

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

## The Exchange Reaction of Organic Halides with Iodine Monochloride

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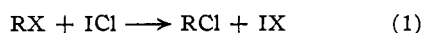
The kinetics of the dark reactions of benzyl iodide, benzyl bromide and isopropyl iodide with iodine monochloride in dilute solutions in carbon tetrachloride at 25° have been investigated. The benzyl halides (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>X) react to liberate one mole of IX per mole of iodine monochloride used as starting material. In the isopropyl iodide reaction one mole of iodine is liberated per two moles of consumed iodine monochloride. The reaction rates have been followed by spectrophotometric determination of the concentrations of iodine or iodine monobromide produced. In solutions containing a large excess of the organic halides the reactions of the benzyl halides follow the rate law,  $d(\text{IX})/dt = k(\text{C}_6\text{H}_5\text{CH}_2\text{X})(\text{ICl})$ .<sup>2</sup> The rate of the isopropyl iodide reaction also shows a second-order dependence on iodine monochloride concentration but is not directly proportional to isopropyl iodide concentration. This observation can be explained if one considers the fact that in the isopropyl iodide solutions a large fraction of the iodine monochloride exists in the form of a 1:1 complex, (CH<sub>3</sub>)<sub>2</sub>CHI·ICl. Equilibrium constants for the complex formation can be derived from the kinetic data. They are closely similar to those obtained by direct experimental measurement. Under the above reaction conditions the benzyl halides form benzyl chloride. Isopropyl iodide is presumed to form mainly propylene chloriodide, although from solutions of high concentration of reactants only isopropyl chloride can be isolated. Possible mechanisms for these reactions are discussed. It seems likely that in the rate-determining steps for the reaction of the three halides an iodine monochloride molecule attacks the 1:1 complex, RX·ICl.

Aliphatic iodides undergo rapid exchange reactions with free halogens at room temperature.<sup>1</sup> For example isopropyl iodide reacts vigorously with bromine to yield isopropyl bromide and iodine.<sup>1b</sup> It has been suggested<sup>1c</sup> that these reactions proceed through the formation of 1:1 organic halide-halogen addition complexes as intermediates.<sup>1c</sup> While such addition complexes can be precipitated from solutions of halogens in simple aliphatic iodides only at low temperatures,<sup>2</sup> there is ample evidence to indicate that they are present in these solutions in significant quantity at room temperature.<sup>3</sup>

To obtain more specific information concerning the mechanism of this type of exchange, the kinetics of reaction of iodine monochloride with certain organic halides in carbon tetrachloride have been studied. The results of measurements on three different halides (benzyl iodide, benzyl bromide and isopropyl iodide) provide evidence that addition complexes do function as reaction intermediates.

**The Kinetic Studies.**—In a series of preliminary experiments it was observed that the rate of formation of iodine in dilute solutions of benzyl iodide and iodine monochloride in carbon tetrachloride occurred at a reasonably rapid rate in the dark and that the rate of reaction increased markedly when the solutions were exposed to light. All kinetic measurements reported in this paper were restricted to reactions in the dark at 25°.

The reactions of both benzyl iodide and benzyl bromide under the conditions of the kinetic experiments were presumed to be of the type



since in the presence of a large excess of organic halide the reactions reached completion with the evolution of one mole of iodine (or iodine monobromide) per mole of iodine monochloride used as starting material. The initial iodine monochloride concentrations of the solutions were chosen so that

the rate of liberation of iodine or iodine monobromide could be determined by following the increase in the intensity of visible absorption of the solutions. Wave lengths of 518 and 540 mμ were chosen as most suitable for measuring, respectively, the absorption of iodine and iodine monobromide. In calculating the concentrations of the halogen products from measured optical densities at these wave lengths small corrections for absorption by unreacted iodine monochloride were required.<sup>4</sup>

If one assumes that the measured optical density,  $d$ , is given by the expression

$$d = (\text{ICl})\epsilon_a + (\text{IX})\epsilon_b \quad (2)$$

where  $\epsilon_a$  and  $\epsilon_b$  represent the extinction coefficients associated with the absorption of the two halogens, and that the initial optical density,  $d_i$ , of the solution at the beginning of the rate run is given by

$$d_i = (\text{ICl})_i\epsilon_a \quad (3)$$

it can be shown that at any time during a run

$$(\text{IX})_t = \frac{d - d_i}{\epsilon_b - \frac{d_i}{(\text{ICl})_i}} \quad (4)$$

The (IX) values during the course of the runs were calculated from the spectrophotometric data using equation (4) and the experimentally determined  $\epsilon_b$  values for solutions of iodine or iodine bromide in carbon tetrachloride. The  $\epsilon_b$  value for iodine (940) was not influenced by the presence of benzyl iodide in the solutions in the concentrations employed in the rate runs. However, as discussed in the Experimental section, it was found that  $\epsilon_b$  for iodine monobromide (*ca.* 200) was subject to small variations with changes in the benzyl bromide concentration of the solutions.

For both benzyl bromide and benzyl iodide the reaction rate was found to be first order with respect to organic halide concentration and second order with respect to iodine monochloride concentration.

(1) (a) A. Geuther, *Ann.*, **123**, 124 (1862); (b) C. Friedel, *ibid.*, **135**, 206 (1865); (c) F. Viebock and A. Schwappach, *Ber.*, **63**, 2813 (1930).

(2) J. Thiele and W. Peter, *ibid.*, **38**, 2842 (1905).

(3) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **74**, 1891 (1952).

(4) For details concerning the spectra of the three halogens in carbon tetrachloride see (a) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (b) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950); (c) A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, *ibid.*, **73**, 514 (1951).

Since in all runs the organic halide was present in large excess, the reactions obeyed the rate law

$$-d(\text{ICl})/dt = k(\text{ICl})^2 \quad (5)$$

and the observed  $k$  values for the several runs were directly dependent on the benzyl halide concentration of the solutions. The integrated form of equation (5) is given by equation (6)

$$kt = \frac{1}{(\text{ICl})_t} - \frac{1}{(\text{ICl})_i} \quad (6)$$

in which  $(\text{ICl})_t = (\text{ICl})_i - (\text{I}_2)_t$  and in which the subscripts  $i$  and  $t$  refer to concentrations at times zero and  $t$ , respectively. Values of  $k$  were, therefore, determined conveniently by measuring the slope of the straight lines obtained by plotting  $1/(\text{ICl})_t$  values against time.

Typical examples of the graphical procedure for evaluation of the rate constants are given in Fig. 1, and a summary of the kinetic studies of the benzyl halide reactions is given in Table I.

TABLE I  
RATE CONSTANTS FOR THE REACTION OF IODINE MONOCHLORIDE WITH ORGANIC HALIDES IN CARBON TETRACHLORIDE AT 25°

Run	(RX) <sub>i</sub> , mole/liter	(ICl) <sub>i</sub> , mole/liter × 10 <sup>3</sup>	$k$ , hr. <sup>-1</sup> moles <sup>-1</sup> liters	$k/(\text{RX})_i$ , hr. <sup>-1</sup> moles <sup>-2</sup> liters <sup>2</sup>
<b>C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>I</b>				
1	0.0528	0.505	206	3900
2	.0528	1.01	209	3960
3	.0528	2.02	190	3600
4	.0264	1.01	107	4060
5	.1056	1.01	414	3920
<b>C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br</b>				
6	0.203	1.97	14.4	70.9
7	.203	3.93	14.5	71.4
8	.203	7.86	17.8	87.5
9	.396	3.84	27.2	68.6
10	.103	3.98	7.6	73.8
<b>Isopropyl iodide</b>				
11	0.2425	2.00	26.5	109
12	.2425	4.00	28.9	119
13	.2425	8.00	29.7	122
14	.123	4.00	33.1	269
15	.474	3.86	23.0	48.5

Reactions of the two benzyl halides with iodine monochloride in carbon tetrachloride solutions in which the concentrations of the reactants were of the order of 1–2  $M$  were run to permit isolation of the organic products. The reaction of benzyl iodide appeared to proceed to completion almost instantaneously as evidenced by the immediate heavy precipitation of iodine on mixing of the reactants. With benzyl bromide the rate of halogen precipitation was slower than was observed for the benzyl iodide reaction. Reasonably good yields of benzyl chloride were isolated from the benzyl iodide reaction; but the product mixture obtained from benzyl bromide contained only small amounts of benzyl chloride and appeared to be mainly ring halogenated material, which presumably was produced by a reaction of high order with respect to halogen concentration. Since the

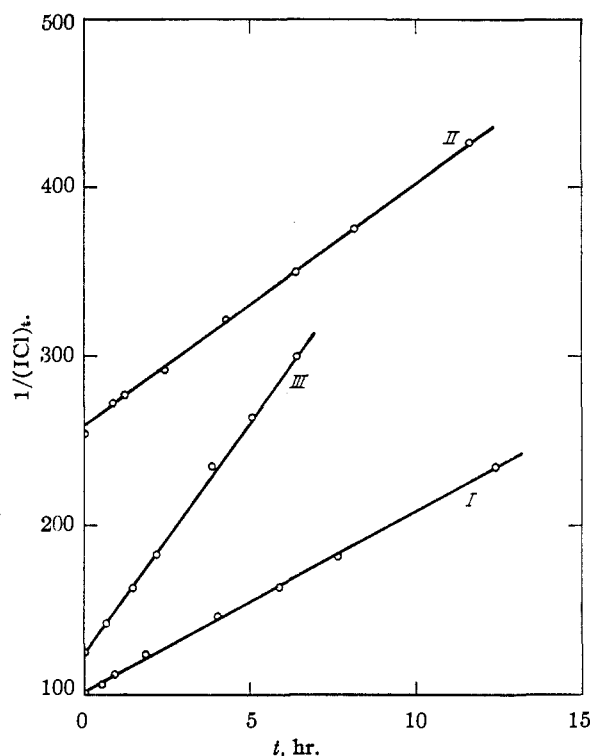


Fig. 1.—Graphical evaluation of rate constants for the reactions of organic halides with iodine monochloride: I (run 4), benzyl iodide; II (run 7), benzyl bromide; III (run 13), isopropyl iodide. For curve I multiply the plotted ordinate values by ten to obtain correct  $1/(\text{ICl})_t$  values.

exchange reaction of benzyl bromide is much slower than that of benzyl iodide, one might anticipate that side reactions would contribute more to the over-all reaction of benzyl bromide than to that of benzyl iodide. There seems little doubt, however, that under the conditions of the kinetic experiments the observed reaction of benzyl bromide was of the exchange type and was accompanied by little or no ring halogenation. It is significant that the iodine monochloride concentration of solutions of toluene and the halogen (in concentrations comparable to those used in these kinetic experiments) remains unchanged over long periods of time if the solutions are not exposed to light.

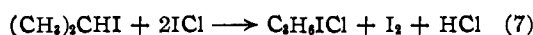
Kinetic experiments on the rate of reaction of trityl bromide and iodine monochloride were also planned. However, when carbon tetrachloride solutions of these substances were mixed, an addition compound, which analysis indicated was very likely  $(\text{C}_6\text{H}_5)_3\text{CBr} \cdot 2\text{ICl}$ , precipitated. Similar addition compounds of trityl bromide and iodine<sup>5</sup> or bromine<sup>6</sup> have been reported previously.

The kinetic experiments with isopropyl iodide and iodine monochloride were performed using experimental conditions closely similar to those employed in the studies of the benzyl halides. In this case the reaction in the presence of a large excess of isopropyl iodide ceased with the liberation of slightly more than one mole of iodine per two moles of iodine monochloride initially in solution. Pre-

(5) M. Gomberg, *THIS JOURNAL*, **20**, 790 (1898).

(6) J. U. Nef, *Ann.*, **308**, 304 (1899).

sumably the predominant reaction which occurred under these conditions<sup>7</sup> was



It seems likely that only a small percentage of the iodine monochloride was reacting according to equation (1) to give isopropyl chloride. Attempts were made to determine the relative contributions of reactions (1) and (7) to the formation of iodine on the basis of iodine analyses at the completion of the reaction. However, because of a very slow side reaction to produce iodine (presumably by the decomposition of isopropyl iodide), it was not possible to decide with accuracy that point at which the main reactions reached completion. This side reaction was sufficiently slow so that it could be disregarded during the time interval over which kinetic measurements were made.

The total halogen concentration of the solutions at any time  $t$ ,  $(\text{X}_2)_t$ , could be related by equation (8) to the iodine and iodine monochloride concentrations.

$$(\text{X}_2)_t = (\text{I}_2)_t + (\text{ICl})_t = (\text{I}_2)_t + (\text{ICl})_t - A(\text{I}_2)_t \quad (8)$$

The iodine concentration of the solutions was also related to the optical densities at  $518 \text{ m}\mu$  by equation (9), a modification of equation (4), in which  $A$  represents the number of moles of iodine monochloride required to produce 1 mole of iodine.

$$(\text{I}_2)_t = \frac{d_{518\text{m}\mu} - \bar{d}_t}{\epsilon_b - A(d_t/(\text{ICl})_t)} \quad (9)$$

In isopropyl iodide solutions of the concentrations used in the rate runs  $\epsilon_b$  for iodine was again 940.

The data needed to calculate  $A$  values using equations (8) and (9) were obtained from two runs in which samples of the solution were removed occasionally for optical density measurement at the same time as samples were removed and analyzed for total halogen by titration with standard sodium thiosulfate solution. The concentrations of reactants in these two runs were closely similar to those of runs 13 and 14 of Table I. The  $A$  values thus determined remained reasonably constant during that phase of the reaction over which kinetic measurements were made and averaged 1.89. It is likely therefore that the main reaction which was followed in the kinetic measurements was that given by equation (7).

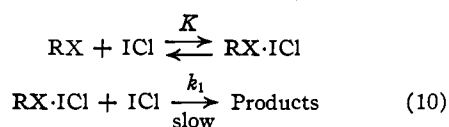
For all rate runs values of  $(\text{I}_2)_t$  and  $(\text{ICl})_t$  were calculated from the measured optical densities using equation (9) and the right-hand expression of equation (8) and assuming this same value for  $A$ . The data for the individual runs in the presence of a large excess of isopropyl iodide could be analyzed satisfactorily by assuming the rate law (5), and rate constants were determined by graphical procedures based on equation (6). A typical run and the summary of runs for isopropyl iodide are included in Fig. 1 and Table I.

As is required if the reaction is second order with respect to iodine monochloride concentration, the rate constants,  $k$ , calculated for the isopropyl iodide runs were independent of changes in initial iodine monochloride concentration in solutions of

fixed isopropyl iodide concentration. Although one would expect this reaction, like those of the benzyl halides, to be first order with respect to organic iodide concentration, values of  $k/(\text{isopropyl iodide})$  did not remain constant but diminished as the isopropyl iodide concentrations of the solutions were increased. This apparent anomaly can be explained if one considers the function of the isopropyl iodide-iodine monochloride addition complex in the reaction mechanism.

An attempt was made to isolate propylene chloroiodide from the reaction of isopropyl iodide and iodine monochloride at higher concentration (2.5  $M$   $\text{ICl}$  and 1.25  $M$  isopropyl iodide) in carbon tetrachloride. None of this high boiling product was obtained, but significant quantities of isopropyl chloride were recovered. It was noted, however, that some hydrogen chloride, which should be produced as a by-product during the formation of the chloroiodide (see equation (7)) was liberated during the reaction.

**The Reaction Mechanisms.**—It seems probable that the three organic halides investigated undergo reaction with iodine monochloride by the path



The second reaction is presumed to be rate determining.

This mechanism requires a rate law of the form

$$\frac{d(\text{IX})}{dt} = -\frac{1}{A} \frac{d(\text{ICl})}{dt} = k_1(\text{RX}\cdot\text{ICl})(\text{ICl})_t \quad (11)$$

where  $(\text{ICl})_t$  represents the concentration of uncomplexed iodine monochloride. The equilibrium constant for the formation of  $\text{RX}\cdot\text{ICl}$  is given by equation (12)

$$K = \frac{(\text{RX}\cdot\text{ICl})}{(\text{RX})(\text{ICl})_t} \quad (12)$$

Equation (11) can be therefore rewritten in the form

$$\frac{d(\text{IX})}{dt} = \frac{k_1 K (\text{RX})(\text{ICl})_t^2}{[1 + K(\text{RX})]^2} \quad (13)$$

where  $(\text{ICl}) = (\text{ICl})_t + (\text{RX}\cdot\text{ICl})$ .

The rate constants,  $k$ , (see equation (5)) calculated from the experimental data according to equation (6) were based on the total iodine monochloride (both free and complexed) concentrations of the solutions. If mechanism (10) is the correct one for the reactions under investigation, one should not expect a direct dependence of observed  $k$  values on the  $\text{RX}$  concentration of the solutions unless under the experimental conditions the term  $[1 + K(\text{RX})]^2$  (see equation (13)) is close to unity. One must infer therefore that if mechanism (10) correctly accounts for the reactions of benzyl iodide and benzyl bromide, very little of the iodine monochloride was bound in the form,  $\text{RX}\cdot\text{ICl}$ , in the solutions prepared for kinetic measurement.

The fact that the observed  $k$  values for the isopropyl iodide reaction did not depend directly on the isopropyl iodide concentration of the solutions can, however, be accounted for on the assumption

(7) The reaction of isopropyl iodide with bromine to yield isopropyl bromide has been reported to produce in addition some hydrogen bromide and a compound  $\text{C}_3\text{H}_7\text{Br}_2$ .<sup>1b</sup>

that appreciable amounts of iodine monochloride were complexed in the solutions investigated.

If mechanism (10) correctly explains the isopropyl iodide reaction,  $k_1$  is related to  $k$  by equation (14).

$$k_1 = \frac{k[1 + K(\text{RX})]^2}{AK(\text{RX})} \quad (14)$$

Since  $k_1$  values should be independent of the concentrations of isopropyl iodide in the reacting solutions, one can then substitute the experimental values for  $k$  and  $(\text{RX})$  in equation (14) and, by using data for two separate runs, solve for  $K$ . From the data of runs 14 and 15 (Table I) a value of  $K = 7.4$  was calculated. Using the average  $k$  value for runs 11–13 and the data of run (14) and of run (15)  $K$  values of 7.9 and 6.6 were calculated.

In view of the relatively slow rate of reaction of isopropyl iodide with iodine monochloride in dilute solutions in carbon tetrachloride it seemed feasible to attempt to check these  $K$  values by the direct evaluation of the equilibrium constant for  $\text{RI} \cdot \text{ICl}$  complex formation by the spectrophotometric procedures used previously in studying  $\text{RI} \cdot \text{I}_2$  complexes.<sup>3</sup> Preliminary measurements indicated that such solutions displayed marked absorption in the 325–350  $m\mu$  region which was not characteristic of either isopropyl iodide or iodine monochloride but which presumably was characteristic of a 1:1 complex. By making rapid optical density measurements on freshly prepared carbon tetrachloride solutions (25°) of the alkyl iodide and iodine monochloride in this wave length region data were obtained from which equilibrium constants for the complex formation could be calculated. The average value of  $K$  as determined from these measurements was 7.4. This figure is in excellent agreement with  $K$  values calculated from the kinetic data.

The observed rate law for the reactions of the three halides with iodine monochloride might also be explained in terms of a mechanism in which the rate-determining step is a termolecular reaction involving one molecule of alkyl halide and two molecules of the halogen. This mechanism, however, seems much less reasonable than that based on the alkyl halide-halogen complex.

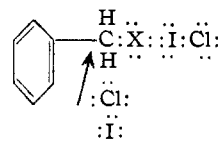
The reaction of isopropyl iodide with mercuric chloride in ether solution to form isopropyl chloride and mercuric iodide appears to be similar in type to the reactions under consideration in this paper. The reaction is autocatalytic and the rate of formation of mercuric iodide is dependent to the first order on the concentrations of isopropyl iodide, mercuric chloride and mercuric iodide.<sup>8</sup> The reaction is presumed to proceed through the formation of a 1:1 isopropyl iodide-mercuric iodide complex as an intermediate. It is interesting to note that the kinetic data taken in the present investigation give no indication that the reactions are autocatalytic. It therefore seems unlikely that a complex between the reacting alkyl halide and the halogen product, IX, can function simultaneously with  $\text{RX} \cdot \text{ICl}$  as a reaction intermediate.

(8) B. H. Nicolet and W. McD. Potts, *THIS JOURNAL*, **50**, 212 (1928).

This point was further investigated in the benzyl iodide and isopropyl iodide runs by introducing iodine into the solutions at the start of the reactions. No significant changes in the reaction rates were observed. Neither, incidentally, did isopropyl chloride react with iodine monochloride in carbon tetrachloride solution when the concentrations of the alkyl chloride and the halogen were comparable to those of isopropyl iodide and iodine monochloride in the rate runs. Therefore isopropyl chloride cannot be formed as an intermediate in the reaction of isopropyl iodide in dilute solution.

Numerous kinetic studies of photochemically or thermally induced radical-type organic halide-halogen exchange reactions have been reported.<sup>9</sup> The experiments described in this paper, however, appear to be the first to be directed toward elucidation of the mechanism of the dark reaction at room temperatures. It seems very doubtful that under these conditions the reactions can proceed by a radical mechanism. It is noteworthy that attempts to suppress the benzyl iodide-iodine monochloride reaction rate by adding small amounts of hydroquinone to the reaction mixtures were unsuccessful.

In these dark reactions the iodine monochloride, through complex formation, probably serves to weaken the carbon-halogen bond of the alkyl halide in much the same fashion as does a hydroxylic solvent (through hydrogen bond formation) in the nucleophilic displacement reaction. The rate-determining step in the reaction of the benzyl halides might then be pictured as one in which a molecule of iodine monochloride attacks a molecule of the complex at the side chain carbon to

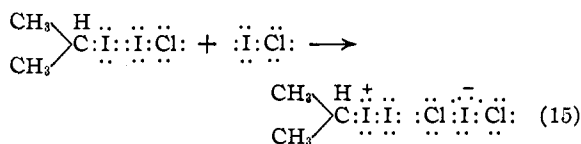


displace  $\text{XICl}^-$  by a Walden inversion process.<sup>10</sup> A series of rapid follow reactions would then lead to the formation of benzyl chloride, iodine and IX. Such a mechanism does not, however, account for the formation of propylene chloriodide from the reaction of isopropyl chloride and iodine monochloride.

In an alternate description of the rate-determining step the iodine monochloride molecule is presumed to initiate a nucleophilic displacement reaction on carbon by attacking the chlorine atom of the organic halide-iodine monochloride complex. The product of this reaction may be considered as an ion pair or at least as a short-lived polar intermediate. Equation (15) represents the formation of this intermediate in the reaction of isopropyl iodide.

(9) See for example (a) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945); (b) R. M. Noyes, *ibid.*, **70**, 2614 (1948); (c) A. A. Miller and J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949); (d) N. Davidson and J. H. Sullivan, *ibid.*, **17**, 176 (1949).

(10) This reaction path is similar to that suggested to explain the kinetics of formation of trityl methyl ether from the reaction of trityl halides and methanol in benzene solution. See C. G. Swain, *THIS JOURNAL*, **70**, 1119 (1948).



Further decomposition of this intermediate can be pictured as proceeding through the formation of isopropylcarbonium ion. The carbonium ion could then either react with iodine monochloride to yield isopropyl chloride or lose a proton to form propylene and subsequently propylene chloriodide. A similar carbonium ion mechanism has been proposed for the iodine-catalyzed dehydration of alcohols.<sup>11</sup> However in the present case in which the reaction occurs at 25° in a medium of low polarity, carbonium ion formation seems unlikely. It is possible that decomposition of the reaction product of equation (15) to form either isopropyl chloride or propylene occurs by internal cyclic processes.<sup>12</sup>

For the moment the details of the mechanisms of these reactions must remain obscure. It seems likely that the mechanisms of other reactions of organic halides and halogens to form dihalides in the presence of electrophilic reagents must be similar to that of the reaction of isopropyl iodide and iodine monochloride to form propylene chloriodide. Examples of such reactions are the formation of propylene dibromide from isopropyl bromide in the presence of iron wire,<sup>13</sup> the iron-catalyzed reaction of isobutyl or *t*-butyl chloride with bromine to form isobutylene dibromide<sup>14</sup> and the formation of isobutylene dibromide from *t*-butyl chloride and bromine in liquid sulfur dioxide.<sup>15</sup>

### Experimental

**Benzyl Iodide.**—This material was prepared by refluxing an acetone solution of benzyl chloride and sodium iodide.<sup>16</sup> The crude product, m.p. 23.5–25°, was freed from traces of iodine by shaking its ether solution with a dilute aqueous sodium thiosulfate solution. The ether phase was dried over calcium chloride and evaporated to yield white crystals of benzyl iodide. *Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>I: I, 58.1. Found: I, 57.4.

**Benzyl Bromide.**—This was prepared by the photobromination of toluene.<sup>17</sup> The crude product was redistilled at reduced pressure, and a cut of b.p. 130–132° (100 mm.) was

(11) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. J. Woolf, *J. Chem. Soc.*, 2113 (1948).

(12) The objection to a mechanism involving ion formation in a non-polar solvent may also be raised in connection with the Walden inversion process discussed previously for the reaction of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>X·ICl with iodine monochloride. It should be noted, however, that this process may be so formulated that the iodine atom of the attacking iodine monochloride molecule may be bonding to the terminal chlorine atom of the 1:1 complex as the C–X bond breaks. In this sense the two alternate reaction paths which have been proposed become identical.

It should be noted that the *A* values determined in connection with the kinetic experiments on isopropyl iodide were relatively constant during the course of the runs and were essentially the same for solutions of different iodine monochloride concentration. In other words the product ratio of isopropyl chloride to propylene chloriodide seems to be independent of iodine monochloride concentration in dilute solutions. This cannot however be the case in more concentrated iodine monochloride solutions in which isopropyl chloride is formed preferentially.

(13) E. Linnemann, *Ann.*, **136**, 51 (1865).

(14) A. D. Herzfelder, *Ber.*, **26**, 1260 (1893).

(15) E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1271 (1937).

(16) G. H. Coleman and C. R. Hauser, *THIS JOURNAL*, **50**, 1196 (1928).

(17) J. Schramm, *Ber.*, **18**, 608 (1885).

retained for use in the kinetic work. *Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>Br: Br, 46.7. Found: Br, 47.2.

**Isopropyl Iodide.**—A sample prepared for use in earlier work<sup>3</sup> was redistilled just before it was used, b.p. 88.2–89.0°.

**Kinetic Experiments.**—Dilute solutions of iodine monochloride in carbon tetrachloride were prepared and standardized as described previously.<sup>18</sup>

For the rate studies solutions of iodine monochloride and of the organic halides in carbon tetrachloride at 25° were mixed in black bottles which had previously been warmed to the thermostat temperature. Samples of the resultant solutions were removed from time to time, transferred to 1-cm. absorption cells for optical measurement on the Beckman spectrophotometer at 518 or 540 mμ against a carbon tetrachloride blank. The reactions, in general, were followed to at least two-thirds completion.

While the extinction coefficient (940) of iodine in carbon tetrachloride at 518 mμ was unaffected by low concentrations of benzyl or isopropyl iodide, the extinction coefficient of iodine monobromide in carbon tetrachloride at 540 mμ varied somewhat with the benzyl bromide concentration of the solutions. Illustrative data are given in Table II. In analyzing the benzyl bromide rate data, ε<sub>b</sub> values needed to calculate iodine monobromide concentrations by use of equation (4) were obtained by graphical interpretation of the data of this table. The iodine bromide solutions used in these studies were prepared by mixing equal quantities of iodine and bromine solutions of the same concentrations.

TABLE II

THE EXTINCTION COEFFICIENT OF IODINE MONOBROMIDE IN CARBON TETRACHLORIDE SOLUTIONS CONTAINING BENZYL IODIDE

(IBr), mole/l.	(C <sub>6</sub> H <sub>5</sub> - CH <sub>2</sub> Br), mole/l.	ε <sub>540mμ</sub>	(IBr), mole/l.	(C <sub>6</sub> H <sub>5</sub> - CH <sub>2</sub> Br), mole/l.	ε <sub>540mμ</sub>
1.90	0	202	3.80	0.095	193
2.53	0	201	3.80	.189	187
3.80	0	200	3.80	.379	176
			1.52	.189	188

**The Reaction of Benzyl Iodide and Iodine Monochloride.**—A solution of 25.2 g. (0.115 mole) of benzyl iodide in 80 ml. of carbon tetrachloride was treated in a darkened room with a solution of 18.8 g. (0.115 mole) of iodine monochloride<sup>19</sup> in 40 ml. of carbon tetrachloride. A heavy precipitate of iodine formed immediately and the mixture warmed slightly. The iodine was removed by filtration, and the filtrate was decolorized with aqueous sodium thiosulfate solution and dried over calcium chloride. This material was fractionated through a centered rod column. After removal of the carbon tetrachloride a fraction of b.p. 175.0–177.0° (750 mm.), n<sub>D</sub><sup>20</sup> 1.5378, was collected. This material (6.1 g.) was benzyl chloride. *Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>Cl: Cl, 28.01. Found: Cl, 27.81. Including the weight of slightly lower and higher boiling cuts a total of 9.8 g. of reasonably pure benzyl chloride was collected (67.5% yield). About 5 ml. of high-boiling residue remained in the boiler.

**The Reaction of Benzyl Bromide and Iodine Monochloride.**—To 149 g. (0.0825 mole) of benzyl bromide in 25 ml. of carbon tetrachloride was added 13.4 g. (0.0825 mole) of iodine monochloride in 25 ml. of carbon tetrachloride. The mixture warmed slightly, a halogen precipitate began to form and hydrogen halide gas was evolved slowly. The following day the mixture was decolorized with aqueous sodium thiosulfate. The dried organic phase was distilled to remove carbon tetrachloride. The residue was distilled under reduced pressure. Two fractions, b.p. 120–126° (99 mm.) and 126–136° (99 mm.), were collected. A considerable quantity of high-boiling residue, presumably ring halogenated material, remained in the boiler. This material underwent extensive decomposition when its distillation was attempted. The n<sub>D</sub><sup>20</sup> values for the two fractions were 1.5550 and 1.5667, respectively, and the lower boiling fraction gave d<sub>20</sub><sup>20</sup> 1.2842. The higher boiling fraction was

(18) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **72**, 5170 (1950).

(19) Prepared by the directions of A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 846.

probably impure benzyl bromide and the lower boiling fraction a mixture of benzyl bromide and benzyl chloride.<sup>20</sup> A differential halogen analysis indicated that the mole ratio of bromine to chlorine in the lower boiling fraction was 1.89/1.

**The Reaction of Isopropyl Iodide with Iodine Monochloride.**—A solution of 47.8 g. (0.294 mole) of iodine monochloride in 120 ml. of carbon tetrachloride was added dropwise with stirring over a one-half hour period to 25 g. (0.147 mole) of isopropyl iodide contained in a flask which was wrapped to exclude light. The reaction mixture warmed, iodine precipitated and hydrogen chloride gas was evolved during the addition. The following day the mixture was shaken with sodium thiosulfate solution to remove iodine. The carbon tetrachloride phase was dried and distilled rapidly from a modified Claisen flask. Only about 0.5 ml. of product boiling above the boiling point of carbon tetrachloride was isolated. This material vigorously evolved iodine when subjected to distillation from a small flask. Therefore there was no significant quantity of propylene chloroiodide in the reaction product. The distillate was subjected to fractionation from a modified Claisen flask. Four grams of isopropyl chloride, b.p. 38–41°, was isolated in this fashion (35% yield).

**The Reaction of Triphenylbromomethane with Iodine Monochloride.**—To 1.0 g. of trityl bromide<sup>21</sup> in 30 ml. of carbon tetrachloride was added 0.60 g. of iodine monochloride in 20 ml. of carbon tetrachloride. During the addition an amorphous suspension formed and subsequently redissolved. After the mixture was allowed to stand at room temperature for two hours and was then cooled in an ice-bath, an abundance of brick-red crystals precipitated. These were filtered and quickly air-dried. This material, m.p. 77–78.5°, weighed 0.45 g. The melting point remained

(20) For physical properties see E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(21) Prepared from triphenylcarbinol by the method of H. Wieland, *Ber.*, **42**, 3024 (1909).

unchanged after the material was recrystallized from heptane. The equivalent weight (based on adding a weighed sample to sodium iodide solution followed by titration with standard sodium thiosulfate solution) was 170; calcd. equiv. wt. for C<sub>19</sub>H<sub>15</sub>Br·2ICl, 162.

**The Equilibrium Constant for the Isopropyl Iodide–Iodine Monochloride Complex.**—Carbon tetrachloride solutions of isopropyl iodide and iodine monochloride, in which the organic halide concentration varied from 0.50–0.06 *M* and the halogen concentration varied from 1.9 × 10<sup>-2</sup>–1.0 × 10<sup>-3</sup> *M*, were prepared at 25°. Optical density measurements of these solutions at 328, 335 and 340 mμ were made immediately after mixing of the reagents, using carbon tetrachloride solutions of isopropyl iodide in the blank cells. The experimental data taken at the several wave lengths were found, by graphical interpretation, to fit the equation

$$\frac{(ICl)_1}{d_o} = \frac{1}{K\epsilon_o} \times \frac{1}{(RI)} + \frac{1}{\epsilon_o} \quad (16)$$

TABLE III

THE EQUILIBRIUM CONSTANT (25°) FOR THE ISOPROPYL IODIDE–IODINE MONOCHLORIDE COMPLEX

λ, mμ	328	335	340
<i>K</i>	8.0	6.8	7.4
ε <sub>o</sub>	590	370	270

where (ICl)<sub>1</sub> and (RI) represent the total iodine monochloride and isopropyl iodide concentrations of the solutions and *d*<sub>o</sub> is the measured optical density corrected for the small absorption of free iodine monochloride. The details of the method of calculation have been described in earlier publications.<sup>3,18</sup> The calculated equilibrium constants, *K*, and extinction coefficients for the complex, ε<sub>o</sub>, at the various wave lengths are given in Table III.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

## The Formation of the Imine Radical in the Electrical Discharge

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When an electrical discharge is passed through hydrazoic acid at low pressures, the NH radical is formed and may be condensed on a liquid nitrogen cooled surface as a blue solid. This is the most convenient way of preparing the material. Cyanic acid under similar conditions yields a purple deposit which appears to be a mixture of NH and undecomposed cyanic acid. We were unable to detect NH in the gases leaving a discharge tube when ammonia, hydrazine or nitrogen–hydrogen mixture passed through it under a variety of conditions. The greenish-blue glow at a liquid-air cooled surface formed by the gases leaving an ammonia discharge tube appears not to be due to NH.

(1) **Introduction.**—This is a continuation of work described in a previous paper<sup>1</sup> in which we prepared the NH radical by the thermal decomposition of hydrazoic acid. When this acid is passed through a hot tube at low pressure, the NH radical in the gases leaving the furnace can be frozen out on a liquid-nitrogen cooled finger and appears as a beautiful blue solid.

Experiments using cyanic acid were not successful, since the acid did not decompose appreciably in passing through our furnace at the highest temperature (1250°) attainable with our quartz apparatus. Subsequently we did decompose cyanic acid in a special apparatus in which a platinum furnace was heated to 1400° but no blue material formed on the cold finger. We have continued this work by studying the conditions necessary to produce NH in a discharge tube.

(2) **Electrical Discharge in Ammonia, Hydrazine and Nitrogen–Hydrogen Mixture.**—A number of investigators have studied reactions in the electrical discharge with the expectation of obtaining the nitrogen hydrides, NH or NH<sub>2</sub>. Lavin and Bates<sup>2</sup> showed that when ammonia was passed through a discharge tube at low pressures, an active gas was obtained which had in part the properties of atomic hydrogen. However, in addition, a greenish-blue glow emanated from the solid ammonia condensed in a liquid air trap 1.5 meters from the discharge tube. Lavin and Bates were unable to obtain any spectroscopic evidence of the presence of NH in the gases leaving the discharge tube, but concluded from chemical evidence that the active gas leaving the discharge tube "seems to consist of atomic hydrogen and NH or NH<sub>2</sub>"

(2) G. I. Lavin and J. R. Bates, *Proc. Natl. Acad. Sci.*, **16**, 804 (1930); also see E. J. B. Willey, *Proc. Faraday Soc.*, **30**, 230 (1934).

(1) F. O. Rice and M. Freamo, *This Journal*, **73**, 5529 (1951).