368. *The Photochemical Addition of Bromine to Bromobenzene in Carbon Tetrachloride Solution.*

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It is shown that there is no thermal reaction at ordinary temperatures between bromine and bromobenzene in carbon tetrachloride solution. When, however, the system is irradiated with light of wave-length λ 4360 A., addition of bromine takes place by a comparatively simple mechanism. The photo-addition is of low quantum efficiency (0·01—0·005), is unaffected by the presence or absence of oxygen, and is uncomplicated by substitution.

Chlorine and bromine interact with benzene and benzenoid substances to give halogenated derivatives by addition and by substitution of nuclear hydrogen. When both types of reaction are taking place concurrently, the kinetics of halogenation must necessarily be complicated, especially, as has been shown to be the case with the interaction between bromine and benzene, if the halogen acid produced by substitution makes the reaction autocatalytic (Meidinger, *Z. physikal. Chem.*, 1929, *B*, **5**, 29).

It was held for a long time that addition and substitution processes in the aromatic series were intimately connected, the former being regarded as the precursors of the latter. This view has been generally abandoned, mainly for theoretical reasons. Nevertheless, an experimental confirmation of this particular prediction of the modern electronic theory of benzenoid reactivity is desirable, and we have therefore initiated experiments designed to disentangle the kinetics of the halogenation processes. In the present communication we record the results of experiments on the addition of bromine to bromobenzene in carbon tetrachloride solution under the influence of light. We have chosen this particular halogenation process because, at room temperature and in dilute solution, no substitution occurs either in the dark or in the light, and we were thus able to isolate the kinetics of the photo-addition, which we find proceeds by a fairly simple mechanism and in which reproducible results are easily obtained. Dissolved oxygen has no effect, the rate of reaction being the same whether the solution is saturated with oxygen, air, or nitrogen.

Experimental.

Preparation of Materials.—Bromobenzene. This was prepared from "AnalaR" benzene, frozen out three times to remove homologues, and pure bromine. The crude product was steam-distilled, dried over calcium chloride, and fractionated; b. p. 157·0—157·2°/760 mm.

Bromine. Commercial bromine was extracted three times with 10% sodium hydroxide solution to remove chlorine (Cohen, *J. Amer. Chem. Soc.*, 1930, **52**, 2827), dried with phosphoric oxide, and fractionated in an all-glass apparatus.

Carbon tetrachloride. Medicinal carbon tetrachloride was refluxed over and then distilled from phosphoric oxide in a current of dried air.

Light Source and Filters.—The light used consisted almost entirely of the mercury 4360 A. line, which was filtered out from the spectrum given by a quartz mercury-vapour lamp running at 72 volts and 4·3 amps. Owing to the long exposures required, the lamp was fitted with an automatic striking mechanism which came into operation whenever the current through the lamp failed. The mercury 4360 A. line, which is completely absorbed by dilute bromine solutions, was isolated from the spectrum by means of two filtering solutions:

(*a*) 15 G. of "AnalaR" copper sulphate crystals, 200 c.c. of aqueous ammonia (*d* 0·880), and 300 c.c. of water. A 1-cm. layer of this solution transmits 90% of the 4360 A. line but absorbs light of higher wave-length. The absorption for the 4920 A. line, the adjacent intense line in the mercury arc, is 90%.

(*b*) A saturated aqueous solution of sodium nitrite. This solution, for a 1-cm. layer, also transmits 90% of the required light, but absorbs the light of lower wave-length given by the mercury arc, the absorption for the nearest line, 4050 A., being greater than 95%.

The filtering solutions were contained in the outer vacuum spaces of Dewar vessels filled inside with dust-free distilled water, the least thickness of filtering solution which the light travelled being greater than 1 cm. The two Dewar vessels acted as containers for the filters and also as lenses to concentrate the light source.

Estimation of Bromine Concentration.—The change in bromine concentration of the carbon tetrachloride solution during reaction was measured by means of a Hilger–Nutting spectrophotometer. The instrument was calibrated at the end of each reaction by observing the readings for two or more bromine solutions of known concentration (found by treatment with potassium iodide and titration with standard sodium thiosulphate).

Measurement of Light Intensity.—The light intensity was measured by the method of Leighton and Forbes (*J. Amer. Chem. Soc.*, 1930, **32**, 3139), using the photochemical decomposition of uranyl oxalate. A solution containing 8·5 g. of uranyl sulphate and 12·6 g. of recrystallised oxalic acid per litre was exposed to the light in the reaction cells, and the amount of oxalic acid decomposed determined by titration with permanganate. The light intensity is given by the expression

$$I = \text{c.c. of } \mathrm{N}/10\text{-}\mathrm{KMnO_4}/t \times Q \times \varepsilon \times 2 \times 10^4$$

Q, the quantum efficiency of the reaction for light of wave-length 4360 A., was taken as 0·57. The fractional absorption of the solution, ε, was measured in the spectrophotometer and found to be 0·40.

Reaction Cells.—The reactions were carried out in quartz cells with plane faces, of diameter *ca.* 5·5 cm., internal thickness 1·0 cm., and capacity 23—25 c.c. Stirring was effected by a small glass tube, sealed at both ends, containing a piece of iron wire. This was moved up and down in the cell by an electro-magnet fed with an intermittent current. Experiment showed that the stirring was adequate, the observed rate of reaction being independent of the rate of stirring over a wide range.

Preparation of Solutions.—Mixtures of known amounts of carbon tetrachloride, bromobenzene, and bromine in the presence of either dry nitrogen or oxygen were made up in the reaction cell by the following procedure. An all-glass apparatus was constructed in which, after evacuation (3 times) with a Hyvac pump, solvent and solutes could be distilled from phosphoric oxide in two stages into the reaction cell against countercurrents of the appropriate gases. [Nitrogen from a cylinder was freed from oxygen by passing it through towers containing pumice soaked in the following mixture : 75 c.c. of saturated solution of " silver salt " (sodium anthraquinone-β-sulphonate) ; 12 c.c. of sodium hydroxide solution (*d* 1·45) ; 6 g. of sodium hyposulphite. Both the nitrogen and the oxygen entered the apparatus through calcium chloride tubes and sulphuric acid towers.]

The reaction cell could be detached from the rest of the apparatus, and the amounts of carbon tetrachloride and of bromobenzene in it were found by direct weighing. The bromine present was estimated colorimetrically with the spectrophotometer.

Results.—*Influence of light intensity.* The light intensity was varied by interposing wire-gauze screens between the light source and the reaction cells. To obtain the fraction of light transmitted by the screen, a calibration was carried out by means of a photoelectric cell to which was connected an electrometer. A comparison of the time taken for a constant light source to produce a given increase in the electrometer current, with and without the screen in position, was made ; in Table I, I_t/I_0 is the ratio of transmitted to incident light.

Two determinations of the influence of the light intensity on the velocity of the reaction

TABLE I.

Times for rise of 50 divisions.

No screen.	Screen A.	Screen B.	I_t/I_0.	No screen.	Screen A.	Screen B.	I_t/I_0.
46·2	103·0	—	0·449	49·6	—	134·8	0·378
46·4	—	128·4	0·362	50·2	114·6	—	0·439
46·4	103·8	—	0·451	51·4	—	141·1	0·365

Mean ratios of I_t/I_0 : screen A = 0·45; screen B = 0·37.

are given in Table II, where N_0 is the initial normality of bromine in carbon tetrachloride solution, N_t the normality after t minutes, and R the ratio of the mean slopes of the experimental velocity curves, *i.e.*, the ratio of the rates of reaction. In these four experiments the light used was inhomogeneous, but absorption was practically complete.

TABLE II.

Expt.	Screen.	$N_0 \times 10^2$.	$N_t \times 10^2$.	t.	R.	Expt.	Screen.	$N_0 \times 10^2$.	$N_t \times 10^2$.	t.	R.
A_1	None	6·70	5·14	215	0·45	B_1	None	5·44	3·12	180	0·36
A_2	A	6·70	5·60	340		B_2	B	5·44	3·68	380	

Influence of concentration of reactants. A series of experiments was carried out in which the concentrations of the bromine, bromobenzene, and dissolved oxygen were varied, and the results are tabulated in Table III; v is the volume, in c.c., of solution irradiated, I the light intensity in g.-mol. quanta per minute, PhBr the initial concentration of bromobenzene in g.-mols. per litre, and N_0, N_t, and t have the same significance as in Table II. All these reactions were carried out with homogeneous light, 4360 A.

TABLE III.

Expt.	v.	PhBr.	$I \times 10^5$.	$N_0 \times 10^2$.	$N_t \times 10^2$.	t.
1	22·2	0·59	1·16	5·3	4·38	540
2	24·2	0·76	1·20	4·9	3·80	540
3	22·0	1·0	1·16	5·1	4·19	420
4	24·2	1·1	1·20	5·3	4·48	420
5	24·4	2·4	1·20	5·3	3·97	420
6	24·7	3·6	1·20	5·3	3·82	420
7	22·7	4·0	1·16	5·2	3·76	420
8	24·4	6·3	1·20	4·8	3·41	390
9	23·7	0·51	1·20	5·7	4·79	570
10	21·8	0·64	1·16	5·1	4·05	570
11	22·0	2·1	1·16	5·5	3·58	660
12	23·9	2·8	1·20	5·3	3·32	660
13	22·3	4·0	1·16	5·7	2·27	1500
14	24·2	4·7	1·20	5·1	1·84	1500
15	23·6	0·48	1·20	5·9	5·19	510
16	22·0	0·50	1·16	5·7	4·86	510
17	25·4	4·0	1·20	6·2	4·99	420
18	22·6	4·5	1·16	6·7	5·43	360
19	21·8	1·3	1·16	11·2	9·39	600
20	24·4	2·7	1·20	10·2	8·23	540
21	24·1	4·0	1·20	2·2	1·31	360
22	24·1	4·1	1·20	8·4	6·80	390
23	18·5	1·9	1·16	3·8	2·36	426
24	24·4	4·4	1·20	3·1	1·81	426

The solutions for reactions 1—8 were distilled into the reaction cell in an atmosphere of nitrogen, those for 9—14 in oxygen, and those for 15—24 in air. The individual readings for the first three reactions are given in Table IV to illustrate the nature of the measurements from which the quantities in Table III are derived; ΔN is the change in normality at time t minutes.

TABLE IV.

Expt.	$t =$	0.	60.	120.	180.	300.	360.	420.	540.
1	$\Delta N \times 10^2$	0	0·09	—	0·21	0·51	—	0·76	0·92
2		0	0·14	—	0·39	0·66	—	0·89	1·10
3		0	0·12	0·26	0·45	0·70	0·82	0·91	—

That light is essential to the primary process in the addition of bromine to bromobenzene was shown by allowing a solution of these substances in carbon tetrachloride to remain in the dark at 25°. After 168 hours there was no change in the thiosulphate titre of the iodine liberated from a solution of potassium iodide, whereas for the same solution exposed to the light the titre had dropped to less than one-half of its original value after 24 hours.

The absence of hydrogen bromide after irradiation was established by shaking the solution with an excess of aqueous phenol to remove free bromine as tribromophenol, bromine ions then being precipitated by the addition of a known excess of standard silver nitrate solution. The change in the thiocyanate titre of the silver nitrate gave the total hydrogen bromide present, and on subtracting the amount of acid produced by the phenol, which is known from the thiosulphate titre of the iodine equivalent of the original bromine–bromobenzene mixture, the amount of free hydrogen bromide present in the original reaction solution is obtained. This test showed that the photo-reaction is solely one of addition, since practically no hydrogen bromide was detected when the titration was carried out rapidly.

On exposure of a concentrated solution of bromine and bromobenzene to a mercury lamp for several days, heptabromo*cyclo*hexane was produced, confirming van der Linden's observations (*Rec. Trav. chim.*, 1936, **55**, 282); m. p. (after crystallisation from ethyl alcohol) 148·5° (Found : Br, 88·5. Calc. for $C_6H_5Br_7$: Br, 87·9%). It may be noted that Matthews (J., 1892, **61**, 104) found that in the photochlorination of chlorobenzene the end-product was $C_6H_5Cl_7$. It is also of interest to note that boiling the heptabromo*cyclo*hexane in carbon tetrachloride solution alone or in the presence of substitution catalysts such as iodine and iron was quite ineffective in converting the addition compound into substituted benzenes.

DISCUSSION OF RESULTS.

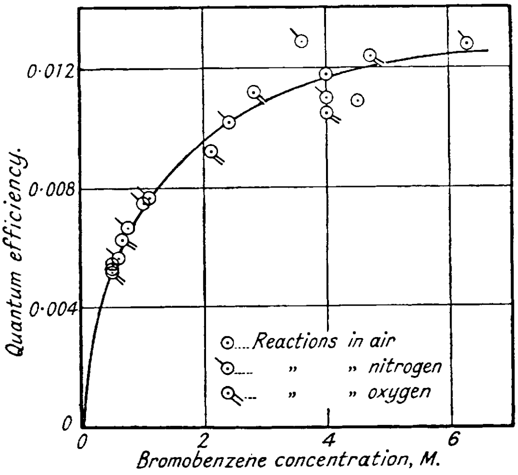
Since no hydrogen bromide was produced under the conditions in which reactions 1—24 were measured, we feel justified in assuming that the whole course of the photoreaction is

$$C_6H_5Br + Br_2 = C_6H_5Br_3 \text{ (photo)}$$
$$C_6H_5Br_3 + Br_2 = C_6H_5Br_5 \text{ (thermal)}$$
$$C_6H_5Br_5 + Br_2 = C_6H_5Br_7 \text{ (thermal)}$$

and that only the first molecule of bromine which adds on to any bromobenzene molecule requires activation by light. In this way one quantum of light is usefully used for every six atoms of bromine which disappear, and the quantum efficiency is equal to the velocity in g.-mols. of bromobenzene disappearing per cell per minute when the light intensity is 1 g.-mol. quantum per minute. The quantum efficiencies (γ) calculated on this basis from the experimental data are given in col. 2 of Table V.

The observed quantum efficiencies of reactions 1—18, in which the bromine concentration was kept as constant as was compatible with distillation of the reagents into the reaction vessels, are plotted against bromobenzene concentration in the figure, and it is evident that the oxygen content of the solution has no noticeable effect on the rate of reaction.

The primary process in the photo-addition of bromine to bromobenzene in carbon tetrachloride solution may be either the dissociation of the bromine into atoms or the activation of bromine molecules. Meidinger (*loc. cit.*), for the addition of bromine to benzene, suggested a mechanism involving the former assumption. Franck and Rabinowitsch (*Trans. Faraday Soc.*, 1934, **30**, 120) have shown that it is most probable that the concentration of bromine atoms in solution would be almost negligible even when illuminated by light which would cause dissociation in the gas phase. For this reason we have assumed that in the addition of bromine to bromobenzene the primary process is the production of activated bromine molecules, not atoms. The direct proportionality of the reaction rate to the first power of the light intensity is further evidence in support of this view.



The mean energy of the light absorbed by activated bromine molecules is 66·8 kg.-cals. per g.-mol. (calculated for 4360 A.). The energy required to destroy the resonance of the benzene nucleus and raise the energy content of the molecule to that of bromo*cyclo*hexatriene is approximately 36 kg.-cals. For addition of bromine molecules to this unsaturated substance at ordinary measurable rates an activation energy of 20—30 kg.-cals. would be necessary. (The thermal data in the foregoing statements are derived from *Ann. Reports*, 1937, **34**, 216.) It thus appears that the light absorbed can provide all the energy of activation required and that the slowness of the reaction is due to deactivation by the solvent.

TABLE V.

		γ (calc.).*				γ (calc.).*	
Expt.	γ (obs.).	A.	B.	Expt.	γ (obs.).	A.	B.
			Reactions in nitrogen.				
1	0·0057	0·0057	0·0056	5	0·0102	0·0108	0·0106
2	0·0067	0·0065	0·0065	6	0·0129	0·0120	0·0117
3	0·0075	0·0076	0·0075	7	0·0110	0·0122	0·0120
4	0·0077	0·0080	0·0079	8	0·0128	0·0129	0·0130
			Reactions in oxygen.				
9	0·0052	0·0053	0·0051	12	0·0112	0·0113	0·0110
10	0·0063	0·0060	0·0059	13	0·0105	0·0125	0·0120
11	0·0092	0·0105	0·0102	14	0·0124	0·0125	0·0124
			Reactions in air.				
15	0·0055	0·0051	0·0049	20	0·0125	0·0126	0·0110
16	0·0053	0·0052	0·0050	21	0·0090	0·0093	0·0120
17	0·0118	0·0127	0·0120	22	0·0149	0·0135	0·0121
18	0·0109	0·0132	0·0123	23	0·0114	0·0092	0·0098
19	0·0097	0·0099	0·0085	24	0·0107	0·0107	0·0122

* The methods of calculation of A and B are given on p. 1964.

The simplest mechanism for the photoreaction is

(1) $Br_2 + h\nu = Br_2^*$ . . . . (k_1)

(2) $Br_2^* + X$ (deactivators) $= Br_2 + X$ . . . . . . (k_2)

(3) $Br_2^* + C_6H_5Br = C_6H_5Br_3$ . . . . (k_3)

(5) $Br_2 + C_6H_5Br_3 = C_6H_5Br_5$ . . . . (k_5)

(6) $Br_2 + C_6H_5Br_5 = C_6H_5Br_7$ . . . . (k_6)

If the absorption of the light is complete, the rate of formation of activated bromine molecules is independent of the bromine concentration and should vary with the first power of the light intensity. Reaction (2) includes normal deactivation by the solvent and also by any added inhibitor. That k_2 is large is shown by the low quantum efficiency. Taking these five stages, and assuming that the concentrations of Br_2^*, $C_6H_5Br_3$, and $C_6H_5Br_5$ are stationary, we have

$$[Br_2^*] = k_1I/(k_2[X] + k_3[C_6H_5Br])$$

$$[C_6H_5Br_3] = k_1k_3I[C_6H_5Br]/(k_2[X] + k_3[C_6H_5Br])(k_5[Br_2])$$

and

$$[C_6H_5Br_5] = k_1k_3k_5I[C_6H_5Br]/k_5k_6[Br_2](k_2[X] + k_3[C_6H_5Br])$$

But

$$-\,d[Br_2]/dt = k_3[Br_2^*][C_6H_5Br] + k_5[C_6H_5Br_3][Br_2] + k_6[C_6H_5Br_5][Br_2].$$

Substituting and rearranging, we have

$$\frac{-\,d[Br_2]}{dt} = \frac{3k_1k_3I[C_6H_5Br]}{k_2[X] + k_3[C_6H_5Br]} \text{ or } \frac{K_1I[C_6H_5Br]}{K_2 + [C_6H_5Br]}$$

The predicted direct proportionality of the rate of reaction to the first power of the light intensity is in complete agreement with the observations given in Tables I and II. The ratio of the rates, *R*, is the same as the fraction of the light transmitted by the screens used.

By using, in the above equation, the constants $K_1 = 0·015$ and $K_2 = 1·0$, found by trial and error, the quantum efficiencies for reactions 1—24 have been calculated, and are given in col. B of Table V. The agreement between the observed and the calculated rates is fair, but a closer scrutiny of the results shows that the quantum efficiency is not quite independent of the bromine concentration and increases very slowly with it. Two reasons can be given for this effect. (i) Although light absorption is complete at the maximum of absorption, this is not the case elsewhere in the region of absorption and a small increase in the number of activated bromine molecules with increase in bromine concentration is therefore to be expected. (ii) It can be readily shown that reversibility to any extent of the first addition process, *i.e.*,

$$(4)\quad C_6H_5Br_3 \rightleftharpoons C_6H_5Br + Br_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (k_4)$$

leads with the same assumptions as in the first mechanism, to a quantum efficiency equation

$$\frac{-\,d[Br_2]}{dt} = \frac{3k_1k_4I[C_6H_5Br]}{k_2[X]/k_3 + [C_6H_5Br]} \times \frac{[Br_2]}{k_4/k_5 + [Br_2]}$$

or

$$\frac{K_1[C_6H_5Br]}{K_2 + [C_6H_5Br]} \times \frac{[Br_2]}{K_3 + [Br_2]}$$

By using the constants $K_1 = 0{\cdot}02$, $K_2 = 1{\cdot}0$, and $K_3 = 0{\cdot}016$, the quantum efficiencies given in col. A of Table V are obtained. In almost all cases the agreement with the observed rates is good, and it is noteworthy that in order to obtain such close correlation it is necessary to take into account the reversibility of the bromine addition process only. This may be taken as an indication that the first step in the bromination process may be a complex C_6H_5Br,Br_2, and that the subsequent rearrangement of the complex into tribromo*cyclo*hexadiene is not instantaneous. The magnitude of the effect of varying bromine concentration is, however, too small for the above suggestion to be tested quantitatively. This kind of dependence on the bromine concentration was found by Meidinger (*loc. cit.*) for the bromine–benzene interaction.

A preliminary investigation has shown that the photobrominations of nitrobenzene and benzil proceed along very similar lines. Both reactions show a first-order dependence on the light intensity, and at room temperature no hydrogen bromide is produced in either case.

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