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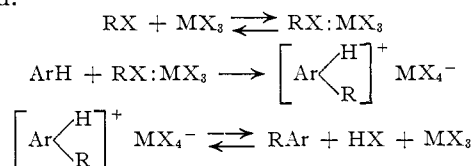
Kinetics of Methylation and Ethylation of Benzene and Toluene in 1,2,4-Trichlorobenzene under the Influence of Aluminum Bromide; Mechanism of the Alkylation Reaction^{1,2}

BY HANS JUNGK,³ CHARLES R. SMOOT³ AND HERBERT C. BROWN

RECEIVED OCTOBER 26, 1955

The kinetics of the reaction of methyl and ethyl bromide with benzene and toluene have been determined. The alkylations were found to proceed homogeneously in 1,2,4-trichlorobenzene with aluminum bromide as the catalyst. However, the rate could be followed only over the early stages of the reaction. In the later stages, the instantaneous rate decreased much more rapidly than any reasonable order would predict. The large decrease in rate is attributed to the removal of the aluminum bromide catalyst through formation of a stable σ -complex. By restricting the measurements to the early portion of the reaction, the alkylation reaction was observed to be third order, first order in each component: aluminum bromide, alkyl halide, aromatic. The rate expression for the reaction is $d[\text{HBr}]/dt = -d[\text{RBr}]/dt = k_3 [\text{RBr}][\text{AlBr}_3] \cdot [\text{ArH}]$. The kinetic data demonstrate that toluene reacts faster than benzene—the relative rates are 5.10 in methylation and 2.89 in ethylation. Furthermore, ethylation of benzene proceeds at a rate approximately 57 times more rapid than methylation. The energies of activation for methylation and ethylation of benzene are 14.6 and 10.7 kcal. mole⁻¹, respectively, with entropies of activation of -20.4 and -25.1 e.u. Isopropylation of benzene proved too fast to measure, even at very low concentrations. The relative rates of these reactions with benzene are: methylation (1), ethylation (57), isopropylation (>2500). It is proposed that methylation proceeds essentially by a displacement mechanism involving a nucleophilic attack by the aromatic nucleus on the polarized alkyl bromide-aluminum bromide addition compound. As the alkyl group becomes better able to accommodate a positive charge, *i.e.*, methyl < ethyl < isopropyl < *t*-butyl, there will be an increase in the amount of ionic character in the carbon-bromide bond in the transition state, accompanied by a decrease in the nucleophilic contribution by the aromatic. It is probable that isopropylation represents the limiting case and that no additional decrease in nucleophilic assistance occurs in extending the reaction to *t*-butylation. Attempts to measure the rate of reaction of *n*-propyl bromide with benzene under these conditions showed that the elimination of hydrogen bromide and the alkylation of benzene proceed at comparable rates. Consequently, a kinetic study of the system was not possible.

In an earlier paper it was suggested that the Friedel-Crafts reaction of aromatic nuclei with primary halides proceeds by a displacement mechanism, with the aromatic contributing to the breaking of the carbon-halogen bond in the transition state.⁴ The following reaction sequence was proposed.



The observation that the isomer distributions and the toluene/benzene reactivities are not independent of the halogen in methylation by methyl bromide and methyl iodide⁵ precludes the possibility of a free carbonium ion intermediate and provides further evidence for a displacement mechanism.

As the alkyl group in the alkyl bromide becomes more branched, it becomes more able to accommodate a positive charge. Consequently, there should be an increasing tendency for the alkyl bromide to be converted into ions in the series: methyl, ethyl, isopropyl and *t*-butyl. At some point along this series it would be expected that the formation and reaction of alkyl carbonium ions will provide the favored reaction path for aromatic alkylations.⁶ At that point the concentration of

the aromatic may no longer be involved in the rate expression.

It appeared that a detailed study of the kinetics of reaction of a series of alkyl halides with aromatic nuclei under Friedel-Crafts conditions might provide information with regard to the possible change in mechanism from predominantly displacement to essentially ionization. Consequently, the kinetics of the alkylation of benzene and toluene with several alkyl halides were investigated.⁷

Results

The aluminum bromide catalyzed reactions of methyl and ethyl bromides with benzene and toluene were found to proceed smoothly in 1,2,4-trichlorobenzene solution with no appreciable alkylation of the solvent.⁹ A detailed study was made of the reaction of ethyl bromide with benzene in this solvent. The reaction was entirely homogeneous providing the catalyst concentration was maintained at less than 0.2 *M*. A number of runs were made using low catalyst concentrations with excess benzene and ethyl bromide. Although the initial rate was extremely rapid, the instantaneous rate decreased much faster than any reasonable order would predict. The data for four kinetic studies at different aluminum bromide concentrations are shown in Fig. 1. It is obvious that the reactions become extremely slow after a short reaction period, even though considerable alkyl halide and

(1) The Catalytic Halides. XV11.

(2) Based upon the theses submitted by Hans Jungk and Charles R. Smoot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Company (Indiana) Fellow at Purdue University, 1952-1954.

(4) H. C. Brown and M. Grayson, *THIS JOURNAL*, **75**, 6285 (1953).(5) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; C. C. Price, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1946, Vol. 111, Chapt. 1; M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949.

(7) J. Ulich and G. Heyne [*Z. Elektrochem.*, **41**, 509 (1935)] report a study of the reaction of *n*-propyl chloride with benzene in the presence of gallium chloride. Unfortunately, the rate data suffer from several serious difficulties. The reaction was followed by the evolution of hydrogen chloride. However, under the experimental conditions *n*-propyl chloride both eliminates hydrogen chloride and isomerizes into isopropyl chloride (ref. 8). Consequently, it is not certain to what extent the rate of evolution of hydrogen chloride measures the rate of reaction of the aromatic with the alkyl halide.

(8) Unpublished work with R. Wong.

(9) A brief summary of the search for suitable solvents is given in the Experimental Part.

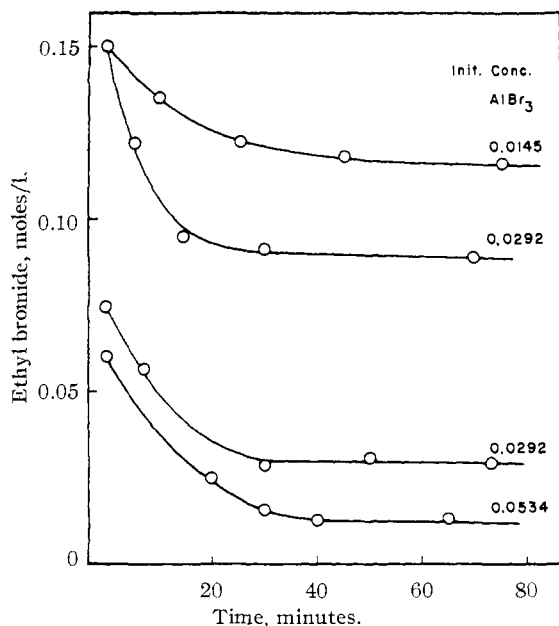


Fig. 1.—Effect of changes in aluminum bromide concentration on the rate of ethylation of benzene in 1,2,4-trichlorobenzene.

benzene remain. The reaction exhibited satisfactory kinetics in the initial portion of its progress, however, and this system was utilized for the kinetic study of the reaction.

In order to provide sufficient time for samples to be taken during this early phase of the reaction, low concentrations of reactants were used. As a result, the solutions were extremely sensitive to moisture. Exploratory trials indicated that a particular catalyst solution might maintain essentially constant catalytic activity for several days. However, in order to avoid this uncertainty, a new catalyst solution was made up for each series of runs and all runs in the series were carried out on the same day. Attempts to make catalyst solutions of reproducible catalytic activity indicated a variation of approximately 10% between the "active concentration" and the concentration as determined by titrimetric analysis (see Experimental Part). This difficulty could not be avoided and resulted in some variation in the rate constants in experiments with different catalyst solutions.

The rates of the reactions were followed by measuring the rate of production of hydrogen bromide, corresponding to the rate of disappearance of the alkyl bromide. The data thus obtained for the reaction of benzene with methyl bromide fit a rate expression first order in the methyl bromide.

Variation in the initial concentrations of the benzene and the aluminum bromide resulted in changes in the value of k_1 . However, by dividing the first-order rate constants, k_1 , by the concentrations of benzene and aluminum bromide, a new quantity resulted which is essentially constant over all concentrations of the three reactants. It must be concluded that the reaction is actually third order—first order in each of the three components of the reaction mixture. These data are summarized in Table I.

TABLE I
RATE CONSTANTS FOR THE REACTION OF BENZENE AND TOLUENE WITH METHYL BROMIDE AND ALUMINUM BROMIDE IN 1,2,4-TRICHLOROBENZENE

Reactants, moles/l.			Temp., °C.	First-order constant $k_1 \times 10^3$ (sec. ⁻¹)	Third-order constant $k_3 \times 10^3$ (l. ² mole ⁻² sec. ⁻¹)
Aromatic ^a	CH ₃ Br	Al ₂ Br ₆			
0.636	0.106	0.0318	25.0	7.19	3.56
.509	.106	.0318	25.0	5.66	3.51
.382	.106	.0318	25.0	4.84	3.99
.305	.106	.0318	25.0	3.97	4.10
.673	.251	.0278	25.0	5.22	2.78
.673	.201	.0278	25.0	5.22	2.78
.673	.151	.0278	25.0	6.38	3.40
.673	.120	.0278	25.0	6.74	3.61
.685	.181	.0353	25.0	8.80	3.64 ^c
.700 ^f	.181	.0353	25.0	46.0	18.6 ^c
.685	.181	.0359	25.0	8.63	3.51 ^d
.700 ^b	.181	.0359	25.0	49.98	17.9 ^d
.615	.103	.0369	25.0	9.91	4.36
.615	.103	.0185	25.0	4.93	4.34
.330	.246	.0103	45.0	4.76	13.5
.333	.248	.0104	35.0	3.10	8.92
.336	.250	.0105	25.0	1.42	4.02

^a Benzene except where otherwise indicated. ^b Toluene. ^c Relative rate, $k_T/k_B = 5.11$. ^d Relative rate, $k_T/k_B = 5.10$.

The ethylation of benzene and toluene was investigated using the same procedures and similar third-order rate constants were obtained. The data are summarized in Table II.

TABLE II
RATE CONSTANTS FOR THE REACTION OF BENZENE AND TOLUENE WITH ETHYL BROMIDE AND ALUMINUM BROMIDE IN 1,2,4-TRICHLOROBENZENE

Reactants, moles/l.			Temp., °C.	First-order constant $k_1 \times 10^3$ (sec. ⁻¹)	Third-order constant k_3 (l. ² mole ⁻² sec. ⁻¹)
Aromatic ^a	C ₂ H ₅ Br	Al ₂ Br ₆			
0.213	0.134	0.0173	25.0	0.860	0.233 ^c
.254 ^b	.134	.0173	25.0	2.99	.682 ^c
.378	.134	.0173	25.0	1.44	.222 ^d
.390 ^b	.134	.0173	25.0	4.21	.624 ^d
.549	.103	.0132	25.0	1.70	.235
.330	.151	.0161	45.0	3.24	.609
.333	.153	.0163	35.0	2.43	.448
.336	.154	.0164	25.0	1.32	.240

^a Benzene except where otherwise indicated. ^b Toluene. ^c Relative rate, $k_T/k_B = 2.93$. ^d Relative rate, $k_T/k_B = 2.84$.

Relative reactivities of toluene and benzene in methylation and ethylation may be determined from the kinetic results. In Tables I and II values have been calculated from rate constants obtained in experiments using the same catalyst solutions and reactants of similar concentration.

An attempt was made to determine the rates of reaction of *n*-propyl bromide with benzene in trichlorobenzene, but hydrogen bromide formation was observed in ampules containing all of the reactants with the exception of the aromatic. This indicated that dehydrohalogenation was occurring as a side-reaction. The dehydrohalogenation was first-order in *n*-propyl bromide, but the order with

respect to the catalyst was not determined. Assuming the reaction to be first order with respect to aluminum bromide, the second-order rate constant was calculated to be $0.0120 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Since the rate of dehydrohalogenation of *n*-propyl bromide is comparable to its rate of alkylation of benzene, clean kinetics could not be realized. The rate of dehydrohalogenation of *n*-propyl bromide is at least 50 times greater than that of ethyl bromide.

Attempts to extend the kinetic measurements to isopropyl bromide were unsuccessful. Even at the lowest possible concentrations, the rate was too fast to measure—the reaction being complete before the first sample could be taken. A minimum third-order rate constant of $10 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ may be estimated. In view of these results, no attempt was made to include *t*-butyl bromide.

By comparing the rates of methylation and ethylation of benzene determined under identical conditions, it is possible to calculate the relative reactivity of these two halides.

$$\frac{k_3^{\text{EtBr}}}{k_3^{\text{MeBr}}} = \frac{0.220}{3.99 \times 10^{-3}} = 55.2$$

$$\frac{k_3^{\text{EtBr}}}{k_3^{\text{MeBr}}} = \frac{0.240}{4.02 \times 10^{-3}} = 59.7$$

Incorporating the minimum value estimated for k_3 for isopropyl bromide results in the following order of reactivity: methylation, 1; ethylation, 57; isopropylation, >2500.

From third-order rate constants determined at 25, 35 and 45° for methylation (Table I) and ethylation (Table II) of benzene, energies of activation were calculated (Fig. 2). The resultant values are 14.7 kcal. mole⁻¹ for methylation and 10.7 kcal. mole⁻¹ for ethylation of benzene. The entropies of activation for these reactions are -20.4 and -25.1 e.u., respectively.¹⁰

Discussion

The kinetic data for the reactions of both methyl and ethyl bromide with benzene and toluene obey a rate expression first order in the alkyl bromide.

$$\frac{d[\text{HBr}]}{dt} = -\frac{d[\text{RBr}]}{dt} = k_1[\text{RBr}]$$

However, the rate constant, k_1 , varies linearly with changes in the initial concentration of both the aluminum bromide and the aromatic. Consequently, the complete expression must involve each of the three compounds to the first power.

$$\frac{d[\text{HBr}]}{dt} = -\frac{d[\text{RBr}]}{dt} = k_3[\text{ArH}][\text{AlBr}_3][\text{RBr}]$$

It was considered that in the initial stages of the reaction, with low concentrations of both hydrogen bromide and the more basic aromatic formed in the alkylation reaction, the σ -complex¹¹ is largely dissociated, regenerating the catalyst. As the reaction

(10) Because of the experimental limitations we were unable to measure the rate constants over a temperature range greater than 20°. This, coupled with the possible variation of the rate constants previously mentioned, means that the values for the energies and entropies of activation must be considered to possess a relatively large uncertainty.

(11) H. C. Brown and W. J. Wallace, *THIS JOURNAL*, **75**, 6268 (1953).

proceeds, the higher concentrations of the products results in the formation of the σ -complex and the effective removal of the aluminum bromide.¹² The large decrease in the instantaneous rate in the later stages of the reaction is attributed to this removal of the catalyst.

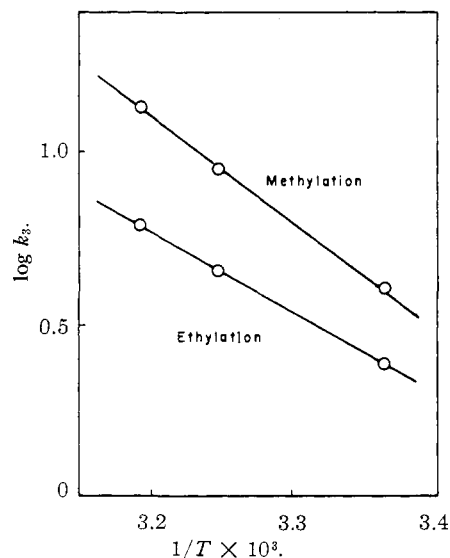
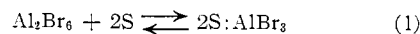


Fig. 2.—Energies of activation for the reaction of methyl and ethyl bromides with benzene in 1,2,4-trichlorobenzene (methylation: $k_3 \times 10^3$).

The alkylation of the aromatic produces a mono-alkyl derivative whose rate of alkylation should be similar to that of the original aromatic. Consequently, to a first approximation the molar concentration of the aromatic does not change. As a result the reaction obeys pseudo-first order kinetics.

The experimental observation that the reaction is first order in the aromatic in both methylation and ethylation rules out as a possible mechanism the rate-determining ionization of the alkyl halide, followed by the rapid reaction of the carbonium ion with the aromatic. In view of the tremendous rapidity with which carbonium ions must react with simple aromatic hydrocarbons,¹³ we can also eliminate any mechanism involving a fast ionization of the alkyl halide, followed by a rate-determining reaction of the carbonium ion with the aromatic nucleus.

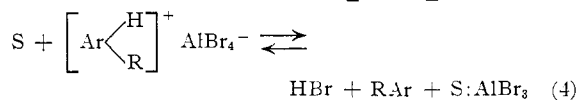
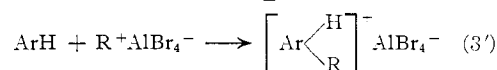
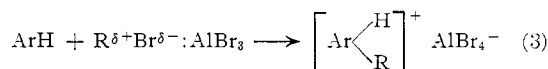
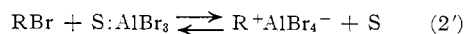
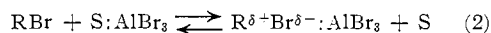
The results would appear to be consistent with a slow nucleophilic attack by the aromatic on a polarized alkyl bromide-aluminum bromide complex, or with an attack of the aromatic on an ionized ion-pair,¹⁴ in mobile equilibrium with the addition compound. The following mechanism would appear to be in accord with the observed kinetics and the known facts about the alkylation reaction ($S = 1,2,4$ -trichlorobenzene).



(12) It has been demonstrated previously that methyl bromide does not react with toluene at any significant rate when the catalyst is in the form of toluene-HBr-Al₂Br₆ σ -complex.⁵

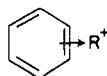
(13) F. E. Condon and M. P. Matuszak, *THIS JOURNAL*, **70**, 2539 (1948).

(14) For a discussion of the role of ion-pairs in solvolytic reactions, see S. Winstein *et al.*, *Chemistry and Industry*, 664 (1954).

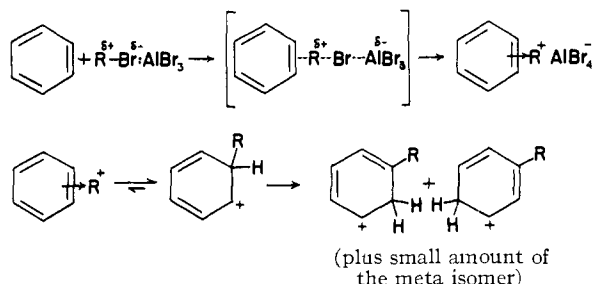


In the first step (1) we postulate that the aluminum bromide must be coordinated with the trichlorobenzene used as solvent. Although we have not established this point experimentally, we have observed that aluminum bromide coordinates readily with methyl bromide and other alkyl halides.¹⁵ The reaction of ethyl bromide with benzene and toluene in the presence of free aluminum bromide is extraordinarily fast, with the reaction being complete in less than 0.005 sec.¹⁶ The decrease of the reaction rate to a measurable velocity must in large part be due to a competition of the trichlorobenzene and the alkyl bromide for the available aluminum bromide (2,2').

In the third step the alkyl group is transferred to the aromatic ring (3,3'). It was previously suggested that a localized π -complex appears to be in-



involved as a high energy intermediate in the isomerization, disproportionation and alkylation reactions of alkylbenzenes.¹⁷ On this basis, the transfer of the alkyl group would involve the mechanism



The alternative mechanism involving reaction of the aromatic with the ion-pair (3') would be quite similar.

Finally, in the last step the solvent again participates by facilitating the dissociation of the σ -complex. Under similar reaction conditions, in the absence of the solvent, the alkylation proceeds to form but one mole of product per mole of aluminum bromide present.⁵ It is apparent that the solvent plays an important role in the reaction. A solvent of relatively high basicity, such as nitrobenzene,

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

(16) H. C. Brown and H. Jungk, *ibid.*, **78**, 2182 (1956).

(17) For discussion and pertinent literature references, see H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

coordinates so strongly with the aluminum bromide that the alkyl bromide cannot compete. A solvent of very low basicity provides too little competition and the alkylation reaction proceeds too rapidly for measurement. Such a solvent fails to dissociate the σ -complex and it tends to separate from the solution.

At the present time there does not appear to be any experimental basis for deciding between the alternative formulations of an attack by the aromatic on a polarized alkyl bromide-aluminum bromide addition compound, $R^{\delta+}Br^{\delta-}:AlBr_3$ (3), or with a reaction of the aromatic with an ion-pair intermediate, $R^+AlBr_4^-$ (3'). Indeed, a careful consideration of the problem suggests that the decision between these two alternatives may become primarily a matter of defining at what stage the polarized species is more conveniently considered to be an ion-pair.

We have previously demonstrated that in the methylation of benzene and toluene different toluene/benzene reactivity ratios and isomer distributions are obtained with methyl bromide and iodide.⁵ If we assume that no covalent bonding exists in the ion pair, then the fact that the reaction shows a dependence on the nature of the halogen appears to be more simply explained by the mechanism based on a polarized addition compound than by the ion pair intermediate.

The results show that the aromatic is also involved in the rate expression for the ethylation reaction. It is concluded that here also we are dealing with a rate-determining nucleophilic attack of the aromatic on a polarized ethyl bromide-aluminum bromide intermediate. There is a marked increase in the rate of ethylation as compared to methylation: k_3^{EtBr}/k_3^{MeBr} is 57. This increase is contrary to the order observed for typical bimolecular displacement reactions.¹⁸ The increase must be attributed to the greater ability of the ethyl group to accommodate a positive charge, leading to a more reactive polarized addition compound (3) or a higher equilibrium concentration of ion-pairs (3').

In this connection the observed entropies of activation, -20.4 e.u. for methylation and -25.1 e.u. for ethylation, are in good agreement with the values of -20 to -30 e.u. commonly observed in bimolecular displacement reactions. Moreover, the formation of pure ethyl- β -C¹⁴-benzene from the condensation of benzene with ethyl- β -C¹⁴ chloride and aluminum chloride¹⁹ is also quite consistent with a displacement reaction of the type under discussion. The toluene/benzene reactivity ratio is 5.10 in the methylation reaction and 2.89 in the ethylation reaction. In other words, methylation is a more selective²⁰ reaction than ethylation. In an attack by carbonium ions, the reactivity ratio would be expected to increase with increasing stability of the attacking species, $CH_3^+ < C_2H_5^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$. Since a decrease is observed, the results further support the conclusion that the substitution reactions do not proceed

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

(19) R. M. Roberts, G. A. Ropp and O. K. Neville, *THIS JOURNAL*, **77**, 1764 (1955).

(20) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).

through attack by free methyl- and ethylcarbo-
nium ions.²¹

With increased branching of the alkyl group, the ability to accommodate a positive charge increases. At some stage in the series, we may expect to find that the aromatic is no longer involved in the rate-determining stage.²³ From stereochemical evidence²⁴ it appears that this stage may be realized in *sec*-butyl and related secondary alkyl derivatives. Unfortunately, it was not possible to extend the kinetic measurements to isopropyl or *t*-butyl bromide, so that we cannot present kinetic evidence bearing on this point. However, the large increase in rate of alkylation with isopropyl bromide (relative rate >2500) is consistent with this interpretation.

In conclusion, the present study supports the view that the alkylation of aromatics by primary halides in the Friedel-Crafts reaction proceeds through a nucleophilic displacement by the aromatic on a polarized alkyl bromide-aluminum bromide addition compound. With increasing ability of the alkyl group to accommodate a positive charge, there appears to be an increase in the ionic character of the carbon-bromine bond in the transition state, accompanied by a decrease in the amount of nucleophilic assistance by the aromatic. Accordingly, with increased branching of the alkyl halide, as in the series, methyl, ethyl, isopropyl and *t*-butyl, there appears to occur a gradual change in the nature of the transition state until the limiting case is reached where the aromatic no longer contributes significantly to the breaking of the carbon-bromine bond. In terms of this picture, the reactions of alkyl halides with aromatic nuclei in the Friedel-Crafts reaction is closely related to other types of displacement reactions of alkyl halides.^{18,23,25}

Experimental Part

Study of Possible Solvents.—Initially attempts were made to utilize nitrobenzene as a solvent for the rate studies. This solvent had previously proved satisfactory for the study of the reactions of aromatics with substituted benzyl halides.⁴ However, neither methyl nor ethyl bromide reacted at any measurable rate with benzene in nitrobenzene solutions of aluminum chloride and bromide. For example, a maximum of 2% reaction was observed in an experiment in which 0.67 *M* benzene, 0.67 *M* methyl bromide and 0.3 *M* aluminum bromide, all in nitrobenzene solution, was permitted to stand at 25° for 86 hours. Less basic solvents were also investigated. In trichlorocumene phase separation was observed after only 4% reaction. In *o*-dichlorobenzene the alkylation of the solvent by ethyl bromide was almost as rapid as the reaction with the dissolved benzene.

Carbon disulfide and *n*-heptane proved unsatisfactory since phase separations occurred very shortly after mixing the reactants. Use of a milder catalyst, gallium trichloride,

(21) The toluene/benzene reactivity ratios obtained in the present study differ from those observed previously for competitive alkylation in the aromatic as solvent with the aluminum bromide and alkyl bromide present in equimolar amounts.¹⁶ This provides further evidence that the reactivity ratios and isomer distributions can be modified by changes in the experimental conditions.²²

(22) H. C. Brown and C. W. McGary, Jr., *THIS JOURNAL*, **77**, 2306 (1955).

(23) In terms of the discussion provided by S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951), the reaction would have attained the "limiting" stage where no nucleophilic assistance is required from the aromatic.

(24) R. L. Burwell, Jr., and S. J. Archer, *ibid.*, **64**, 1032 (1942); R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952); C. C. Price and M. Lund, *ibid.*, **62**, 3105 (1940).

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

did not avoid this difficulty. Addition of weakly basic coordinating agents, such as *p*-chloronitrobenzene or 2-nitro-4-chlorotoluene, to prevent phase separation, completely inhibited the reaction.

Solvents such as benzonitrile, nitromethane and liquid sulfur dioxide formed precipitates with the aluminum bromide.

One interesting possibility was examined in considerable detail. Methyl iodide had previously been observed to react with toluene at a rate approximately 200 times more slowly than methyl bromide.⁵ Accordingly it appeared that methyl iodide might serve as solvent for a study of the reaction of methyl bromide with benzene in the presence of aluminum bromide. Some success was achieved. It was possible to follow the reaction rate without undue reaction of the solvent with the aromatic. Two difficulties led us to abandon this system. The volatility of the methyl iodide made manipulations of the solutions awkward and free iodine, formed in the reactions, complicated the analyses. The use of 1,2,4-trichlorobenzene avoided these difficulties and it was therefore adopted for the kinetic studies.

Materials.—The 1,2,4-trichlorobenzene was obtained by careful fractionation of a mixture of all trichlorobenzene isomers (Hooker Electrochemical Co.) in an adiabatic packed column rated at 70 theoretical plates. Sufficient material was fractionated so that all of the kinetics could be determined using the same batch of solvent.

The purification of benzene, toluene, methyl and ethyl bromide have been previously described.^{5,16}

After purifying the aluminum bromide as described,¹⁶ the catalyst was again treated to ensure the removal of all impurities. For this purpose the aluminum bromide was transferred in stages through a glass tube under vacuum and then distilled into small tubes containing break tips. Approximately 2 to 8 g. of catalyst was sealed off in each of these tubes. The aluminum bromide was obtained in the form of colorless, transparent crystals.

Preparation of Solutions.—The solutions of aromatic and alkyl bromides were made up in scrupulously dried volumetric flasks. After the reactants had been diluted to the measured volume, chips of calcium hydride were added and the solutions stored at 25° for at least 8 hours before use in order to remove the last traces of moisture.

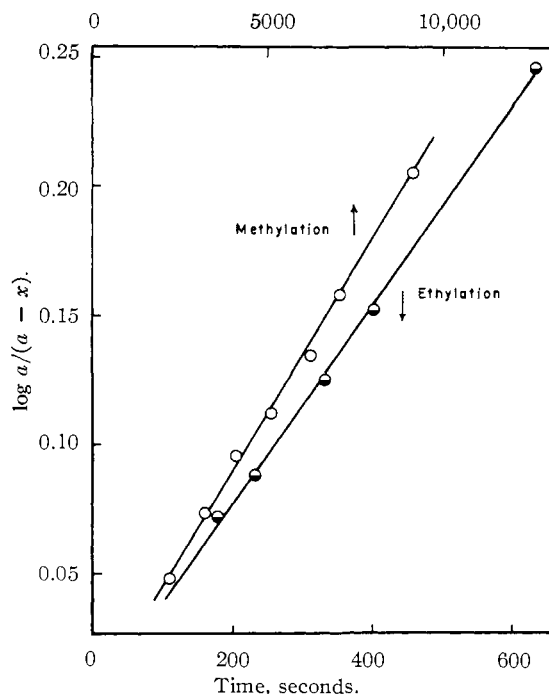


Fig. 3.—Rates of reaction of benzene with methyl and ethyl bromides in 1,2,4-trichlorobenzene.

The catalyst solution was made up in a calibrated distilling flask fitted with a ground glass joint and stopper at the neck and a stopcock at the side arm. The ampule con-

taining the aluminum bromide was placed in the neck of the flask, the flask evacuated through the side arm and the break tip on the ampule broken against the bottom of the stopper in the flask. The catalyst was transferred into the flask by gentle heating, dry nitrogen admitted through the side arm, and the empty ampule removed in a steady flow of the gas. The flask was again evacuated and the solvent drawn up into the flask through the side-arm. An approximate concentration could be calculated from the weight of the ampule before and after transfer of the catalyst. The exact concentration was determined by titration (see below). Samples were removed from the flask only in a stream of dry nitrogen to minimize the introduction of traces of moisture.

Procedure for Kinetic Determination.—The rates were measured using a "fragile bulb technique."⁴ The reactants were added with a 1-cc. rapid delivery pipet at 25°. The reaction bulbs were immediately closed with a rubber cap slipped over the stem, then shaken and immersed in a constant temperature bath. It was necessary to wash and dry the pipet between each addition of the catalyst solution. The reaction time was measured from the start of addition of the catalyst solution. At the proper time, each bulb was removed from the bath, the outside washed off with distilled water, and then placed in a 250-ml. wide mouth erlenmeyer flask containing 30 cc. of cold distilled water. After stoppering the flask, the bulb was broken by shaking the flask, quenching the reaction.

The titration procedure was described previously.⁴ The concentration of the catalyst was determined by titration

of blanks which were carried through the same procedure as the reaction samples, but without having aromatic and alkyl bromide present. The amount of reaction was determined by titration from the difference between the hydrogen bromide present in the sample and that found in the blanks.

The pseudo-first order rate constants were determined graphically. Typical data are shown in Fig. 3. The values of k_2 were determined by dividing the graphical k_1 values by the concentrations of benzene and alkyl bromide.

Side Reactions.—The absence of any significant side reactions during methylation and ethylation of benzene and toluene was established by treating methyl and ethyl bromides with aluminum bromide in 1,2,4-trichlorobenzene at the temperatures and reaction times used in the alkylation studies. Failure to observe any significant change with time in the titer for the catalyst eliminated the possibility of a competitive alkylation of the solvent or of an elimination reaction of the alkyl bromide. An approximate rate constant for the formation of hydrogen bromide from ethyl bromide at 25°, $k_2 = 1.7 \times 10^{-4}$ l. mole⁻¹ sec.⁻¹, shows it to be much smaller than the alkylation rate and unimportant in the kinetics.

Acknowledgment.—We wish to acknowledge the financial assistance provided by the Standard Oil Company (Indiana) in the form of two fellowship grants.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. VI. The Effect of the Steric Requirements of the Alkyl Group on the Direction of Bimolecular Elimination

BY HERBERT C. BROWN, ICHIRO MORITANI¹ AND M. NAKAGAWA¹

RECEIVED OCTOBER 26, 1955

A series of related tertiary bromides, $RCH_2CBr(CH_3)_2$, has been dehydrobrominated by pyridine and by potassium ethoxide (1 *M* solution in ethanol). With increased branching of the group R (Me < Et < *i*-Pr < *t*-Bu) there is observed a regular increase in the ratio of 1- $\frac{1}{2}$ -olefin in the product. This transition from Saytzeff- to Hofmann-type elimination is attributed to the steric requirements of the alkyl group R. It is proposed that with the increasing steric requirements of the group R the transition state leading to the 2-olefin becomes less favored energetically than that leading to the 1-olefin.

Directive effects in elimination reactions have been discussed previously by Hughes, Ingold and their co-workers.² They pointed out for the first time the existence of two conflicting rules governing the direction of elimination. They proposed that all unimolecular eliminations as well as bimolecular eliminations of uncharged molecules should proceed to give the most branched olefin (Saytzeff rule), while bimolecular eliminations of σ onium salts should proceed to give the least branched olefin (Hofmann rule). They attributed the Saytzeff rule to control by the electromeric factor, and the Hofmann rule to control by the polar factor rendered important by the positive charge in the σ onium ion.

The observation that the solvolysis of dimethyl-nopentylcarbonyl chloride proceeds to give predominantly 2,4,4-trimethyl-1-pentene,³ a case of Hofmann-type elimination in an unimolecular reaction, led us to question this interpretation. We therefore undertook an examination of the possi-

ble role of steric effects in controlling the direction of olefin formation in both unimolecular and bimolecular elimination. The role of steric effects in unimolecular elimination reactions has been discussed previously.⁴ The importance of the steric factor in directing elimination in bimolecular reactions is the subject of the present group of papers.

Consideration of the possible role of steric effects in bimolecular elimination reactions suggested that the direction of elimination might be influenced by (a) the steric requirements of the alkyl groups on the incipient double bond, (b) the steric requirements of the attacking base, and (c) the steric requirements of the leaving group. The first of these factors was examined by studying the effects of the steric requirements of the group R in the series of tertiary bromides, $RCH_2CBr(CH_3)_2$, on the nature of the olefins formed in eliminations by potassium ethoxide and by pyridine. The results are reported in the present paper.

Results

The four tertiary bromides $RCH_2CBr(CH_3)_2$, with R = Me, Et, *i*-Pr and *t*-Bu, were dissolved in a

(1) Post-doctorate assistants at Purdue University, 1951-1953 and 1953-1954, respectively, on a contract supported by the Office of Naval Research and a grant provided by the National Science Foundation.

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