain in total pressures below 20 mm., this does not seem an unreasonable conclusion. However, no other evidence has been offered in support of this assumption, and in a recent article—after the initiation of this research—Bodenstein[16] pointed out that this phase of the reaction is one of the unsolved problems of these studies.

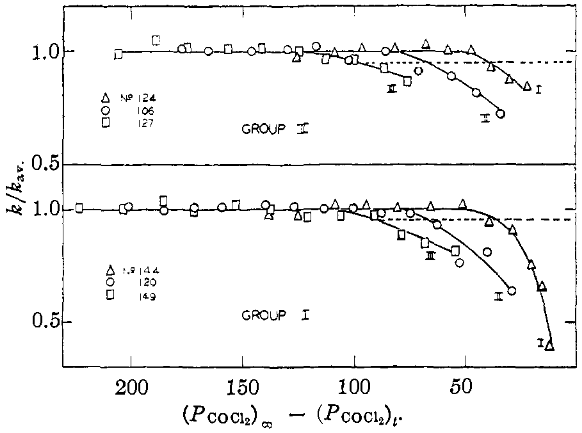

Fig. 2.—To permit comparison of the position of the "break" for three different light intensities the ratio $k_t/k_{av.}$ is plotted against the difference of $(P_{COCl_2})_\infty$ and $(P_{COCl_2})_t$. $k_{av.}$ is the average value of the rate constant for the experiment as indicated in the tabulation of data and k_t is the constant at any time (t). $(P_{COCl_2})_\infty$ represents the pressure of phosgene on completion of the reaction and $(P_{COCl_2})_t$ is the pressure at time (t). Group I represents three experiments in which the initial pressures of carbon monoxide are in excess over chlorine by 120 mm. or more. In Group II the pressures of chlorine and carbon monoxide are more nearly equal—chlorine being in small excess. In both cases the incident light curve I is greater than that of curve II which is greater than curve III.[15]

Since the over-all rate expression (I) is proportional to the square root of the light absorbed and (II) is proportional to the first power of the light absorbed, the most direct method of studying this change in mechanism should be an investigation of the effect of various light intensities. This investigation showed that an increase in the incident light intensity extended the linear part of the curve, *i. e.*, the normal mechanism of the reaction was maintained longer with high intensities than with low intensities. The extent of this effect is shown in Fig. 2.

Due to the gradual deviation of the curve from the normal value the position of the "break" from linearity is indeterminate without further definition. Therefore we shall arbitrarily establish the rule that the "break" from the normal rate equation has occurred when the constant deviates 5% from the normal value. This is just outside the ordinary experimental error of these experiments and is indicated by the broken line in Fig. 2. The position of the "break" was determined as closely as possible (usually within ± 5 mm.) at the point where the constants had decreased by 5%.

In addition to this change in position of the "break" with variation of light intensity, the following conclusions may be derived from the summary of experimental data in Tables II and III. The decrease in the constants near the end of the reaction was not a function of the total pressure in the reaction vessel, nor of the initial concentrations of the reacting gases. Moreover, the point of "break" was not a function of the amount of phosgene present nor of the percentage completion of the reaction mixture. It was found, however, to be a function of the proportionate

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(14) Bodenstein, *Z. physik. Chem.*, **130**, 444 (1927).

(15) It is of considerable importance that light intensities be sufficiently standardized to permit the comparison of the rates of reactions as established by different laboratories. A comparison of the light intensities and rates of this investigation with the data of Manninen (private communication) showed a check within the experimental error. The incident light intensities for all the experiments unless otherwise specified was an intensity of 1.12×10^{-2} watts. This was obtained from the filtered light of two 100-watt lamps using the glass filters (GG3 & BG12, Schott).[8] For the highest intensity of Fig. 2 (Expts. 124 and 144, curve I), the cell was illuminated by the 100-watt lamps without the presence of the glass filters. This increased the light intensity 13.0 times over that used in Expts. 106 and 120. In this case no quantitative correlation can be expected between the light intensities and the rates of reaction, because of the decrease in the molar extinction coefficient at wave lengths longer than 4500 Å. [Halban and Sedentopf, *Z. physik. Chem.*, **103**, 71 (1922)]. The lowest intensity used (Expts. 127 and 149, curve III) was obtained by placing a 16-mesh copper screen in the path of each light beam. Each screen transmitted 39.2% of the light and the total energy entering the cell was 7.28×10^{-3} watts.

(16) Bodenstein, Schumacher and Brenshede, *ibid.*, **B40**, 121 (1938).

amounts of the carbon monoxide and chlorine present at this point.

TABLE II

(Illumination, 0.242 watt)

		Pressures at the "Break"				
Expt.	$k_{av.} \times 10^3$	P_{total}, mm.	P_{COC}	P_{CO},	P_{Cl_2}	$[P_{Cl_2}/P_{CO}]^{1/2}$
122	1.11 ± 0.02	229	116	35	76	1.49
123	1.09 ± .002	232	97	26	109	2.05
124	1.13 ± .02	208	110	57	41	0.848
126	1.03 ± .02	189	51	19	119	2.50
128	1.08 ± .03	532[a]	128	63	58	0.960
130	1.10 ± .02	371	143	205	23	.335
136	1.10 ± .02	476	120	328	28	.292
144	1.13 ± .03	326	119	171	36	.459
152	1.05 ± .02	389	86	273	30	.332
153	1.07 ± .02	260	78	159	23	.380
161	1.08 ± .03	272	131	20	121	2.46

[a] This pressure includes 283.0 mm. of CCl_2F_2.

TABLE III

(Illumination, 0.0186 watt)

		Pressures at the "Break"				
Expt.	$k_{av.} \times 10^3$	P_{total} mm.	P_{COCl_2} mm.	P_{CO} mm.	P_{Cl_2} mm.	$[P_{Cl_2}/P_{CO}]^{1/2}$
101	3.42 ± 0.03	238	67	60	111	1.36
103	3.17 ± .05	279	88	71	90	1.13
105	3.26 ± .05	330	129	34	167	2.22
106	3.37 ± .05	277	123	67	87	1.14
107	3.30 ± .10	272	115	56	101	1.34
113	3.29 ± .07	289[a] (72)	64	73	80	1.05
115	3.15 ± .05	212	58	46	108	1.53
116	3.43 ± .18	510 (315)	51	48	96	1.41
117	3.27 ± .04	239	74	87	78	0.947
118	3.20 ± .07	585 (295)	79	143	68	.690
120	3.29 ± .05	404	152	186	66	.596
121	3.15 ± .07	479 (191)	110	91	87	.978
125	3.15 ± .03	282	91	126	65	.718
133	3.32 ± .04	344	123	151	70	.681
134	3.24 ± .05	444	192	195	57	.541

[a] The numbers in parentheses indicate pressures of CCl_2F_2 that are included in the total pressures.

Here we may note that there is no relationship between total pressures and the position of the "break." For example, in Expt. 118 the total pressure at the point of "break" was 585 mm., of which 295 mm. was the inert gas CCl_2F_2, and for Expt. 125 was 282 mm.; however, the "break" in terms of the limiting component chlorine occurs at the same point in each. Furthermore, the initial pressures of CO and Cl_2 in Experiment 120 are about 1.4 times the initial pressures in Expt. 125—and again the positions of the "break" for the two experiments are within five millimeters of each other. These facts indicate that the "break" will occur at the same place regardless of total pressure or pressures of $COCl_2$ provided the relationship between CO and Cl_2 remains the same.

That the position of the "break" in terms of the pressure of chlorine is a function of the ratio of the pressure of chlorine to the pressure of carbon monoxide is best shown in Fig. 3. Theoretical considerations based on either the Bodenstein or Rollefson mechanism and discussed below predict that the pressures at the "break" may be represented by a function

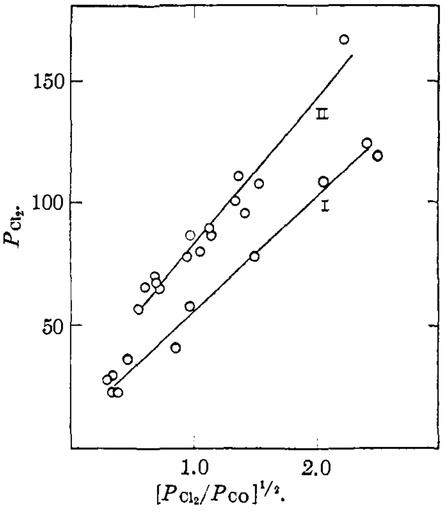

Fig. 3.

$$P_{Cl_2} = k\left[\frac{P_{Cl_2}}{P_{CO}}\right]^{1/2} + B$$

where P_{Cl_2} and P_{CO} are the pressures of chlorine and carbon monoxide, respectively, at the "break" and k and B are characteristic constants. The validity of this function has been investigated for two light intensities over a range of concentrations. The ratio of P_{Cl_2}/P_{CO} for the higher light intensity (curve 1) was varied from 0.110 to 6.26 and for the lower intensity (curve II) ranges from 0.292 to 4.92. The results are shown graphically in Fig. 3. The deviations from linearity are within the experimental error of such determinations, and it may be concluded that this function correctly represents the experimental data concerning the position of this "break."

Discussion

Both Bodenstein[2] and Rollefson[3] postulate the same chain-breaking processes—reactions (4) and (5). Although both of these reactions occur throughout the entire course of the experiment, it may be assumed that the frequency of occurrence of reaction (4) is so much greater than of reaction (5) during the first part of the reaction (*i. e.*, when the rate is dependent upon the square root of the absorbed light) that (5) may be disregarded in comparison to (4). This is justifiable since dependence on the square root of the light absorbed requires that two chlorine atoms be removed simultaneously. Further, the consideration of reaction (4) as the chain-breaking process yields the correct rate equation. However, when the "break" appears in the rate curve the reaction mechanism has changed. If we assume that this change in the reaction mechanism arises from the fact that reaction (5) is occurring sufficiently often so that it is now no longer insignificant in comparison to reaction (4), then we may derive the following rate equation from the complete mechanism including both reactions (4) and (5)

$$\mathrm{d(COCl_2)/d}t = k'\,[\mathrm{Cl_2}]\,\left(-1 + \sqrt{1 + k''\,I_a\,[\mathrm{CO}]}\right)$$

Both the Bodenstein and Rollefson mechanisms yield the same net result. The exact mathematical solution of this equation is so sensitive to experimental errors that no precise evaluation of these constants can be made. By a series of arithmetical approximations using the data of Expt. 123 it was found that the order of magnitude of k' was (3.0 ± 0.5 × 10^{-3} and k'' was 2.0 ± 0.5 × 10^{-2}.

However, we may derive from this complete mechanism relationships which are more specifically descriptive of what is actually happening at the "break" in the following manner.

Using the Bodenstein mechanism—including reactions (1) to (5)—it may be shown that the rates of disappearance of Cl atoms for (4) and (5) are given by

$$-\,(\mathrm{dCl/d}t)_4 = I_a$$
$$-\,(\mathrm{dCl/d}t)_5 = [K_5/k_4K_{\mathrm{COCl}}]^{1/2}I_a^{1/2}[1/\mathrm{CO}]^{1/2}$$

where the reaction rate constants have their usual significance.

Since the Rollefson mechanism yields completely analogous equations it is apparent that by either mechanism the first chain-breaking process (4) is directly proportional to the absorbed light while that of the secondary chain-breaking process (5) is proportional to the square root of the light energy absorbed. Therefore, an increase of the light intensity and the resulting increase in absorbed light will increase reaction (4) more than reaction (5) and thus increase the range wherein reaction (4) is the only effective chain-breaking process. The experimental confirmation of this conclusion as shown in Fig. 2 constitutes evidence in favor of this mechanism of terminating the chain.

But this argument may be carried further and correlated with the complete mechanism of the reaction. If we assume that the "break" appears at the point where the reaction (5) is becoming significant in comparison to (4) it follows, with careful definition of the position of this "break," that it always occurs when the rate of (5) has reached a definite value in comparison to the rate of (4). Then at the "break," as defined above, the difference in the rates of (4) and (5) will have a constant value, thus

$$-\left(\frac{\mathrm{dCl}}{\mathrm{d}t}\right)_4 - \left(-\frac{\mathrm{dCl}}{\mathrm{d}t}\right)_5 = k'I_a - k''\left[\frac{I_a}{P_{\mathrm{CO}}}\right]^{1/2} = \text{constant}$$

But the light absorbed is proportional to the concentration of chlorine, and

$$P_{\mathrm{Cl_2}} = K\left[\frac{P_{\mathrm{Cl_2}}}{P_{\mathrm{CO}}}\right]^{1/2} + B$$

where k and B are characteristic constants and are equal to the individual rate constants as indicated above and $P_{\mathrm{Cl_2}}$ and P_{CO} are the pressures of these gases at the point of "break."

That this function, which may be derived from the complete mechanism including both chain-terminating processes, correctly represents the experimental data at the defined "break" is shown in Fig. 3. Since the experimental data do obey this function, and whereas no other chain-breaking processes have been found that comply with this derived function, we may conclude that this is good evidence in favor of the establishment of this chain-terminating mechanism as correct and that the occurrence of the typical "break" in the reaction curve near the completion of the reaction has been explained.

Summary

The third-body effect of dichlorodifluoromethane on the photochemical formation of phosgene has been studied and discussed in the terms of the Bodenstein and Lenher–Rollefson mechanisms.

The effect of varying light intensities on the decrease of the rate toward the end of the reaction has been studied and explained.

The position of the "break" in the experimental curve has been investigated over a variety of total pressures and ratios of the components and found to be represented by the function

$$P_{\mathrm{Cl_2}} = K[P_{\mathrm{Cl_2}}/P_{\mathrm{CO}}]^{1/2} + B$$

This function is derived from the postulated mechanism and the concurrence of experiment with theory is offered as evidence for the assumed chain-breaking processes which adequately explain the decrease in reaction rate as the reaction nears completion.

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