

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 %	Ethyl bromide reacted Mole	Rate constants ^b	
			$10^2 k_0$, mole l. ⁻¹ min. ⁻¹	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.

(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.

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

[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}

BY CHARLES R. SMOOT³ AND HERBERT C. BROWN

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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

(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.

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

(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).

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 S_N1 for ionization and S_N2 for displace-

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

ment mechanisms. More recently, Winstein⁶ and Swain⁷ have proposed that such reactions do not fall into two distinct classes, but involve a continuous change in mechanism from the one limit of pure displacement, SN₂, to the other limit of pure ionization, SN₁. On this basis the Friedel-Crafts alkylation reaction would appear to be closely related to other substitution reactions of alkyl halides with the major difference being the relatively weak nucleophilic character of the displacing base and the strong electrophilic properties of the metal halide catalyst.

In spite of the importance of the Friedel-Crafts reaction, there have been very few kinetic studies.^{4,8} In particular, no kinetic study is now available for the complete series of alkyl halides methyl, ethyl, isopropyl and *t*-butyl. We originally attempted to carry out such a study with aluminum bromide as a catalyst, but encountered difficulties with side reactions, such as isomerization⁹ and disproportionation,¹⁰ particularly with the branched alkyl groups. In 1,2,4-trichlorobenzene these side reactions could be controlled and the rates of reaction of methyl and ethyl bromide with aromatics established.^{4b} However, isopropyl bromide reacted so rapidly that only a minimum value could be estimated.

In the preceding paper^{4c} evidence was presented that the gallium bromide catalyzed reaction is far more favorable for such a kinetic study. This reaction appeared to be free of the undesirable side reactions, and the reaction rates appeared to fall within a range that could be followed conveniently, even in the case of the more branched halides. Accordingly, a detailed study was undertaken of the rates of reaction of methyl, ethyl, *n*-propyl, isopropyl and *t*-butyl bromides with benzene and toluene under the influence of gallium bromide. In this paper the relative rates of reaction of these alkyl halides at 15, 25 and 40° are reported, along with the results on the energies and entropies of activation for the reactions.

Results

The kinetics of the reaction of ethyl bromide with benzene were established in detail in a previous paper.^{4c} In a similar manner pseudo zero order kinetics were observed in the kinetic studies with methyl and *n*-propyl bromides with benzene and toluene. The absolute and relative rates of reaction of methyl, ethyl and *n*-propyl bromide with benzene and toluene are shown in Table I. The values of k_2 in Table I are the average of two or three runs with different catalyst solutions in most cases. The values of k_2 for methyl, ethyl and *n*-propyl bromides were determined by a complete kinetic study. The reactions with isopropyl and *t*-butyl bromides, however, proved to be too rapid to follow in the same manner. Thus, the reactions of both isopropyl and *t*-butyl bromides with benzene and toluene were complete within experimental error 30 seconds after mixing. The values of k_2 for

the reactions of isopropyl and *t*-butyl bromides with toluene were estimated by the use of a flow apparatus.⁹ By the use of this flow apparatus, in which two solutions could be mixed and the reaction rapidly quenched, reaction periods as brief as 0.005 sec. were possible. Second-order rate constants were estimated for isopropyl and *t*-butyl bromides from the extent of reaction during a very short reaction time, assuming that pseudo zero-order kinetics were followed.

TABLE I
RATES^a OF REACTION OF ALKYL BROMIDES WITH BENZENE AND TOLUENE

Alkyl bromide RBr	Temp., °C.	Benzene		Toluene	
		Rate constant ^b k_2 , l. mole ⁻¹ min. ⁻¹	Rel. rate	Rate constant ^b k_2 , l. mole ⁻¹ min. ⁻¹	Rel. rate
Methyl	15	0.137 ± 0.006	1.00	0.86 ± 0.01	1.00
Ethyl	15	4.52 ± .02	33	11.5 ± .3	13.4
<i>n</i> -Propyl ^c	15	9.39	68	14.2 ± .1	16.5
Methyl	25	0.300 ± .002	1.00	1.71 ± .1	1.00
Ethyl	25	9.55 ± .16	32	23.5	13.7
<i>n</i> -Propyl ^c	25	20.0 ± .3	67	26.9 ± 2.2	15.7
Isopropyl	25			4.5 × 10 ⁵	3 × 10 ⁵
<i>t</i> -Butyl	25			14 × 10 ⁵	8 × 10 ⁵
Methyl	40	0.785 ± .028	1.00	4.60 ± 0.08	1.00
Ethyl	40	25.5 ± 1.1	33	61.2 ± 1.6	13.3
<i>n</i> -Propyl ^c	40			73	15.9

^a Initial concentrations: RBr, approximately 0.4 *M*; GaBr₃, 0.025 to 0.045 *M*. ^b Average of 2 or 3 values with different catalyst solutions. ^c Total rates of reaction, including both direct alkylation and isomerization. See discussion in text.

From the average values of k_2 as shown in Table I, energies of activation and log *PZ* terms were calculated from plots of log k_2 versus the reciprocal of the absolute temperature for the reactions of alkyl bromides with benzene and toluene. Values of ΔH^\ddagger and ΔS^\ddagger were also calculated according to the method of Cagle and Eyring¹¹ and the values obtained by these two methods are shown in Table II.

TABLE II
ENERGIES AND ENTROPIES OF ACTIVATION FOR REACTIONS OF ALKYL BROMIDES WITH BENZENE AND TOLUENE

Alkyl bromide	Aromatic	E_{act}^a	log <i>PZ</i> ^b	ΔH^\ddagger ^a	ΔS^\ddagger ^c
Methyl	Benzene	12.5	8.56	11.9	-29.3
Ethyl	Benzene	12.4	10.13	11.8	-22.6
<i>n</i> -Propyl	Benzene	12.9	10.76	12.4	-19.2
Methyl	Toluene	12.0	9.02	11.5	-27.4
Ethyl	Toluene	12.0	10.15	11.4	-22.2
<i>n</i> -Propyl	Toluene	11.8	10.08	11.2	-22.7

^a Kcal. mole⁻¹. ^b Calculated in terms of k_2 l. mole⁻¹ min.⁻¹. ^c Cal. mole⁻¹ deg.⁻¹.

The reaction of *n*-propyl bromide differs from that with methyl and ethyl bromide in that it can react by two different paths. The *n*-propyl bromide-gallium bromide addition compound can react with the aromatic directly, or the halide may first be isomerized to isopropyl bromide, which would then react with the aromatic. The rates reported in Table I are the total rates, calculated from the amount of hydrogen bromide liberated per unit time. Analysis of the product by infrared showed the presence of 28% *n*- and 72% isopropylbenzene. The product from the reaction with tolu-

(6) S. Winstein, E. Grunwald and H. W. Jones, *THIS JOURNAL*, **73**, 2700 (1951).

(7) C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).

(8) N. N. Lebedev, *J. Gen. Chem. (U.S.S.R.)*, **24**, 664 (1954).

(9) H. C. Brown and H. Jungk, *THIS JOURNAL*, **77**, 5579 (1955).

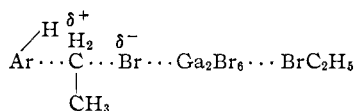
(10) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

(11) F. W. Cagle and H. Eyring, *ibid.*, **73**, 5628 (1951).

ene could not be analyzed conveniently by infrared since a mixture of six isomers is formed.

Discussion

The relative rates of reaction of methyl, ethyl and *n*-propyl bromides with benzene are 1.00, 32 and 67, and the rates with isopropyl and *t*-butyl bromides are much faster. Thus the order of reactivity is *t*-butyl > isopropyl > ethyl > methyl. It follows that the ability of the alkyl group to tolerate a positive charge in the transition state must be more important than its susceptibility to SN2 reactions. In other words, the bond breaking provided by the gallium bromide must be making a larger contribution to the transition state than the bond making by the aromatic.



The relative rates of reaction of methyl, ethyl and *n*-propyl bromides with toluene are 1.00, 13.7 and 15.7, much closer together than those observed in benzene (1.00, 32 and 67). This indicates that in the reaction with toluene the ability of the alkyl group to tolerate a partial positive charge is less important than in the corresponding reaction with benzene so that toluene, the more basic hydrocarbon,¹² must be contributing to the bond making process to a greater degree than benzene. This is consistent with a displacement mechanism. In an ionization mechanism, where the rate-determining step would be the formation of the carbonium ion, the relative rates of reaction of these alkyl halides would be expected to be the same, or nearly so, in both benzene and toluene.

Isopropyl and *t*-butyl bromides react about 10⁵ to 10⁶ times faster than the primary derivatives. Since branching of the alkyl group results in a decrease in rate in typical SN2 reactions, it appears that the transition state of the secondary and tertiary halides must be either largely or entirely ionic in character.

The energies of activation for the reactions of benzene with methyl, ethyl and *n*-propyl bromides are 12.5, 12.4 and 12.9 kcal. mole⁻¹, respectively. The differences in absolute rates are due primarily to differences in ΔS^\ddagger . Similarly, the values for the same reactions with toluene are 12.0, 12.0 and 11.8 kcal. mole⁻¹. The differences in rates between benzene and toluene arise primarily from the differences in the energies of activation, with similar values of ΔS^\ddagger observed for both aromatics (except for *n*-propyl bromide, discussed later).

The low values observed for the activation energies are also compatible with a displacement mechanism. Considerably higher values for the activation energy would be anticipated for an ionization process in non-polar media such as benzene and toluene.

This interpretation is supported by recent data of Sixma on the isomerization of ethyl-1-C¹⁴ bromide

(12) (a) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); (b) D. A. McCaulay and A. P. Lien, *This Journal*, **73**, 2013 (1951); (c) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

to ethyl-2-C¹⁴ bromide under the influence of aluminum bromide in carbon disulfide solution.¹³ The energy of activation for this reaction is 19.1 kcal./mole. Since aluminum bromide is a far more powerful catalyst than gallium bromide, the activation energy for the latter catalyst should be much larger.¹⁴ This compares with the activation energies of 12–13 kcal. mole⁻¹ observed for the alkylation reaction.

Some support for the proposed interpretation is provided by the entropies of activation. Thus, in unimolecular processes, such as ionization reactions, entropies of activation are usually near zero, while in typical second-order, or displacement processes, values of -20 to -30 cal. mole⁻¹ deg.⁻¹ are commonly observed. Many reactions now appear not to be strictly unimolecular or bimolecular, but concerted, with bond-making and bond-breaking of varying importance to the transition state.^{6,7} It may be expected that gradual changes in values of ΔS^\ddagger would be noted in such intermediate reactions. From this viewpoint, lower values of ΔS^\ddagger (more negative) would represent a stronger bond in the transition state between the atoms forming a new bond. The inverse should also be true. On this basis, a more negative value of the entropy of activation would indicate that the atom undergoing reaction requires a stronger contribution from the bond-making process. In the alkylation of both benzene and toluene the values for ΔS^\ddagger are about -28 cal. mole⁻¹ deg.⁻¹ for methylation and -22 cal. mole⁻¹ deg.⁻¹ for ethylation. These values correspond to those expected for a process involving bond-making by the aromatic in the transition state. The lower value for methylation may be rationalized on the basis that the methylation reaction proceeds with more displacement character, *i.e.*, requires a greater contribution from the aromatic in the transition state.

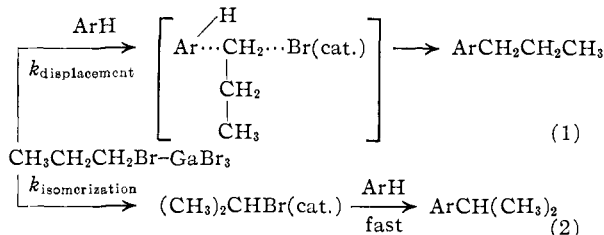
While values of ΔE_{act} and ΔS^\ddagger could not be determined for the reactions of isopropyl and *t*-butyl bromides, it is of interest to consider such values as would be consistent with the absolute rates. The reactions are 10⁵ to 10⁶ times faster than the corresponding reactions of primary alkyl bromides. If the differences in rate were attributed solely to differences in the energies of activation, it would require that the energies of activation for the reactions of isopropyl and *t*-butyl bromides be only 4 to 5 kcal. mole⁻¹. Such very low values for the energies of activation are somewhat unreasonable. If this conclusion is accepted, it follows that a large increase in the values of ΔS^\ddagger for these reactions must be responsible for the very large increase in rates. Thus, if these two reactions can be assumed to occur predominantly by ionization, with little or no participation of the aromatic, the values of ΔS^\ddagger should be approximately zero, and this would predict an increase in rate of approximately fifty thousand. This

(13) F. L. J. Sixma and H. Hendriks, *Proc. Koninkl. Ned. Acad. Wetenschap.*, **B59**, 61 (1956); F. L. J. Sixma, H. Hendriks and D. Holtzapffel, *Rec. trav. chim.*, **75**, 129 (1956); F. L. J. Sixma and H. Hendriks, *ibid.*, **75**, 169 (1956).

(14) In this discussion it is assumed that the isomerization reaction is proceeding through an ionization of the ethyl bromide-aluminum bromide complex. It is possible that the reaction does not involve an ionization. This would mean that the ionization path is a less favorable one and presumably involves an even higher activation energy.

factor alone could account for the greater part of the observed enormous increases in rate.

In the previous discussion of the reaction data for *n*-propyl bromide, the rates referred to were the total rates of reaction as measured by the rate of formation of hydrogen bromide. In this case, however, two concurrent reactions are possible for the *n*-propyl bromide-gallium bromide complex.



In (1) the *n*-propyl complex undergoes a nucleophilic attack by the aromatic, and the halide is alkylated without rearrangement of the alkyl group. In (2) the *n*-propyl complex isomerizes to the isopropyl complex, which subsequently reacts to yield the isopropyl derivative. The experimental rate constant for the total reaction is the sum of the rate constants for the displacement and isomerization reactions.

$$k_{\text{total}} = k_{\text{displ.}} + k_{\text{isom.}} \quad (3)$$

As k_{total} is known for benzene, it should be possible to determine both $k_{\text{displ.}}$ and $k_{\text{isom.}}$ from the ratio of *n*- to isopropylbenzene in the product. The isomer distribution in the reaction of *n*-propyl bromide with benzene was determined, under the same conditions in which the kinetics were measured, to be 28% *n*- and 72% isopropylbenzene. Since k_{total} is 20.0 l. mole⁻¹ min.⁻¹, $k_{\text{displ.}}$ and $k_{\text{isom.}}$ are 5.6 and 14.4 l. mole⁻¹ min.⁻¹, respectively.

The relative rates of reaction of methyl, ethyl and *n*-propyl bromides with benzene *via* a displacement reaction are, therefore, 1.00, 33 and 19. The decrease in rate in going from ethyl to *n*-propyl bromide is further evidence for a displacement mechanism. The electrical effects of the ethyl and *n*-propyl groups are very similar, but a decreased rate with *n*-propyl derivatives is usually observed in typical displacement reactions, presumably as a consequence of steric considerations. Thus, in a typical displacement reaction, that of the reaction of pyridine with ethyl and *n*-propyl iodides,¹⁵ the relative rates were found to be 1.00 to 0.39. These values are to be compared with 1.00 to 0.57 which were observed in this study of the relative rates of the displacement reaction of ethyl and *n*-propyl bromides with benzene.

From the rate of isomerization of the *n*-propyl bromide-gallium bromide addition compound in benzene, it is possible to calculate the rate of the displacement reaction with toluene. This calculation is based on the assumption that the rate of isomerization is not appreciably affected by the very slight change in solvent in going from benzene to toluene. From the value for toluene of k_{total} 26.9 l. mole⁻¹ min.⁻¹, and the value in benzene of $k_{\text{isom.}}$

(15) Unpublished work of K. Blackwood and N. Kornblum, Purdue University. The k_2 values of the reaction of pyridine with ethyl and *n*-propyl iodides in acetonitrile at 25° were 18.0×10^{-3} and 7.0×10^{-3} l. mole⁻¹ sec.⁻¹, respectively.

14.4 l. mole⁻¹ min.⁻¹, the value of $k_{\text{displ.}}$ may be calculated to be 12.5 l. mole⁻¹ min.⁻¹. The relative rates of reaction of methyl, ethyl and *n*-propyl bromides with toluene *via* a displacement reaction are, therefore, 1, 13.7 and 7.3. The relative rates of reaction of alkyl halides *via* a displacement with benzene and toluene are shown in Fig. 1. In both cases, a decrease in the rate is noted in going from ethyl to *n*-propyl bromide and the decrease is of the same order of magnitude as observed for other typical displacement reactions. The relative rate of the reaction of *n*-propyl bromide with benzene and toluene by displacement is 2.25, which is in good agreement with the value of 2.47 which was observed for the relative rate of reaction of ethyl bromide with these aromatics.

Some interesting predictions on the gallium bromide catalyzed reaction of *n*-propyl bromide with aromatic hydrocarbons can be made. Since two concurrent reactions occur, the ratio of the products is determined by the rate of displacement by an aromatic, relative to the rate of isomerization of the *n*-propyl bromide. As the rate of isomerization should be reasonably constant, the use of more basic hydrocarbons should increase the rate of the displacement reaction, and likewise the proportion of *n*-propyl derivative in the product. Conversely, the use of less basic aromatic hydrocarbons, such as chlorobenzene, should decrease the rate of displacement and lead to a higher proportion of the isopropyl derivative in the product.

If the partial rate factors for the reaction of *n*-propyl bromide *via* displacement are assumed to be the same as those observed for the reaction of ethyl bromide, then the ratio of the products can be calculated for more basic hydrocarbons, in the manner described in the Experimental Part. The rates for the more basic hydrocarbons are calculated by the method of Condon¹⁶ and Brown and McGary¹⁷ and the predicted values are shown in Table III. The agreement between the experimental and calculated values for benzene and toluene is quite satisfactory. Further study of the reaction with higher methylated benzenes is planned in order to check these predictions.

TABLE III

RATES^a OF REACTION OF *n*-PROPYL BROMIDE *via* DISPLACEMENT WITH HIGHER METHYLATED BENZENES

Aromatic	Rates of displacement	Total rate ^b	<i>n</i> -Propyl derivative, %	
			Calcd.	Found
Benzene	6	21.3	28.2	28 ^c
Toluene	14.8	30.1	49.2	47 ^d
<i>p</i> -Xylene	17.7	33.0	53.6	
<i>m</i> -Xylene	44.7	60.0	74.2	
Mesitylene	145	160	90.7	
Pentamethylbenzene	355	370	95.9	

^a Predicted values; see discussion in text. ^b Total of rate of displacement plus 15.3, the rate of isomerization. ^c Determined by infrared analysis. ^d Determined from the rate constants with benzene and toluene.

Experimental Part

Materials.—The purification and physical properties of benzene, toluene, ethyl bromide and gallium bromide were

(16) F. E. Condon, *THIS JOURNAL*, **70**, 1963 (1948).

(17) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).

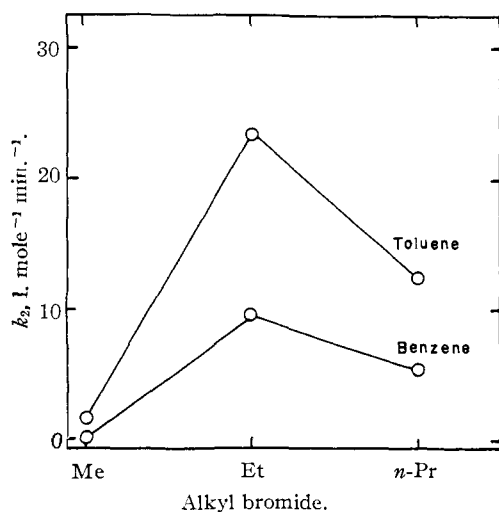


Fig. 1.—Rates of reaction of alkyl bromides with benzene and toluene *via* displacement.

described previously.⁴⁰ *n*-Propyl, isopropyl and *t*-butyl bromides were purified in a similar manner and the following physical properties noted: *n*-propyl bromide, b.p. 70.8° at 744 mm., n_D^{20} 1.4342; isopropyl bromide, b.p. 59.8° at 747 mm., n_D^{20} 1.4247; and *t*-butyl bromide, b.p. 73.4° at 744 mm., n_D^{20} 1.4278. Methyl bromide (Matheson Chemical) was condensed onto calcium hydride to ensure dryness, passed through a tube containing glass beads coated with phosphorus pentoxide and then added to the benzene or toluene solution.

Procedure for Kinetic Studies.—The details of the procedure for kinetic studies were described previously.⁴⁰ In all of these kinetic studies, the "effective" gallium bromide concentrations were determined by measuring the rate of a standard reaction. As the second-order rate constant for the reaction of ethyl bromide at 25° was known most accurately, it was used as a standard reaction to determine the "effective" activities or concentration of catalyst solutions. The rates of reaction of methyl, ethyl and *n*-propyl bromides with benzene at 25° are shown in Fig. 2. The "effective"

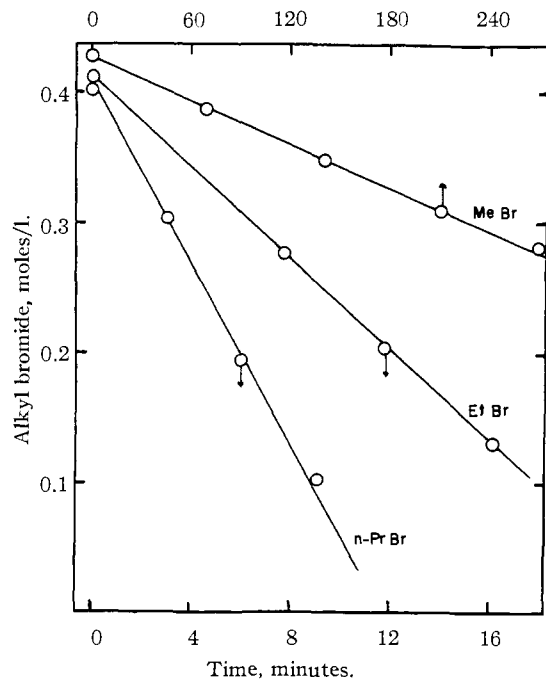


Fig. 2.—Rates of gallium bromide catalyzed reactions of alkyl bromides with benzene at 25°.

(and actual) catalyst concentration for this series of rates was 0.0423 mole/l. The rates of the same reactions with toluene are shown in Fig. 3 and the "effective" catalyst

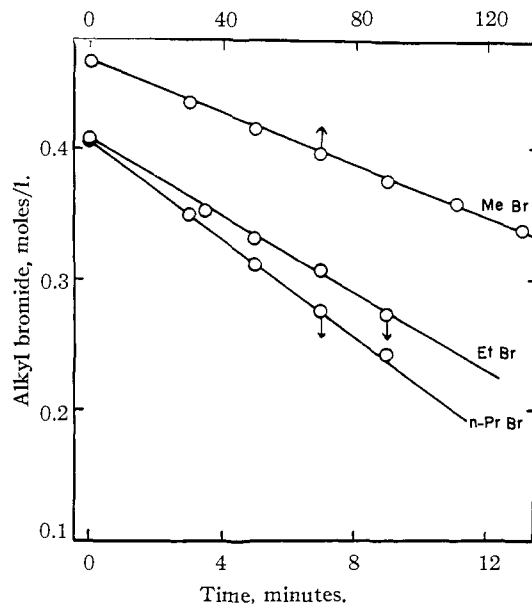


Fig. 3.—Rates of the gallium bromide catalyzed reactions of alkyl bromides with toluene at 25°.

concentration for this series was 0.0245 mole/l. The initial concentrations and rate constants for all runs are summarized in Tables IV and V. The energies of activation and $\log PZ$ terms were calculated from plots of $\log k_2$ versus the reciprocal of the absolute temperature. The data for the reactions of methyl, ethyl and *n*-propyl bromides with toluene are shown in Fig. 4. Similar data were obtained

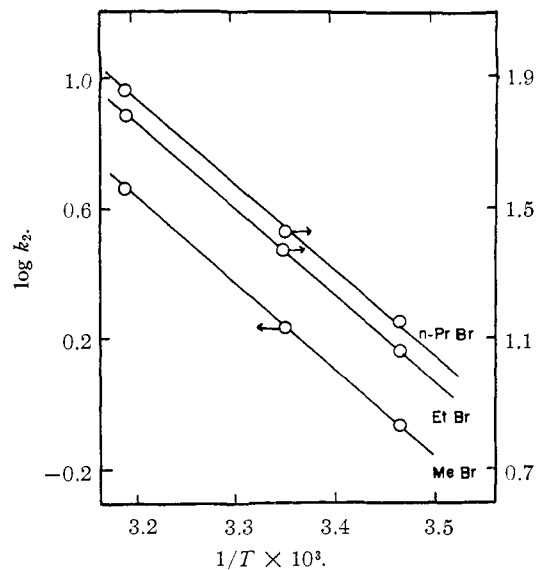


Fig. 4.—Variation of $\log k_2$ with temperature in the gallium bromide catalyzed reactions of alkyl bromides with toluene.

with benzene but are not shown. Values of ΔH^\ddagger and ΔS^\ddagger were obtained in a similar manner from plots of $\log k_2/\text{temp.}$ versus the reciprocal of the absolute temperature. The slopes of the lines and the intercepts were determined in every case by the method of least squares.

Estimation of Rate Constants for the Reactions of Isopropyl and *t*-Butyl Bromides with Toluene.—Second-order rate constants were estimated from the extent of reaction of isopropyl and *t*-butyl bromides with toluene in a flow

TABLE IV

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

Alkyl bromide	Init. concn., M RBr	Init. concn., M GaBr ₃ ^a	Temp., °C.	Rate constants	
				$10^4 k_0^b$	k_2
Methyl	0.364	0.0409	15	2.40	0.143
Methyl	.402	.0347	15	1.58	.132
Methyl	.427	.0423	25	5.36	.300
Methyl	.359	.0403	25	4.87	.300
Methyl	.398	.0343	25	3.50	.298
Methyl	.352	.0395	40	11.6	.744
Methyl	.392	.0337	40	9.16	.806
Methyl	.391	.0360	40	10.4	.806
Ethyl	.412	.0236	15	25.2	4.53
Ethyl	.432	.0340	15	54.0	4.51
Ethyl	.407	.0370	25	132	9.70
Ethyl	.411	.0423	25	173	9.69
Ethyl	.411	.0463	25	198	9.30
Ethyl	.399	.0228	40	127	24.4
Ethyl	.422	.0330	40	301	26.5
<i>n</i> -Propyl	.416	.0469	15	207	9.39
<i>n</i> -Propyl	.412	.0423	25	353	19.7
<i>n</i> -Propyl	.411	.0463	25	434	20.2

^a Effective catalyst concentration. ^b Moles l.⁻¹ min.⁻¹.

reactor, assuming the reaction to be zero order and second order with respect to the catalyst. Using the flow apparatus described by Brown and Jungk,⁹ equal quantities of 0.836 *M* isopropyl bromide solution and 0.094 *M* gallium bromide solutions in toluene were mixed with a contact time of approximately 0.005 sec. The reaction mixture was quenched with water at 25°. In two separate runs 20 and 22% reaction were observed, and the second-order rate constants calculated from these data were 4×10^5 and 5×10^5 l. mole⁻¹ min.⁻¹, respectively. In a similar reaction with *t*-butyl bromide, a 0.868 *M* *t*-butyl bromide solution in toluene was mixed with a 0.094 *M* gallium bromide solution in a similar manner and 58% reaction was observed. The second-order rate constant was calculated to be 14×10^5 l. mole⁻¹ min.⁻¹.

Calculations.—The rate of isomerization of *n*-propyl to isopropyl bromide was also calculated from the kinetic data. The calculation is based on the assumption that the rate of isomerization of *n*-propyl bromide is the same in benzene and toluene media (and also in higher methylated benzenes). It further assumes that the $k_{\text{toluene}}/k_{\text{benzene}}$ ratio and isomer distribution of the reaction of *n*-propyl bromide *via* displacement may be considered to be the same, or nearly so, as in the reaction of ethyl bromide.¹⁸ The total

(18) It was necessary to make these assumptions as $k_{\text{toluene}}/k_{\text{benzene}}$ and the isomer distribution of the displacement reaction of *n*-propyl bromide could not be determined experimentally, due to the concurrent isomerization. The value for k_T/k_B for the reaction of ethyl bromide is 2.47 and the isomer distribution in the reaction with

TABLE V

RATE CONSTANTS FOR THE REACTION OF ALKYL HALIDES WITH TOLUENE UNDER THE INFLUENCE OF GALLIUM BROMIDE

Alkyl bromide	Init. concn., M RBr	Init. concn., M GaBr ₃ ^a	Temp., °C.	Rate constants	
				$10^4 k_0^b$	k_2
Methyl	0.404	0.0232	15	4.57	0.86
Methyl	.473	.0248	15	5.18	0.85
Methyl	.400	.0225	25	8.80	1.71
Methyl	.468	.0245	25	10.2	1.70
Methyl	.393	.0220	40	22.7	4.68
Methyl	.461	.0241	40	26.3	4.52
Ethyl	.424	.0180	15	36.4	11.2
Ethyl	.413	.0261	15	77.0	11.3
Ethyl	.412	.0249	15	75.1	12.0
Ethyl	.419	.0200	25	94.0	23.5
Ethyl	.408	.0266	25	167	23.5
Ethyl	.412	.0175	40	194	63.6
Ethyl	.402	.0253	40	383	59.8
Ethyl	.401	.0241	40	352	60.2
<i>n</i> -Propyl	.414	.0269	15	104	14.3
<i>n</i> -Propyl	.411	.0248	15	86.5	14.1
<i>n</i> -Propyl	.410	.0266	25	176	24.9
<i>n</i> -Propyl	.410	.0258	25	166	25.0
<i>n</i> -Propyl	.407	.0245	25	181	30.0
<i>n</i> -Propyl	.407	.0245	25	166	27.6
<i>n</i> -Propyl	.400	.0241	40	420	73

^a Effective catalyst concentration. ^b Moles l.⁻¹ min.⁻¹.

rates of reaction of *n*-propyl bromide in benzene and toluene are 20.0 and 26.9 l. mole⁻¹ min.⁻¹. The k_T/k_B ratio is very low due to the concurrent isomerization reaction. Assuming the k_T/k_B ratio to be the same as with ethyl bromide, 2.47, the rate of isomerization can be calculated kinetically. Let x represent the rate of isomerization; then the total rate minus x represents the rate of the displacement reaction. Therefore

$$(26.9 - x)/(20.0 - x) = 2.47; x = 15.3$$

This value is in good agreement with the value of 14.4 which was obtained by direct analysis of the products of the reaction with benzene. Using the partial rate factors obtained from the reaction of ethyl bromide, the rates of reaction of *n*-propyl bromide with polymethylated benzenes *via* displacement were calculated by the method of Condon¹⁶ and Brown and McGary.¹⁷

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toluene is 38.3% *o*-, 21.1% *m*- and 40.6% *p*-ethyltoluene (ref. 19). From these values the partial rate factors were calculated to be: o_f , 2.84; m_f , 1.56; and p_f , 6.02.

(19) H. C. Brown and C. R. Smoot, *THIS JOURNAL*, **78**, 6255 (1956).