

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## Photochemical Studies. XXIV. The Photochemical Chlorination of the Dichlorobenzenes

BY CHARLES F. FISK AND W. ALBERT NOYES, JR.

The photochemical chlorination of benzene and of its chlorine substitution products has been the subject of several previous investigations.<sup>1</sup> In the gas phase, the initial reaction proceeds by short chains and results largely in the addition of chlorine to the aromatic nucleus. Products soon condense on the walls and most of the reaction after the initial stages must take place in the solid or liquid phase. With prolonged photochemical chlorination both benzene and chlorobenzene give eventually  $C_6Cl_{12}$ .

The present study was undertaken to compare the rates of addition of chlorine to *o*-, *m*- and *p*-dichlorobenzene and to investigate particularly the mechanism of the latter by measuring the rate of pressure decrease as a function of several different variables. The extent of the chlorination and a value for the quantum yield have also been obtained. An explanation of the data is given.

### I. Experimental

The preparation of the chlorine was similar to that previously used.<sup>1c</sup> The dichlorobenzenes were all c. p. products from the Eastman Kodak Company. The *p*-dichlorobenzene was subjected to several fractional crystallizations from its own liquid. The fraction chosen melted sharply at 52.2–52.3° (corr.). Finally this 1-g. sample was fractionally distilled in vacuum and stored behind a mercury trap so that it was not exposed to the air once it had been freed from volatile substances by evacuation. Somewhat less care was taken with the *o*- and *m*-dichlorobenzenes since they were investigated much less completely than the para compound. They were both fractionally distilled, the middle fraction being treated by vacuum distillation before use.

All other chemicals were of standard c. p. quality.

The reaction vessel was a cylindrical fused quartz cell attached to the main vacuum line, pressure gages, etc., by a quartz to Pyrex graded seal. The vessel was held in a fixed clamp on an optical bench so that its position could be duplicated.

The technique of filling the reaction vessels has already been described.<sup>1</sup> All pressure measurements were made with an all glass gage of the Bourdon type. For determining the rate of pressure change with time it became necessary to measure pressure changes of about 0.04 mm. with an accuracy of about 5% at a total pressure of around 40 mm. For this purpose the Bourdon gage was modified

by making the primary pointer operate a lever swung on a glass axle and bearing to give a magnification of fifteen to thirty times that obtained with the unmodified gage. With good luck a sensitivity of 0.001 mm. pressure per 0.01 mm. motion (as measured by a filar micrometer) could be obtained. This gage was calibrated and used as a direct deflection instrument for rate measurements. Although the experiments were carried out at room temperature, this was sufficiently constant during a run so that when the gage was balanced at 40 mm. pressure the needle position was constant in time, since small temperature variations operated nearly equally on both sides of the gage. This modified gage was used in the study of the dependence of rate on light intensity. For other experiments the ordinary gage was used.

For measuring the outside pressure used to balance the gages when they served as null point instruments a dibutyl phthalate manometer was employed.

The light source was a water cooled capillary mercury arc similar to that described by Forbes and Harrison.<sup>2</sup> It was operated at atmospheric pressure on 35 volts and 5 amperes. The light was filtered by 3 mm. of greenish window glass plus 3 mm. or more of number 986 red purple Corex. A number 586 violet ultra filter was used for low intensities.<sup>3</sup> From the intensity distribution in the arc, the transmissions of the various glasses and the absorption coefficients of chlorine it is possible to show that approximately 97% of the radiation absorbed by the chlorine in these experiments was in the group of lines around 3660 Å.

Although parallel light is to be desired in experiments involving chain reactions, it was necessary to use a focused beam in order to obtain the desired intensity. However, a simple calculation showed that the effect due to divergence in these experiments is negligible. The arc lamp was clamped in such a way that its position was reproducible. The lens was mounted on the optical bench so that an image of the arc was produced in the center of the reaction vessel without any part of the beam hitting the walls. The light intensity was varied by changing the number of filters. The shape of the light beam always remained the same. Light intensities were measured by means of a photoelectric cell which could be placed in reproducible positions either in front or in back of the reaction vessel.

The *p*-dichlorobenzene was first admitted to the desired pressure, controlled by the temperature of the supply bulb, and the reaction vessel sealed off. The chlorine was then admitted by breaking a capillary magnetically. The ingoing chlorine undoubtedly concentrated the *p*-dichlorobenzene slightly in the reaction vessel, but this effect was minimized as much as possible by the geometry of the system. An hour was always permitted to elapse after

(1) (a) Lane and Noyes, *THIS JOURNAL*, **54**, 161 (1932); (b) Smith, Noyes and Hart, *ibid.*, **55**, 4444 (1933); (c) Hart and Noyes, *ibid.*, **56**, 1306 (1934). These articles contain references to earlier work.

(2) Forbes and Harrison, *ibid.*, **47**, 2449 (1925).

(3) The authors wish to express their appreciation to the Corning Glass Co. for furnishing these filters.

filling the cell for the attainment of equilibrium of mixing. The total pressure was measured and the chlorine pressure obtained by difference.

The arc lamp was started and a Wratten green filter interposed to prevent reaction. The ratio of intensity in front to that in back as determined by the photo-cell was used as a check on the optical system. The color filters to be used during the run were then placed in position and the zero deflection obtained by interposing a Wratten number 2 filter which cuts off quite sharply at 4000 Å.

The pressure was always found to remain constant for an hour before the actual run was started. After a definite time of irradiation, during which the variations in intensity were obtained by measurements behind the cell, a shutter was interposed and upon moving the photocell to the front of the reaction vessel the incident intensity was again noted. The pressure stayed constant, except for the Budde effect, after the light was cut off. This procedure will be called Technique I.

The magnitude of the quantum yield was obtained by comparing intensities as measured with the photo-cell with the decomposition produced in a uranyl sulfate-oxalic acid actinometer.<sup>4</sup> Corrections were applied for absorption and reflection by the windows, but a high accuracy for the absolute values of the quantum yields is not claimed.

Some early runs were made in all Pyrex reaction vessels made by sealing optically plane windows on the necks of Erlenmeyer flasks. Two identical cells, one containing the actinometer solution, were operated on opposite sides of the mercury arc in a thermostat. Color filters similar to those previously mentioned were used and pressure measurements were made in the manner already described. The over-all intensity was about one hundred times that used in the other technique. This less accurate method will be referred to as Technique II.

Since the vapor pressures of the *o*-, *m*- and *p*-dichlorobenzenes are low (approximately 1.05, 1.35 and 0.64 mm. at 20°, respectively), the rate measurements were much more difficult of execution than those for benzene and chlorobenzene. The total pressure change (assuming negligible vapor pressures for the addition products) is four times the initial pressure of the dichlorobenzene in a given run. The smoothness of the total pressure-time curves indicated definitely that this assumption is valid.

## II. Results

(a) **The Vapor Pressures of the Dichlorobenzenes.**—In order to obtain the effect of pressure of dichlorobenzene on the reaction rate, it was necessary to measure the vapor pressures of the three substances at a series of temperatures. This was accomplished by the use of the pressure gages described in the previous section and while a high order of accuracy was not obtained the results were accurate enough for the purpose at hand. Since these vapor pressures do not seem to be given in the literature they are presented (interpolated to even temperatures) in Table I.

(4) Leighton and Forbes, *THIS JOURNAL*, **52**, 3138 (1930).

TABLE I  
VAPOR PRESSURES OF THE DICHLOROBENZENES

Temp., °C.	Dichlorobenzene vapor pressure, mm.		
	<i>p</i> -(solid)	<i>m</i> -(liquid)	<i>o</i> -(liquid)
0	0.07	0.30	0.25
5	.15	.47	.38
10	.25	.68	.55
15	.40	.96	.76
20	.64	1.35	1.05
24	.90	1.75	1.35

(b) **The Dark Reaction.**—The dark reaction had been found to be appreciable in the case of benzene and small, although negligible compared to the photochemical rate, in the case of chlorobenzene. Several bulbs were prepared containing chlorine at a pressure of 40 mm. and *p*-dichlorobenzene at a pressure of 0.7 mm. At various intervals over a period of months the chlorine was determined by standard procedure.<sup>1</sup> The results showed no disappearance of chlorine. Similarly no pressure decrease was observed due to dark reaction over periods of several days in the apparatus used for photolysis.

(c) **The Budde Effect.**—A Budde effect was always observed when the reaction mixture was irradiated. That this was due to the transformation of radiant energy into thermal energy was demonstrated by the fact that it was proportional to the light intensity but independent of the pressure of *p*-dichlorobenzene. The effects were of the order of hundredths of a millimeter.

(d) **Effect of Impurities, etc.**—The following seemed to have no influence on the results: (1) air or oxygen at pressures below 0.5 mm.; (2) mercury or mercury chlorides in small amounts (due to the presence of mercury vapor before the admission of the chlorine); (3) quite large variations in the treatment of the reaction vessel by flaming, baking out, etc. There may possibly be some effect due to the condition of the walls, but no definite statement in this connection is possible.

Some chlorine compounds of silicon may have been formed at the moment the reaction vessel was sealed off from the chlorine supply bulb. However, attempts to exaggerate this effect by longer heating, etc., produced no noticeable change in the results. There still remains the possibility that chlorine atoms may react with the walls to produce silicon compounds which would act as inhibitors.<sup>5</sup> However, this effect must have been reproducible from run to run if it exists at all.

(5) Cf. Bodenstein and Unger, *Z. physik. Chem.*, **11B**, 253 (1931); Schumacher and Steiger, *ibid.*, **7B**, 369 (1930).

(e) **The Magnitude of the Absolute Quantum Yield.**—By comparison of the uranyl sulfate-oxalic acid actinometer with the photoelectric cell it was found that 1 cm. deflection was equivalent to  $5.9 \times 10^{14}$  quanta per second. If the initial reaction leading to pressure change is the addition of one molecule of chlorine to one molecule of *p*-dichlorobenzene (see later discussion), then one-half of the initial rate of pressure change is equal to the rate of disappearance of chlorine by the addition reaction. In one run (number 13a) the following data were obtained: chlorine pressure, 31.2 mm.; *p*-dichlorobenzene pressure, 0.64 mm.; intensity, 7.45 cm. deflection; window transmission, 0.85; fraction of radiation absorbed by the chlorine, 0.441; volume of system, 45 cc.; quanta

absorbed per sec.,  $1.65 \times 10^{15}$ ; molecules of  $\text{Cl}_2$  disappearing per second,  $6.44 \times 10^{14}$ ; quantum yield, 0.39.

This value of the quantum yield may not be compared directly with values for benzene and chlorobenzene which were obtained at higher pressures. Rough estimates indicate that the value for *p*-dichlorobenzene is lower if anything than for the other two substances under comparable conditions.

(f) **The Form of the Total Pressure-Time Curve.**—In all some seventy different runs were made and it would be useless to present the data in detail. Table II shows the data obtained for one typical run with Technique I.

TABLE II  
ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE  
(Run 11)  
(Press. *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ : 0.64 mm.; press.  $\text{Cl}_2$ , 32.6 mm.)

Time, min., <i>t</i>	Pressure decrease, mm. $\Delta P_t$	Fraction final pressure change, $\Delta P_t/\Delta P_\infty$	Intensity behind cell (arbitrary units), $D_{b_t}$	$(D_{b_t}/D_{b_0})/(D_{t_0}/D_{t_1})$	$(dP/dt)/(dP/dt)_0$ (corr. to const. <i>D</i> )
0	0				
0.5	0.047	0.020	4.10	1.00	(1.00)
1	.093	.041	3.70	0.95	
2	.174	.076	3.60	.94	0.98
3	.254	.111	3.45	.92	
5	.428	.188	3.46	.92	.95
6	.506	.222	3.60	.94	
7	.580	.255	3.70	.95	.88
8	.658	.289	3.35	.91	
9	.729	.320	3.35	.90	.85
10	.800	.351	3.70	.95	.81
12	.937	.412	3.50	.92	.80
13	1.005	.441	3.40	.91	
14	1.068	.469	3.40	.91	.77
15	1.122	.493	3.35	.91	
16	1.191	.523	3.40	.91	
17	1.251	.551	3.25	.89	.75
19	1.368	.601	3.20	.88	.70
21	1.478	.649	3.15	.88	.67
23	1.577	.692	3.15	.88	.61
25	1.667	.732	3.20	.88	.55
32	1.925	.847	3.00	.86	.47
36	2.027	.893	2.70	.81	.35
41	2.113	.930	2.62	.80	.22
46	2.178	.957	2.61	.80	.17
52	2.200	.972	2.60	.80	.07
$\infty$	2.265	(1.000)	2.30	.75	(0.00)

( $D_t$  is the intensity in front of the cell in arbitrary units.) The final pressure change is not exactly four times the pressure of the *p*-dichlorobenzene because some of the tubing was not included in the reaction zone and diffusion was slow enough to prevent all of the substance initially present from reacting. The difference is quite closely accounted for on this basis.

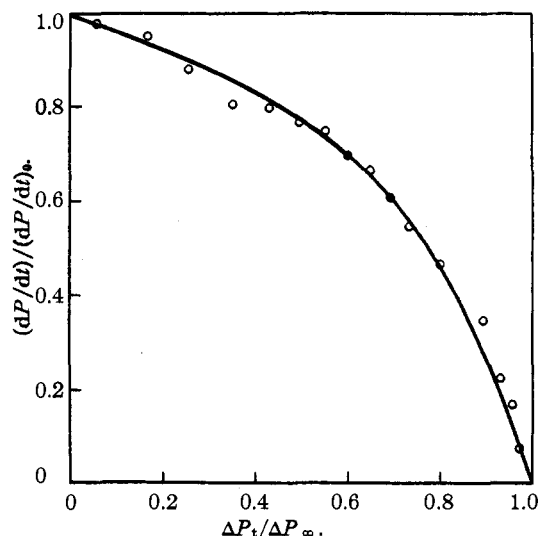


Fig. 1.—Behavior of rate at low light intensity.

Figure 1 shows a plot of  $(dP/dt)/(dP/dt)_0$  against  $\Delta P_t/\Delta P_\infty$  for the data in Table II (run 11). Figure 2 shows a similar plot for a run at very high light intensity using Technique II. The fact that the plot is curved at low light intensities would seem to signify that a steady state is not reached as regards all of the chemically stable intermediate addition products. At high intensities such a steady state seems to be reached. Little can be said concerning the mechanism of the reaction after the early stages because a mist is produced which settles out on the walls and a large fraction of the reaction must occur at the interface between the liquid or solid and the gas phase.

In benzene and chlorobenzene the amount of substitution occurring during the early stages of the reaction was small.<sup>1</sup> It was impossible to ob-

tain an adequate proof of this point for *p*-dichlorobenzene due to the small amount of it which could be obtained in the vapor phase. However, the results indicated that this substance did behave in much the same way as the other two. It is assumed, therefore, in treating the rate data that the main initial reaction is one of addition. The next problem is to study the rate of the initial reaction as a function of the different variables using total pressure change as a measure of reaction rate.

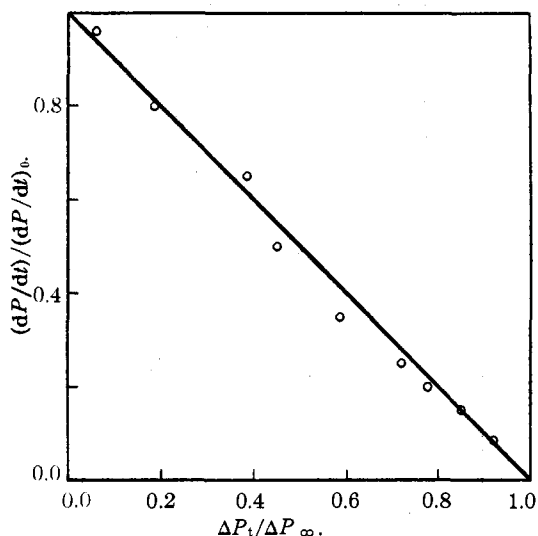


Fig. 2.—Behavior of rate at high light intensity.

(g) The Effect of Light Intensity on the Rate.

—Table III presents data showing the effect of light intensity on the rate for the runs made at fairly low light intensities. It will be noted, however, that the intensity has been varied by a factor of nearly fifty. In the sixth column the intensity (expressed in cm. deflection) is multiplied by the fraction absorbed by the chlorine and in the seventh column the rate of pressure change in mm./min. is divided by the corresponding figure in column six. The values in the seventh column are reasonably constant, indicating that within experimental error the rate of pressure change is proportional to the light intensity when the intensity is fairly low.

In ascertaining whether the rate is proportional to a particular power of the light intensity for chain reactions, the number of quanta absorbed per cc. per second is the really important quantity. Thus variations in intensity from one part of the beam to another, the geometry of the beam and the volume of the reaction vessel must all be taken into account in making comparisons. As pointed

TABLE III

EFFECT OF VARIATION IN INTENSITY AT LOW LIGHT INTENSITIES ON THE RATE OF ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE

(Pressure *p*-dichlorobenzene, 0.64 mm. Volume, 45 cc.)

Run	$(dP/dt)_0$ mm./min. $\times 10^2$	Intensity in front (cm. de- flection) $D_t$	Chlorine pressure	Fraction absorbed, $F_A$	$\frac{I_A}{D_t}$ ( $= F_A \times D_t$ )	$\frac{(dP/dt)_0}{I_A}$ $\times 10^2$
11	8.66	10.20	32.6	0.455	4.65	1.86
13a	5.27	6.34	31.2	.441	2.80	1.88
13b	0.84	1.04			0.46	1.83
13c	2.64	2.79			1.23	2.14
13d	4.93	5.89			2.60	1.89
14	3.13	3.56	32.5	.454	1.62	1.93
17	12.22	12.50	44.2	.562	7.03	1.74
18a	11.18	11.50	43.8	.558	6.42	1.74
18b	3.75	3.92			2.19	1.71
19a	9.06	8.97	45.4	.573	5.14	1.76
19b	4.65	4.58			2.63	1.77
19c	1.09	1.06			0.61	1.78
19d	0.32	0.33			.19	1.68

( $D_t$  is already corrected for window transmission.)

out above the runs at very high light intensity were made with a different technique from those at low intensity and hence a direct comparison between the two sets of data is difficult. In Table IV the data obtained at high intensities are presented. The figure of 0.33 cc. of 0.1 *N* potassium permanganate per minute for the average intensity of the first group of runs corresponds to about ten times the highest number of quanta absorbed per cc. per second in Table III. It is seen that over the data in both tables the number of quanta absorbed per cc. per second has been varied by a factor of nearly 500.

TABLE IV

EFFECT OF VARIATION IN INTENSITY AT HIGH INTENSITIES ON THE RATE OF ADDITION OF CHLORINE TO *p*-DICHLOROBENZENE

(Calculated to pressure of *p*-dichlorobenzene = 1 mm.)

Run no.	$(dP/dt)_0$ mm./min.	$I_A$ (cc. 0.1 <i>N</i> KMnO <sub>4</sub> per min.)	$\frac{(dP/dt)_0}{I_A}$	$\frac{(dP/dt)_0}{I_A^{1/2}}$	$\frac{(dP/dt)_0}{I_A^{45}}$
o-4	1.10	0.37	3.0	1.8	2.1
o-5	0.89	.28	3.2	1.7	2.0
o-28	1.20	.39	3.1	1.9	2.2
o-31	1.18	.28	4.2	2.2	2.7
Av.	1.09	.33	3.3	1.9	2.24
o-29	0.57	.09	6.3	1.9	2.7
o-30	.43	.11	3.9	1.3	1.8
o-32	.39	.06	6.5	1.6	2.4
o-33	.47	.08	5.9	1.7	2.4
Av.	.465	.085	5.5	1.6	2.26

It is seen that the proportionality to light intensity which is found within experimental error

at low light intensities cannot be extrapolated to very high intensities. This will be taken up in the Discussion of Results. The quantum yield for the first four runs in Table IV averages about 0.08, while for the second group of runs it is 0.14.

(h) **The Effect of Pressure of *p*-Dichlorobenzene on the Rate.**—The effect of *p*-dichlorobenzene pressure on the rate was determined with runs made at intensities similar to those in Table III. The technique was Technique I previously described. Table V presents the results.

TABLE V

EFFECT OF *p*-DICHLOROBENZENE PRESSURE ON RATE

Run	$(dP/dt)_0$ mm./min. $\times 10^2$	Chlorine pressure, mm., $P_1$	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> pressure, mm., $P_2$	$I_a$	$(dP/dt)_0$ $I_a$	$(dP/dt)_0$ $I_a \times P_2$
22	2.27	37.1	0.64	1.56	1.46	2.3
23	5.06	37.3	.30	5.98	0.85	2.8
24	6.89	36.4	.47	5.68	1.21	2.6
26	2.62	34.1	.22	4.39	0.60	2.7
27	4.84	28.1	.64	3.18	1.52	2.4
29	7.03	29.9	.91	3.14	2.24	2.5

The results in Table V indicate quite clearly that the rate is proportional to the pressure of *p*-dichlorobenzene within experimental error.

(i) **Dependence of Rate on Chlorine Pressure.**—Here again the same technique was used as for the runs in Table III. Table VI presents the results.

TABLE VI

EFFECT OF CHLORINE PRESSURE ON RATE

Pressure *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, 0.64 mm.

Run	$(dP/dt)_0$ mm./min. $\times 10^2$	$D_f$ de- flection, cm.	% absorbed	$I_a$	Chlorine pressure, mm.	$(dP/dt)_0$ $I_a$
27	4.84	13.9	22.9	3.18	28.1	1.52
30	3.06	12.9	13.9	1.80	16.1	1.70
31	1.16	11.5	6.5	0.75	7.1	1.55
32	3.51	10.0	23.9	2.39	29.2	1.47
11 <sup>a</sup>	8.66	10.2	45.5	4.65	32.6	1.86
19 <sup>a</sup>	9.06	8.97	57.3	5.14	45.4	1.76

<sup>a</sup> Runs 11 and 19 were made in a different quartz cell from the others, the length being twice as great as for the other runs.

(j) **The Extents of Addition and Substitution.**—Benzene and chlorobenzene could be chlorinated eventually to the cyclic compound C<sub>6</sub>Cl<sub>12</sub>. Chlorination of the dichlorobenzenes to the same final product should lead to the disappearance of 7 molecules of chlorine per molecule of dichlorobenzene present at the beginning of a run. That this seems to be the case is indicated by the data in Table VII. If the final product has a negligible vapor pressure, the total pressure should

change by an amount equal to four times the initial pressure of *p*-dichlorobenzene. Final chlorine pressures were determined by titration.

TABLE VII

EXTENTS OF SUBSTITUTION AND ADDITION (*p*-DICHLOROBENZENE)

Run	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> pressure, mm., $P_1$	Change in total pressure, $\Delta P$	$\Delta P/P_1$	Change in chlorine pressure, $\Delta P_2$	$\Delta P_2/P_1$
o-26	0.98	2.89	2.95	4.87	5.0
o-25	.79	1.82	2.3	2.97	3.8
o-24	.99	3.69	3.7	6.87	6.9
o-23	.98	3.86	3.9	5.86	6.7
o-28	.91	3.28	3.6	5.10	5.6

(k) **Comparison of the Ortho, Meta and Para Compounds under Similar Conditions.**—The three dichlorobenzenes were compared as to reaction rate using technique similar to that for the data in Table III. Table VIII gives the data.

TABLE VIII

COMPARISON OF RATES OF CHLORINATION OF ORTHO, META AND PARA DICHLOROBENZENES

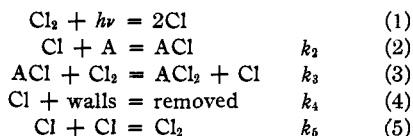
Run	Com- pound	$(dP/dt)_0$ mm./min. $\times 10^2$	Intensity in front (cm. deflec- tion) $D_f$	Chlorine pressure, mm.	$I_a$	$(dP/dt)_0$ $I_a \times 10^2$
32	para	3.51	10.0	29.2	2.39	1.47
33	meta	4.85	11.2	32.1	2.91	1.66
34	meta	3.76	10.2	34.4	2.81	1.34
35	ortho	4.40	11.0	34.8	3.06	1.44
36	ortho	4.40	10.2	36.5	2.95	1.49

The three compounds do not exhibit differences in behavior greater than experimental error.

### III. Discussion of Results

The following facts seem to stand out from the results of the experimental work: (1) the rate of pressure change in a system of chlorine and *p*-dichlorobenzene is proportional to the pressure of the latter and independent of the pressure of the former except in so far as the amount of radiation absorbed is dependent on this quantity; (2) at moderate light intensities the rate is proportional to the intensity within experimental error, but at very high intensities (and also in a larger vessel) the rate depends on some power of the light intensity between 0.5 and 1.0; (3) the rates for the ortho, meta and para compounds do not differ appreciably.

As happens so frequently in studies of kinetics of reactions, one mechanism cannot be selected as fitting the data better than any other on the basis of reaction rate studies alone. One which is adequate is represented by the following equations



where A represents a molecule of dichlorobenzene. The rate of disappearance of chlorine is

$$-dP_2/dt = (k_2 k_4 / 2k_5) P_1 (1 + 8k_3 I_a / k_1^2)^{1/2} - 1) \quad (6)$$

Equation (6) gives a dependence on a power of  $I_a$  between 1.0 and 0.5 at high intensities and reduces to

$$-dP_2/dt = 2k_2 I_a P_1 / k_4 \quad (7)$$

at low light intensities. ( $P_1$  = pressure of  $\text{C}_6\text{H}_4\text{Cl}_2$ ;  $P_2$  = pressure of  $\text{Cl}_2$ ;  $I_a$  = intensity absorbed in the proper units.)

The mechanism represented by equations (1) to (5) resembles in one respect those postulated for benzene and chlorobenzene in that the addition of a chlorine atom to the substance being chlorinated is postulated as the first step following absorption of radiation.

To account for the effect of intensity, the recombination of chlorine atoms (or some other unsaturated groups) must be allowed to proceed both on the walls and homogeneously in the gas phase. Since the rate of diffusion of atoms to the walls will depend on the pressure, decreasing as the pressure increases, whereas the homogeneous recombination will take place as the result of three-body collisions which increase in number with the pressure, the effect of total pressure on the rate of reaction may not be very marked over quite large changes in that quantity.<sup>6</sup> Nevertheless, one will expect wall recombination to be most important at low pressures and in vessels of small diameter, while three-body collision recombination will be most important at high pressures and in vessels of large diameter. The transition from preponderance of one to preponderance of the other may take place over a relatively short pressure interval.<sup>7</sup> An exact treatment would necessarily include both the rate of diffusion of atoms to the walls and the effect of total pressure (or more specifically of the partial pressures of all of the constituents of the gas phase) on the rate of recombination of chlorine atoms.

The results in Table VI show no pronounced effect of the total pressure (which will depend almost entirely on the chlorine pressure since the

(6) Jost and Jung, *Z. physik. Chem.*, **33**, 92 (1929), find little change in the value of the reaction rate constant for the hydrogen-bromine reaction at pressures greater than thirty or forty mm.

(7) Rabinowitch and Wood, *Trans. Faraday Soc.*, **33**, 907 (1936).

pressure of  $p\text{-C}_6\text{H}_4\text{Cl}_2$  is always small). It seems necessary to conclude, therefore, that in a small vessel over the pressure range investigated the rate of diffusion to the walls is rapid. If one assumes that the concentration of chlorine atoms is not far from uniform throughout the reaction vessel, one finds the number of chlorine atoms hitting the walls per second to be

$$N_1 = 1.69 \times 10^{22} P_3 \quad (8)$$

where  $P_3$  is the pressure of chlorine atoms in mm. and the area of the walls is 49 sq. cm. Turning to run 13a in Table III, one finds the rate of production of chlorine atoms to be

$$2 \times 6.34 \times 0.441 \times 5.9 \times 10^{14} = 3.30 \times 10^{16} \text{ per sec.} \quad (9)$$

If  $\alpha$  is the fraction of the collisions with the walls which lead to removal of chlorine atoms, the postulation of a steady state leads to

$$P_3 = 1.95 \times 10^{-7} / \alpha \text{ mm.} \quad (10)$$

In a steady state the rates of reactions (2) and (3) are equal, the rate of removal of chlorine molecules by the formation of the addition product will be equal to the number of collisions between  $p\text{-C}_6\text{H}_4\text{Cl}_2$  molecules and chlorine atoms multiplied by a steric factor,  $\beta$ , multiplied by the fraction of the collisions involving sufficient energy to produce reaction which may be written as  $\exp(-E/RT)$ . If  $\sigma$ , the distance between centers at closest approach for these collisions, is taken as  $6 \times 10^{-8}$  cm., the total number of collisions per second in a volume of 25 cc. will be

$$z = 1.43 \times 10^{26} P_1 P_3 \quad (11)$$

if  $P_1$  and  $P_3$  are expressed in millimeters.

The rate of change of chlorine pressure is one-half the rate of change of total pressure and multiplying by  $3.26 \times 10^{16}$  (the number of molecules per cc. at 1 mm. pressure at  $25^\circ$ ) and by the volume gives the number of molecules of chlorine disappearing per second. Equating this to the effective number of collisions per second gives

$$\alpha/\beta = 4.33 \times 10^3 \exp(-E/RT) \quad (12)$$

where  $\beta$  is the steric factor. In round numbers, therefore

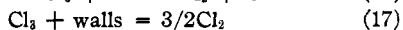
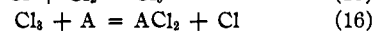
$$E = 5000 - 1365 \log_{10} \alpha/\beta \quad (13)$$

If the proper collision radius has been chosen both  $\alpha$  and  $\beta$  must be fractions and will probably not differ greatly from unity. The heat of activation of reaction (2) is thus of the order of magnitude of 5000 calories per mole. This may be compared to 6100 calories for the reaction  $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$ .<sup>8</sup> If the reaction between chlorine and  $p\text{-}$

(8) Rodebush and Klingelhoefer, *THIS JOURNAL*, **55**, 130 (1933).

dichlorobenzene could be studied at higher pressures comparable to those used in the hydrogen chlorine reaction, the lengths of the chains would probably become quite large.

A word might be said with regard to other possible mechanisms for the reaction. Equations (2) and (3) may not be combined into one equation involving Cl, A and Cl<sub>2</sub> without introducing a factor of the chlorine pressure in the final rate equation. This is contrary to the experimental evidence. The evidence for or against the molecule Cl<sub>3</sub> is not conclusive. At low light intensities the proper form of rate equation may be based on the following series of reactions



With this mechanism the numerical factors will be changed somewhat due to differences in the masses of the molecules involved and in the collision radius, but the heat of activation of reaction (16) will be of the order of that given by equation (13).

Most of the other mechanisms tried gave equations disagreeing very definitely with the experimental data.

It should be reemphasized that at high light intensities it is necessary to introduce a homogeneous recombination of atoms or radicals which is partly responsible for the stopping of chains.

Since the treatment of the rate data applies only to the addition reaction, under conditions such that the substitution reaction is small, it should be noted that the possible mechanisms bear some resemblance to those postulated by other authors to explain reactions of a similar type.<sup>9</sup>

Some mention of the relationship of the work described in the present article to the work on benzene and chlorobenzene may be made. Two runs were made in the present apparatus with benzene (Technique II). The rate for *p*-dichlorobenzene, corrected to the same pressure and intensity, was two-thirds to one-half that for benzene, indicating that the heat of activation for the reaction corresponding to (2) or (16) is lower for the latter substance.

(9) Dickinson and Carrico, *THIS JOURNAL*, **56**, 1473 (1934); Stewart and Weidenbaum, *ibid.*, **57**, 2036 (1935). See articles under Ref. 1 for other references. Booher and Rollefson, *ibid.*, **56**, 2293 (1934), feel that the use of triatomic halogen molecules offers satisfactory explanations of many different halogenation reactions. See also Rollefson, "Symposia on Quantitative Biology," The Biological Laboratory, Cold Spring Harbor, L. I., N. Y., Vol. 111, 1935, p. 42.

At low light intensities the rate of chlorination of benzene was found to be proportional to the pressure of chlorine, or in other words to the intensity absorbed. At higher intensities and in vessels of fairly large volume so that the distance the chlorine atoms had to traverse to reach the walls was much larger than in the present experiments, the rate was found to be proportional approximately to the square root of the light intensity, the pressure of the chlorine and the pressure of the benzene. With chlorobenzene the incident intensity could not be varied conveniently with the apparatus used, but the volume of the apparatus was again large and the rate was again best represented by an expression involving the square root of the light intensity. As regards the effect of light intensity the agreement between the expressions for the three substances may be said to be complete. The differences center largely upon the effects of the chlorine pressure and of the pressure of the substance being chlorinated. The pressure of benzene was varied from about 1.6 mm. to about 12.5 mm., while that of chlorobenzene was varied from about 1.5 mm. to about 8.3 mm. In both cases the initial rate was found to be proportional to the pressure of the substance being chlorinated, thus agreeing with the work on the dichlorobenzenes.<sup>10</sup> The square root of the chlorobenzene pressure (or of some quantity proportional to the amount of uncompleted addition reaction) seemed to be involved in calculating constants for the course of runs beyond the initial stages.

For both benzene and chlorobenzene the chlorine pressure appeared in the final rate expression, thus disagreeing with the work on the dichlorobenzenes. This may possibly be due to the fact that when the pressure of the substance to be chlorinated is higher than in the present experiments reactions (2) and (3) follow each other so rapidly that their sum may be written as one step. It is probable also that in the case of chlorobenzene where the volume of the vessel was large and the intensity high, the total gas pressure (primarily dependent on the pressure of the chlorine) affected the rate of diffusion of atoms to the walls, thus making it necessary to introduce this quantity into the rate expression.

Thus while there are some superficial differences in the rate expressions obtained for these various substances, many aspects of the reactions

(10) Ref. 1b, p. 4457, Ref. 1c, Table IV, p. 1307.

are similar and the mechanisms probably are not widely different.

### Summary

1. The rates of photochemical chlorination of the three dichlorobenzenes have been investigated. Most of the measurements were made on the para compound, although little difference in behavior between the three was noted.

2. The rate of chlorination is proportional to the intensity at low intensities, but depends on

some power of the intensity between 0.5 and 1.0 at higher intensities.

3. The rate is independent of the chlorine pressure, except in so far as this determines the light absorption, but is proportional to the pressure of the dichlorobenzene.

4. Various possible mechanisms of the reaction have been discussed and a brief comparison with the results for benzene and chlorobenzene has been made.

PROVIDENCE, R. I.

RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

## The Determination of the Heat Capacities and the Heat Capacity Ratios of Gaseous Hydrogen Cyanide and of Hydrogen Sulfide<sup>1</sup>

BY W. A. FELSING AND G. W. DRAKE

**Object of the Investigation.**—The purpose of this investigation was the experimental determination of the heat capacities and of the heat capacity ratios at different temperatures of gaseous hydrogen cyanide and hydrogen sulfide. Heat capacity data for gaseous hydrogen cyanide were necessary for the thermodynamic treatment of the thermal decomposition data for monomethylamine obtained in this Laboratory.<sup>2</sup> Hydrogen cyanide is one of the products of this decomposition, and since published data for the heat capacities of this substance are meager and discordant it was decided to measure these needed quantities. It constitutes an integral part of the study of the methylamines as refrigerating fluids in the absorption type refrigerating units as carried out in this Laboratory.<sup>3</sup>

Since the apparatus was available and the heat capacity data for gaseous hydrogen sulfide are rather meager, this substance was included in this investigation.

**Previous Investigations.**—Bryant proposed,<sup>4</sup> on the basis of spectroscopic measurements, the following relation for gaseous hydrogen cyanide

$$C_p(\text{cal./mole}) \text{HCN}(g) = 7.01 + 0.006600T - 0.000001641T^2$$

This relation is claimed to apply over the region 300–2000°K. with an accuracy of about 3%. Usherwood,<sup>5</sup> Partington and Carroll<sup>6</sup> and Bredig and Teichmann<sup>7</sup> have determined heat capacity ratios for gaseous hydrogen cyanide at different temperatures. The latter investigators also calculated values of  $C_p$  and  $C_v$  from their heat capacity ratios.

Eastman proposed a relation for gaseous hydrogen sulfide,<sup>8</sup> which he based upon a review of all existing data; for the region 300–600°K. he proposed

$$C_p(\text{cal./mole}) \text{H}_2\text{S}(g) = 7.2 + 0.0036T$$

for which he claimed only a 5–10% accuracy. Bryant<sup>4</sup> proposed a relation based upon spectroscopic measurements

$$C_p(\text{cal./mole}) \text{H}_2\text{S}(g) = 6.48 + 0.00558T + 0.000001204T^2$$

This relation is to apply over the range 300–2000°K. with an accuracy of about 2%. Partington and Shilling<sup>9</sup> give a résumé of all heat capacity ratios for gaseous hydrogen sulfide as determined through 1923. Recently Giauque and Blue<sup>10</sup> determined the heat capacities of solid and liquid hydrogen sulfide.

**The Method of this Investigation.**—The method selected for the experimental determination of the heat capacities was the closed system continuous flow method of

(1) From a thesis presented by George Wilson Drake to the Graduate Faculty of the University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) F. W. Jessen, Ph.D. Dissertation, University of Texas, 1933.

(3) (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, *THIS JOURNAL*, **54**, 1442 (1932); (c) Felsing and Jessen, *ibid.*, **55**, 4418 (1933); (d) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

(4) Bryant, *Ind. Eng. Chem.*, **25**, 820 (1933).

(5) Usherwood, *J. Chem. Soc.*, **121**, 1604 (1922).

(6) Partington and Carroll, *Phil. Mag.*, **49**, 1665 (1925).

(7) Bredig and Teichmann, *Z. Elektrochem.*, **31**, 449 (1925).

(8) Eastman, *Bur. Mines Tech. Paper* 445 (1929).

(9) Partington and Shilling, "The Specific Heats of Gases," Ernest Benn Limited, London, 1924, pp. 139, 199.

(10) Giauque and Blue, *THIS JOURNAL*, **56**, 831 (1936).