Summary

The activity coefficients of molecular salicylic acid have been determined in various aqueous salt solutions.

For the hydroxybenzoic acids the "salting-out" constants diverge from the values for benzoic acid as one progresses from salts having the highest "salting-out" effects to salts having the lowest effects.

A comparison of the "salting-out" constants for ortho, meta and para-hydroxybenzoic acids in potassium chloride solutions shows that the constants decrease with the transfer of the hydroxy group to the meta and para positions, respectively.

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Photochemical Studies. XVI. A Further Study of the Chlorination of Benzene

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In a previous article[1] a report was made of an investigation of certain phases of the chlorination of benzene vapor. The results may be briefly summarized as follows. (1) The rate of reaction was at least approximately proportional to the pressure of the chlorine. Benzene and chlorine pressures of comparable magnitude (several centimeters) were used. (2) A liquid was formed first on the walls, followed by the gradual growth of crystals. The liquid was not analyzed. It may have been either phenyl chloride or a solution of benzene in some of the reaction products. (3) The only product isolated and for which a definite analysis was obtained was benzene hexachloride ($C_6H_6Cl_6$). (4) From measurements of pressure change and determination of the chlorine used up it was obvious that both addition and substitution were taking place.

In the present investigation an attempt has been made to elucidate certain aspects of benzene chlorination through measurements of quantum yields, pressure changes and reaction rates. In so far as the experimental results may be compared with those previously reported, complete agreement is noted. It was hoped to simplify the results by using benzene pressures so low that the first substitution product (phenyl chloride) would not condense.

I. Experimental Procedure

(a) **Chlorine.**—In some of the experiments the chlorine was prepared by heating anhydrous cupric chloride. Water was first removed from hydrated cupric chloride by heating for several days at 135° under a high vacuum. The chlorine was evolved at

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[1] Lane and Noyes, THIS JOURNAL, **54**, 161 (1932).

temperatures of several hundred degrees, was dried by phosphorus pentoxide and fractionally distilled repeatedly. It was kept at the temperature of solidification of ammonia (−77°) and was admitted to the reaction system as desired.

In most of the experiments carefully purified commercial chlorine was used. A diagram of the purification system is shown in Fig. 1. The chlorine cylinder was attached at A, and G was connected to a water pump through drying columns. The system between G and A was evacuated with the water pump and chlorine admitted from the cylinder at first intermittently and then in a steady stream. The trap C was surrounded with solid–liquid ammonia mush and an appreciable amount of chlorine condensed. The vapor pressure of chlorine at this temperature is about 6 cm., so that danger of back diffusion of water vapor was very small. The drying tube E was filled with magnesium perchlorate. When sufficient chlorine had collected in C, the tube at A was sealed off. After further removal of some of the chlorine, the tube at G was sealed off and most of the chlorine was distilled into the trap F, the final portion being left in C by sealing the tube at B. The chlorine was distilled back and forth between F and D in order to dry it.

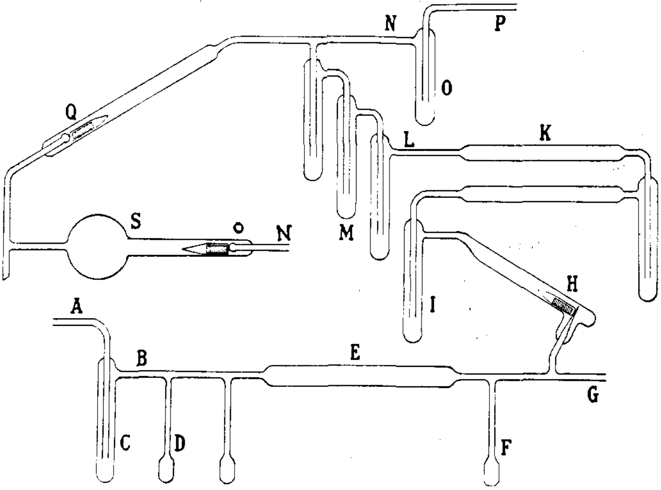

Fig. 1.

The rest of the line as far as H had been thoroughly evacuated with continual flaming, liquid air being kept around the trap at O to remove mercury vapor and other impurities. By means of the glass-surrounded iron bar in H the tip was broken while the chlorine in F was kept cold by liquid air. The entire system was next evacuated to remove traces of non-condensable gases and then the chlorine was distilled into the trap I. There followed repeated distillation through the drying tubes K filled with magnesium perchlorate, succeeded by a fractional distillation in which most of the chlorine was finally sealed off in the main line at L. The chlorine was now distilled through the three traps M, a high vacuum being maintained during each distillation to eliminate the last traces of uncondensable gases. Finally the line was sealed off at N.

The flasks in which the chlorine was finally collected are shown at S. They had been maintained at a high vacuum in a furnace heated to a high temperature (about 400–450°) for several days, the mercury vapor and other condensable impurities being removed by a trap immersed in liquid air. When the purified chlorine was collected in the final trap M, the tip in Q was broken and the chlorine admitted to the flasks S at any desired pressure. The flasks were sealed off and kept for use. In some cases the chlorine reservoir was attached to a series of breakable tips such as that shown at Q so that it could be used repeatedly to admit chlorine to reaction vessels without allowing contact with the air.

(b) **Benzene.**—The benzene used in these experiments had been specially purified by Dr. R. A. Vingee[2] for use in freezing point determinations. It showed no test for thiophene and gave a constant and reproducible melting point of 5.452 ± 0.003°. It was kept over phosphorus pentoxide and after outgassing was never allowed to come into contact with the air.

(c) **Pressure Measurements.**—Pressures in systems where chlorine was present were measured by Pyrex gages of the Bodenstein type used as null instruments. The sensitivities of the gages varied from about 1 millimeter to about 0.02 millimeter. The outside pressures were usually read with sulfuric acid manometers. Temperature corrections were always applied.

(d) **Quantum Efficiency Determinations.**—The absorption coefficients of chlorine have been determined by von Halban and Siedentopf.[3] The values given by these authors were used in the calculations. Several determinations of the absorption coefficient were made using the 4358 Å. line of mercury. The average value agreed with that of von Halban and Siedentopf for this wave length to better than one per cent.

One source of error in these determinations is due to the formation of a solid product on the window of the reaction vessel, particularly at the point where it is traversed by a beam of radiation. In early runs no attempt was made to eliminate this error and values for the quantum yield were found to show little consistency.

A large variety of different chlorinated products may be formed during the course of the reaction. For this reason the apparent quantum efficiency probably will change with the ratio of molecules of chlorine disappearing to molecules of benzene initially present. It was decided, therefore, to attempt to determine the quantum efficiency only for the early stages of the reaction. Under these conditions the accuracy of the quantum yield will be determined largely by the error in the difference between the initial and final chlorine pressures. Since the difference is small compared to either quantity alone the precision will leave something to be desired.

The preparation of the reaction vessels may be best described by reference to Fig. 1. A chlorine bulb of the type S was sealed through the tube N to a Pyrex flask which in turn was sealed to a vacuum line. The flask was evacuated with continual flaming for several hours and benzene vapor admitted to the desired pressure. The vessel was then sealed off. In some cases the benzene vapor was condensed in the reaction vessel with liquid air in order to avoid any thermal decomposition upon sealing. The tip o was broken and the chlorine admitted to the reaction vessel. After waiting a few seconds for pressure equilibrium to be attained but before benzene could diffuse into S, the tube N was sealed off. The reaction vessel then contained a mixture of chlorine and benzene whose total pressure equaled the pressure of the chlorine remaining in S. After exposure of the reaction vessel to radiation the tip was broken under a potassium iodide solution and the flask filled. After emptying and rinsing the liberated iodine was titrated with approximately $N/20$ sodium thiosulfate. In the same manner the chlorine in the bulb S was determined. The volumes of all parts of the apparatus were accurately determined by filling with water from calibrated burets. The calculation of the amount of chlorine disappearing was accomplished as follows. If p_1 is the initial pressure of the benzene in the reaction vessel up to the breakable tip in o and V_1 is the volume of the reaction vessel, then if V_2 is the volume of the reaction vessel after being sealed off, the pressure of the benzene in the reaction vessel as exposed to radiation is

$$p_3 = V_1p_1/V_2 \tag{1}$$

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[2] R. A. Vingee, Thesis, Brown University, 1931.

[3] Von Halban and Siedentopf, *Z. physik. Chem.*, **103**, 71 (1922).

The pressure of the chlorine (p_4) in the bulb S may be determined from the volume and the analysis. The initial pressure of chlorine in the reaction vessel before exposure to radiation is, therefore

$$p_5 = p_4 - p_3 \qquad (2)$$

The final pressure of chlorine in the reaction vessel after exposure (p_6) is obtained from the volume and the titration. All of the information for calculating the number of moles of chlorine which have disappeared during exposure to radiation is now available.

In any chain reaction involving chlorine the effects of impurities are difficult to estimate and account for. In our opinion most of the error is to be ascribed to the quantity ($p_6 - p_5$) which is always small compared to either p_6 or p_5.

Careful test showed that for times of exposure similar to those indicated in Table I the thermal reaction may usually be ignored.

The thermopile was of the Moll micro type with small surface. It was calibrated at frequent intervals with two radiation standards furnished by the Bureau of Standards. The value obtained was 4.76 ergs/sq. mm./sec./cm. deflection.

Due to the fact that the reaction vessel had a curved surface it was necessary to use a beam of radiation of small cross section. The transmission of the walls did not seem to vary greatly with the wave length (4358 and 3660 Å.) and the thickness of the glass. The average of several determinations gave 0.85 as the fraction of the radiation transmitted. At 3130 Å. corex flasks were used and these showed a wall transmission of 0.84 for this wave length.[4]

A shield of asbestos board perforated by a hole 6.355 mm. in diameter was placed in the path of an approximately parallel beam of radiation. In most of the runs a quartz monochromator was used, although an attempt was made to use color filters at 4358 Å. in order to secure greater intensity. Capillary quartz mercury arc lamps somewhat similar to those described by Forbes and Harrison[5] were used. The thermopile, whose surface was slightly larger than that of the opening in the shield, was used to measure the total radiation penetrating the opening. The deflection obtained with the shield in position was 0.818 times the deflection obtained with the shield removed, whereas the ratio of the area of the spot to the area of the thermopile window was 0.846. The ratio was determined for several different types of beam and was surprisingly constant as long as the area of the beam was slightly larger than that of the thermopile window. Some error would undoubtedly be introduced by a non-homogeneous beam or by a highly diverging or converging beam, but such errors are small in this case compared to errors due to other causes. In the calculations, therefore, the observed deflection is divided by 0.818 and the area of the perforation is taken as the area to be used in the calculation.

The intensity of the radiation penetrating the perforation was determined at frequent intervals and the flask exposed for measured time intervals. The product of the galvanometer deflection and the time was determined and used. The fraction of the radiation absorbed by the chlorine was calculated from the pressure, the diameter of the flask and the absorption coefficients of von Halban and Siedentopf.[3] For 3660 Å. and 3130 Å. the reflection from the back wall of the flask could be neglected.

During the run the flask was turned at frequent intervals to avoid areas covered by solid deposit.

(e) **Pressure Change during Reaction.**—In order to follow the course of the reaction a system of the type shown in Fig. 2 was used. The entire apparatus was built of Pyrex. The mercury arc lamp in the center was surrounded by a water jacket which in turn was surrounded by a tube containing a solution of iodine and bromine dissolved in

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(4) The authors wish to express their appreciation to the Corning Glass Co. for furnishing the corex bulbs and tubing.

(5) Forbes and Harrison, THIS JOURNAL, **47**, 2449 (1925).

carbon tetrachloride. The radiation was, therefore, not strictly monochromatic, although the 3660 Å. line was the most intense by far. This apparatus had, however, the advantage of giving reproducible results with sufficient energy absorption to permit carrying the reaction to near completion in a finite length of time. Crude estimates of the quantum efficiency agreed as to order of magnitude with those obtained by the other method. The total pressure in the system was followed with a Bodenstein manometer.

In some instances attempts were made to determine the chlorine pressure by optical absorption in an auxiliary cell. For various reasons, mainly due to a slight deposition of solid on the windows of the auxiliary cell, great accuracy was not attained by this method. At the end of the run chlorine was determined as described above. After the end-point had been reached with thiosulfate, the hydrogen chloride was titrated using approximately $N/100$ sodium hydroxide with methyl orange as the indicator. In this way it was possible to determine the relative amounts of addition and substitution.

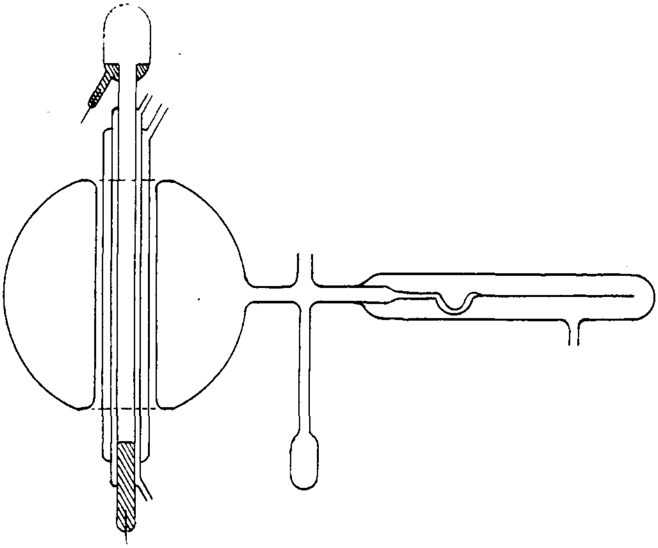

Fig. 2.

II. Results

Preliminary investigations by several different methods served to show definitely that the reaction is of the chain type and that the quantum yield tends to increase with the ratio $(P_a - P_x)/P_m$ (P_a = initial chlorine pressure, P_x = chlorine pressure at time t, P_m = initial benzene pressure). It seems probable that the recombination of chlorine atoms is effective in stopping the chains so that the geometry of the beam of radiation would affect the apparent yield. For these reasons Table I includes only results obtained by the method described in the preceding section for which the above ratio is between 0.15 and 0.50. Disagreement between found and calculated values may be accounted for, with one exception, by variations in the distribution of the absorbed intensity. Correction for dark reaction has been made where necessary.

TABLE I

QUANTUM EFFICIENCY OF BENZENE CHLORINATION, 25 ± 2°

Wave length	Galv. defl., av.	Percentage absorbed	Initial pressure of Cl_2, mm.	Initial pressure of C_6H_6, mm.	Pressure change of Cl_2, mm.	Quantum efficiency Found	Quantum efficiency Calcd.
3660	4.8	84	94.7	8.56	1.54	22	(22)
	18.6	91	125.2	8.40	2.52	12	14
	...	..	113.1	8.00	0.07	..	..
	2.4	90	119.3	8.51	1.91	23[a]	..
	8.5	89	116.1	8.30	4.64	25[b]	..
	35.5	83	97.1	40.8	10.23	46	40
	17.3	90	122.2	40.9	5.81	34	69
3130	8.8	99	121.3	9.65	3.00	16	22
	5.5	99	126.4	8.40	2.50	17	25
	...	..	150.5	9.3	+0.44[c]	..	..
	...	..	178.6	8.1	2.00[d]	..	..

[a] Pressure of added oxygen, 0.162 mm. [b] Pressure of added oxygen, 0.153 mm. [c] Blank run 74 min. at 97°. [d] Blank run twenty hours at room temp.

In all of the runs shown in Table I titrations for hydrogen chloride were made. As will be shown later the initial reaction is almost entirely one of addition, so that with a small ratio of molecules of chlorine used to benzene pressure little hydrogen chloride should be found. The amount did not

TABLE II

PRESSURE CHANGES DURING BENZENE CHLORINATION

Run	Time, hrs.	Initial pressure of Cl_2, mm.	Initial pressure of C_6H_6, mm.	Final total pressure, mm.	Final pressure of Cl_2, mm.	Final pressure of HCl, mm.	Temp., °C.
1[a]	58	44.3	9.2	22.45	10.95	..	24
2	14.25	35.64	1.80	30.29	...	10.0	24.5
3	1.75	40.01	12.5	22.43	4.79	12.20	26
4	0.33	139.0	9.54	113.72	85.37	27.52	27
5[b]	20.5	61.30	4.61	49.70	33.96	15.80	24.7
6	1.13	40.06	2.32	34.18	27.27	7.54	24.7
7	1.15	39.27	2.49	35.36	28.43	6.08	34.6
8	1.55	40.65[c]	1.63	37.75	30.73	6.79	34.2
9	15.00	71.98	3.25	63.91	49.69	12.51	25.1
10	0.17	55.42	1.66	54.23	51.29	0.57	25.0
11	.24	40.74	1.95	40.92	37.90	.85	35.2
12	.24	40.07	2.18	38.43	35.17	1.90	25.1
13[d]	.88	38.64	1.54	34.62	28.93	5.54	24.8
14	1.02	39.16	2.32	38.71	35.15	2.07	34.7
15	0.565	38.18	2.13	37.96	34.55	1.70	34.8
16[e]	.667	40.47	2.22	...	32.24	4.03	35.0
17[e]	.50	40.28	3.03	...	27.92	4.45	25.0

[a] Run No. 1 was made with a dichromate filter. All others were made with approximately monochromatic 3660 Å. radiation. [b] A thermostat was used beginning with Run No. 5. [c] A small amount of air was probably present in Run No. 8. [d] Beginning with Run No. 13 a new reaction vessel was used. [e] No pressure gage was used during Runs 16 and 17.

exceed the experimental error in those runs shown. The dark reaction, however, seemed to be mainly one of substitution, for the chlorine pressure change usually agreed approximately with the pressure of the hydrogen chloride found.

Table II presents data obtained with the apparatus shown in Fig. 2.

From the data in Table II it is possible to calculate empirical formulas for the products by assuming that the benzene is completely used up. Since most of the runs did not approach complete chlorination, the empirical formulas will not be in accord. Table III gives the empirical formulas together with the ratio of molecules of chlorine added to molecules substituted.

TABLE III

EMPIRICAL FORMULAS OF PRODUCTS, $C_dH_eCl_f$ ($d = 6$)

Run	e	f	$e + f$	Molecules added/ molecules subs.	Temp., °C.
2	0.4	11.5	11.9	0.53	24.5
3	5.0	4.7	9.7	1.9	26
4	3.1	8.4	9.5	0.95	27
5	2.6	8.4	11.0	.73	24.7
6	2.8	7.8	10.6	.70	24.7
7	4.1	5.7	9.8	.78	34.6
8	1.8	8.0	9.8	.46	34.2
9	2.2	9.9	12.1	.78	25.1
10	5.7	4.6	10.3	6.25	25.0
11	5.6	2.5	8.1	2.34	35.2
12	5.1	2.6	7.7	1.58	25.1
13	2.4	9.0	11.4	0.75	24.8
14	5.1	2.6	7.7	.94	34.7
15	5.2	2.6	7.8	1.14	34.8
16	4.2	5.6	9.8	0.96	35.0
17	4.5	6.7	11.2	1.78	25.0

It is evident that both addition and substitution take place to a large extent in the chlorination of benzene. At 25° the ratio of molecules added to molecules substituted approaches 0.5 as a lower limit and the number of molecules reacting per benzene molecule approaches 9. This indicates definitely that the chlorination may, if carried on for a sufficient length of time, go as far as dodecachlorocyclohexane (C_6Cl_{12}). The only sharp melting point for products was obtained after run 2. This product melted at 66–68° which may be taken tentatively as the melting point of C_6Cl_{12}.

At 25° it is found empirically that

$$\text{Moles substituted/moles added} = 2/9(P_a - P_x)/P_m \tag{3}$$

Since the vapor pressure of benzene hexachloride is negligible we may write, if there are no intermediate addition products

$$\text{Chlorine added} = 3/4(P_0 - P) \tag{4}$$

where P_0 is the initial total pressure and P is the total pressure at the time t.

Hence

$$(P_0 - P) = 12\,P_m(P_a - P_x)/(9P_m + 2(P_a - P_x)) \qquad (5)$$

At 35° it is found empirically that

$$(P_0 - P) = 12.552\,P_m(P_a - P_x)/(9P_m + 2(P_a - P_x)) - 1.27 \qquad (6)$$

Figure 3 shows the applicability of equations (5) and (6). These equations may be used with some certainty to calculate the chlorine pressure after early stages of a run.

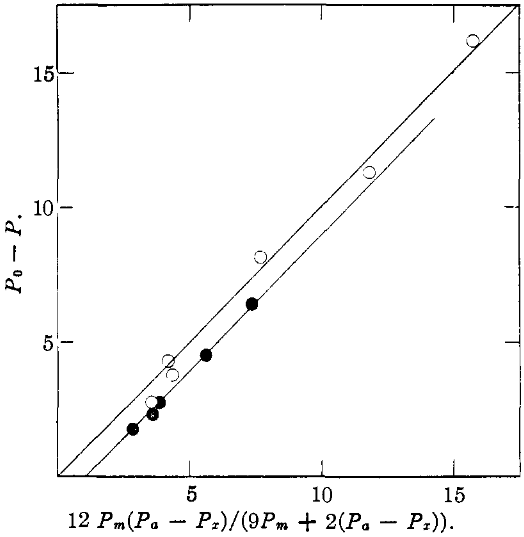

Fig. 3.—Upper line —25°. Lower line —35°.

At 25°

$$P_H = 2(P_a - P_x)^2/(9P_m + 2(P_a - P_x)) \qquad (7)$$

and

$$-dP_H/dP_x = 0,\ P_a = P_x \qquad (8)$$

where P_H is the pressure of the hydrogen chloride formed. The addition reaction is, therefore, predominant at the beginning of a run at this temperature. At 35° the analogous expression for hydrogen chloride pressure agrees well within experimental error with the observations.

Several rate expressions were tried, especially the following. *I. Rate* proportional to absorbed intensity[6]

$$aI_0t = P_a - P_x + (1/k)\log_{10}(e^{-kP_a} - 1)/(e^{-kP_x} - 1) \qquad (9)$$

where $k = 2.303\,Kd$, d is the thickness of the cell (3.5 cm. av.) and K is the absorption coefficient in the expression $I = I_0\,10^{-KdP_x}$, I_0 = incident intensity, I = intensity transmitted.

II. Rate proportional to square root of absorbed intensity

$$aktI_0^{1/2} = 4.606\log_{10}(e^{kP_a/2} + \sqrt{e^{kP_a} - 1})/(e^{kP_x/2} + \sqrt{e^{kP_x} - 1}) \qquad (10)$$

III. Rate proportional to chlorine pressure

$$2.303\log_{10} P_a/P_x = k_1t \qquad (11)$$

IV. Rate proportional to square of chlorine pressure

$$(1/P_x - 1/P_a) = k_2t \qquad (12)$$

Table IV illustrates the application of equations 9, 10, 11 and 12 to three different runs. Constants are calculated for alternate pressure readings.

A slight deposition of solid product always occurs so that a slight decrease in light intensity during a run is to be expected. In no case is k_2 satisfactory, whereas in agreement with previous work,[1] k_1 holds approxi-

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(6) Romeyn and Noyes, THIS JOURNAL, **54**, 4149 (1932).

TABLE IV

DEPENDENCE OF RATE ON CHLORINE PRESSURE

Time, min.	P, mm.	$k_1 \times 10^3$ Eq. 11 1/min.	$k_2 \times 10^4$ Eq. 12 1/min./mm. P	aI_0 Eq. 9	$aI_0^{1/2}$ Eq. 10
Run No. 3 (26°)					
0	52.51				
3.5	45.95	39	11.3	4.1	2.4
7.0	41.57	36	12.6	3.6	1.9
14.5	35.42	36	16.8	3.5	1.7
25.5	29.83	34	20.6	3.1	1.3
35.0	27.45				
Run No. 13 (24.8°)					
0	40.18				
2.0	39.57	7.7	2.0	0.81	0.49
3.5	39.00	10.0	2.7	1.05	.63
5.0	38.42	11.9	3.2	1.24	.74
6.4	37.88	12.4	3.5	1.29	.77
9.8	36.92	13.8	4.0	1.43	.83
12.0	36.31	15.7	4.7	1.61	.91
14.5	35.80	15.8	4.9	1.61	.90
17.8	35.25	15.9	5.2	1.61	.89
21.3	34.82				
Run No. 15 (34.8°)					
0	40.31				
3.8	40.25	4.2	1.11	0.45	0.26
8.8	39.90	1.9	0.51	.20	.14
11.5	39.68	2.2	.62	.24	.14
13.5	39.51	2.1	.59	.23	.12
19.0	39.11	2.1	.58	.22	.13
24.0	38.77	2.5	.70	.26	.16
29.0	38.35	2.5	.70	.26	.15
33.9	38.07				

mately for high benzene pressures. The choice between aI_0 and $aI_0^{1/2}$ is not clear-cut, although the latter shows the smallest average deviation from the mean. For other reasons the square root equation is probably to be preferred.

When one compares different runs it becomes obvious that the values of none of the constants are independent of either the initial chlorine or the initial benzene pressure. During the course of a given run it is difficult to introduce a quantity dependent on the unchlorinated benzene, but attempts showed that such terms were relatively unimportant. It seems difficult if not impossible to arrive at a formulation of the reaction rate for a complete run in terms of an equation which would have an unambiguous theoretical significance. A comparison of the rates of change of total pressure at the beginning of the various runs indicated that a relatively simple equation would hold. This equation may be written

$$-\mathrm{d}P/\mathrm{d}t = aI_0^{1/2}(1 - e^{-kP_a})^{1/2}P_aP_m \qquad (13)$$

Integration of equation (13) is impossible without expressing the benzene pressure as a function of the chlorine pressure. This would involve the introduction of doubtful assumptions. It is possible to use equation (13) only to evaluate the initial slope of the total pressure–time curve.

In Table II five runs, Nos. 5, 6, 9, 10 and 12, were carried out in the same reaction vessel under comparable conditions. Of these No. 5 showed a very slow initial rate of change of total pressure. This phenomenon was occasionally encountered and has not been completely elucidated. Table V shows the applicability of equation (13) to the other four runs. The initial slopes were obtained graphically from large-scale plots of total pressure against time.

TABLE V

INITIAL RATE OF CHANGE OF TOTAL PRESSURE AT 25°

Run	6	9	10	12
$-\mathrm{d}P/\mathrm{d}t$, $t = 0$, mm./min.	0.208	0.775	0.282	0.260
$(1 - e^{-kP_a})^{-1/2}$	1.631	1.323	1.445	1.631
$-(P_aP_m)^{-1}(1 - e^{-kP_a})^{-1/2}\mathrm{d}P/\mathrm{d}t$	3.7×10^{-3}	4.4	4.4	4.9

Similar calculations for Runs 7, 8, 11 at 35° gave 1.7, 1.7 and 2.5×10^{-3} for the quantity in row 4.

The agreement in the fourth row of Table V is probably as good as one could expect. Reference to the quantum efficiencies in Table I shows that with one exception they may be fairly well accounted for by equation (13). The calculated quantum efficiencies are relative values based on the first. For reasons already discussed there should be some difference between the values at 3660 Å. and those at 3130 Å. When the rate of a reaction is proportional to the square root of the light intensity, the quantum efficiency will be inversely proportional to that quantity.

A comparison of the runs at 35° with those at 25° indicates in every case that less chlorine disappears in unit time at the higher temperature. Since the pressure gage was always at room temperature, it was suspected that some of the products might have condensed in the cooler parts of the system thus removing them from the zone in which chlorine atoms were produced. Two runs (Nos. 16 and 17) were made in which no pressure gage was used and in which all parts of the reaction system were at the temperature of the thermostat.

There are several runs at the two temperatures which may be compared more or less directly. For this purpose a constant was calculated from the initial and final chlorine pressures by the equation

$$2(P_a^{1/2} - P_x^{1/2}) = k_{1/2}\,t \qquad (14)$$

Since the pressure of the chlorine is relatively low and the light absorption not large, this constant ($k_{1/2}$) should be very approximately proportional to a $I_0^{1/2}$ in equation (10). Table VI shows values of $k_{1/2}$ for pairs of comparable runs at 35° and at 25° together with $k_{1/2}/P_aP_m$ which should be roughly comparable to the values in the fourth row of Table V.

TABLE VI

EFFECT OF TEMPERATURE ON REACTION RATE

Run	$k^1/_2$	$R = k^1/_2/P_aP_m$	R_{35}/R_{25}
6	0.0338	3.64×10^{-4}	0.76
7	.0271	2.77×10^{-4}	
12	.0547	6.26×10^{-4}	.62
11	.0310	3.90×10^{-4}	
13	.0339	5.70×10^{-4}	.67
16	.0342	3.81×10^{-4}	
17	.0742	6.08×10^{-4}	.63

Since Runs 6 and 7 were for longer time intervals than the others shown in Table VI, R_{35}/R_{25} for this pair should be nearer unity than for the others.

It is evident that the net rate of chlorine disappearance is lower at 35° than it is at 25° under comparable conditions. The current through the mercury arc and the potential drop were maintained as nearly the same for the various runs as possible, but there remained the possibility of a variation in intensity either due to the arc itself or to the transmission of the color filter. In order to test this point the uranyl sulfate–oxalic acid actinometer was employed. This system has been studied with great care by Leighton and Forbes.[7] Due to the type of cell employed in these runs all of the precautions observed by these authors could not be followed. In particular the solution could not be stirred. Although too great accuracy should not be claimed for the variation of light intensity with temperature, the evidence indicated little or no change between 25 and 35°. It seems necessary to conclude, therefore, that not only the rate of disappearance of chlorine is lower at the higher temperature but that the quantum efficiency and the rate of change of total pressure are both lower. Possible explanations of this fact will be brought out in the discussion.

III. Discussion of Results

In the previous section empirical equations correlating most of the results on the chlorination of benzene have been given. It remains to give some theoretical justification for these equations and, if possible, to indicate the relationship between these results and the accepted facts of organic chemistry.

In the present experiments the benzene and chlorine have been purified as carefully as possible. With the exception of two quantum efficiency determinations the effect of oxygen was not studied. Even in these two runs the amount of oxygen was relatively small and its effect not marked. It is quite possible that a different type of reaction would have been ob-

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(7) Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

served with larger amounts of this gas. In a few preliminary runs the effect of water vapor was found also not to be very marked.

Previous studies on the chlorination and bromination of benzene under the influence of radiation have been carried out largely either in liquid benzene or in benzene dissolved in some solvent.[8,9,10,11,12,13] In these studies it either has been shown or assumed that the main product in the chlorination is benzene hexachloride ($C_6H_6Cl_6$). In the bromination both phenyl bromide and benzene hexabromide have been found. In the present work it has been shown that both substitution and addition take place and that as many as nine molecules of chlorine may react with one benzene molecule in the limit to give dodecachlorocyclohexane (C_6Cl_{12}). It is known that α-benzene hexachloride reacts slowly or not at all with chlorine.[14] Therefore either the α modification is not formed in the present work or it will react with chlorine atoms on the walls of the vessel. It seems more probable that when a small amount of benzene is present in a large excess of chlorine containing chlorine atoms, simultaneous addition and substitution take place at all stages of the reaction and it would be hopeless to try to isolate any one substance in the pure form until the reaction is complete. As shown in the previous work[1] if the chlorine is not in large excess benzene hexachloride will be one of the main products, although as judged by the melting point the α modification is not the principal one formed.

There are two simple ways in which chlorine atoms might react with benzene

$$Cl + C_6H_6 = C_6H_5Cl + H \qquad (15)$$
$$Cl + C_6H_6 = C_6H_5 + HCl \qquad (16)$$

These would be followed by either

$$H + Cl_2 = HCl + Cl, \text{ or} \qquad (17)$$
$$C_6H_5 + Cl_2 = C_6H_5Cl + Cl \qquad (18)$$

Reaction (15) is exoenergetic. This is probably also true of (16). Chains leading to substitution might be initiated either way providing neither has too high a heat of activation. The experiments indicate, however, that substitution is relatively unimportant at the start of a run (at least at 25°), so that it seems doubtful whether either (15) or (16) takes place to any large extent in the present experiments. Attempts have been made to estimate heats of activation for (15) and (16) by the methods of Eyring and Polanyi[15] and of Eyring.[16]

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(8) Slator, *Z. physik. Chem.*, **45**, 540 (1903).

(9) Luther and Goldberg, *ibid.*, **56**, 43 (1906).

(10) Bodenstein, *ibid.*, **85**, 329 (1913), has estimated the quantum efficiency for the chlorination to be very high.

(11) Meidinger, *ibid.*, **5B**, 29 (1929).

(12) Rabinowitsch, *ibid.*, **19B**, 190 (1932).

(13) Alyea, THIS JOURNAL, **52**, 2743 (1930), finds the yield per ion pair in the reaction induced by alpha particles to be very high.

(14) *Cf.* Mathews, *J. Chem. Soc.*, **59**, 166 (1891).

(15) Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

(16) Eyring, THIS JOURNAL, **53**, 2537 (1931).

As first approximations the reactions C–H + Cl = C + H–Cl and C–H + Cl = C–Cl + H were studied. The necessary constants for evaluating approximate Morse functions for the Franck–Condon curves for C–H and H–Cl molecules are known.[17] For C–Cl the value of r_0 (the equilibrium distance between centers) was assumed to be 1.8 Å.[18] and ω (the first constant in the equation for vibration levels) was taken as 712 cm.^{-1}.[19] The values of the energies of activation are sensitive to the assumed ratio of coulombic to interchange binding. If 0.1 is taken for all three molecular species, the calculated heat of activation for the first reaction (C–H + Cl = C + H–Cl) is about 26 kcal., while this is lowered considerably if a higher value for this ratio is assumed. About all one may predict with certainty concerning this reaction is that the heat of activation is probably higher than for the reaction Cl + H–H = H–Cl + H which is involved in the hydrogen–chlorine reaction. For the other reaction (with formation of C–Cl and H) the calculations lead one to expect the formation of a stable complex. It is possible to estimate roughly the effect of other parts of the benzene molecule on these activation energies[20] but the accuracy of the calculations would leave something to be desired. From a theoretical standpoint one is not justified in excluding either reaction (15) or (16), although little can be said concerning their probability. It is possible that the larger amount of substitution at 35° than at 25° may be due to the high heat of activation of (18).

It has been shown recently by Ritchie and Norrish[21] that the hydrogen–chlorine reaction follows the same type of equation as that obeyed by the hydrogen–bromine reaction.[22] In both reactions the chains may be stopped largely by the recombination of halogen atoms although other chain-stopping steps are conceivable. Recently Leermakers and Dickinson[23] have studied the photochlorination of tetrachloroethylene in carbon tetrachloride solution. These authors find the rate to be proportional to the square root of the intensity absorbed and to the chlorine concentration. They state that a satisfactory rate equation may be derived in several ways. In particular one may assume either a triatomic chlorine molecule, Cl_3,[24] or an intermediate free radical C_2Cl_5. Dickinson and Leermakers[25] have shown that a sensitized reaction between oxygen and tetrachloroethylene takes place when oxygen is present.

Since the substitution reaction should lead to no pressure change the

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[17] *Cf.* Kimball and Eyring, THIS JOURNAL, **54**, 3876 (1932); Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 274.

[18] Pierce, *Phys. Rev.*, **43**, 145 (1933).

[19] Harkins and Bower, *ibid.*, **38**, 1845 (1931).

[20] *Cf.* Eyring, THIS JOURNAL, **54**, 3191 (1932).

[21] Ritchie and Norrish, *Proc. Roy. Soc.* (London), **A140**, 99, 112 (1933).

[22] Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **121**, 127 (1926).

[23] Leermakers and Dickinson, THIS JOURNAL, **54**, 4648 (1932).

[24] Rollefson and Eyring, *ibid.*, **54**, 170 (1932).

[25] Dickinson and Leermakers, *ibid.*, **54**, 3852 (1932).

empirical equation (13) which accounts fairly satisfactorily for the rate of total pressure change at the beginning of a run should be dependent entirely on the addition reaction. There are several different ways in which this equation may be derived. One may assume either Cl_3 molecules, or an intermediate complex C_6H_6Cl or a three-body collision between a chlorine atom, a chlorine molecule and a benzene molecule. All of these methods are equivalent to postulating an intermediate compound of the formula $C_6H_6Cl_3$ which may have a mean life comparable to the duration of a collision or much longer. With this in mind one may write the equations

$$\mathrm{Cl_2} + h\nu = \mathrm{Cl}(^2P_{1/2}) + \mathrm{Cl}(^2P_{3/2});\ +\mathrm{d(Cl)/d}t = k_1I_\mathrm{a} \tag{19}$$

$$\mathrm{Cl + Cl_2 + C_6H_6 = C_6H_6Cl_3};\ +\mathrm{d(C_6H_6Cl_3)/d}t = k_2\mathrm{(Cl)(Cl_2)(C_6H_6)} \tag{20}$$

$$\mathrm{C_6H_5Cl_3 = C_6H_6Cl_2 + Cl};\ -\mathrm{d(C_6H_6Cl_3)/d}t = k_3\,\mathrm{(C_6H_6Cl_3)} \tag{21}$$

$$\mathrm{C_6H_6Cl_3 = C_6H_6 + Cl_2 + Cl};\ -\mathrm{d(C_6H_6Cl_3)/d}t = k_4\mathrm{(C_6H_6Cl_3)} \tag{22}$$

$$\mathrm{Cl + Cl = Cl_2};\ -\mathrm{d(Cl)/d}t = k_5\mathrm{(Cl)}^2 \tag{23}$$

It follows that

$$\begin{aligned} +\mathrm{d(C_6H_6Cl_2)/d}t &= (k_1I_\mathrm{a}/k_5)^{1/2}(k_2k_3/(k_3 + k_4))\mathrm{(Cl_2)(C_6H_6)} \\ &= -K\,\mathrm{d}P/\mathrm{d}t \end{aligned} \tag{24}$$

where I_a is the intensity of the absorbed radiation. Equation (26) is identical with equation (13) in form. There should, perhaps, be included in k_5 a term dependent on the total pressure since the recombination of chlorine atoms would probably take place as the result of a three-body collision.

While equation (24) accounts satisfactorily for the observed rate of change of total pressure at the beginning of a run, it contains no step in its derivation which leads to the formation of hydrogen chloride. Neither does it account for the rate of disappearance of chlorine during the course of a run.

The fact that substitution takes place to a very small extent at the beginning of a run may be explained in one of the following ways. (1) An intermediate compound may be formed which slowly splits out hydrogen chloride. This would be in accord with mechanisms frequently postulated in organic chemistry. (2) The addition compounds ($C_6H_6Cl_2$, $C_6H_6Cl_4$ and $C_6H_6Cl_6$) may react with chlorine atoms (probably on the walls) to form hydrogen chloride, the resulting free radicals then reacting with molecular chlorine. That reactions of this type must occur is indicated by the nature of the ultimate product which is formed on complete chlorination of benzene. (3) A condensed layer may form on the walls which would dissolve some of the benzene and the substitution reaction may take place entirely in this layer. (4) Reactions (15) and (16) may simply be slow compared to the addition reaction.

There was usually a small but definite decrease in pressure after turning off the mercury arc lamp providing this was done before the reaction had proceeded too far. This did not continue indefinitely. This indicates that the first addition compound ($C_6H_6Cl_2$) adds chlorine in the dark according to the equation

$$C_6H_6Cl_2 + 2Cl_2 = C_6H_6Cl_6 \qquad (25)$$

Reaction (25) is in accord with well-known facts of organic chemistry concerning molecules with conjugated double bonds.

No reference to dichlorocyclohexadiene ($C_6H_6Cl_2$) could be found except in textbooks which give it as an intermediate in the production of benzene hexachloride. The only compound of this empirical formula mentioned is 3,5-dichloro-1,2-dihydrobenzene,[26] which is almost certainly not the first compound formed when chlorine adds to benzene. It has been shown, however, that α-benzene hexachloride loses hydrogen chloride upon heating to form 1,2,4-trichlorobenzene.[27] Whether $C_6H_6Cl_2$ would lose hydrogen chloride easily is problematical. It is impossible to estimate the heat of the reaction $C_6H_6Cl_2 = C_6H_5Cl + HCl$ precisely, but a crude calculation shows that it would probably be endothermic, perhaps to the extent of 30 kcal. It seems very doubtful, therefore, whether this reaction could account for the amount of substitution actually observed, although it would undoubtedly have a high temperature coefficient.

It seems probable, therefore, that the main initial reaction is addition according to equation (21), accompanied by small amounts of either (15) or (16). It is possible that the substitution might take place by means of the complex $C_6H_6Cl_3$, *viz.*, $C_6H_6Cl_3 = C_6H_5Cl + HCl + Cl$. If most of the chlorine atoms form Cl_3 this mechanism would be quite plausible unless one wishes to postulate that chlorine atoms and Cl_3 are both present in appreciable quantity and react with benzene in different manners. No definite proof exists for such an assumption.

The increased amount of substitution with increasing temperature finds a ready explanation in the temperature coefficients of the substitution reactions, whereas the slower rate of disappearance of chlorine at the higher temperature is due in part to the smaller amount of reaction (25). It is possible also that the rate of recombination of chlorine atoms will be increased considerably by an increase of temperature.

A further discussion of theoretical aspects of chlorination will be given at a later date when data on chlorination of phenyl chloride are published.

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Summary

1. The photochemical chlorination of benzene in the gas phase proceeds by a short chain reaction.

2. The rate of pressure change at the beginning of the reaction is pro-

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[26] Crossley and Haas, *J. Chem. Soc.*, **83**, 501 (1903).

[27] Sho-e Tei and Shigeru Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **10A**, 325 (1927).

portional to the square root of the light intensity, the pressure of the chlorine and the pressure of the benzene.

3. Both addition and substitution take place, but the main initial reaction is addition.

4. The mechanism of the reaction has been discussed.

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Actinometry with Uranyl Oxalate at λλ 278, 253 and 208 mμ, Including a Comparison of Periodically Intermittent and Continuous Radiation

BY F. PARKHURST BRACKETT, JR., AND GEORGE S. FORBES

Following several investigations by others of the photolysis of uranyl oxalate, W. G. Leighton and one of us[1] determined quantum yields, ϕ, in monochromatic light at each of nine wave lengths, and urged a wider use of the reaction for purposes of actinometry. An identical value of ϕ, 0.59 (λ = 313 mμ) at comparable concentrations, has been obtained by Heidt and Daniels.[2] Using a zinc spark, we have now measured quantum yields at 208 mμ. Also by redetermining ϕ at 278 and 253 mμ, we were able to compare the relative efficiencies of periodically intermittent and continuous radiation, a question already investigated by Lazareff and Perrin[3] with dyestuffs in polychromatic light, but well worthy of additional study if uranyl oxalate is to be used for actinometry.

We used a spark apparatus[4] maintaining constant intensity within a few per cent. for two hours, and simpler than that described by Boas.[5] The monochromator[4] with its train of crystal quartz was used without change. Including so far as possible only λλ 206 and 210 mμ, 16,000 ergs/sec. were available at the exit slit, at λ 253 mμ 30,000 ergs/sec., at λ 278 mμ 14,000 ergs/sec. The fused quartz reaction vessels, 90 mm. high, 40 mm. broad and (1) 5.3 mm. or (2) 5.5 mm. thick, when containing the actinometer solution, completely intercepted and absorbed the highly divergent beam. A motor-driven spiral of flattened platinum wire provided adequate stirring. The system was not thermostated, but the temperature was consistently recorded.

Our radiometric apparatus, as well as our procedure, agreed for the most part with that previously employed in this Laboratory[6,1] and discussed

(1) Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930); with bibliography.

(2) Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

(3) Lazareff and Perrin, *Compt. rend.*, **177**, 1436 (1923).

(4) Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

(5) Boas, *Z. Physik*, **60**, 690 (1930).

(6) P. A. Leighton and G. S. Forbes, THIS JOURNAL, **51**, 3549 (1929)