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The Reaction of *t*-Butyl Bromide and *t*-Butyl Iodide with Iodine Monochloride

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In connection with a study of reactions which require the function of organic halide–halogen complexes as intermediates the rates and products of the dark reactions of *t*-butyl iodide and *t*-butyl bromide with iodine monochloride in carbon tetrachloride have been investigated. The formation of iodine and *t*-butyl chloride in the reactions of *t*-butyl iodide, which even in dilute solution at 25° is too rapid for kinetic study, is accompanied by the production of a high boiling product which is probably mainly isobutylene chloroiodide. The *t*-butyl bromide reaction also leads to the formation of both *t*-butyl chloride and an isobutylene dihalide. This reaction, which becomes complex in nature in its later stages, can be studied kinetically in its earlier phases at room temperature, by employing iodometric and spectrophotometric methods to follow the iodine monochloride and iodine monobromide concentrations of the solutions as a function of time. The rate of disappearance of iodine monochloride shows a second-order dependence on iodine monochloride concentration but is not directly dependent on *t*-butyl bromide concentration. The kinetic data can be interpreted successfully on the assumption that the rate-determining step in the reaction involves the attack of a molecule of iodine monochloride on a 1:1 *t*-butyl bromide–iodine monochloride complex.

In the dark benzyl bromide and benzyl iodide undergo exchange reaction 1

$$C_6H_5CH_2X + ICl \longrightarrow C_6H_5CH_2Cl + IX \quad (1)$$

with iodine monochloride in carbon tetrachloride solution which obey the rate law given in equation 2.[1] In relatively concentrated solutions isopropyl

$$d(IX)/dt = k(C_6H_5CH_2X)(ICl)^2 \quad (2)$$

iodide reacts with iodine monochloride to yield isopropyl chloride. However, in solutions of low iodine monochloride concentration the major reaction which occurs leads to the production of only one mole of iodine per two moles of iodine monochloride consumed and to an organic product which is presumed but not proved to be propylene chloroiodide.[1] The rate of this reaction in the dark in dilute iodine monochloride solution (10^{-2} – 10^{-3} M) is second order with respect to iodine monochloride but it is not directly dependent on isopropyl iodide concentration (0.1–0.4 M i-C_3H_8I). The reaction kinetics for the isopropyl iodide reaction can best be interpreted on the assumption that the rate-determining step involves the reaction of a 1:1 addition complex of isopropyl iodide and iodine monochloride with a molecule of iodine monochloride. The exchange reactions of the benzyl halides may also proceed through organic halide–halogen complex formation, although the evidence favoring such a reaction path is less direct than that for the isopropyl iodide reaction.

Investigation of non-radical types[2] of reactions of organic halides with halogens is being continued in the hope that a kinetic demonstration of the function of organic halide–halogen complexes as reaction intermediates may be made under conditions in which the structure of the organic product may be established with certainty. This paper presents the results of a study of the rates and products of the dark reaction of *t*-butyl bromide and *t*-butyl iodide with iodine monochloride in carbon tetrachloride solution. Tertiary halides have been chosen since previous work[3] suggests that they have a marked capacity to form halogen addition complexes, a feature which is essential if complex formation is to be detected kinetically. Unfortunately these reactions have been found, like other reactions of similar nature,[4] to provide a complex mixture of products and are, therefore, not ideally suited to the purposes of the investigation. The results obtained in this study are, nevertheless, of value in amplifying certain phases of the discussion of possible mechanisms for organic halide–halogen dark reactions.

The Reaction of *t*-Butyl Iodide with Iodine Monochloride.—Even in dilute solutions in carbon tetrachloride the reaction of iodine monochloride with *t*-butyl iodide to form iodine proceeds to completion too rapidly to permit a study of the reaction kinetics. It has been shown by spectrophotometric methods that a solution made up in a black bottle to contain 0.160 M *t*-butyl iodide and 4.77×10^{-3} M iodine monochloride produces the maximum quantity of iodine within two minutes after its preparation. The resultant solution of products evolves hydrogen halide gas, an indication that the reaction which occurs is not entirely of the simple halogen exchange type.

A few measurements have been made to determine the effect of changes in concentration of reactants on the halogen stoichiometry of the reaction. Samples of various reaction mixtures which, as established by spectrophotometric investigation, had generated the maximum quantity of iodine were analyzed for iodine content by titration with sodium thiosulfate solution. The results of these measurements are given in Table I in which the tabulated A values represent the ratio of initial iodine monochloride concentration $(ICl)_i$ to the final iodine concentration $(I_2)_f$ of the solutions. The observed A factors range between 1.1 and 1.2, whereas a theoretical A factor of 1.0 is required for a normal exchange reaction leading to the formation of *t*-butyl chloride and iodine, and an A factor of 2.0 is required for a reaction in which two molecules of iodine monochloride are consumed in forming one molecule each of isobutylene chloroiodide, hydrogen chloride and iodine. It is clear, therefore, that if the observed A factor is truly indicative of a competition between these two reaction processes, the normal exchange reaction predominates over a wide range of concentration of reactants.

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[1] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953).

[2] As distinguished from reactions which proceed through atomic halogen as an intermediate. *Cf.* R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953), and preceding papers.

[3] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

[4] A. Kronstein, *Ber.*, **54**, 1 (1921).

TABLE I

THE HALOGEN STOICHIOMETRY OF THE *t*-BUTYL IODIDE–IODINE MONOCHLORIDE REACTION IN CARBON TETRACHLORIDE (25°)

$(t\text{-BuI})_i$, moles/liter	$(\mathrm{ICl})_i$, moles/liter $\times 10^3$	$(\mathrm{I_2})_f$, moles/liter $\times 10^3$	*A*
1.37	4.06	3.39	1.20
1.09	110.3	100.8	1.10
0.160	4.77	4.39	1.09
.160	0.477	0.394[a]	1.21
.0162	4.85	4.20	1.15

[a] Determined by spectrophotometric rather than volumetric procedures by measurement of the solution at 518 mμ (molar extinction coefficient of I_2 at 518 mμ in 0.160 *M* *t*-butyl iodide is 928).

To check the identity of the reaction products a 1.4 *M* solution of *t*-butyl iodide was treated dropwise with 1.2 times its molar equivalent of iodine monochloride. Hydrogen chloride was produced during the addition, and from the resultant product solution a considerable quantity of *t*-butyl chloride was recovered by fractionation. The high-boiling residue remaining from this fractionation decomposed vigorously to form iodine when further attempts to distil it were made. In view of its high boiling point, it seems certain that the residue contained an organic polyhalide.

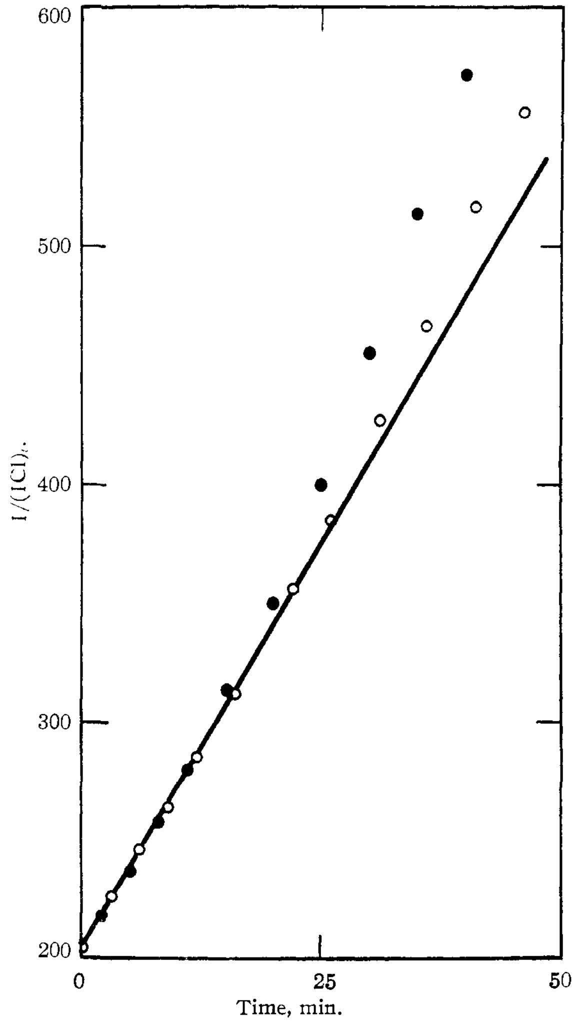

Fig. 1.—The rate of reaction of *t*-butyl bromide with iodine monochloride: $(t\text{-BuBr})_i$ = 0.0865 *M*, $(\mathrm{ICl})_i$ = 4.92×10^{-3} *M*: ○, data at 490 mμ; ●, data at 540 mμ.

The Reaction of *t*-Butyl Bromide with Iodine Monochloride.—In dilute solution in carbon tetrachloride *t*-butyl bromide and iodine monochloride react rapidly in the dark at 25° to form iodine monobromide. Before the iodine monochloride is completely consumed, iodine begins to form in the solutions apparently as a product of a reaction following the initial reaction leading to iodine monobromide formation.

To follow the rate of disappearance of iodine monochloride in the early phase of this reaction, during which iodine monobromide was the only halogen product present in the solutions, both spectrophotometric analyses for iodine monobromide and volumetric analyses for total halogen were made. The spectrophotometric studies of iodine monobromide formation as a function of time were made by following the increase in optical density of the solutions at 490 and 540 mμ. The measured optical densities d_t, of the solutions at these wave lengths at time *t*, are related to the corresponding concentrations of the halogens by equation 3

$$d_t = (\mathrm{ICl})_t\epsilon_{\mathrm{ICl}} + (\mathrm{IBr})_t\epsilon_{\mathrm{IBr}} \qquad (3)$$

in which $\epsilon_{\mathrm{ICl}} = d_i/(\mathrm{ICl})_i$. This extinction coefficient was determined from optical density measurements at the start of the reaction. In all rate runs *t*-butyl bromide was kept in large excess so that ϵ_{IBr} values remained constant during rate runs and could be determined by direct measurement of the optical density of iodine monobromide in *t*-butyl bromide–carbon tetrachloride solutions. A table of the variations in ϵ_{IBr} values with changing *t*-butyl bromide concentration is given in the Experimental section. The iodine monobromide concentration of the rate samples was calculated from the expression

$$(\mathrm{IBr})_t = \frac{d_t - (\mathrm{X_2})_t\epsilon_{\mathrm{ICl}}}{\epsilon_{\mathrm{IBr}} - \epsilon_{\mathrm{ICl}}} \qquad (4)$$

in which the term $(\mathrm{X_2})_t$, as determined by iodometric methods, is equivalent to $(\mathrm{IBr})_t + (\mathrm{ICl})_t$.

The rate of disappearance of iodine monochloride was found to be second order with respect to iodine monochloride concentration as expressed by the rate law

$$-\mathrm{d}(\mathrm{ICl})_t/\mathrm{d}t = k(\mathrm{ICl})_t^2 \qquad (5)$$

Rate constants, *k*, were determined from the slopes of the straight lines obtained by plotting values of $1/(\mathrm{ICl})_t$ against time. A plot of data for a typical run is given in Fig. 1. Spectrophotometric data taken both at 490 and 540 mμ are interpreted in this graph. In this run the deviation of the reaction rate from equation 5 becomes serious after the reaction has proceeded for about 25 minutes. This deviation, which results from marked light absorption of small amounts of accumulated iodine in the reaction mixtures, is more pronounced in the 540 mμ data than in those recorded at 490 mμ. The resultant error in estimating the iodine monobromide concentration spectrophotometrically is lower at the shorter wave length because of the relatively high iodine monobromide extinction coefficient at 490 mμ as compared to that at 540 mμ. Although the later phases of these reactions did not lend themselves to kinetic analysis, the iodine error in general did not become appreciable until the ratio $(IBr)_t/(X_2)_t$ was of the order 0.3–0.4.

Rate constants for a series of runs at varying initial concentrations of reactants, as determined from data taken in the early stages of the reactions, are presented in Table II. The second-order dependence of the reaction rate on iodine monochloride concentration at fixed *t*-butyl bromide concentration is demonstrated by the results of runs 3–5. The fact that values of $k/(t\text{-butyl bromide})$ increase with decreasing *t*-butyl bromide concentration suggests that in the rate-determining step of the reaction a 1:1 *t*-butyl bromide–iodine monochloride complex is attacked by a molecule of iodine monochloride.

TABLE II

RATE CONSTANTS FOR THE REACTION OF IODINE MONOCHLORIDE WITH *t*-BUTYL BROMIDE IN CARBON TETRACHLORIDE AT 25°

Run	(*t*-BuBr) mole/ liter	(ICl), milli-moles/ liter	*A'*	*k*, min.$^{-1}$ moles^{-1} liters	*k*/(*t*-BuBr) min.$^{-1}$ moles^{-2} liters^2
1	0.336	4.60	1.42	13.1	39.0
2	.336	4.70	1.48	15.4	45.8
3	.168	9.60	..	10.9	64.9
4[a]	.171	4.90	1.44	10.4	60.6
5[a]	.173	2.40	1.46	10.9	63.0
6	.0865	4.90	1.36	6.92	80.0
7	.0433	4.83	1.41	4.71	109
8	.0220	2.46	1.45	2.22	101

[a] Average of two runs for which rate constants did not differ by more than 2%.

The *A'* factors listed in Table II are defined by the expression

$$A' = \frac{(\mathrm{ICl})_i - (\mathrm{ICl})_t}{(\mathrm{IBr})_t} \qquad (6)$$

and represent the number of moles of iodine monochloride consumed in the formation of one mole of iodine monobromide. The observed *A'* factors remained relatively constant during the course of individual runs and were approximately 1.4 for all of the runs. It therefore is obvious that the disappearance of iodine monochloride is not accounted for exclusively by the reaction

$$\mathrm{C_4H_9Br + ICl \longrightarrow C_4H_9Cl + IBr} \qquad (7)$$

but must also involve a competitive reaction leading to the formation of a dihalide. Equations 8 and 9 represent the stoichiometry of possible competitive processes.[5]

$$\mathrm{C_4H_9Br + 2ICl \longrightarrow C_4H_8ICl + HCl + IBr} \qquad (8)$$

$$\mathrm{C_4H_9Br + ICl \longrightarrow C_4H_8IBr + HCl} \qquad (9)$$

To check the composition of the reaction products a 1.4 *M* solution of *t*-butyl bromide in carbon tetrachloride was treated dropwise with iodine monochloride. During the addition process hydrogen chloride containing a small percentage of hydrogen bromide was evolved. The solution acquired the color of iodine monobromide during the initial phases of the addition and iodine precipitation occurred in the later stages of the reaction. From the product an appreciable quantity of *t*-butyl chloride was isolated by fractionation. A high boiling residue of complex character remained after complete removal of the solvent. Further investigation showed that this material contained a substantial amount of isobutylene dihalide of which isobutylene dibromide was a major constituent and in which isobutylene chloroiodide (or a mixture of isobutylene iodobromide and chlorobromide) was present in small quantity. Presumably the dibromide was formed in the later stages of the reaction through the reaction of isobutylene bromoiodide or chloroiodide with iodine monobromide.

The Reaction Mechanisms.—Since *A'* values determined in the kinetic studies of the *t*-butyl bromide–iodine monochloride reaction are about 1.4 even in the early stages of the reaction, one must conclude that the observed rate law 5 accounts for the disappearance of iodine monochloride to form both *t*-butyl chloride and isobutylene dihalide. One may also conclude, because of the constancy of *A'* values reported for the several runs in Table II, that the ratio of the monohalide and dihalide in the product is independent of initial concentrations of reactants. These comments apply to that phase of the reaction in which iodine formation is not significant.

The effects of changing *t*-butyl bromide concentration on the observed *k* values can be explained in terms of the following reaction scheme in which the second step is rate determining

$$\mathrm{RBr + ICl \xrightleftharpoons{K} RBr{\cdot}ICl}$$

$$\mathrm{RBr{\cdot}ICl + ICl \xrightarrow[\text{slow}]{k_1} products} \qquad (10)$$

As shown previously[1] a mechanism of this type requires a rate law of the form

$$\mathrm{d(IBr)}/\mathrm{d}t = -(1/A')\mathrm{d(ICl)}_t/\mathrm{d}t = \frac{k_1K(\mathrm{RBr})(\mathrm{ICl})_t^2}{[1 + K(\mathrm{RBr})]^2} \qquad (11)$$

where *K* is the equilibrium constant for complex formation as defined by equation 12.

$$K = (\mathrm{RBr{\cdot}ICl})/(\mathrm{RBr})(\mathrm{ICl}) \qquad (12)$$

The rate constants *k* and k_1 should then be related by the expression

$$k = k_1A'K(\mathrm{RBr})/[1 + K(\mathrm{RBr})]^2 \qquad (13)$$

which may be rewritten in the form

$$[(\mathrm{RBr})/k]^{1/2} = 1/(k_1A'K)^{1/2} + (K/k_1A')^{1/2}(\mathrm{RBr}) \qquad (14)$$

A plot of experimental values of $[(\mathrm{RBr})/k]^{1/2}$ *vs.* (RBr) should provide a straight line from the slope and intercept of which the value of *K* may be calculated. The data of Table II were treated graphically according to equation 14. From the resultant plot (Fig. 2) values of $K = 1.8$ mole^{-1} l. and $k_1A' =$

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[5] Reaction 8 might be regarded as the summation of two successive reactions, 8a and 8b

$$\mathrm{C_4H_9Br + ICl \longrightarrow C_4H_8ICl + HBr} \qquad (8a)$$

$$\mathrm{HBr + ICl \longrightarrow HCl + IBr} \qquad (8b)$$

Experiment shows that hydrogen bromide gas reacts rapidly with a solution of iodine monochloride in carbon tetrachloride to form iodine monobromide.

60.6 mole^{-1} min.$^{-1}$ l., were obtained. The magnitude of this K value was checked independently by the procedure utilized previously[3] in the evaluation by spectrophotometric methods of equilibrium constants for organic halide–halogen interaction. The values of ϵ_{ICl} at 490 mμ for iodine monochloride in various solutions of *t*-butyl bromide in carbon tetrachloride (determined in connection with the rate runs summarized in Table II) were used in this calculation. A value of K = 2.1 mole^{-1} l. was thus obtained.

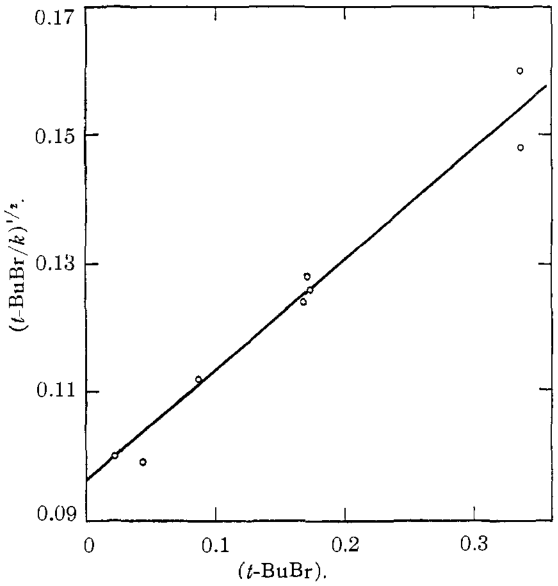

Fig. 2.—Evaluation of K from kinetic data.

The possibility that a complex of the type $C_4H_9Br \cdot IBr$ might function competitively with $C_4H_9Br \cdot ICl$ in the rate-determining step of the reaction to consume iodine monochloride was tested by repeating one of the rate runs (run 5, Table II) with iodine monobromide present initially at a concentration of 7×10^{-4} M, in the reaction mixture. The observed rates of disappearance of iodine monochloride and of formation of iodine monobromide were identical with those measured in run 5. It was observed in a series of independent measurements that iodine monobromide (3×10^{-3} M) undergoes a direct reaction with *t*-butyl bromide (0.6 M) in carbon tetrachloride solution to form iodine. This reaction is slow as compared to the reaction of *t*-butyl bromide with iodine monochloride, but may account in part for the formation of iodine in the later phases of the rate studies summarized in Table II. *t*-Butyl chloride showed no evidence of reacting with iodine monochloride in dilute solutions in carbon tetrachloride.

It seems likely that the dihalide produced directly by the reaction of *t*-butyl bromide with iodine monochloride is either isobutylene chloroiodide or bromoiodide (see equations 8 and 9). It also seems probable that a reactive intermediate produced in the rate-determining step (equation 10) is the common precursor to both *t*-butyl chloride and the dihalide.

A structure for this intermediate, which includes one molecule of *t*-butyl bromide and two molecules of iodine monochloride and is similar in type to that proposed previously for the reaction of isopropyl iodide with iodine monochloride, is in accord with the experimental observations. It has been suggested[1] that decomposition of such an intermediate to form an organic chloride or a dihalide might occur by internal cyclic processes. This point might be further clarified through studies of the temperature coefficient of the reaction rate. However, the reaction is so complex in nature that such data would probably be of very limited value in the interpretation of the reaction mechanism.

Such a cyclic process would account for the production of isobutylene bromoiodide as a primary reaction product (equation 9) without the formation of an olefin intermediate. This process seems attractive, since the substantial quantity of isobutylene dibromide in the product very likely derives from isobutylene bromoiodide (by reaction with iodine monobromide) rather than from isobutylene chloroiodide. The bromoiodide certainly should not form in preference to the chloroiodide through an olefin intermediate, at least in the initial stages of the reaction in which the iodine monobromide concentration is low. The composition of the dihalide product is, however, not well enough established to make conclusive comment on this point.

The reaction of *t*-butyl iodide and iodine monochloride undoubtedly follows a course parallel to that of the *t*-butyl bromide reaction. It seems certain that *t*-butyl iodide should be readily susceptible to complex formation with iodine monochloride. Indeed its pronounced capacity to form an iodine complex already has been demonstrated.[3]

Experimental

Materials.—The *t*-butyl iodide was prepared from *t*-butyl alcohol, phosphorus and iodine.[6] Eastman Kodak Co. *t*-butyl bromide was refractionated for use in these experiments. Iodine monochloride was prepared by the procedure of Vogel.[7] Eastman Kodak sulfur-free carbon tetrachloride was used without further purification.

Determination of A Factors for the *t*-Butyl Iodide–Iodine Monochloride Reaction.—To dilute solutions of *t*-butyl iodide in carbon tetrachloride contained in black bottles at 25° were added known volumes of a standard solution of iodine monochloride in carbon tetrachloride. Samples of the resultant solution were removed from time to time. Some were analyzed iodometrically and others were diluted with known volumes of carbon tetrachloride to permit a study of the visible absorption spectrum of the halogen in the solutions. The diluted samples were measured on the Beckman spectrophotometer against a carbon tetrachloride blank in the 400–600 mμ wave length region.

Within a few minutes after their preparation, the reaction mixtures for which data are recorded in Table I showed the characteristic iodine absorption maximum in the 518 mμ region. In terms of the known extinction coefficient of iodine in carbon tetrachloride[3] ($\epsilon_{518 m\mu}$ 940) it could be calculated on the basis of the iodometric and spectrophotometric analyses that the halogen in these solutions even after very short reaction time was essentially pure iodine.

The Products of the *t*-Butyl Iodide–Iodine Monochloride Reaction.—To a well-stirred solution of 46 g. (0.25 mole) of *t*-butyl iodide in 150 ml. of carbon tetrachloride 49 g. (0.3 mole) of iodine monochloride was added dropwise over a one-half hour period. Heavy iodine precipitation occurred and a gas was evolved during the addition. Some of this gas was trapped in water and was identified as hydrogen chloride through its behavior on treatment with silver nitrate in the presence and absence of ammonium hydroxide.

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(6) M. T. Bogert and E. M. Slocum, This Journal, **46**, 764 (1924).

(7) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 846.

The iodine was removed from the resulting product by washing with aqueous sodium thiosulfate. The resultant carbon tetrachloride solution of organic products was dried over calcium chloride. Iodine formed rapidly in this solution even at room temperature. The material in this solution which boiled below 90° was removed by simple distillation. The remaining high-boiling residue decomposed vigorously to form iodine on further distillation at low pressures. This residue very likely was composed, at least in part, of isobutylene chloroiodide. The low-boiling distillate was fractionated through a four foot sintered glass column to yield *t*-butyl chloride[8] (b.p. 52.2–53.0° (753 mm.), $n^{24}D$ 1.3846). *Anal.* Calcd. for C_4H_9Cl: Cl, 38.3. Found: Cl, 36.9 (based on precipitation of silver chloride by treatment of a sample with alcoholic silver nitrate). From the refractive indices of the various fractions taken it was estimated that a total of 9.4 g. of *t*-butyl chloride was formed in the reaction (40.7% yield). Because of decomposition of the boiler residue to form iodine, complete removal of the carbon tetrachloride and isolation of high-boiling product could not be accomplished.

Kinetics of Reaction of *t*-Butyl Bromide and Iodine Monochloride.—Carbon tetrachloride solutions of the reactants were prepared in black bottles at 25° in much the same fashion as were the solutions used in determining *A* factors for the *t*-butyl iodide–iodine monochloride reaction. A sample was transferred immediately to an absorption cell for measurement on the Beckman spectrophotometer against a carbon tetrachloride blank. The cell housing was maintained at 25°. From time to time optical density readings of the sample at 490 and 540 mμ were recorded. Samples of the reaction mixture were also withdrawn at various times and were analyzed for total halogen content, after addition to potassium iodide solution, by titration with standard sodium thiosulfate solution.

Values of the optical densities of the solutions at zero time were determined by extrapolation of data taken in the first few minutes of each run. The extinction coefficients of iodine monobromide (ϵ_{IBr}) in carbon tetrachloride–*t*-butyl bromide solutions were determined by independent spectrophotometric measurements of *t*-butyl bromide solutions containing equal concentrations of iodine and bromine. The variation in extinction coefficients with changing iodine monobromide concentration is shown in Table III. The ϵ_{IBr} values required for calculation of rate constants using equations 4 and 5 were obtained by graphical interpolation of these data.

TABLE III

THE EXTINCTION COEFFICIENTS OF IODINE MONOBROMIDE IN CARBON TETRACHLORIDE–*t*-BUTYL BROMIDE SOLUTIONS

(IBr), moles/l. × 10^3	*t*-BuBr mole/l.	$\epsilon_{490m\mu}$	$\epsilon_{540m\mu}$
3.80	0	380	200
1.90	0	...	202
2.54	0.084	369	195
2.54	.168	361	188
2.54	.336	341	173

The Reaction of Hydrogen Bromide with Iodine Monochloride.—A 5×10^{-3} *M* solution of iodine monochloride in carbon tetrachloride was treated with gaseous hydrogen bromide for a period of a few minutes. Within the first few seconds of hydrogen bromide addition the color of the solution changed from violet to deep brown. The halogen in the resultant solution was readily characterized as iodine monobromide on the basis of spectrophotometric and iodometric analyses. The solution showed the characteristic iodine monobromide absorption peak at 490 mμ (ϵ_{490} 370) and an $\epsilon_{540\ m\mu}$ value of 195 (*cf.* Table III).

The Equilibrium Constant for *t*-Butyl Bromide–Iodine Monochloride Complex Formation.—From the optical densities at 490 mμ of the solutions prepared for rate measurement (Table II) value of ϵ_{ICl} ($\epsilon_{ICl} = d_i/(ICl)_i$) for solutions of iodine monochloride in *t*-butyl bromide–carbon tetrachloride mixtures were calculated. The experimental data were found by graphical interpretation to fit the equation

$$\frac{1}{\epsilon_{ICl} - \epsilon_{X_2}} = \frac{1}{\epsilon_C - \epsilon_{X_2}} \times \frac{1}{K(t\text{-BuBr})} + \frac{1}{\epsilon_C - \epsilon_{X_2}}$$

where ϵ_{X_2} and ϵ_C refer, respectively, to the extinction coefficients of free and complexed halogen. The details of this method of calculation have been given previously.[9] The value of ϵ_{X_2} was established as 120 at 490 mμ by direct spectrophotometric measurement of a solution of iodine monochloride in carbon tetrachloride. Values of ϵ_{ICl} and the corresponding *t*-butyl bromide concentrations are listed in Table IV. Data for a 0.650 *M* *t*-butyl bromide solution are included. Kinetic data for this solution are not reported since reaction occurred too rapidly to permit accurate iodometric analyses.

TABLE IV

VALUES OF ϵ_{ICl}(490mμ) FOR *t*-BUTYL BROMIDE–CARBON TETRACHLORIDE SOLUTIONS AT 25°

(*t*-BuBr)	0.650 *M*	0.336 *M*	0.173 *M*	0.0865 *M*
ϵ_{ICl}	75	87	100	108

The Products of the *t*-Butyl Bromide–Iodine Monochloride Reaction.—A solution of 34.3 g. (0.25 mole) of freshly distilled *t*-butyl bromide in carbon tetrachloride was treated dropwise with stirring with 57 g. (0.35 mole) of iodine monochloride over a one hour period. During the addition the mixture warmed. Iodine monobromide coloration of the solution was observed; and a hydrogen halide gas, some of which was trapped in water, was evolved. Iodine precipitation was first observed when about one-third of the total iodine monochloride was added. Qualitative differential analyses[10] followed by semi-quantitative analysis of the trap contents indicated that the hydrogen halide gas was about 90% hydrogen chloride and 10% hydrogen bromide.

The reaction mixture was allowed to stand for one hour after the iodine monochloride addition was completed. It was then decolorized with sodium thiosulfate solution and dried over calcium chloride. By simple distillation material boiling below 100° was separated. Fractionation of this distillate through a four-foot sintered glass column provided a total of 9.0 g. (39% yield) of *t*-butyl chloride (b.p. 52.2–53.0° (764 mm.), $n^{25}D$ 1.3844). The remaining carbon tetrachloride residue provided no other product which could be characterized.

The high-boiling residue remaining after the original distillation of the reaction products decomposed to yield iodine on further distillation at atmospheric pressure. On reduced pressure distillation of this residue 9.0 g. of product, b.p. 78–82° (85 mm.), contaminated with halogen only to a moderate degree was isolated. After this material had been decolorized with sodium thiosulfate solution, a small sample was refluxed for 12 hours with 5% potassium carbonate solution. A differential analysis of the resultant aqueous solution indicated the following mole percentages of halide ion: Cl, 18.3; Br, 70.6; I, 11.1.

Redistillation of the high-boiling product provided 4.4 g. of material of b.p. 69–70° (63 mm.), $n^{24}D$ 1.5045, $d^{25}{}_4$ 1.7073, which was only slightly contaminated with free halogen as evidenced by its light pink color. The boiling point and refractive index are similar to those reported for isobutylene dibromide.[11]

A 1.1-g. sample of this distillate was refluxed for four hours with alcoholic sodium ethoxide. The resultant solution was neutralized with nitric acid and diluted to 100 ml. with water. Volumetric analysis of this solution indicated that it was 0.0626 *M* in halide ion. Gravimetric analysis by silver halide precipitation indicated a halide ion concentration of 0.0620 *M* assuming that the precipitate was silver bromide. The procedure would not, however, distinguish a bromide ion solution from one containing equivalent quantities of chloride and iodide ions.

A test to characterize the distillate as a vicinal dihalide[12] was made using a solution of 0.1833 g. of distillate and 2 g. of potassium iodide in a total volume of 100 ml. in absolute methanol. After the solution stood at room temperature overnight, iodometric analysis indicated that its iodine concentration was 1.41×10^{-3} *M*. No further increase in iodine concentration was observed for samples of the solution

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[8] *Cf.* E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 955.

[9] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

[10] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1921, p. 326.

[11] C. M. Suter and H. D. Zook, THIS JOURNAL, **66**, 741 (1944).

[12] R. T. Dillon, W. G. Young and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

maintained at room temperature for 11 days. Another sample of this solution heated at 100° in a sealed tube for 11 days gave an iodine analysis of 6.03×10^{-3} *M*. These results suggested that the unknown was primarily isobutylene dibromide containing a small amount (as indicated by its reaction with iodide ion at room temperature)[13] of isobutylene chloroiodide.

The unknown was characterized as an isobutylene dihalide through its conversion to isobutyraldehyde on hydrolysis.[14] A 0.6-g. sample was heated at 100° with 10 cc. of water in a sealed tube for 24 hours. By this time the lower dihalide phase had disappeared and an oily phase had formed on the surface of the water. The water phase gave a positive Fehling test and provided a methone derivative, according to standard procedures,[15] of m.p. 152–154°. This material showed no depression in a mixed melting point determination with an authentic sample of isobutyraldehyde dimethone.

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[13] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 836 (1948).

[14] W. L. Evers, H. S. Rothrock, H. M. Woodburn, E. E. Stahly and F. C. Whitmore, *ibid.*, **55**, 1136 (1933).

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Rates of Ionization of Pseudo Acids. VI.[1,2] Catalytic Behavior of Alkylamines in the Ionization of Nitroethane

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The effect of structure of the amine on the velocity of the reaction $C_2H_5NO_2 + B \rightarrow C_2H_4NO_2^- + BH^+$ has been studied. When the rate constants and corresponding equilibrium constants of the various amines are compared, it is found that successive replacement of the hydrogen atoms in ammonia by alkyl groups leads to an *increase* in the relative rates. A comparison of quinuclidine and piperidine with triethylamine and diethylamine shows that tying back the alkyl groups to prevent shielding of the nitrogen lone pair causes a further increase in rate. These results are interpreted as meaning that there is some slowing down of the rate of proton removal by alkylamines due to F-strain. However, this is more than compensated for by another factor which is rate increasing. This is the inductive effect which increases the electron density at the nitrogen atom. The usual ionization constants in water, which show tertiary amines to be weaker bases than secondary amines are not a true measure of this electron density. The ionization constants are reduced by decreased solvation energy in the 'onium ion whenever an N–H group is replaced by an N-alkyl. The effect of B-strain appears to be unimportant.

In studying the influence of structure of amine catalysts on the rates of two reactions of the type $HA + B \rightarrow BH^+ + A^-$ it has been noticed that increasing alkyl substitution in ammonia and in aniline increases the catalytic efficiency above what would be expected on the basis of a Brönsted relationship between rates and equilibria.[3] Thus trimethylamine reacts with nitroethane twice as fast as methylamine, though it is only one-tenth as strong as a base. This accelerating effect was ascribed to the circumstance that the ordinary basic ionization constant of an amine in water is not a true measure of the electron availability at the nitrogen atom.[3,4] In particular solvation energies, which are important in stabilizing the 'onium ion, would be progressively less as hydrogen atoms on the nitrogen are replaced by alkyl groups. Thus trimethylamine is not as extensively ionized as it should be because the trimethylammonium ion is not strongly solvated.

However, Brown[5] has blamed the low ionization constant of trimethylamine, and other trialkylamines, on B-strain in the 'onium ion. That is, the methyl groups are forced back on the addition of a fourth group to the nitrogen atom till they interfere with each other and cause steric strain. This effect, unlike frontal or F-strain,[5] is independent of the steric requirements of the incoming group so that even a proton could cause B-strain. Pitzer and Spitzer[6] have argued that in the case of the trimethylamine complex with trimethylboron, B-strain is too small to be significant whereas F-strain is important.

The present work was done to determine the relative importance of solvation and steric effects in the reaction rates of a series of aliphatic amines with nitroethane in water at 0°

$$B + C_2H_5NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH^+ + C_2H_4NO_2^- \qquad (1)$$

By sufficient variation of the structure of B it was hoped to get enough information to sort out the several factors affecting the rates.

Experimental

Materials.—The more volatile amines were purified by crystallization of their chloride salts and fractional distillation of an aqueous solution made alkaline with sodium hydroxide. They were collected as aqueous solutions and titrated to determine concentrations. Quinuclidine was obtained as the picrate salt through the kindness of Dr. Stanley Wawzonek and distilled as above.

The nitroethane, piperidine and *n*-hexylamine were fractionated through a 10-plate column and small middle cuts taken. Diisopropylamine, a gift from the Carbon and Carbide Chemical Corp., and *t*-butylamine, a gift from the Rohm and Haas Co., were treated in the same manner.

Reaction 1 goes essentially to completion for the amines used in this study. It is complicated by the simultaneous reaction of nitroethane with hydroxide ion

$$OH^- + C_2H_5NO_2 \xrightarrow{k_3} H_2O + C_2H_4NO_2 \qquad (2)$$

However, k_3 is known and its effect can be corrected for.

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[1] For previous papers see R. G. Pearson and F. V. Williams, THIS JOURNAL, **75**, 3073 (1953).

[2] Presented at the American Chemical Society National Meeting, March, 1953, San Francisco.

[3] (a) R. G. Pearson, THIS JOURNAL, **70**, 204 (1948); (b) R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1286 (1949).

[4] A. F. Trotman-Dickenson, *ibid.*, 1293 (1949).

[5] H. C. Brown, M. D. Taylor, M. Gerstein and H. Bartholomay, THIS JOURNAL, **66**, 431, 435 (1944).

[6] K. S. Pitzer and R. Spitzer, *ibid.*, **70**, 1261 (1948).