[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XVII. The Chlorination of Chlorobenzene; a Comparison with Benzene

BY EDWIN J. HART[1] AND W. ALBERT NOYES, JR.

In previous articles[2] results of studies of the photochemical chlorination of benzene in the gas phase have been reported. At low benzene pressures almost the sole initial photochemical reaction is that of addition. During most of the course of the reaction, however, both substitution and addition take place simultaneously, the final reaction product after long periods approaching the composition of dodecachlorocyclohexane (C_6Cl_{12}). After the first stages the reaction must take place to a large extent in the condensed phase on the walls, thus rendering any detailed discussion of reaction mechanism largely meaningless. It was possible, however, to obtain an approximate rate equation for the addition reaction at zero time.

The present study was undertaken with the object of obtaining further information, if possible, on the mechanisms of addition and substitution in the benzene ring and to contrast the behavior of the symmetrical benzene molecule with that of chlorobenzene. One or two runs have been made on the dichlorobenzenes, but brief mention only will be made of these.

I. Experimental

The method of purification of the chlorine has been described.[2b] In some instances the elaborate precautions for drying the chlorine were eliminated and after allowing the first part of the chlorine in a cylinder to escape as a means of carrying away impurities, a certain amount was collected, thoroughly outgassed and fractionally distilled repeatedly. Chlorine prepared in this manner gave results agreeing with the chlorine prepared by the previous method.

The chlorobenzene was purified by repeated fractional distillation at reduced pressure. The portion utilized gave a refractive index n^{25}_{D} 1.525. It was dried by means of magnesium perchlorate.

Very few determinations of the quantum yield were made, as the information to be obtained from such sources for this type of reaction is rather meager. The method of making these determinations has been described.[2b] The results served to show merely that under the conditions of these experiments the photochemical chlorination of chlorobenzene proceeds by a short chain reaction. If anything the chains were somewhat shorter than in the case of benzene, although the difference was not particularly significant.

Attention was focused at first on the relative amounts of addition and substitution and on a determination of the variation of rate with different conditions of pressure and temperature. The technique for these experiments has been described.[2b] Instead of filling the reaction vessel from a bulb containing gaseous chlorine, the chlorine was admitted from a vessel containing the liquid. The chlorobenzene was first admitted to the desired pressure and then chlorine admitted as the trap containing it was allowed to warm up from the temperature of liquid air. The reaction vessel was sealed off when the proper chlorine pressure had been reached. The initial pressures of the reactants were determined by simple calculations based on the volumes involved. No stopcocks or wax joints were present in the system and although moisture has been shown not to be of much importance, the vessel was always carefully dried by continual flaming under a high vacuum. The main source of impurity may lie in the formation of traces of volatile chlorine compounds of silicon at the time the reaction vessel was sealed off,[3] or by action of the radiation.

All runs were made in a thermostat.

II. Results

(a) Relative Amounts of Substitution and Addition.—Empirically it was found that equations (1) and (2) represent satisfactorily the amounts of substitution and addition in the various runs. The agreement of these equations with experiment is shown graphically in Fig. 1.

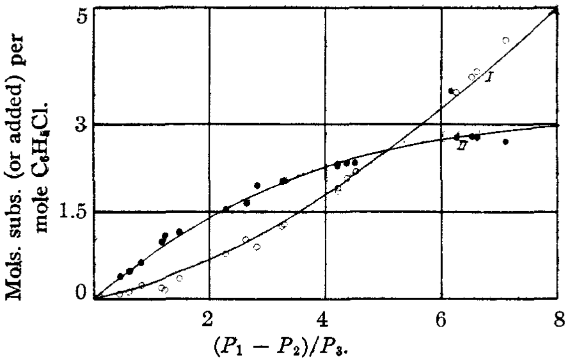

Fig. 1.—Curve I, substitution; Curve II, addition.

$$\frac{\text{No. moles Cl}_2\text{ added}}{\text{moles C}_6\text{H}_5\text{Cl}} = a/(1/x + b) \qquad (1)$$

$$\frac{\text{No. moles Cl}_2\text{ substituted}}{\text{moles C}_6\text{H}_5\text{Cl}} = (1 + bx - a)/(1/x + b) \qquad (2)$$

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[1] Jesse Metcalf Fellow, 1933–34.

[2] (a) Lane and Noyes, THIS JOURNAL, **54**, 161 (1932); (b) Smith, Noyes and Hart, *ibid.*, **55**, 4444 (1933).

[3] *Cf.* Schumacher and Stieger, *Z. physik. Chem.*, **7B**, 369 (1930).

$x = (P_1 - P_2)/P_3$, $a = 0.93_{16}$, $b = 0.175_{85}$, P_1 = initial pressure of chlorine, P_2 = final pressure of chlorine, P_3 = initial pressure of chlorobenzene.

Equations (1) and (2) were found to be applicable both at 25 and at 35°, so that the ratio of substitution to addition does not change markedly with temperature.

(b) **The Thermal Reaction.**—In studying the photochemical reaction, particularly with low light intensities, some correction seemed to be necessary for the thermal reaction. Table I shows data obtained during a few runs of this type.

TABLE I

THERMAL CHLORINATION OF CHLOROBENZENE, 24 ± 1°

Run no.	82	83	84	85	90[a]
Initial press. Cl_2 (P_1), mm.	41.57	44.12	81.74	23.78	42.16
Final press. Cl_2 (P_2), mm.	34.50	43.19	68.51	19.36	33.89
Initial press. of chlorobenzene (P_3), mm.	7.94	2.47	8.32	7.52	6.47
Final press. HCl (P_H), mm.	5.79	0.42	8.89	3.38	5.93
Time, hrs.	40.5	57.0	48.0	72.0	49.8
$P_H/(P_1 - P_2)$	0.82	0.45	0.67	0.76	0.72
$P_H/(P_1 - P_2)$ eqs. (1) and (2)	.17	.05	.27	.09	.31

[a] The reaction vessel for Run 90 was packed with glass tubing which increased the surface about ten-fold.

Comparison of the last two rows in Table I shows that the substitution reaction is relatively much more important for the thermal than for the photochemical reaction.

The mechanism of the dark reaction has not been considered in detail. The rate is very roughly proportional to the product of the chlorine and chlorobenzene pressures. There seems to be a definite but not large effect due to increased surface, although the relative amounts of substitution and addition are not affected.

(c) **The Nature of the Reaction Products.**—If the final reaction product is the same as with benzene, a maximum of eight molecules of chlorine could react per molecule of chlorobenzene, three undergoing the addition reaction and five substitution. Inspection of Fig. 1 indicates that these figures are being approached in the longest runs. The final chlorination product for both benzene and chlorobenzene is, therefore, dodecachlorocyclohexane (C_6Cl_{12}).

Further evidence that the final reaction products in the two cases are identical is obtained from melting points. In the present experiments the final product melted at 66–71° as against 66–69° in the case of benzene.

It was hoped to isolate the first substance formed by condensing it in a side tube cooled slightly below the temperature of the reaction vessel. With high light intensities crystals were formed in the light path as usual. With very low light intensities and in runs of several hours duration a liquid was collected. Refractive index and freezing and boiling point determinations indicated that this liquid was largely a mixture of ortho and para dichlorobenzenes. It seemed to be formed almost solely by the thermal reaction, which agrees well with the facts presented above concerning the relative amounts of substitution and addition.

(d) **Factors Affecting the Rate of Reaction.**—Tables II, III and IV show the influence of various factors on the reaction rate. For the sake of comparison, but without implying any great theoretical significance, the constants k_1, k_2 and k_3 have been calculated from equations (3), (4) and (5) and included.

$$k_1 = 1/t \log_{10} P_1/P_2 \qquad (3)$$

$$k_2 = \left(P_1^{\frac{1}{2}} - P_2^{\frac{1}{2}}\right)/t \qquad (4)$$

$$k_3 = \left(P_2^{-\frac{1}{2}} - P_1^{-\frac{1}{2}}\right)/t \qquad (5)$$

The effect of light intensity is difficult to determine. Two series of runs were made with a ratio of light intensities of 5 ± 1 to 1. For the short runs the rate of disappearance of chlorine depends on a power of the light intensity between 0.5 and 1.0. Since for the low chlorine pressures employed the percentage of radiation absorbed is closely proportional to the pressure, the preceding statement is in general agreement with the data in Tables II and III.

As regards the addition reaction only, some theoretical justification for the observed effect of light intensity may be found (see equation (15)).

In view of the large number of possible intermediate chlorination products, no satisfactory equation was found for calculating the amount of unreacted chlorobenzene during the course of a run. It is possible, from the change in total pressure, to estimate the extent to which the addition

TABLE II

VARIATION OF CHLORINE PRESSURE WITH TIME

(T = 35°. P_1, P_3 approx. constant)

Run no.	61	62	63
Initial press. Cl_2 (P_1), mm.	48.80	48.16	46.83
Final press. Cl_2 (P_2), mm.	43.03	38.16	29.66
Initial press. chlorobenzene (P_3), mm.	3.75	3.78	3.92
Time, min.	30	60	120
$k_1 \times 10^3$	1.58	1.69	1.65
$k_2 \times 10^2$	1.23	1.27	1.16
$k_3 \times 10^4$	2.70	2.97	3.13

TABLE III

DEPENDENCE OF RATE UPON CHLORINE PRESSURE

(T = 25°. P_3 approx. const. High light intensity)

Run no.	86	88	89
Initial press. Cl_2 (P_1)	26.94	16.54	12.22
Final press. Cl_2 (P_2)	18.31	11.40	8.70
Initial press. C_6H_5Cl (P_3)	7.35	8.33	7.81
Time, min.	15	15	15
$k_1 \times 10^3$	11.2	10.8	10.5
$k_2 \times 10^2$	6.1	4.6	3.6
$k_3 \times 10^4$	27.4	33.5	35.1

reaction alone has taken place (see equation (9)), but for estimating the effect of the chlorobenzene pressure on the reaction rate some other method must be used. Since the nature of the reaction changes with $(P_1 - P_2)/P_3$ (see equations (1) and (2)), intercomparison of runs should be made only when the light intensities are the same and the time interval not too long. In any case the over-all rate of disappearance of chlorine would be expected to follow a different rate equation from the addition reaction alone.

For one series of runs with approximately equal initial chlorine pressures equation (6) was found to be obeyed within experimental error.

$$(P_1 - P_2)/P_3 = at/(1 + bt) \qquad (6)$$

where $a = 0.05454$ and $b = 0.004705$. Since for a given initial chlorobenzene pressure the rate of disappearance of chlorine is approximately given by equation (3), it is evident that k_1 is not strictly independent of time. In addition it must include some function of the chlorobenzene pressure since this quantity is known to affect the rate. Combining equations (3) and (6) one finds

$$k_1/P_3 = (a/(P_1 - P_2) - b/P_3) \log (P_1/P_2) \qquad (7)$$

Since the data in Table IV indicate that k_1/P_3 is reasonably constant for those runs for which equation (6) was obtained, it seems probable that the over-all rate of disappearance of chlorine is approximately proportional to the pressure of the chlorobenzene. The light intensity for these runs was relatively low.

TABLE IV

EFFECT OF CHLOROBENZENE PRESSURE ON RATE

(P_1 approx. const.)

Run	P_1, mm.	P_2, mm.	P_3, mm.	Time, min.	$k \times 10^3$ eq. (7)	$k/P_3 \times 10^3$
			T = 25°			
56	43.37	41.11	2.07	15	1.05	0.51
57	45.03	31.83	6.09	60	3.09	.51
59	41.61	34.10	5.07	30	2.78	.55
60	46.51	43.98	4.10	15	2.03	.50
			T = 35°			
61	48.80	43.03	3.75	30	1.46	0.39
62	48.16	38.16	3.78	60	1.61	.43
63	46.83	29.66	3.92	120	1.54	.39

In the absence of a theoretically derived rate equation the variation of the rate with temperature would have little significance. In the case of benzene the rate was appreciably slower at 35° than at 25°. In the present case the difference is less marked and with comparable light intensities amounts to less than ten per cent. The intercomparison of runs with different chlorine and chlorobenzene pressures is uncertain to about this extent in the absence of a completely valid expression for the reaction rate.

III. Discussion

A fairly complete picture of the chlorination of both benzene and chlorobenzene may now be given. The details of the mechanism present, however, many doubtful points. In fact in systems as complex as those under discussion it is wise to confine attention to those points which are not doubtful, realizing that more than one detailed mechanism may usually be found which will not disagree with the experimental facts.

The following points seem to be demonstrated beyond question by the experiments:

(a) The thermal reactions for both benzene and chlorobenzene lead almost entirely to substitution. The thermal chlorination of chlorobenzene is, however, accompanied by a finite amount of addition.

(b) With very low light intensities (Table I, Ref. 2a) the thermal reaction may predominate and benzene may be chlorinated to chlorobenzene which will condense on the walls (if the initial pressure of the benzene is sufficiently high). Since chlorobenzene also undergoes thermal substitution, a mixture of chlorobenzenes will eventually result. Under these conditions the photochemical reaction may take place largely in the condensed phase on the walls, the chlorobenzenes and the dissolved benzene undergoing both substitution and addition with the production of a variety of products.

(c) With light intensities sufficiently high so that the speed of the thermal reaction may be neglected in comparison with that of the photochemical reaction (Table II, Ref. 2a, Tables I, IV and V, Ref. 2b, Tables II, III and IV) the initial reactions for both benzene and chlorobenzene are almost entirely of addition. In the case of chlorobenzene this may be accompanied by a slight amount of substitution, but the data cannot be made sufficiently precise for very short runs to make this point certain.

(d) The photochemical chlorination of both benzene and chlorobenzene leads to the eventual production of dodecachlorocyclohexane (C_6Cl_{12}), although the rate of introduction of the last few atoms of chlorine is exceedingly slow.

(e) For both substances the rate of disappearance of chlorine depends both on the chlorine and on the initial benzene (or chlorobenzene) pressures. The course of any given run indicates, however, that the rate is dependent almost solely on the chlorine pressure (and light intensity) but that factors dependent on the amount of unchlorinated material are relatively unimportant until several molecules of chlorine have been used per molecule of starting material. Two alternative conclusions seem possible from this fact: (1) the reaction (at least after the early stages) may take place almost entirely on the walls so that the gas phase concentration of the material to be chlorinated is unimportant; (2) the chlorination of the first intermediate products proceeds with practically the same facility as that of the parent substance. The evidence indicates that both of these explanations must be considered in the complete elucidation of the reaction rate, but that the second is largely responsible for the course of the reaction during the early stages.

(f) With intermediate and high light intensities (Table II, Ref. 2a, all Tables, Ref. 2b) a steady state as regards intermediate addition products is readily attained in the case of benzene. This must mean that the thermal addition of chlorine to molecules of the type of $C_6H_6Cl_2$ is rapid. This statement is borne out by an examination of the variation of total pressure with time. With chlorobenzene similar conditions do not seem to obtain. With intermediate light intensities (Reactions in Tables II and IV above) the total pressure curves indicate the formation of some relatively long-lived intermediate addition product. Somewhat questionable evidence in support of this statement is found in the analysis of intermediate reaction products obtained in the chlorination of benzene with very *low* light intensities (Ref. 2a, p. 167). These analyses indicated the possible formation of a compound $C_6H_5Cl_3$. With high light intensities the steady state in the chlorination of chlorobenzene seems to be attained rapidly.

An alternative explanation for the facts in the preceding paragraph is also possible. The existence of some inhibitor which was used up during the early stages of a run would explain the form of the total pressure curves with intermediate intensities. The data in Table II indicate, however, that this is not the most probable explanation.

(g) The effect of increase in temperature on the chlorination of benzene is to increase slightly the relative amount of substitution and to decrease slightly the rate of disappearance of chlorine. These facts indicate that addition and substitution in benzene probably proceed from somewhat different starting points, or at least that the "heat of activation" for one reaction is slightly different from that of the other. In the case of chlorobenzene, however, the ratio of addition to substitution is little if at all affected by temperature and the rate of disappearance of chlorine decreases only slightly if at all. This fact indicates that addition and substitution may originate from the same intermediate and that the "heats of activation" for the two reactions may be the same.

(h) For both substances the rate is proportional to some power of the light intensity between 0.5 and 1.0.

(i) The over-all rate of disappearance of chlorine is more rapid with benzene than with chlorobenzene. Direct comparison of the rates of the two reactions, while somewhat meaningless due to the different rate expressions involved, indicates the rate for chlorobenzene to be from one-third to one-half that for benzene. Average quantum efficiencies, while open to the same objection, are just half as great for chlorobenzene.

In the case of chlorobenzene it is not admissible to assume that a steady state is reached as regards the various intermediate chlorination products. A rate equation valid over an entire run is, therefore, difficult to derive. Those which were tried either did not apply or involved arbitrary constants which made them of doubtful theoretical value.

For benzene the rate of total pressure change at the beginning of a run was found to be approximately proportional to $I_a^{1/2}P_aP_m$, where I_a is the intensity of the absorbed radiation, P_a the initial chlorine pressure and P_m the initial benzene pressure. Since at these low pressures the absorbed intensity is proportional closely to P_a, this expression is nearly equivalent to $kP_a^{3/2}P_m$ (see Table VI, Ref. 2b). For chlorobenzene equation (8) applies approximately. P_A is initial total pressure, P_B is the total pressure at time t and A is a constant which does not vary widely.

$$-dP_B/dt = k(A - P_A + P_B) \qquad (8)$$

Figure 2 shows the application of this empirical equation to two different runs.

Since addition predominates at the beginning, the substitution reaction will not lead to a change in total pressure and variations in the latter will be nearly proportional to the rate of the addition reaction. Two runs made with *p*-dichlorobenzene show that the rate of addition of chlorine to this substance is very little different (slightly slower) from the rate of addition to chlorobenzene itself. Both rates are, however, slower than that of benzene.

The data represented in Fig. 1 show that both addition and substitution take place simultaneously. If one assumes that substitution does not affect the rate of addition except in so far as it changes the total pressure of chlorine, the amount of addition which may still take place at any time t will be given by equation (9).

$$P_4 = (4P_3 - P_A + P_B) \qquad (9)$$

From equations (1) and (2) the chlorine pressure should be given by equation (10).

$$P_2 = P_1 - 3(P_A - P_B)P_3/4(aP_3 - 3b(P_A - P_B)/4) \qquad (10)$$

One possible mechanism for the addition reaction is represented by equations (11), (12), (13) and (14).

$$Cl_2 + h\nu = 2Cl \qquad (11)$$

$$Cl + C_6H_5Cl = C_6H_5Cl_2 \qquad (12)$$

$$C_6H_5Cl_2 + Cl_2 = C_6H_5Cl_3 + Cl \qquad (13)$$

$$C_6H_5Cl_2 + Cl = C_6H_5Cl + Cl_2 \qquad (14)$$

Reaction (13) would be followed by subsequent addition of two more chlorine molecules, but if the steady state is assumed (which seems to be valid only at high light intensities) the rate of production of the final addition product will be the same as the rate of production of $C_6H_5Cl_3$.

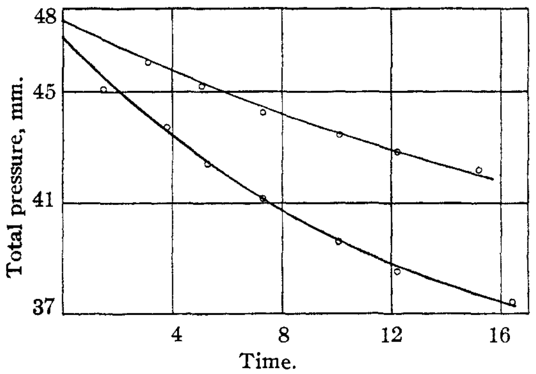

Fig. 2.—Upper curve, P_1 = 46.11; P_3 = 1.47; lower curve, P_1 = 44.02; P_3 = 2.94.

With one reasonable assumption as regards the relative orders of magnitude of the constants involved, the resulting rate equation is

$$-dP_B/dt = KI_a^{\frac{1}{2}}P_2^{\frac{1}{2}}P_4^{\frac{1}{2}} = K'P_2P_4^{\frac{1}{2}} \qquad (15)$$

since the intensity of the absorbed radiation is very closely proportional to the chlorine pressure.

Equations (11)–(14) do not provide a unique way of deriving equation (15). While the facts in this article do not require the postulation of Cl_3,[4] equation (15) may be derived with its use providing the chain stopping step is of the type $Cl + Cl_3 = 2Cl_2$.

Substitution of the expressions in equations (9) and (10) in equation (15) should give an equa-

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[4] *Cf.* Rollefson and Eyring, THIS JOURNAL, **54**, 170 (1932).

tion for the rate of the addition reaction. Since the resulting equation is rather difficult to manipulate in the integrated form, slopes were obtained from the total pressure curves and constants calculated from the differential form. Tables V and VI show how well equation (15) applies to several runs.

Table V

The Rate of the Addition Reaction

(Average constants at 3-minute intervals, 5 constants each run.)

Run no.	73	75	86	88
Initial press. Cl_2	44.02	46.11	26.94	16.54
Initial press. C_6H_5Cl	2.94	1.47	7.35	8.33
$K' \times 10^3$ (Eq. 15)	6.9[a]	5.3	5.6	5.6

[a] The light intensity was slightly higher in this run than in the others. Correction brings this figure down to about 6.

Table VI

The Rate of the Addition Reaction, Run 88

Time	0	3	6	9	12
P_B (mm.)	24.87	23.31	21.90	20.65	19.53
$-dP_B/dt$ (mm./min.)	0.530	0.490	0.435	0.380	0.365
$K' \times 10^3$ (Eq. 15)	5.6	5.7	5.6	5.5	5.8

While equation (15) applies well to the early stages of runs made with high light intensity, the constants show some tendency to increase after longer intervals.

Data for calculating the heat of the reaction

$$C_6H_6 + Cl = C_6H_6Cl- \qquad (16)$$

are not very reliable,[5] but indicate that the value is small. No data are available for calculating the value for the corresponding reaction for chlorobenzene. Conditions in the two molecules are, however, quite different. From the standpoint of symmetry and a consideration of resonance[6] around the ring, one would expect chlorobenzene to behave somewhat more like an aliphatic compound than benzene. The extra valence electrons on the chlorine atom might alter the resonance in such a way as markedly to affect the stability of the double bonds in the ring. Qualitatively it seems probable that reactions of the type of (16) would take place more readily with chlorobenzene than with benzene.

For similar reasons the compound $C_6H_5Cl_3$ might be expected to be more stable than the analogous compound $C_6H_6Cl_2$. Some evidence for the existence of the former is found in the present experiments, whereas $C_6H_6Cl_2$ seemed to have a very brief existence and did not need to be considered even at fairly low light intensities.

The final stages of both reactions must occur on the walls. Chlorine atoms (presumably produced in the gas phase) must be capable of inducing substitution in the various intermediate chlorination products after they are in the solid form.

Summary

1. The extents of addition and substitution during the photochemical chlorination of chlorobenzene have been investigated. The ultimate product is probably the same as for benzene, namely, dodecachlorocyclohexane (C_6Cl_{12}).

2. Various factors affecting the rate have been studied. A possible mechanism for the addition reaction has been given.

3. The behaviors of benzene and chlorobenzene during photochemical chlorination have been contrasted.

4. Temperature affects the rate of chlorination but slightly and, in the case of chlorobenzene, does not change markedly the ratio of addition to substitution.

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[5] The data necessary for the calculation of the heat of this reaction were largely obtained from "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. V, p. 163, ff. 94.5 kcal. is used for the heat of dissociation of the C–H bond [*cf.* Kistiakowsky and Gershinowitz, *J. Chem. Physics*, **1**, 432 (1933)]. The value for the C–Cl bond is that used by Pauling [This Journal, **54**, 3577 (1932)]. This figure is uncertain [*cf.* Hukumoto, *J. Chem. Physics*, **2**, 46 (1934)].

[6] For discussion of resonance in related problems see Hückel, *Z. Physik*, **83**, 632 (1933), and earlier articles and Pauling and Wheland, *J. Chem. Physics*, **1**, 362 (1933), and earlier articles by Pauling