PHOTOCHEMICAL STUDIES.
XIII. THE PHOTOCHEMICAL REACTION BETWEEN CHLORINE AND BENZENE IN THE GASEOUS PHASE[1]

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The photochemical reaction between chlorine and benzene in the liquid phase or in solution has been the subject of previous investigations. A complete bibliography of this work need not be given at this time.[2] The gas phase reaction has received relatively little attention. It would be expected, by comparison of this system with other systems and a study of the literature on the liquid phase reaction, that a rather large quantum efficiency would be obtained and that complications would arise due to the large number of products which might be formed.

I. Experimental

The chlorine used in these experiments was a commercial product. It was introduced into the apparatus through a tube containing phosphorus pentoxide and was then purified by distillation with liquid air. During the fractionation only the middle third was retained for use.

The benzene was thiophene free and was purified by drying with phosphorus pentoxide and by distillation at low pressure.

Some early experiments were carried out with a dynamic system. The chlorine (or benzene) passed through a quartz cell exposed to the full radiation from an iron arc. The chlorine (or benzene) then joined the benzene (or chlorine) at a junction situated immediately at the exit of the cell. No stopcocks or wax joints were present in the apparatus. The interpretation of these experiments was rendered very uncertain due to the possibility of back diffusion of the substance which should not have been exposed to the radiation. The results obtained may be summarized as follows. (1) When the benzene was illuminated and then passed into the chlorine no reaction could be detected which could not, with plausibility, be ascribed to diffusion of chlorine into the illuminated zone. Reaction was detected by determining the gas uncondensed by liquid air, since hydrogen chloride has sufficient vapor pressure at liquid air temperatures to be easily detectable.[3] Illumination of the benzene alone without any chlorine present in the system gave no indication of the formation of uncondensable gas. (2) Illumination of the chlorine with subsequent passage into benzene invariably showed the formation of large amounts of uncondensable gas, presumably hydrogen chloride. In this case, also,

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[1] This paper contains preliminary results obtained with the object of determining the general course of the photochemical reaction between chlorine gas and benzene vapor. Results obtained later at Brown University and bearing more specifically on the mechanism of the reaction will be published at a future date by H. P. Smith and the senior author.

[2] For a summary see Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., New York, 1928, p. 118.

[3] Calculated from the formula of Giauque and Wiebe, THIS JOURNAL, 50, 105 (1928).

there may have been slight diffusion of the benzene into the illuminated zone, although the chlorine atoms produced by the action of radiation should persist for an appreciable distance in the stream of gas. The difficulties in this type of experimentation and the uncertainties in the interpretation of the results led to its abandonment in favor of a static method.

The chlorine and benzene were prepared in the same manner in this type of experiment. The extent of the reaction was determined: (1) by change in pressure (a glass pressure gage similar to that described by Daniels[4] was employed for this purpose); (2) by determination of the amount of chlorine disappearing during the course of the reaction; (3) in some instances by micro-analysis of the solid products formed during the reaction.

Figure 1 shows a diagram of the apparatus used. The pressure gage was attached at G. C_1 was filled with benzene vapor previously purified. Chlorine was admitted at F and the line sealed off at this point. Liquid air was placed around the trap H and the chlorine completely condensed. The tip T was broken by the magnetic device shown just as the liquid air was removed from the trap H. The incoming benzene vapor diffused through the system including the two flasks C_1 and C_2 and the chlorine as it vaporized from H mixed with the benzene vapor and gave a uniform mixture throughout the system with the possible exception of the tubing between C_1 and C_2 which would be filled initially with a relatively large amount of chlorine. The volume of the tubing was small compared to the volume of the system as a whole.

L was a 1000-watt tungsten filament lamp. Running water flowed continuously through the two cells W and the cells E, two inches in thickness, were filled with $M/20$ potassium dichromate solution. The absorption cells were made of ordinary plate glass. The spectral region used in this investigation extended, therefore, between the approximate limits of 4500 and 6000 Å. Due to the fact that absorption by the chlorine is relatively feeble for wave lengths greater than 5000 Å., the practical limits are from about 4500 to 5000 Å.

When it was desired to determine the amount of chlorine remaining at the end of the reaction, rubber tubing leading from a nitrogen tank was slipped over the tip at F and the tip broken inside the rubber tubing. Nitrogen was admitted to the line to atmospheric pressure. Tubing was placed over A and the line flushed with nitrogen, the emerging gases being passed into a potassium iodide solution. The iodine liberated was titrated with sodium thiosulfate solution.

When it was desired to analyze the solid products deposited on the walls of C_1 and C_2, the flasks were removed from the line and washed out with ether. The crystals were dried in a vacuum desiccator. The microanalyses were not entirely satisfactory due to the small amount of material, the difficulty in obtaining completely dry crystals and to the possibility that in some cases the crystals consisted of mixtures of several compounds. The analyses aid somewhat in the final interpretation of the results. Chlorine was determined in some cases by a Carius analysis. In one run the carbon and hydrogen were determined by true microanalysis and the chlorine was obtained by difference.[5]

II. Results and Discussion of Results

Several facts must be kept in mind in considering the results obtained. (1) Only the chlorine absorbs radiation. A detailed discussion of the band spectrum of chlorine need not be given at the present time, but

[4] Daniels, THIS JOURNAL, 50, 1115 (1928).

[5] The authors wish to express their appreciation to Dr. Irving Muskat and Dr. Kenneth Adams for performing the micro-analyses.

according to the ideas of Franck[6] and the analysis of the chlorine band spectrum as carried out by Kuhn,[7] chlorine atoms should be produced in the spectral region used.　(2) Moderate pressures of chlorine and benzene were used and appreciable reaction could not be produced before the products would condense on the walls of the vessel.　Phenyl chloride and m-dichlorobenzene are liquids with appreciable vapor pressures,[8] but most of the other possible products would have relatively low vapor pressures. With the intensities of radiation employed and the pressures used, no single step of the reaction may proceed to completion before other steps have started.　(3) If the reaction is entirely one of substitution, no pressure change would be observed until products of the reaction begin to condense on the walls.　With addition an immediate decrease in pressure should be observed.
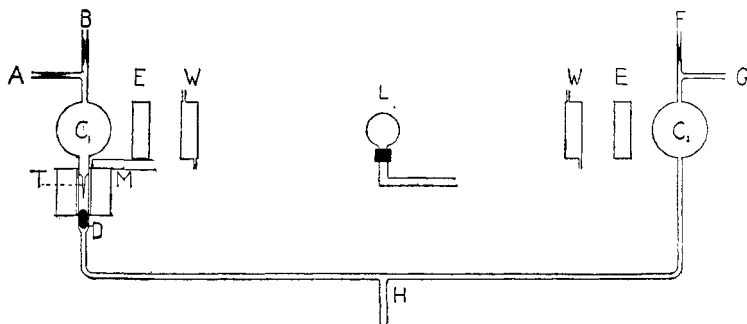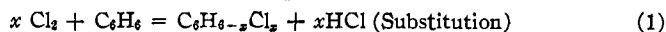

Fig. 1.

The general phenomena observed during the course of a run may be summarized as follows.　(1) With very high radiation intensities, such as would be obtained by removing the dichromate filter (Fig. 1), a cloud of fine droplets would be produced almost immediately.　These droplets must consist of either phenyl chloride or one of the dichlorobenzenes or perhaps a mixture of several compounds.　All of the evidence points to the fact that they consist of phenyl chloride.　(2) The droplets diffuse to the walls and collect there.　Solid products are formed eventually on the walls.　The solids seem to be produced only in and to grow out from the drops of liquid. (3) Solid is formed in the drops only in the illuminated zone.　(4) In the dark no decrease in pressure could be noticed.　(5) Experiments carried out with phenyl chloride in place of benzene showed solid products to be formed, at least with any rapidity, only if the phenyl chloride were admitted in such a way that it condensed on the walls.

[6] Franck, Z. physik. Chem., 120, 144 (1926); Trans. Faraday Soc., 21, 536 (1925).

[7] Kuhn, Z. Physik, 39, 77 (1926).

[8] For the vapor pressure of phenyl chloride see "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, p. 220.

(a)   The Dependence of Rate of Pressure Change on the Concentrations of the Reacting Substances.—The reactions which may occur would follow one of the two general equations

$$x \; Cl_2 + C_6H_6 = C_6H_{6-x}Cl_x + xHCl \text{ (Substitution)} \qquad (1)$$
$$y \; Cl_2 + C_6H_6 = C_6H_6Cl_{2y} \qquad \text{(Addition)} \qquad (2)$$

In the liquid reaction the final product seems to be largely benzene hexachloride ($C_6H_6Cl_6$).[9]   This compound could scarcely form in one step during a homogeneous gas phase reaction.   Since phenyl chloride is formed, at least part of the reaction must proceed according to equation (1).   No pressure change would be observed unless the phenyl chloride condensed on the walls.

It is of interest to ascertain the dependence of rate of pressure decrease on the pressures of the reactants.   Let p_1 be the initial pressure of chlorine, p_2 the initial pressure of benzene, p_3 the vapor pressure of phenyl chloride, p_4 the pressure of chlorine and p_5 the pressure of benzene just at the point when the reaction system becomes saturated with phenyl chloride.   Then

$$p_4 = p_1 - p_3 = p_1 - p_2 + p_5 \qquad (3)$$

If P_1 and P_2 represent the total pressures at the beginning and at the instant phenyl chloride begins to condense, we may write

$$P_1 - P_2 = 0 = p_1 + p_2 - 2p_3 - p_4 - p_5 \qquad (4)$$

Let P_3 be the total pressure at any time subsequent to the attainment of saturation with phenyl chloride and p_6 and p_7 the partial pressures of chlorine and of benzene, respectively, at that time.   Then we may put

$$P_3 = p_3 + p_6 + p_7 + (p_1 - p_6) \qquad (5)$$

where $(p_1 - p_6)$ is equal to the partial pressure of hydrogen chloride   But

$$p_7 = p_2 - p_1 + p_6 \qquad (6)$$

and

$$P_3 = p_3 + p_2 + p_6 \qquad (7)$$

or

$$p_6 = P_3 - p_3 - p_2 \qquad (8)$$

If the reaction is first order with respect to chlorine we would find the equation

$$k = (2.303/(t_2 - t_1)) \log (P_1 - p_3 - p_2)/(P_3 - p_3 - p_2) \qquad (9)$$

to hold for all points after the system had become saturated with phenyl chloride.   Up to that point the equation

$$k = (2.303/t_1) \log (P_1 - p_2)/(P_1 - p_3 - p_2) \qquad (10)$$

should be valid. t_1 is the time required to produce saturation with phenyl chloride.

If addition takes place as well as substitution, the chlorine pressures could be calculated only if the ratio of the rates of the two reactions were

[9] Slator, Z. physik. Chem., **45**, 540 (1903).

known. In this case one molecule of chlorine would disappear without hydrogen chloride formation. Thus, the decrease in total pressure would be equal to twice the decrease in partial pressure of the chlorine, *unless* some substance with low vapor pressure were chlorinated to give another substance with low vapor pressure. In that event equations of the type of equation (9) should be applicable.

In equations (9) and (10) it is possible to use P_1 and P_3 as obtained directly during a run. p_3 may be obtained from tables[8] and p_2 may be calculated from the data. Table I shows the applicability of equations (9) and (10) to the data for one run.

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TABLE I

REACTION RATE AS FUNCTION OF CHLORINE PRESSURE

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$P_1 = 11.70$ cm. $p_1 = 7.70$ cm. $p_2 = 4.00$ cm. $T = 25°$.   (With dichromate filter)

Time. min.	Total pressure, cm.	Chlorine pressure Eq. (8), cm.	k Eqs. (9) and (10)
0	11.70	(7.70)	2.4×10^{-4}
780	11.36	6.24	1.9
2220	10.26	4.80	1.5
3660	9.47	3.85	2.0
5100	8.33	2.87	2.0
7170	7.42	1.88	2.5
8610	6.91	1.33	

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Av. 2.0

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One additional run made with somewhat lower benzene pressure and nearly three times the initial chlorine pressure showed an average constant of 2.2×10^{-4} until the pressure changes became too small to be measured with accuracy.

Table II shows data for a run made without the dichromate filter. In this case solid was deposited in less than ten minutes and condensation of phenyl chloride took place even before the first pressure reading could be taken. Under these conditions the pressure of the chlorine should be equal approximately to its initial pressure minus the change in total pressure. This statement should be especially applicable after the early stages of a run. The constants are calculated on this basis. The pressure changed for some time after the last reading given in the table, but this simple type of calculation is not applicable when the change in total pressure is too large, for the benzene is being converted into substances of very low vapor pressure by addition as well as by substitution. Strictly speaking this method of calculation is valid only when a substance of low vapor pressure is being chlorinated to give another substance of low (or at least the same) vapor pressure. The data in Table II indicate that this condition is fulfilled approximately for a time after the early stages of the run, but negative chlorine pressures would be found toward the end if this calculation were carried to the limit.

TABLE II

REACTION RATE AS FUNCTION OF CHLORINE PRESSURE

$P_1 = 11.10$ cm. $p_1 = 7.25$ cm. $p_2 = 3.85$ cm. $T = 25°$.   (Without dichromate filter)

Time, min.	Total pressure, cm.	Pressure chlorine (calcd.), cm.	k
0	11.10	(7.25)	
10	10.03	6.18	1.6×10^{-2}
18	7.50	3.65	7.2
25	6.05	2.20	6.2
35	5.04	1.19	8.3
45	4.37	0.52	6.6

Av. 7.1 (last four)

One other run with a slightly higher chlorine pressure gave constants for a short time averaging about 7.7×10^{-2}.

Thus we see that with moderate benzene pressures the rate of reaction is, to a first approximation, proportional to the chlorine pressure. The spectral region is such that absorption of the radiation is far from complete, so that the rate is probably proportional to the intensity of the radiation absorbed rather than to the chlorine pressure as such.

The initial benzene pressures did not vary greatly from one run to another (See Table IV), but no direct connection could be found between pressure of benzene and rate under the conditions of these experiments. This means, presumably, that reaction takes place appreciably on the walls, at least after the initial stages of a run. Further investigation of this point will be made later.

(b) **The Analysis by Titration of Chlorine Disappearing.**—An independent check on the value of the reaction rate constant may be obtained from analytical data. Referring to the run given in Table I, the number of moles of chlorine calculated from the initial pressure is 0.00884. At the end 51.38 cc. of 0.1130 sodium thiosulfate was required to react with the iodine liberated by the chlorine. There was, therefore, 0.00290 mole of chlorine left at the end of the run. The total time of exposure was 8630 minutes. Therefore, $k = 2.303/8630 \log (884/290) = 1.3 \times 10^{-4}$, a fair check with the values given in the table. The average constant, for runs with the dichromate filter, calculated in this manner is 3.7×10^{-4}. Without the dichromate filter the results calculated by the two methods are less comparable (Runs 7 and 8) since these runs were continued for some time after noticeable pressure changes had stopped. The small amounts of chlorine at the end gave relatively large chances for error both in removing it from the line and in the titration.

Table III presents a summary of the results obtained from analytical data.

With the exception of the first run, in which some error seems to have been introduced, not more than four atoms of chlorine have been used per

TABLE III

NUMBER OF MOLES OF REACTANTS

Run no.	Initial moles of benzene	Initial moles of chlorine	Final moles chlorine	Atoms Cl used/ moles benzene
1	0.0041	0.0234	0.0061	8.4
2	.0053	.0261	.0163	3.7
3	.0058	.00227	.00032	0.7
4	.0043	.00161	.00088	0.3
6	.0043	.00884	.00290	2.8
7	.0044	.00819	.00020	3.6
8	.0044	.00902	.00035	3.9

initial benzene molecule.   This means, probably, that a mixture of products is always formed.

(c)   The Total Pressure Change during Reaction.—If the reaction is entirely one of substitution, the final pressure should be equal to the initial pressure of the chlorine, providing the vapor pressures of the organic products are negligible.   If the reaction is one of addition, the final pressure should approach the vapor pressures of the products provided neither the chlorine nor the benzene is in too great excess.   Table IV summarizes the data on initial and final pressures.

TABLE IV

TOTAL CHANGE IN PRESSURE

Run no.	Initial pressure of chlorine, cm.	Initial pressure of benzene, cm.	Total initial pressure, cm.	Final pressure, cm.	Time, hrs.	Conditions
1	20.7	3.6	24.3	19.1	43	Dichromate filter
2	22.9	4.6	27.5	22.1	8	
3	2.0	5.1	7.1	4.8	48	
4	1.4	3.7	5.1	2.3	48	
6	7.9	3.8	11.7	6.9	143	
7	7.2	3.9	11.1	2.4	14	No filter
8	7.8	3.7	11.5	1.5	17	

It is obvious that substitution will not account for the entire pressure change in some of the runs.

(d)   Characteristics of the Solid Products Formed.—Carius analyses of the chlorine content of the solid products were carried out for Runs 1 and 2.   Carbon and hydrogen analyses were made for Run 6.[5]

For Run 1 the percentage of chlorine in the solid removed from the walls was 58.18.   For Run 2 it was 57.95.   The only known compound having a composition near this figure is trichlorobenzene ($C_6H_3Cl_3$) with a theoretical percentage of 58.63.   The hypothetical compound $C_6H_5Cl_3$ would contain 57.99% of chlorine.

For Run 6, which lasted 143 hours, the following results were obtained

	Found			Theoretical ($C_6H_6Cl_6$)
Percentage H	2.29	1.99	Av. 2.14	2.08
Percentage C	24.69	25.65	25.17	24.76
Percentage Cl (by difference)	73.02	72.36	72.69	73.16

Melting points were determined for some of the products. In no case were very sharp melting points obtained. In one run (not shown above) the solid melted from 118 to 122°. γ-Benzene hexachloride melts at 112° and the δ-form at 129°. The α- and β-forms melt at widely removed temperatures. The solid obtained in Runs 1 and 2 did not have a sharp melting point, but melted from approximately 50 to 105°.

(e) Conclusions.—The rate of removal of chlorine from the gas phase in the chlorination of benzene under the conditions of these experiments is proportional to the pressure of the chlorine. This means, probably, that the rate is proportional to the intensity of the radiation absorbed and that the production of atoms is sufficient to initiate the reaction. The reaction, at least in the early stages, is unquestionably a chain reaction. Such chains are possible theoretically and facts concerning the mechanism will be brought out at a later date. It is interesting to note, however, that Luther and Goldberg[10] found the rate of photochemical chlorination of liquid benzene to be proportional to the pressure of the chlorine and that Bodenstein[11] estimated the quantum efficiency to be as high as 10^6.

One of the products is unquestionably phenyl chloride and the chain mechanism leads also logically to the formation of hydrogen chloride. The phenyl chloride is soon adsorbed on the walls and before reaction has proceeded very far begins to condense. Later stages probably involve several simultaneous reactions. Slator[9] found benzene hexachloride, $C_6H_6Cl_6$, as one of the main products in the liquid reaction. Meidinger[12] found phenyl bromide and benzene hexabromide in the bromination of benzene. Benzene hexachloride is formed unquestionably as one of the final products in the present experiments. Addition of chlorine to benzene must be taking place, therefore, as well as substitution. The isolation of definite intermediate compounds would be difficult if not impossible. It would seem unreasonable for the addition of chlorine to benzene to be a homogeneous gas phase photochemical reaction and what evidence is presented in this article is distinctly against such an assumption. The addition of a chlorine atom to a benzene molecule could probably take place only as the result of a triple collision and the resulting unsaturated molecule formed would have to acquire another chlorine atom either from some chlorine molecule or by absorbing a free atom produced photochemically. The former step seems improbable and the latter mechanism would involve a peculiar power of the light intensity in the rate equation.

[10] Luther and Goldberg, Z. physik. Chem., **56**, 43 (1906).

[11] Bodenstein, ibid., **85**, 329 (1913).

[12] Meidinger, ibid., **5B**, 29 (1929).

We may offer the following tentative description of the phenomena taking place. (1) A chain reaction is first produced leading to the formation of phenyl chloride and hydrogen chloride. (2) The phenyl chloride condenses on the walls. (3) Several things may now happen. By analogy with the addition of chlorine to phenyl iodide,[13] the compound $C_6H_5Cl_3$ may be formed. While analyses of solids from two different runs give the proper halogen content, too great weight should not be given to this evidence due to the possibility of a mixture being present. This hypothetical compound would probably not be formed by the addition of a chlorine molecule to the ring of phenyl chloride, but would be a molecular compound of some type. It might split out hydrogen chloride and give one of the dichlorobenzenes upon heating. It might, however, act as a good chlorinating agent and play a part in the addition of chlorine to the benzene which would dissolve unquestionably in the phenyl chloride. The fact that crystals are first produced in the liquid drops on the walls in the illuminated zone indicates that the addition reaction takes place in the liquid phase and not as a homogeneous gas phase reaction. The extent of the addition should vary with time, but in agreement with previous work the final product seems to be benzene hexachloride. The results point distinctly to the fact that addition is of primary importance once sufficient phenyl chloride is produced to give a layer on the walls.

Results obtained at sufficiently low pressure to keep the phenyl chloride from condensing will be presented at a later date.

Summary

1. The photochemical chlorination of benzene at moderate pressures has been studied. The rate of reaction is approximately proportional to the chlorine pressure.

2. The first step leads to the production of phenyl chloride, but this substance condenses on the walls and a liquid reaction ensues which involves largely addition, probably to benzene dissolved in the phenyl chloride, the final product being mostly benzene hexachloride.

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[13] Willgerodt, *Chem. Centr.*, **16**, 833 (1885).