ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Kinetics and Mechanism of the Gallium Bromide Catalyzed Alkylation of Aromatics with Ethyl Bromide[1,2]

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A kinetic study of the gallium bromide catalyzed alkylation of benzene and toluene with ethyl bromide has been made. The reaction follows zero-order kinetics in benzene or toluene as solvent. It is zero order with respect to ethyl bromide and second order with respect to gallium bromide. Toluene reacts 2.47 times more rapidly than benzene, suggesting that the aromatic is involved in the rate-determining step of the reaction mechanism. The energy of activation for the ethylation of benzene is 12.4 kcal. mole^{-1} and the entropy of activation is -22.6 cal. mole^{-1} deg.$^{-1}$. The observations are consistent with a rate-determining reaction of the aromatic with two 1:1 ethyl bromide–gallium bromide addition compounds (equation 6). It appears, therefore, that in contrast to aluminum bromide where the 1:1 complex, $C_2H_5Br:AlBr_3$, appears to react rapidly with benzene and toluene, the weaker catalyst, gallium bromide, requires a second mole of catalyst to facilitate the transfer of the alkyl group from the bromide to the aromatic nucleus.

The kinetic study of the aluminum chloride catalyzed reaction of several substituted benzyl halides with various aromatic hydrocarbons in nitrobenzene solution revealed that the reaction is third order, first order in each of the three reactants: the aromatic, the benzyl halide and the aluminum chloride.[4] As the aromatic component is involved in the rate-determining step and the reaction is relatively insensitive to changes in the polarity of the solvent, it appears that the alkylation cannot proceed through a rate-determining ionization of the benzyl halide to carbonium ions. The observations are more consistent with a mechanism involving a nucleophilic attack of the aromatic component on a benzyl chloride–aluminum chloride addition compound. It was proposed that similar displacement reactions are important in Friedel–Crafts alkylations with primary halides. This interpretation provides a reasonable explanation for the relatively large amounts of *n*-alkylbenzenes which have been noted in alkylations utilizing *n*-alkyl halides.[5]

Study of the kinetics and mechanism of the aluminum bromide catalyzed reaction of methyl and ethyl bromide with benzene and toluene in 1,2,4-trichlorobenzene solution provided additional evidence for participation of the aromatic in the rate-determining step.[6] The marked increase in rate with increasing branching of the alkyl bromide (methyl < ethyl < isopropyl) suggests that the carbon-to-bromine bond must be strongly polarized in the transition state. Presumably, with increasing ability of the alkyl group to tolerate a positive charge, the mechanism may alter to one which is based on free carbonium ions and does not involve the aromatic in the rate-determining step.

Unfortunately, we were unable to extend our rate study of the aluminum bromide catalyzed alkylation of aromatics from methyl and ethyl bromides to isopropyl and *t*-butyl bromides. The latter reactions are far too fast for a kinetic study. Moreover, isopropyl and *t*-butyl aromatics are highly susceptible to isomerization and disproportionation under the influence of aluminum bromide.[7] Consequently, it appeared desirable to search for a milder catalyst which might permit a kinetic study of the entire series of alkyl bromides (methyl, ethyl, isopropyl and *t*-butyl) and which would avoid the undesirable side reactions characteristic of the aluminum bromide reaction.

The gallium bromide–alkyl bromide–aromatic solvent system proved to be free of these objectionable side reactions, with no significant isomerization or disproportionation observed under conditions suitable for the alkylation reaction. The reaction offered considerable promise for the objectives of the present investigation and a detailed study of the kinetics and mechanism of the gallium bromide catalyzed reaction of ethyl bromide with benzene and toluene was therefore undertaken.

Results

The gallium bromide catalyzed reaction of ethyl bromide with benzene (in benzene as solvent) proceeds at a rate which is convenient for a kinetic study and major attention was directed to this reaction. Small catalytic quantities of the metal halide were used. The reaction is homogeneous up to 50–80% reaction[8] and the rate of reaction was followed by determining the amount of hydrogen bromide liberated. A linear relationship was obtained when the concentration of ethyl bromide was plotted *versus* time, corresponding to a pseudo zero-order reaction. A series of kinetic runs was made to determine the effect, if any, of the initial concentration of ethyl bromide. With initial ethyl bromide concentrations of 0.212 and 0.423 *M*, the observed rate constants were the same, within experimental error. When the initial concentration was

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[1] The Catalytic Halides. XVIII.

[2] Based upon a thesis submitted by Charles R. Smoot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Standard Oil Co. (Indiana) Fellow at Purdue University, 1952–1954.

[4] H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953).

[5] (a) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); (b) H. Gilman and R. N. Meals, *ibid.*, **8**, 126 (1943); (c) D. V. Nightingale and J. M. Shackelford, THIS JOURNAL, **76**, 5767 (1954).

[6] H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

[7] (a) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579, 5583 (1955); (b) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

[8] At higher catalyst concentrations a second layer formed after 50–80% reaction and the rate was sharply inhibited. This difficulty was avoided by using lower catalyst concentrations and following the rate only over the first 50–70% reaction. This phenomenon is similar to that reported in a previous study (ref. 6).

increased to 0.846 *M*, a small decrease (19%) in rate was observed.[9]

The reaction is pseudo zero order, so the catalyst concentration must remain unchanged during the reaction. The zero-order rate constants, however, increase rapidly with increasing catalyst concentration. Therefore, the order of the reaction with respect to gallium bromide was established by measuring the rates of reaction at a series of different gallium bromide concentrations. The data are shown in Table I. The values for k_0 were obtained graphically from plots of the ethyl bromide concentration *versus* time. The values of k_1 were obtained by dividing k_0 by the catalyst concentration, and values of k_2 were obtained by dividing k_0 by the square of the catalyst concentration. The calculated first-order rate "constants" decreased with decreasing catalyst concentration. The relative constancy of k_2 values indicates that the reaction is second order with respect to gallium bromide. The reaction kinetics do not permit a decision as to whether the second-order term is $[GaBr_3]^2$ or $[Ga_2Br_6]^2$. In view of the fact that such metal halides are monomeric in alkyl halide solution, we have treated the data on the basis of the assumption that we are dealing with the monomeric species, $GaBr_3$, in the reaction mixture.

The average values of k_2, second-order rate constants, for the gallium bromide catalyzed reaction of ethyl bromide with benzene are 4.52, 9.55 and 25.5 l. mole^{-1} min.$^{-1}$ at 15, 25 and 40°, respectively. From these values the energy of activation and log *PZ* term were calculated from the Arrhenius equation to be 12.4 kcal. mole^{-1} and 10.13. Using the equation of Cagle and Eyring,[10] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated to be 11.8 kcal. mole^{-1} and -22.6 cal. mole^{-1} deg.$^{-1}$ for the reaction.

TABLE I

RATE CONSTANTS FOR THE REACTION OF ETHYL BROMIDE WITH BENZENE UNDER THE INFLUENCE OF GALLIUM BROMIDE

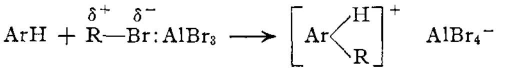
Init. concn., mole/l. C_2H_5Br	Init. concn., mole/l. $GaBr_3$[a]	Temp., °C.	Rate constants 10^4k_0[b]	Rate constants k_1[c]	Rate constants k_2[d]
0.211	0.0301	25	84.8		9.43
.423	.0301	25	86.1		9.51
.846	.0301	25	69.5		7.73
.411	.0423[e]	25	173	0.409	9.69
.411	.0463[e]	25	198	.428	9.30
.407	.0370[e]	25	132	.358	9.70
.410	.0243	25	55.3	.232	9.55
.410	.0161	25	20.2	.126	7.82
.410	.0121	25	13.0	.103	8.90
.412	.0236	15	25.2		4.53
.432	.0340	15	54.0		4.51
.399	.0228	40	127		24.4
.422	.0330	40	301		26.5

[a] "Effective" catalyst concentration unless otherwise noted. See Experimental Part. [b] Mole l.$^{-1}$ min.$^{-1}$. [c] Min.$^{-1}$. [d] L. mole^{-1} min.$^{-1}$. [e] Actual catalyst concentrations as determined by the weight of gallium bromide added.

The reaction of ethyl bromide in toluene was studied in order to determine the effect of the aromatic on the rate of reaction. The value of k_2 for the reaction in toluene at 25° is 23.5 l. mole^{-1} min.$^{-1}$. Therefore, the reaction of toluene is 2.47 times faster than that of benzene.

Discussion

The aluminum bromide catalyzed reaction of ethyl bromide with benzene or toluene in 1,2,4-trichlorobenzene solution is first order in the aromatic, in the ethyl bromide and in the metal halide (either $AlBr_3$ or Al_2Br_6).[6] Toluene reacts 2.89 times faster than benzene. Since the aromatic is involved in the rate expression, the reaction cannot proceed through a rate-determining ionization of the alkyl bromide, followed by a fast attack of the carbonium ion on the aromatic. Instead, it is considered that the reaction probably proceeds either through an attack of the aromatic upon a polarized ethyl bromide–aluminum bromide addition compound (1) or through an attack of the aromatic upon an ion-pair (1′).[11]



$$ArH + \overset{\delta^+}{R}—\overset{\delta^-}{Br}:AlBr_3 \longrightarrow \left[Ar\begin{smallmatrix}H\\R\end{smallmatrix}\right]^+ AlBr_4^- \quad (1)$$

$$ArH + R^+AlBr_4^- \longrightarrow \left[Ar\begin{smallmatrix}H\\R\end{smallmatrix}\right]^+ AlBr_4^- \quad (1')$$

The gallium bromide catalyzed reaction, as investigated in the present paper, is zero order with respect to ethyl bromide, and second order with respect to gallium bromide. Since the aromatic was used as the reaction medium, the order with respect to this component could not be determined. However, it was observed that toluene reacts at a rate 2.47 times faster than benzene. Since this relative rate is similar to that observed in the aluminum bromide catalyzed reaction, it appears reasonable to assume that the aromatic is also involved in the rate-determining stage of the gallium bromide catalyzed reaction.[12]

We are, therefore, faced with the problem of interpreting the unusual kinetics of the gallium bromide catalyzed reaction and in accounting for the remarkable differences in the aluminum bromide and gallium bromide catalyzed reactions.

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[9] It is not established that the decrease is significant. It could be due to a solvent effect arising from the high concentration of ethyl bromide (solution approximately 15% ethyl bromide by weight) or to the presence of minute amounts of impurities in the alkyl bromide which would deactivate a portion of the small amount of the catalyst used.

[10] F. W. Cagle and H. Eyring, THIS JOURNAL, **73**, 5628 (1951).

[11] It was pointed out that there does not appear to be any experimental basis at present for deciding between these two alternative formulations. Moreover, a careful consideration of the problem suggests that the decision between these two alternatives may become predominantly a matter of defining at what stage the polarized species is more conveniently considered to be an ion-pair.

[12] It is necessary to consider the possibility that the difference in the rates of ethylation of benzene and toluene is due to a solvent effect. In the aluminum chloride catalyzed reactions of benzyl chlorides with aromatics in nitrobenzene solution, the addition of a nonpolar solvent, such as methylcyclohexane, results in a mild retardation in rate (ref. 4). The solvent properties of toluene and benzene are quite similar. From one point of view, toluene may be considered equivalent to benzene diluted slightly with a paraffin hydrocarbon. Consequently, no major change in rate would be anticipated from a purely solvent effect, and any such effect would be expected to result in a *decrease* with toluene rather than in an *increase*, as observed. Finally our success in correlating the observed relative rates with the isomer distribution also argues strongly in favor of the view that the observed ratio is due to the differences in reactivity of the two hydrocarbons.

The interactions of gallium bromide with alkyl bromides have not yet been studied. However, the interactions of gallium chloride with alkyl chlorides have been the subject of an intensive examination.[13] In view of the similarity of the systems, it appears reasonable to apply the results to the related gallium bromide–alkyl bromide systems.

Gallium chloride dissolves in methyl chloride to form a 1:1 addition compound in solution, $CH_3Cl:GaCl_3$. This product can be isolated as a crystalline solid. As methyl chloride is removed, a new crystalline phase, the 1:2 addition compound, $CH_3Cl:Ga_2Cl_6$, can be isolated. From the variation in the dissociation pressures with temperature, the $Cl:Ga_2Cl_6$, can be isolated. From the variation in the dissociation pressures with temperature, the heats of dissociation of the following reactions may be calculated.[14]

$$2CH_3Cl:GaCl_3(s) \rightleftarrows CH_3Cl:Ga_2Cl_6(s) + CH_3Cl(g) \qquad \Delta H = 7.1 \text{ kcal.} \quad (2)$$

$$CH_3Cl:Ga_2Cl_6(s) \rightleftarrows Ga_2Cl_6(s) + CH_3Cl(g) \qquad \Delta H = 8.1 \quad (3)$$

$$2CH_3Cl:GaCl_3(s) \rightleftarrows Ga_2Cl_6(s) + 2CH_3Cl(g) \qquad \Delta H = 15.2 \quad (4)$$

From (4) it can be seen that the 1:1 methyl chloride–gallium chloride addition compound is quite stable.

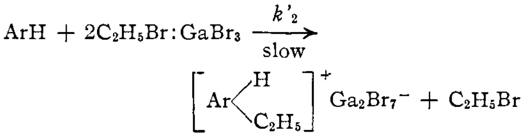
It appears quite reasonable that gallium bromide should form a similar 1:1 complex with ethyl bromide.[15] Since the present reaction mixtures contain a small quantity of gallium bromide in the presence of a large excess of ethyl bromide, it appears likely that the gallium bromide will be present primarily as the 1:1 complex, $C_2H_5Br:GaBr_3$.

The reaction of the aromatic with the polarized 1:1 complex in the rate-determining stage would result in the kinetics being first order in the metal halide. We must conclude that in the 1:1 complex, $C_2H_5Br:GaBr_3$, the relatively weak catalyst gallium bromide fails to provide a sufficient pull on the halogen to transfer the alkyl group to the aromatic.

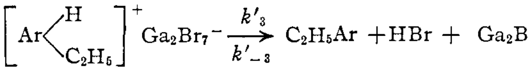
Considerable evidence now exists that the addition complexes of dimeric aluminum bromide and gallium chloride are more stable than the corresponding compounds of the monomeric halides. Thus very weak bases such as benzene form complexes only with the dimeric form of aluminum bromide.[16] Similarly, the addition compound of methyl chloride with dimeric gallium chloride is more stable than the corresponding complex with monomeric gallium chloride.[13] On this basis the squared term in gallium bromide in the rate expression might arise from the need for an additional pull by a second gallium bromide molecule in order to transfer the ethyl group from the bromine atom to the aromatic.

The following mechanism appears to be consistent with the known facts.

$$2C_2H_5Br + Ga_2Br_6 \xrightarrow[k'_{-1}]{k'_1} 2C_2H_5Br:GaBr_3 \quad (5)$$



$$ArH + 2C_2H_5Br:GaBr_3 \xrightarrow[\text{slow}]{k'_2} \left[Ar\begin{matrix}H\\C_2H_5\end{matrix}\right]^+ Ga_2Br_7^- + C_2H_5Br \quad (6)$$



$$\left[Ar\begin{matrix}H\\C_2H_5\end{matrix}\right]^+ Ga_2Br_7^- \xrightarrow[k'_{-3}]{k'_3} C_2H_5Ar + HBr + Ga_2Br_6 \quad (7)$$

This mechanism leads to the kinetic expression

$$\frac{d[HBr]}{dt} = -\frac{d[C_2H_5Br]}{dt} = k'_2[ArH][C_2H_5Br:GaBr_3]^2 \quad (8)$$

In the present study the aromatic was used as the reaction medium and, consequently, its concentration does not appear in the experimental kinetics. Ethyl bromide was used in considerable excess over the gallium bromide used as catalyst. In view of the stability of the 1:1 methyl chloride–gallium chloride addition compounds and the monomeric molecular weight of gallium bromide in methyl bromide, it appears reasonable that the gallium bromide should be essentially completely converted into the 1:1 addition compound. That is to say, the equilibrium represented by equation 5 will lie far to the right. With sufficient ethyl bromide present to convert the gallium bromide into the 1:1 addition compound, the reaction rate will be essentially independent of the ethyl bromide concentration. The rate expression, therefore, reduces down to a zero-order relationship with the rate constant varying with the square of the initial gallium bromide concentration, in agreement with the experimental observations (Table I).

Intuitively, one hesitates to accept a termolecular step in a fast reaction of the present type and seeks an alternative interpretation. One possibly would involve a rate-determining ionization (9) followed

$$2RBr:GaBr_3 \xrightarrow{k'_2} R^+ + Ga_2Br_7^- + RBr \quad (9)$$

by a rapid reaction of the carbonium ion with the aromatic. However, the rate of such a reaction should be independent of the aromatic present, except for minor solvent effects. We believe the evidence is strongly in favor of the aromatic being involved in the rate-determining step,[12] arguing against this interpretation.

Another possibility involves an ionization into an ion-pair (10), followed by a rate-determining reaction of the aromatic with the ion-pair (11).

$$2RBr:GaBr_3 \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} R^+Ga_2Br_7^- + RBr \quad (10)$$

$$ArH + R^+Ga_2Br_7^- \xrightarrow{k'_2} \text{products} \quad (11)$$

This mechanism should lead to a kinetic expression of the form

$$\frac{d[HBr]}{dt} = -\frac{d[RBr]}{dt} = \frac{k'_1k'_2[ArH][RBr:GaBr_3]^2}{k'_{-1}\ [RBr]} \quad (12)$$

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[13] (a) H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953); (b) R. Wong and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).

[14] Corrected values (ref. 13b) are used.

[15] We have observed recently that gallium bromide is monomeric in methyl bromide solution, suggesting its existence as a 1:1 addition compound; work in progress with R. Wong and J. Byrne.

[16] H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6279 (1953).

A mechanism of this kind should exhibit a strong dependence upon the ethyl bromide concentration, contrary to the experimental results. The termolecular mechanism (5–7) appears to provide the most satisfactory interpretation which is consistent both with the kinetic observations and the present knowledge of metal halide–alkyl halide systems.[17]

A possible explanation for the difference in kinetics exhibited by the aluminum bromide and the gallium bromide catalyzed reactions exists in the great difference in the acid strengths of these two substances. The reaction of ethyl bromide with benzene and toluene in the presence of dissolved aluminum bromide is very fast, far too fast to measure.[18] The reaction rate could be reduced to measurable velocities only by utilizing 1,2,4-trichlorobenzene as solvent.[6] (The solvent presumably coördinates with the aluminum bromide and reduces its effective concentration.)

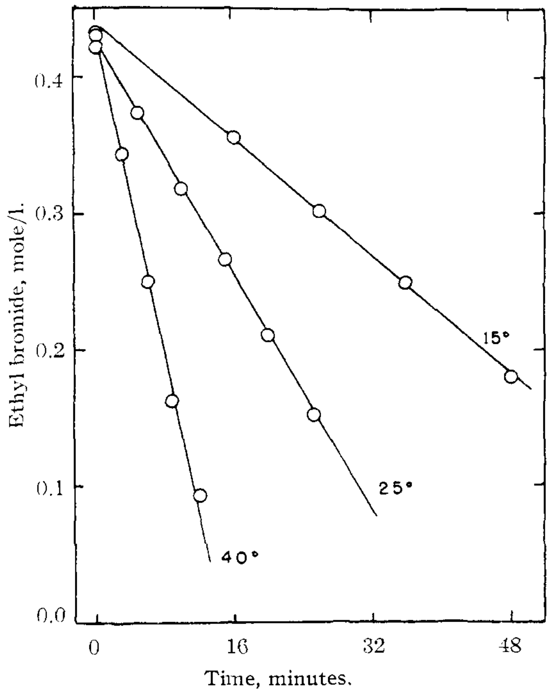

Fig. 1.—Rate data for the gallium bromide catalyzed reaction of ethyl bromide with benzene at 15, 25 and 40°.

In this system also the ethyl bromide presumably exists largely as the 1:1 complex ($C_2H_5Br:AlBr_3$). However, in view of the much stronger coördinating properties of aluminum bromide, it is not unreasonable that the 1:1 aluminum bromide complex should be sufficiently reactive so as to provide the preferred reaction path for the alkylation step.

In other words, the coördinating powers of monomeric aluminum bromide are sufficiently great as to make possible a rapid transfer of the ethyl group from the 1:1 compound ($C_2H_5Br:AlBr_3$), whereas gallium bromide requires the assistance of a second molecule to bring about a similar reaction.

The mechanism proposed for the gallium bromide catalyzed reaction appears to be consistent with the experimental observations. However, a more rigorous test would involve kinetics in an inert solvent which would permit a determination of the reaction order with respect to the aromatic as well as with respect to the alkyl bromide and gallium bromide. We hope to undertake a study of this kind.

Experimental Part

Materials.—Benzene and toluene used in this kinetic study were rectified with an adiabatic column packed with $^1/_{16}''$ steel helices which had been rated at 50 theoretical plates. A high reflux ratio was used and large center cuts were reserved for the kinetic study. The following physical properties were noted: benzene (thiophene free grade) b.p. 80.1° at 740 mm., n^{20}D 1.5008; toluene (reagent grade) 110.2° at 740 mm., n^{20}D 1.4963. The aromatic hydrocarbons were stored over calcium hydride until used in order to ensure complete dryness. Ethyl bromide (Columbia Organic Chemicals) was washed with water to remove traces of alcohols, dried over calcium hydride and rectified with a column (40 theoretical plates) packed with $^1/_{16}''$ glass helices. It was then stored over calcium hydride in an amber bottle. The following physical properties were observed: b.p. 38.0° at 742 mm., n^{20}D 1.4329.

Gallium bromide for use as catalyst was prepared by the direct reaction of gallium metal and hydrogen bromide. In a typical preparation 6 g. of gallium metal was placed in a porcelain boat which was inserted into a 16-mm. glass tube, which had been previously constructed with a constriction so that the tube could be sealed after the reaction was complete. The tube with the gallium metal was placed in a tube furnace at 250° and dried hydrogen bromide was passed through until all the gallium had reacted. The gallium bromide sublimed out of the hot portion of the tube as it formed. The tube was then evacuated and sealed off. The gallium bromide was sublimed into 8-mm. glass side arms with breaker tips, which had been originally sealed to the larger tube. The small tubes were then sealed off under vacuum, each containing 6 to 8 g. of of pure, anhydrous gallium bromide. The yields were essentially quantitative with only minor losses during transfers. When needed, the large samples of gallium bromide were distributed into smaller tubes by vacuum transfer.

Procedure for Kinetic Measurement.—Approximately 0.4 M solutions of ethyl bromide in either benzene or toluene were prepared. Solutions of gallium bromide in the aromatic solvents were prepared in a specially constructed Pyrex volumetric flask. The gallium bromide was sublimed into the flask at reduced pressure and carefully dried benzene or toluene drawn into the flask. The net weight of gallium bromide added was determined by weighing the tube before and after transfer. The solutions were placed in the constant temperature bath at 25.00° and a rapid delivery, 2-ml. transfer pipet was used to transfer 2 ml. of each of two solutions into thin-walled glass capsules. The capsules were sealed immediately with a flame and placed in a constant temperature bath. After the desired

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[17] Note introduced in revision, Aug. 3, 1956; F. L. J. Sixma and H. Hendriks [*Rec. trav. chem.*, **75**, 129 (1956)] have recently examined the exchange of bromine in tagged ethyl bromide with aluminum bromide in carbon disulfide solution. They find that the rate of exchange is proportional to the square of the concentration of aluminum bromide. Since the present reaction also involves a squared term in the metal halide concentration, it may be that such squared terms are general for Friedel–Crafts catalyzed reactions in non-polar media.

N. N. Lebedev [*J. Gen. Chem.* (*U.S.S.R.*), **24**, 664 (1954)] has suggested that the conductivity exhibited by solutions of metal halides in alkyl halides is due to a species $(RCl)_2AlCl_2^+AlCl_4^-$. In a medium of low dielectric constant, such a species would exist as an ion-pair. The reaction (6) above might then proceed through such a species, as

$$2C_2H_5Br:GaBr_3 \rightleftarrows (C_2H_5Br)_2GaBr_2^+GaBr_4^- \quad (6')$$

$$ArH + (C_2H_5Br)_2GaBr_2^+GaBr_4^- \longrightarrow \left[Ar\begin{matrix}H\\C_2H_5\end{matrix}\right]^+ Ga_2Br_7^- + C_2H_5Br \quad (6'')$$

This mechanism would also satisfy the observed kinetics. Without further experimental data with respect to the interaction of metal halides with alkyl halides, it does not appear possible at this time to attempt to define more precisely the nature of the transition state responsible for the squared term in metal halide.

[18] H. C. Brown and H. Jungk, THIS JOURNAL, **78**, 2182 (1956).

reaction times, capsules were removed and placed in a 250-ml. wide-mouth erlenmeyer flask with 40–50 ml. of distilled water. The flask was stoppered and the capsules broken by rapid motion of the flask. After 6 ml. of potassium sodium tartrate solution (15% by weight) was introduced, the hydrogen bromide was titrated with 0.0550 N barium hydroxide solution, using phenolphthalein as the indicator.[19] The amount of base required to neutralize the hydrogen bromide due to the gallium bromide was determined by analyses of blanks, capsules to which no alkyl bromide was added. The hydrogen bromide due to the reaction was determined by difference. A typical kinetic run for the reaction of benzene is shown in Table II.

TABLE II

RATE DATA[a] FOR THE GALLIUM BROMIDE CATALYZED REACTION OF ETHYL BROMIDE WITH BENZENE AT 25°

Time, min.	Ethyl bromide reacted %	Ethyl bromide reacted Mole	Rate constants[b] 10^2k_0, mole l.$^{-1}$ min.$^{-1}$	Rate constants[b] k_2, l. mole^{-1} min.$^{-1}$
5.0	12.7	0.0536	1.07	9.48
10.0	25.7	.1085	1.08	9.57
15.0	38.2	.161	1.07	9.48
20.0	51.4	.217	1.08	9.57
25.3	65.4	.276	1.09	9.66
29.3	75.4	.318	1.08	9.57

[a] Initial concentrations: ethyl bromide, 0.422 M; gallium bromide, 0.0336 M. [b] The value of k_0 determined graphically was 1.08 × 10^{-2} mole l.$^{-1}$ min.$^{-1}$.

The rate data for the reaction of ethyl bromide at 15, 25 and 40° are shown in Fig. 1. The concentration of the catalyst for these runs was 0.0336 mole l.$^{-1}$. In some of the kinetic runs at 40° at higher catalyst concentrations, the data were less precise due to the rapidity of the reaction

The largest uncertainty in the calculation of k_2, however, was the concentration of the catalyst solutions. The concentrations of the gallium bromide solutions were of the order of 0.015 to 0.04 M. These dilute solutions were very sensitive to traces of moisture. The activities of the catalyst solutions were reproducible, *i.e.*, reproducible k_2 rate constants could be calculated from different, freshly prepared solutions, but the activities decreased on standing. Since it was not feasible to prepare a fresh catalyst solution for each kinetic run, an alternate method was used. An accurate second-order rate constant was determined from ethyl bromide at 25.0° by using several freshly prepared catalyst solutions. The reaction of ethyl bromide at 25° was, therefore, adopted as a standard reaction, and it was used to determine the "effective" catalyst concentration during any series of runs. Usually the "effective" concentration differed but little from the actual concentrations. With the aid of minor corrections afforded by this method, very good agreement was obtained between kinetic runs carried out with different catalyst solutions. This method proved of greatest value, however, during the study of the reactions of other alkyl halides as described in a subsequent paper.

Acknowledgment.—We wish to express our appreciation to the Standard Oil Co. (Indiana) for the fellowship grant which made this investigation possible. We also wish to acknowledge the helpful comments of the Referees with regard to the interpretation of the reaction kinetics.

LAFAYETTE, INDIANA

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[19] This method was developed by L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945), for determining hydrogen chloride in the presence of aluminum chloride. The method was adapted for the determination of hydrogen bromide in the presence of gallium bromide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Kinetics and Relative Rates of the Gallium Bromide Catalyzed Reactions of Alkyl Bromides with Aromatics[1,2]

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A kinetic study has been made of the reactions of a number of alkyl bromides with benzene and toluene under the influence of gallium bromide. Excess aromatic was utilized as the reaction medium. In the reaction of methyl, ethyl and *n*-propyl bromides with benzene, the relative rates of reaction are 1.00, 33 and 67, with the energies of activation being 12.5, 12.4 and 12.9 kcal. mole^{-1}, respectively. The entropies of activation for the same reactions are −29.3, −22.6 and −19.2 cal. mole^{-1} deg.$^{-1}$. With toluene the relative rates of reaction of methyl, ethyl, *n*-propyl, isopropyl and *t*-butyl bromides are 1.00, 13.7, 15.9, 3 × 10^5 and 8 × 10^5, respectively. The energies of activation of the reactions of methyl, ethyl and *n*-propyl bromides are 12.0, 12.0 and 11.8 kcal. mole^{-1} while the entropies of activation are −27.4, −22.2 and −22.7 cal. mole^{-1} deg.$^{-1}$, respectively. These data are interpreted as supporting evidence for a displacement mechanism in the Friedel-Crafts reaction of primary alkyl bromides, although the transition state may have considerable carbonium ion character. A gradual change in mechanism is postulated in which the carbonium ion character of the transition state increases with increasing branching of the alkyl group. With isopropyl and *t*-butyl bromides the carbonium ion character of the transition state dominates, and the data may best be interpreted by an ionization mechanism. In the reaction of *n*-propyl bromide with benzene there is formed 28% *n*- and 72% isopropylbenzene. The isopropylbenzene arises from a concurrent isomerization of the *n*-propyl bromide. With increasing basicity of the aromatic component, the isomerization reaction should become less important and the direct alkylation of *n*-propyl bromide should constitute an increasing proportion of the reaction. A kinetic analysis of the reaction with toluene is in agreement with this interpretation.

Evidence has been presented recently that the Friedel–Crafts reactions of aromatics with primary alkyl halides proceeds by an attack of the aromatic upon an alkyl halide–metal halide intermediate.[4] With increasing branching of the alkyl groups, the evidence favors a gradual change in mechanism and the reactions of isopropyl and *t*-butyl halides are believed to proceed *via* an ionization mechanism.

Such changes in mechanism have been studied extensively in other nucleophilic substitutions of alkyl halides.[5] It was originally proposed that such reactions fall into two distinct categories, termed by Ingold as SN1 for ionization and SN2 for displace-

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[1] The Catalytic Halides. XIX.

[2] Based on a thesis submitted by C. R. Smoot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953); (b) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956); (c) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6245 (1956).

[5] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.