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

The Kinetics of Reaction of Bromine with *t*-Amyl Alcohol

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Bromine reacts with *t*-amyl alcohol to form trimethylethylene dibromide presumably through rapid addition of bromine to the olefin formed by bromine-catalyzed dehydration of the alcohol. The kinetics of this reaction in carbon tetrachloride solution at 25° have been studied using both spectrophotometric and iodometric methods of analysis. The oxidizing power of solutions of bromine and *t*-amyl alcohol diminishes less rapidly with time than does the bromine concentration. This fact suggests that a colorless reducible substance is formed as an intermediate in the reaction leading to the production of olefin. The kinetic data indicate that the intermediate is formed by the reaction of a 1:1 alcohol–bromine complex with a molecule of *t*-amyl alcohol. The rate of decomposition of the intermediate to form the olefin is dependent on the concentration of both the intermediate and the alcohol. It seems unlikely that the reducible intermediate is *t*-amyl hypobromite. A structure consistent with the experimental data is proposed.

Little information is available concerning the mechanism of the halogen-catalyzed dehydration of alcohols, although it has been suggested that substances of the type $R\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}I\ I_3^-$ are formed as intermediates in the reaction.[1] To provide further information concerning the mechanism of such reactions a kinetic study of the reaction of bromine with *t*-amyl alcohol has been undertaken. These substances react rapidly to form trimethylethylene dibromide[2] presumably through the rapid addition of bromine to the trimethylethylene produced by dehydration of the alcohol. The rate of disappearance of bromine from solutions of the alcohol should therefore serve as a measure of the rate of the dehydration process.

In the standard method developed for the synthesis of trimethylethylene dibromide, bromine is added dropwise to pure *t*-amyl alcohol at 55°.[3] Under these conditions the reaction is too rapid for convenient kinetic study, and even at 25° the reaction rate is high. However, a satisfactory procedure for measuring the rate of disappearance of bromine from the alcohol solutions at 25° using carbon tetrachloride as an inert diluent has been developed.

Kinetics of Disappearance of Bromine.—In this procedure the bromine concentrations of carbon tetrachloride solutions of *t*-amyl alcohol as a function of time were followed by measuring the optical densities of the solutions at a fixed wave length in the region 530–560 mμ against carbon tetrachloride as a blank. In all cases the mole ratio of alcohol to bromine was high so that the alcohol concentration remained essentially constant during individual rate runs. Under these conditions the rate of disappearance of bromine was first order with respect to bromine concentration. This fact was indicated by the observation that plots of values of log $1/d$ (where d represents the optical density of the solution) *versus* time give straight lines the slopes of which were closely similar for runs in which the initial bromine concentrations were subject to fourfold variation. A plot of the data for a typical run is given in Fig. 1.

The rate constants, k, as defined by equation (1) were calculated

$$k = -\frac{1}{(\mathrm{Br_2})_\mathrm{T}}\frac{d(\mathrm{Br_2})_\mathrm{T}}{dt} = 2.303 \log \frac{d\ \mathrm{init.}}{d_t} \qquad (1)$$

from the slopes of the plots based on the experimental data.[4] The results for a series of runs using solutions of varying bromine and alcohol concentrations are tabulated in Table I.

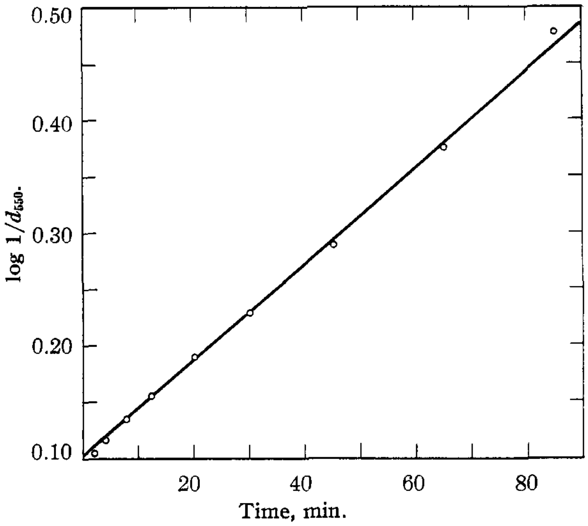

Fig. 1.—The rate of disappearance of bromine by reaction with *t*-amyl alcohol (run 9).

Runs 1, 2 and 3, in which solutions very high in alcohol concentration were employed, proceeded more than two thirds to completion in less than seven minutes. The reported rate constants are therefore based on a series of rapid measurements of limited precision. Nonetheless the first-order dependence of the reaction rate on bromine concentration is apparent even in the results of these fast runs. That this direct dependence of reaction rate on bromine concentration also holds at other alcohol concentrations is evident from the close agreement of k values of runs 5–7 and also of those of runs 8–10.

Runs 4–14 demonstrate the marked sensitivity of k values to changes in *t*-amyl alcohol concentration for runs of low or moderate alcohol concentra-

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[1] 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).

[2] A. Étard, *Compt. rend.*, **114**, 755 (1892).

[3] F. C. Whitmore, W. L. Evers and H. S. Rethrock, *Org. Syntheses*, **13**, 68 (1933).

[4] The term $(\mathrm{Br_2})_\mathrm{T}$ refers to the sum of the concentrations of free bromine and of that complexed with alcohol (see equation (2)). In general it was observed that the rate of disappearance of bromine from the solutions followed first-order kinetics until at least two thirds of the bromine was consumed. In some cases, however, it was observed that the rate constants k, as determined by graphical analysis of the data, tended to increase or decrease as the runs approached completion.

TABLE I

RATE CONSTANTS FOR THE REACTION OF BROMINE WITH *t*-AMYL ALCOHOL IN CARBON TETRACHLORIDE AT 25°

Run	(ROH), mole/l.	$(Br_2)_T$, mole/l.	k, min.$^{-1}$	k_{av}/(ROH)[a]	k_{av}/(ROH)^2
1	4.57	0.0640	0.285	0.065	0.014
2	4.57	.128	.306		
3	4.57	.192	.304		
4	1.52	.0163	.0563	.037	.024
5	0.762	.0325	.0292	.035	.046
6	.762	.0163	.0237		
7	.762	.0081	.0265		
8	.381	.0650	.0117	.027	.071
9	.381	.0325	.0099		
10	.381	.0163	.0092		
11	.191	.0161	.00284	.015	.078
12	.095	.0161	.00072	.0076	.080
13	.0915	.0078	.00088	.0096	.105
14	.0458	.0078	.00023	.0050	.109
15[b]	.758	.0325	.0312		

[a] k_{av} signifies the average value of k for all runs at a given alcohol concentration. [b] Water added, (H_2O) init. = 0.046 *M*.

tion. It is questionable whether or not runs 1–3 should be included in an analysis of the data from this point of view, since the solvent in these runs at high alcohol concentration is highly polar as compared to that in runs 4–14. A comparison of k values of run 4 with those of runs 5–7 indicates that for solutions of relatively high alcohol content, the rate constant is proportional to the alcohol concentration of the solutions. As the alcohol concentration of the medium is reduced, however, values of $k/(\mathrm{ROH})$ diminish markedly (see runs 8–14): and in solutions of low alcohol concentration (runs 13 and 14) the rate constants appear to be proportional to the square of the alcohol concentration. The fifth and sixth columns of Table I indicate the relationship between k values and the alcohol concentrations of the media.

These observations concerning the rate of disappearance of bromine color can be explained if one assumes that the mechanism of decolorization requires as the rate determining step the reaction of a 1:1 alcohol–bromine complex with a molecule of *t*-amyl alcohol. Equilibria with respect to formation of colored halogen–alcohol complexes are presumably established rapidly. Equations consistent with this viewpoint for the reaction of bromine and *t*-amyl alcohol to form a colorless product, tentatively formulated as I, are given below.

$$\mathrm{ROH} + \mathrm{Br_2} \overset{K}{\rightleftarrows} \mathrm{ROH{\cdot}Br_2}$$

$$K = (\mathrm{ROH{\cdot}Br_2})/(\mathrm{ROH})(\mathrm{Br_2}) \quad (2)$$

$$\mathrm{ROH{\cdot}Br_2} + \mathrm{ROH} \xrightarrow{k'} \mathrm{I} \quad (3)$$

If equation (3) represents the rate determining step in the reaction leading to loss of bromine color, then the rate of disappearance of bromine is given by equation (4)

$$\frac{-\,\mathrm{d}(\mathrm{Br_2})_T}{\mathrm{d}t} = k'(\mathrm{ROH{\cdot}Br_2})(\mathrm{ROH}) = k'K(\mathrm{ROH})^2(\mathrm{Br_2}) \quad (4)$$

where

$$(\mathrm{Br_2})_T = (\mathrm{Br_2}) + (\mathrm{ROH{\cdot}Br_2}) \quad (5)$$

From equations (2), (4) and (5) it follows that

$$\frac{-\,\mathrm{d}(\mathrm{Br_2})_T}{\mathrm{d}t} = \frac{k'K(\mathrm{ROH})^2(\mathrm{Br_2})_T}{1 + K(\mathrm{ROH})} \quad (6)$$

Since (ROH) is much larger than $(\mathrm{Br_2})_T$ it may be shown using equations (1) and (6) that k' is related to the experimentally determined rate constant, k, by equation (7).[5]

$$\frac{(\mathrm{ROH})}{k} = \frac{1}{k'K(\mathrm{ROH})} + \frac{1}{k'} \quad (7)$$

If this interpretation of the experimental observations concerning the variation of k with (ROH) is correct, a plot of values of $(\mathrm{ROH})/k$ *versus* corresponding values of $1/(\mathrm{ROH})$ should produce a straight line of intercept $1/k'$ and slope $1/k'K$. As indicated in Fig. 2 the data for runs 1–14 (using average values of k for runs made at the same alcohol concentration) conform reasonably well to graphical analysis according to equation (7). Values of k = 0.055 min.$^{-1}$ mole^{-1} l. and K = 2.2 were calculated from the straight line indicated in this plot. This value for the equilibrium constant is of the same order of magnitude as those determined for the interaction of alcohols with iodine.[6,7]

There was no indication based on kinetic evidence that the reaction of bromine and *t*-amyl alcohol was, under the experimental conditions of the present investigation, subject to catalysis by the water formed as a product.[8] To check this point further run 5 was repeated with sufficient

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(5) It is assumed that under the conditions of the experimental measurements $(\mathrm{Br_2})_T$ is proportional to the optical density throughout the course of any given rate run. This assumption is correct provided both the free and complexed bromine obey Beer's law.

(6) (a) J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952); (b) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 3561 (1953).

(7) In using equation (2) for the derivation of equation (7), it was assumed that the activity coefficient ratio $\gamma_{\mathrm{ROH{\cdot}Br_2}}/\gamma_{\mathrm{ROH}}\gamma_{\mathrm{Br_2}}$ remained constant as the alcohol concentration changed. It has been demonstrated[6b] that concentration equilibrium constants for the formation of the *t*-butyl alcohol–iodine complex in cyclohexane solution do not vary as the alcohol concentration of the solutions increases from 0.065–1 *M*. Since it is likely that *t*-amyl alcohol solutions in non-polar solvents should show smaller deviations from dilute solution laws than should *t*-butyl alcohol solutions, it seems reasonable to assume that the activity coefficient ratio mentioned above is the same for solutions which do not exceed 1.52 *M* in alcohol concentration (runs 4–14). It does, however, seem doubtful whether data taken on 4.57 *M* alcohol solutions should be compared with those taken in more dilute solutions. Actually the data for runs 1–3 were not considered in drawing the straight line in Fig. 2.

In order that equation (7) apply to the data it must also be true that k' does not vary with changing alcohol concentration of the solutions. Since the data of runs 4–14 do fit equation (7), one may conclude that the activity coefficient ratio $\gamma_{A^*}/\gamma_{\mathrm{ROH{\cdot}Br_2}}\gamma_{\mathrm{ROH}}$ remains constant over an alcohol concentration range of 0.0458–1.52 *M* (A* represents the activated complex in reaction (3)). It is possible that for these solutions $\gamma_{A^*}/\gamma_{\mathrm{ROH{\cdot}Br_2}}$ remains constant and that the critical factor which determines the constancy of k' values is the constancy of γ_{ROH}. In the same way one may explain the observed constancy of the equilibrium constant K on the assumption that in the dilute alcohol solutions $\gamma_{\mathrm{ROHBr_2}}/\gamma_{\mathrm{Br_2}}$ is unaffected by changing alcohol concentration and that *t*-amyl alcohol obeys Henry's law. A similar argument may be applied to explain the constancy of the $k_2/(\mathrm{ROH})$ values discussed below over an alcohol concentration range of 0.09–0.76 *M*.

(8) Whitmore and co-workers,[9] infer that the rate of reaction of bromine with the pure alcohol increases at that point at which water first separates from the reaction mixture. V. I. Pansevich-Kolyada and N. A. Prilezhaev, *Zhur. Obshchei Khim.*, **21**, 517 (1951), report that the reaction in carbon disulfide as a solvent is very slow if the solvent is carefully dried.

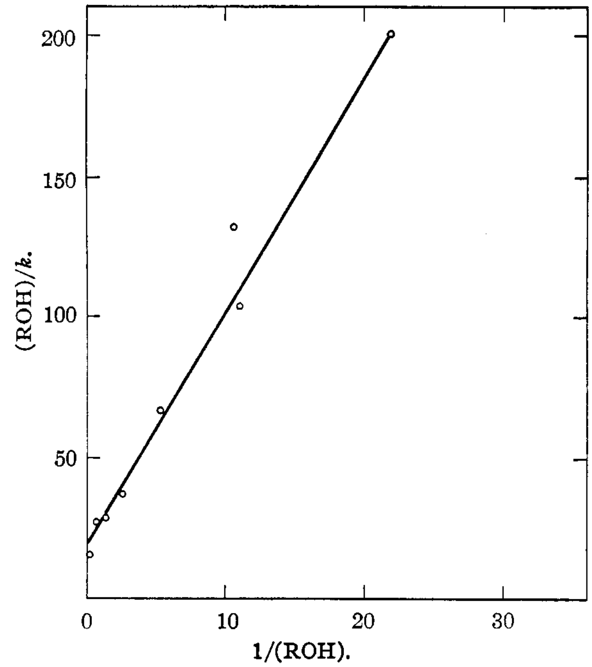


Fig. 2.—Evaluation of *k'* and *K*.

water added initially to exceed in concentration the total amount of water produced in the dehydration reaction. The rate constant for this run (run 15) was essentially the same as that for run 5. In no case were further kinetic measurements made on any run after separation of a water phase was observed. This situation was encountered only in a few of the runs which had proceeded nearly to completion.

The Loss of Oxidizing Power during the Reaction.—In a series of experiments designed originally to check the spectrophotometric method for determining the reaction rate, rate runs were made in which samples of the reacting solutions were analyzed iodometrically to determine their oxidizing power. It was observed that the oxidizing power of the solutions diminished less rapidly than did the intensity of bromine color. This lag in the rate of loss of oxidizing power was markedly apparent in runs at very high alcohol concentration (*e.g.*, run 3) and became less pronounced as the alcohol content of the solutions was diminished.

The possibility that the reaction leading to the disappearance of bromine color produced a colorless reducible intermediate which subsequently underwent decomposition to form trimethylethylene dibromide was considered as an explanation of these observations. With this explanation in mind several runs were made in which samples were removed simultaneously for analysis by both colorimetric and titration procedures. The results of one such run (run 18) are presented graphically in Fig. 3. Curve 1 based on the spectrophotometric measurements represents the percentage of the original bromine present in the solution as a function of time. Curve 2 based on the titration analyses represents the percentage of original bromine converted to non-reducible product as a function of time. **Curve 3 which represents the amount of colorless reducible intermediate (expressed as a** per cent. of the initial bromine concentration) as a function of time can be derived from the data of curves 1 and 2.

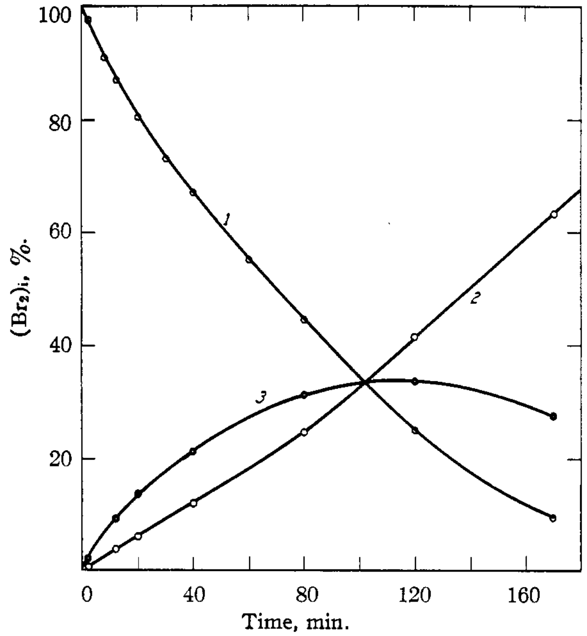


Fig. 3.—The change in concentration of bromine (1), reducible intermediate (3) and reaction product (2) as a function of time (run 18).

To interpret these results it was assumed that the rate of formation of the colorless intermediate, I, is related to the rate of disappearance of bromine color and the rate of formation of non-reducible product, P, by equation (8)

$$\frac{d(I)}{dt} = -\frac{d(Br_2)_T}{dt} - \frac{d(P)}{dt} \qquad (8)$$

and that trimethylethylene dibromide (P) is formed from the intermediate according to rate law (9).

$$\frac{d(P)}{dt} = k_2(I) \qquad (9)$$

If this interpretation is correct, it follows that the experimental data should fit equation (10)

$$k_2(I) = -\frac{d(Br_2)_T}{dt} = k(Br_2)_T \qquad (10)$$

at that point in the reaction at which the concentration of I reaches a maximum. Using the maximum value of (I), the corresponding value of $(Br_2)_T$ and the k value obtained through spectrophotometric measurement, one can calculate k_2. A series of runs, the results of which were interpreted by this procedure, are summarized in Table II.

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF THE INTERMEDIATE (25°)

Run	(ROH) mole/l.	$(Br_2)_T$ mole/l.	k, min.$^{-1}$	k_2, min.$^{-1}$	k_2/(ROH) min.$^{-1}$ mole^{-1} l.
16	0.762	0.0301	0.025	0.016	0.022
17	.762	.0151	.020	.017	
18	.381	.0301	.0095	.0073	.019
19	.191	.0151	.0035	.0038	.020
13	.0915	.0078	.00088	.0020	.022

The results of experiments 16 and 17 indicate that k_2 values are independent of the initial bromine concentrations of the solutions. However, values of k_2 are directly dependent on the alcohol concentration of the solutions over a wide concentration range, as may be seen by inspection of the right-hand column of Table II. This fact suggests that the rate determining step in the formation of the final reaction product from the reducible intermediate involves an attack on the intermediate by an alcohol molecule.

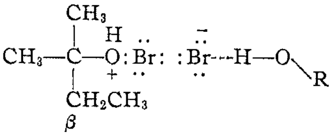
It is interesting to note that in a run at very low alcohol concentration (run 14) no appreciable tendency for accumulation of the colorless intermediate in the reaction mixture was observed experimentally. Using the k value for this run and the established value of $k_2/(\mathrm{ROH})$ one can calculate that at this low alcohol concentration the ratio of $(\mathrm{Br}_2)_\mathrm{T}/(\mathrm{I})$ should be of the order of magnitude of 5/1 when (I) reaches a maximum value.

The Reducible Intermediate.—The fact that the colorless intermediate can be titrated by iodometric methods suggests that it is a hypohalite.[9] Also there is some evidence that hypohalites function as intermediates in other halogen–alcohol reactions. The results of an extension[10] of the work of Bugarszky[11] on the kinetics of oxidation of ethanol by bromine in aqueous solution strongly suggest that ethyl hypobromite and hydrogen bromide are formed as products of the rate determining step. Under these conditions the hypobromite is presumed to be unstable with respect to decomposition to form acetaldehyde and hydrogen bromide.

There are, however, several reasons for concluding that *free t*-amyl hypobromite is not the colorless intermediate formed in the reaction of bromine with *t*-amyl alcohol. First of all, the intermediate accumulates to an appreciable degree in the reaction mixture. It would appear from the results of other work[12] that if equilibria are established in alcohol–bromine solutions with respect to alkyl hypobromite formation, the equilibrium concentration of the hypohalite must be very small. It should be noted, however, that this evidence is based on measurements in which a pure alcohol is used as the solvent. The kinetic data taken in the present investigation give no indication that an equilibrium situation exists with regard to the formation of *t*-amyl hypobromite and hydrogen bromide. Furthermore it does not seem reasonable that the decomposition of *t*-amyl hypobromite to yield trimethylethylene dibromide should proceed independently of any hydrogen bromide present in the reaction system. Yet kinetically the final reaction product is formed by a reaction the rate of which is dependent on the concentration of intermediate to the first power, rather than to the second power as would be required if both a free hypobromite and free hydrogen bromide took part in the reaction.

There is no evidence which suggests that in these solutions an alkyl hypobromite is present which is decomposing to a large degree by some process which does not require the consumption of hydrogen bromide. One of the runs at high alcohol concentration (run 3) was repeated and allowed to proceed until the bromine color had disappeared completely from the solution. The reaction product was then analyzed for hydrogen bromide by titration with sodium hydroxide solution. While no accurate estimate of the acid concentration of the solution could be made because of the tendency for trimethylethylene dibromide to consume sodium hydroxide, it was evident that hydrogen bromide was not a major reaction product. In addition it was demonstrated that trimethylethylene dibromide was formed in appreciable amount by the reaction of *t*-amyl alcohol with bromine at high dilution in carbon tetrachloride.[13]

The experimental evidence provides no clear picture of the structural nature of the colorless intermediate. Since the results of the kinetic studies indicate that this intermediate is formed through the reaction of the alcohol–bromine complex with a second molecule of alcohol (ROH), a formulation of its structure as the ion pair



seems worthy of consideration. This description of the structure, in which the bromine–bromine bond is severed through solvation of bromide ion by ROH, is consistent with the fact that the intermediate appears to be colorless. One may speculate further that the breakdown of the intermediate to form olefin, is initiated by the attack of an alcohol molecule on a hydrogen at the beta carbon of the ion pair. This mechanism is in keeping with the observed kinetics of the decomposition of the intermediate.[14] There is not sufficient experimental

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[9] F. D. Chattaway and O. G. Backeburg, *J. Chem. Soc.*, **123**, 2999 (1923).

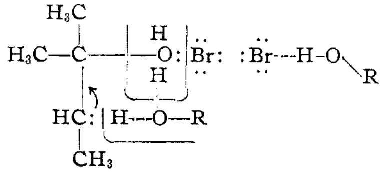
[10] L. Farkas, B. Perlmutter and O. Schächter, THIS JOURNAL, **71**, 2829 (1949).

[11] S. Bugarszky, *Z. physik. Chem.*, **38**, 561 (1901); **42**, 545 (1903).

[12] P. D. Bartlett and D. S. Tarbell, THIS JOURNAL, **58**, 466 (1936).

[13] There is also no evidence that free hydrogen bromide produced simultaneously with a free alkyl hypobromite catalyzes dehydration of the alcohol and indirectly the formation of trimethylethylene dibromide. If this were the case, one should anticipate that, because of rapid accumulation of reducible intermediate and hydrogen bromide at the outset of the reaction, the first-order rate constants for disappearance of bromine color should increase with time even in the initial phases of the reaction. It is possible that the gradual accumulation of small amounts of free hydrogen bromide in the solutions, possibly from side reactions, may account for the increase in rate constants, k, observed toward completion of some of the runs. It should be noted that H. S. Davis, THIS JOURNAL, **50**, 2769 (1928), has reported the formation of some hydrogen bromide during the bromination of trimethylethylene in carbon tetrachloride.

[14] It is possible that the transition state intermediate for the reaction in which ROH attacks the ion pair at the beta carbon is cyclic in nature and that its decomposition to form olefin, bromine and water occurs by a process in which the critical bond ruptures are as indicated below. A similar picture of the transition state intermediate has been



suggested for the reaction of the isopropyl iodide–iodine monochloride complex with iodine monochloride in carbon tetrachloride to form propylene chloroiodide (R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953)).

evidence to substantiate any predictions concerning the details of this breakdown process.

Experimental

***t*-Amyl Alcohol.**—The *t*-amyl alcohol (Eastman Kodak Co.) was dried over potassium carbonate and then fractionated using a four-foot helix packed column. A cut of b.p. 100.9–101.0° (760 mm.) was retained for use in the kinetic experiments.

Kinetic Experiments.—Dilute solutions of bromine (Mallinckrodt Reagent grade) in carbon tetrachloride (Eastman Kodak Co., white label) were prepared at 25° and standardized iodometrically. For the rate studies samples of the bromine solutions were mixed with known amounts of *t*-amyl alcohol, and the resultant solutions were stored in the constant temperature bath at 25°. Samples of these solutions were removed from time to time for analysis by spectrophotometric or volumetric methods.

In the spectrophotometric procedure the samples were transferred to 1-cm. absorption cells for optical density measurements against a carbon tetrachloride blank. In general the wave length at which readings were made in any given run was chosen so that initial optical density readings were less than 1.0 and greater than 0.30. The rate constants based on data obtained in following an individual run by making a series of measurements at two different wave lengths were closely similar. For the fast runs (1–10) there was not sufficient time to take fresh samples for each optical density determination. In these runs the optical measurements were made using a single sample kept in the 1-cm. cell which in turn was stored at 25° within the cell housing of the spectrophotometer.

In the volumetric analytical procedure samples of known volume were removed and added to aqueous potassium iodide. The resultant mixture was then titrated with standard sodium thiosulfate solution.

Test for Hydrogen Bromide in the Reaction Products.—To 3 cc. of *t*-amyl alcohol was added 3 cc. of 0.38 *M* bromine in carbon tetrachloride and the resultant solution (*cf.* run 3) was allowed to decolorize completely. A few drops of phenolphthalein were added, and the solution was titrated with 0.1 *N* sodium hydroxide. Addition of several drops of base caused a temporary pink coloration which faded when the mixture was shaken vigorously. Further additions of base caused a similar behavior. A suspension of trimethylethylene dibromide in water responded in a similar fashion to titration with sodium hydroxide. Results of these experiments would indicate that little or no hydrogen bromide was present in the reaction medium after the bromine had been decolorized.

The Reaction of *t*-Amyl Alcohol with Bromine in Carbon Tetrachloride Solution.—Ten cc. of *t*-amyl alcohol (0.091 mole) was added to a solution of 14.5 g. of bromine (0.091 mole) in 220 cc. of carbon tetrachloride. The resulting solution was allowed to stand in diffuse light at room temperature. Separation of a water phase became noticeable within one-half hour. Two days later the bromine color had disappeared entirely. The reaction mixture was then washed with aqueous sodium bicarbonate and dried over calcium chloride. The carbon tetrachloride was removed under reduced pressure, and the residue was distilled from a modified Claisen flask. Five and one-half grams of trimethylethylene dibromide ((b.p. 100–103°) (101 mm.) and n^{27}_{D} 1.5070)[15] was collected. About 3 g. of lachrymatory residue which underwent decomposition on further attempts at distillation remained in the distilling flask. This residue probably contained a substantial quantity of the dibromide.

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

DAVIS, CALIFORNIA

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Equilibrium Constants for the Interaction of Halogens with Alcohols and Ethers

BY R. M. KEEFER AND L. J. ANDREWS

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The visible absorption of iodine in cyclohexane or carbon tetrachloride solutions is markedly altered by the addition to the solutions of small amounts of isopropyl, *t*-butyl or *t*-amyl alcohol or *n*-butyl ether. These changes are explained on the assumption that 1:1 halogen–alcohol or ether complexes are formed in these solutions. Spectrophotometric methods have been used to evaluate the equilibrium constants for the interaction of iodine with certain of these oxygenated substances in cyclohexane or carbon tetrachloride at 25°. Data on the interaction of bromine with *t*-butyl alcohol are also presented. Solutions of widely varying alcohol concentration were used in the studies of the *t*-butyl alcohol–iodine complex in cyclohexane. The results have been examined to determine the range of alcohol concentration over which the equilibrium constants for complex formation remain constant.

The results of a kinetic study of the reaction of *t*-amyl alcohol with bromine to form trimethylethylene dibromide in carbon tetrachloride solution indicate that a 1:1 alcohol–bromine complex is formed as a reaction intermediate.[1] From the kinetic data, obtained for the most part by measurements on solutions in which the *t*-amyl alcohol concentration was 1 *M* or less, it was calculated that the value of the concentration equilibrium constant K_c, as defined by equation (1), was 2.2 mole^{-1} l. at 25°.

$$K_c = (\mathrm{ROH{\cdot}X_2})/(\mathrm{ROH})(\mathrm{X_2}) \qquad (1)$$

It has seemed desirable to check the magnitude of this constant by direct determination of the concentration of the complex in the alcohol–bromine solutions. Unfortunately the reaction of *t*-amyl alcohol to form trimethylethylene dibromide occurs too rapidly to permit such a determination. However dilute carbon tetrachloride solutions of bromine in *t*-butyl alcohol and of iodine in *t*-amyl alcohol are relatively stable. Equilibrium constants for halogen–alcohol complex formation in these solutions have therefore been determined on the assumption that in order of magnitude they should be comparable with the equilibrium constant for the interaction of *t*-amyl alcohol with bromine.

The constants reported in this communication have been evaluated through studies of the visible absorption of the solutions using procedures similar to those previously employed to study complex formation of iodine with alcohols and ethers[2] and with dioxane[3] in inert solvents. This method is feasible since the visible absorption maxima of the complexes lie further toward the ultraviolet than do those of the free halogens. With bromine

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[1] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **75**, 3557 (1953).

[2] J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).

[3] J. A. A. Ketelaar, C. van de Stolpe and H. R. Gersmann, *Rec. trav. chim.*, **70**, 499 (1951).