used to obtain the very short contact times required for the isomerization of *p*-ethyl- and *p*-isopropyltoluene. The equipment contained two reservoirs, A and B. The tubes leading to the bottom of the reservoirs were attached with 24/40 ground glass joints S, and these assemblies were attached to the remainder of the apparatus by means of ball joints D.

In operation, the toluene–hydrogen bromide–aluminum bromide solution was made up in reservoir A as described above for the batch experiments. The alkyltoluene to be isomerized was placed in reservoir B. The relative quantities of reagents passing into the mixing chamber was controlled by adjustment of stopcock C. Nitrogen under pressure, applied at N and M, forced the liquids through tubes E and F into the mixing chamber H. It was established that with the capillaries in use, a nitrogen atmosphere of 18 p.s.i.g. caused the liquid to flow at a rate of 10 cc./sec. With a mixing chamber volume of 0.05 cc., the contact time was approximately 0.005 sec.

After mixing, the reaction solution entered the quenching chamber I and was mixed with the quench solution entering through K. The quench solution and reaction mixture were mixed by baffles J before flowing into the receiver L. The quench solution was made up of three parts of methanol and one part of water, cooled to −80° and forced into the quenching chamber with air pressure. The receiver, consisting of a 2-l., 3-necked flask, was also maintained at −80°.

After the reaction was over, the quenched reaction mixture was allowed to warm. Upon dilution with an equal volume of water, the organic layer was separated and dried with Drierite. The isomer distribution of the alkyltoluenes was determined by quantitative infrared analysis.

Acknowledgment.—We wish to express our appreciation to Mrs. L. Walsh and Mr. P. Kinsey for their coöperation in determining the infrared spectra, to the Bureau of Standards for the standard samples of the isomeric dialkylbenzenes, and to the Standard Oil Company (Indiana) for the fellowship grant which made this investigation possible.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Reaction of Benzene and Toluene with Methyl Bromide and Iodide in the Presence of Aluminum Bromide; Evidence for a Displacement Mechanism in the Methylation of Aromatic Compounds[1,2]

BY HERBERT C. BROWN AND HANS JUNGK[3]

RECEIVED DECEMBER 29, 1954

The reaction of benzene and toluene with methyl bromide in the presence of molar quantities of aluminum bromide results in the formation of toluene and xylenes in very high yield. The low yield of polymethylated derivatives is attributed to the essentially complete removal of the more basic product as a σ-complex with hydrogen bromide–aluminum bromide. The methylation reaction is exceedingly rapid, being essentially complete in the case of toluene in 30 seconds or less at 0°. Under the same conditions, the reaction of methyl iodide with benzene and toluene proceeds considerably slower, at a rate less than 1/200 that for the bromide. The slower rate for the iodide is attributed to the weaker basic properties of the iodine atom with a resulting weaker coördination with the aluminum bromide. Competitive methylation of toluene and benzene with methyl bromide and aluminum bromide at 0, 25 and 45° resulted in relative rates of methylation of 3.8, 3.0 and 2.5, respectively. A similar study with methyl iodide gave a value of 4.8 for the relative rates of methylation of the two hydrocarbons at 0°. Similar differences are found in the isomer distributions observed in the xylenes obtained in the methylation of toluene by the two halides at 0°. Such differences in the isomer distributions and the relative rate values are not compatible with a mechanism involving attack by methylcarbonium ions. The results are consistent with the proposal that the reaction involves a nucleophilic attack by the aromatic on a polarized methyl halide–aluminum bromide addition compound.

In the past, the Friedel–Crafts alkylation reaction generally has been assumed to proceed through the formation and reaction of carbonium ions.[4-7] Recent studies of the aluminum chloride catalyzed reaction of substituted benzyl halides with aromatic hydrocarbons in nitrobenzene solution revealed that the reaction is third order, first order in the catalyst, alkyl halide and aromatic.[8] It was suggested that in the case of primary halides the kinetics and other characteristics of the alkylation reaction are in better accord with a displacement[9] mechanism in which the aromatic hydrocarbon serves as a nucleophilic component which attacks the alkyl halide–metal halide addition compound.[10,11]

It appeared that a study of the reaction of different methyl halides with benzene and toluene[12] might provide a test of this proposal. If the reaction proceeds through the formation of free methylcarbonium ions (1), it would be expected that the isomer distribution in the methylation of toluene (2)

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(1) The Catalytic Halides. XII.

(2) Based upon a thesis submitted by Hans Jungk to the faculty of Purdue University 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) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(5) C. C. Price, "Organic Reactions," Vol. III, Chapt. I, John Wiley and Sons, Inc., New York, N. Y., 1946.

(6) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949.

(7) D. V. Nightingale, *Chem. Revs.*, **25**, 325 (1939).

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

(9) There does not appear to be available today a simple term to designate substitution reactions in which bond making is occurring concurrently with bond breaking. The symbol introduced by Ingold and Hughes, S_N2, is awkward in general discussion and is not appropriate for a reaction such as that here discussed which is first order in three components. It is proposed, therefore, that the term ionization mechanism be used for reactions in which the formation of ions (bond breaking) is primarily involved in the transition state and the term displacement mechanism be used to refer to reactions in which bond making is of major importance in the transition state.

(10) H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953).

(11) H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6279 (1953).

(12) For an earlier study of the methylation of benzene and toluene see J. F. Norris and D. Rubinstein, *ibid.*, **61**, 1163 (1939).

would be independent of the nature of the halogen. Similarly, the relative rate of attack of benzene and toluene in the competitive methylation of these two hydrocarbons (k_T/k_B) likewise should be independent of the particular methyl halide present.

$$CH_3X + Al_2X_6 \rightleftarrows CH_3^+ + Al_2X_7^- \qquad (1)$$

$$CH_3^+ + CH_3C_6H_5 \xrightarrow{k_T} (CH_3)_2C_6H_4 + H^+ \qquad (2)$$

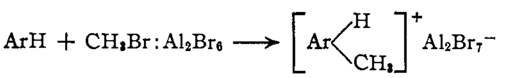
$$CH_3^+ + C_6H_6 \xrightarrow{k_B} CH_3C_6H_5 + H^+ \qquad (3)$$

It was desired that the reaction be run under homogeneous conditions. A convenient means of carrying out the methylation reaction was suggested by observations on the behavior of aromatic hydrocarbon–aluminum bromide–hydrogen bromide systems.[13] Preliminary experiments showed that alkyl halides react smoothly and homogeneously in a 6:1 molar solution of aromatic hydrocarbon and aluminum bromide (Al_2Br_6) to which one mole of alkyl bromide is added. Accordingly, this system was adopted for the methylation studies.

Previous work had shown that methyl chloride undergoes relatively rapid exchange with aluminum bromide, whereas methyl iodide does not exhibit a similar tendency for such exchange. In order to avoid possible complications which might arise as a result of such exchange, the study was restricted to the use of methyl bromide and iodide as methylating agents with aluminum bromide as the metal halide.

Results

Methylation of Benzene and Toluene.—The methylation experiments were carried out at two temperatures, 0 and 25°. At 25°, the solution of one mole of aluminum bromide in six moles of the aromatic was perfectly homogeneous, light yellow in color. The reaction mixture remained homogeneous, with the color changing to a deep reddish-brown, as a mole of the methyl halide was added. At 0°, the aluminum bromide was not completely soluble in the aromatic. However, the undissolved catalyst went into solution immediately following the addition of the methyl halide and remained clear, with no separation of product. Evolution of hydrogen bromide did not occur—the gas was evidently tied up in the form of the σ-complex (4).



$$ArH + CH_3Br{:}Al_2Br_6 \longrightarrow \left[Ar\begin{matrix} H \\ CH_3 \end{matrix} \right]^+ Al_2Br_7^- \qquad (4)$$

The rapid addition of 8.2 g. (0.0864 mole) of methyl bromide to a mixture of 47.0 g. (0.511 mole) of toluene and 45.5 g. (0.0911 mole) of aluminum bromide at 0° caused a noticeable evolution of heat. Rapid sampling of the reaction mixture at 0.5, 1.0, 2.0 and 3.0 minutes, followed by titration for hydrogen bromide formed in the reaction, revealed that the reaction had proceeded to the extent of 92 ± 2%. Evidently, the reaction is essentially complete in less than 30 sec. Similar results were observed for benzene.

Apparently, aluminum bromide in the form of the σ-complex must possess a much lower catalytic activity in this reaction than does free aluminum bromide. Thus, when one mole of methyl bromide was added at 25° to a solution of the toluene σ-complex in toluene (6 moles of toluene, 1 mole each of Al_2Br_6 and hydrogen bromide), no methylation of toluene was observed in a reaction time of 3 minutes.

Several larger methylations were carried out by the above procedure. Fractionation of the reaction products revealed that only toluene was formed in significant amounts in the methylation of benzene and only the three isomeric xylenes in the methylation of toluene. Yields of 92–94% of the monomethylation products were isolated easily. Consequently, the amount of higher methylation products can be no higher than 6–8% and may be considerably less.[14] Examination of the infrared spectra of these products supported the conclusion that the methylation reaction under these conditions proceeds almost quantitatively to the formation of the monomethyl derivatives, with only minor amounts of higher methylated compounds present in the products.

No significant change in the essentially pure monomethylation nature of the reaction was observed even when the reaction time was extended to two hours.

The reaction of methyl iodide with toluene is considerably slower. Under identical conditions, the reaction of methyl iodide with toluene was only 38% complete in 17 minutes. A minimum rate constant for the reaction of methyl bromide with toluene can be estimated from the observation that the reaction is essentially complete in 30 sec. (Table I). Comparison with the estimated first-order rate constant for the methyl iodide reaction (Table I), shows that the reaction of methyl iodide must proceed at least 1/200 as fast as the corresponding reaction of methyl bromide.

TABLE I

SUMMARY OF DATA FOR THE METHYLATION OF BENZENE AND OF TOLUENE AT 0°

Reactants[a]					Reacn.		First-order
C_6H_6	CH_3-C_6H_5	Al_2Br_6	CH_3Br	CH_3I	time, sec.	Reacn.,[b] %	rate constant k_1, sec.$^{-1}$
	0.511	0.0911	0.0864		30	92	>0.1
	.511	.0911	.0864		60	90	
	.511	.0911	.0864		120	92	
	.511	.0911	.0864		180	94	
0.547		.0909	.0908		120	93	
0.547		.0909	.0908		240	92	
	0.359	.0596		0.0599	1020	38	4.7×10^{-4}
	.359	.0596		0.0599	1740	65	6.1×10^{-4}

[a] Moles. [b] Estimated by titration for hydrogen halide.

The methylation of toluene by methyl iodide also does not appear to result in measurable polymethylation. This point was established by examination of the infrared spectra of the products.

Isomer Distribution in Methylation of Toluene.—Determination of the isomer distribution was complicated by the isomerization of *p*- and *o*-xylene under the alkylation conditions.[15] In the case of the reaction of toluene with methyl bromide at 0 and 25°, it was possible to minimize the iso-

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[13] H. C. Brown and W. J. Wallace, THIS JOURNAL, 75, 6268 (1953).

[14] It should be mentioned that loss of methyl bromide by volatilization from the reaction system may, in part, be responsible for the failure to realize even higher yields.

[15] H. C. Brown and H. Jungk, *ibid.*, 77, 5579 (1955).

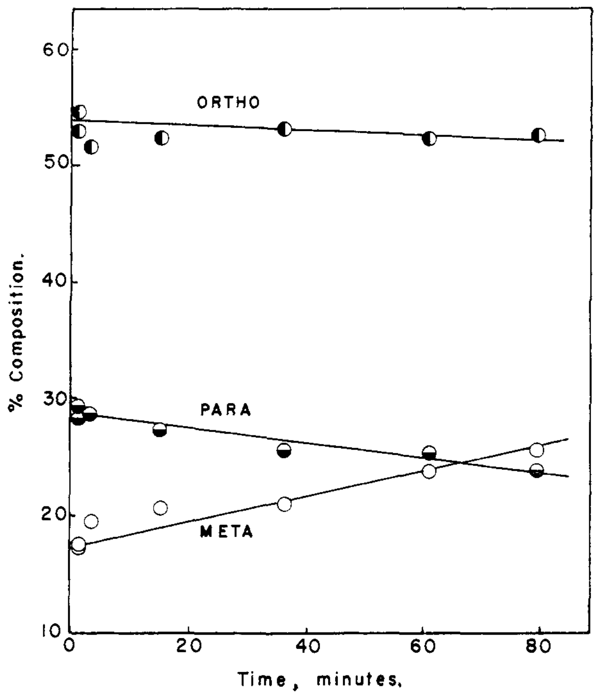

Fig. 1.—Effect of time on the distribution of xylene isomers resulting from reaction of toluene with methyl bromide at 0°.

merization by rapid addition of the methyl halide and immediate removal of a reaction sample. By thus reducing the reaction time to approximately one minute, any significant change in the initial distribution as a result of isomerization was made negligible.

At the same time, the short reaction time introduced another problem. Considerable heat was evolved in the course of the reaction and it was impossible to remove this heat over the short reaction time. Consequently, the reaction proceeded with a rise in temperature. We attempted to compensate for this effect by starting the reaction at a lower temperature, so that the temperature reached at the end of the reaction would straddle the desired reaction temperature.

The change in the isomer distribution with time in the reaction of methyl bromide with toluene at 0° is shown in Fig. 1. The data are collected in Table II. The results both confirm the initial isomer distribution, determined as described above, and agree with the isomerization data previously described.[15]

The methyl iodide reaction offers a more difficult problem. The rate of the methylation reaction is quite slow, and consequently a considerably longer reaction time is necessary in order to obtain an adequate yield of the xylenes for analysis. Unfortunately, the longer reaction time causes the isomerization of the initially formed isomers to become a serious factor, especially at 25°.

TABLE II

CHANGE IN XYLENE ISOMER DISTRIBUTION AFTER METHYLATION OF TOLUENE WITH METHYL BROMIDE AT 0°

Reacn. time, min.	Isomer distribution, %		
	p-	*m*-	*o*-
1	28.3	17.2	54.5
1	29.6	17.5	52.9
3	28.7	19.8	51.5
15	27.0	20.9	52.1
36	25.7	21.1	53.2
45	26.5	23.8	49.6
61	25.3	23.2	52.4
79	23.8	24.8	51.4

We examined the possibility that the initial isomer distribution might be obtained by determining the product distribution at various time intervals, followed by an extrapolation back to zero time. However, such a procedure assumes instantaneous reaction with all isomerization beginning at zero time. Since this is not the case, results obtained in this way would be open to question. Accordingly, we abandoned our attempt to obtain the isomer distribution at 25°.

Fortunately, at 0°, the rate of isomerization proved to be considerably slower and it was possible to utilize a reaction time of 20 min., sufficiently short so that the possible isomerization was smaller than the experimental uncertainty of the infrared analytical procedure.

The experimental results on the isomer distribution are summarized in Table III.

TABLE III

ISOMER DISTRIBUTION IN THE METHYLATION OF TOLUENE

Methyl halide	Temp., °C.	Av. temp., °C.	Isomer distribution, %		
			o-	*m*-	*p*-
Iodide	− 1 to 2	0.5	49.0	10.9	40.1
	0 to 2	1	47.6	12.9	39.5
Bromide	−10 to 7	−1.5	54.5	17.2	28.3
	− 5 to 15	5	52.9	17.5	29.6
Bromide	22 to 36	29	49.8	20.9	29.3

Relative Reactivities of Toluene and Benzene in Methylation.—Since the methylation of benzene and toluene proved to be so very rapid, there did not appear to be much hope in determining the relative reactivities by kinetic studies. Accordingly, recourse was had to a competitive procedure.

In a typical experiment, 110.0 g. (0.207 mole) of aluminum bromide was dissolved in a mixture of 48.4 g. (0.620 mole) of benzene and 57.1 g. (0.620 mole) of toluene. To this solution 19.6 g. (0.206 mole) of methyl bromide was added. Since no change in the relative reactivities of benzene and toluene with time was anticipated, it was possible to add the methyl bromide more slowly than in the isomer distribution experiments. Consequently, the temperature could be controlled within relatively narrow limits. Similar reactions were carried out at 0, 25 and 45°. The relative rate of methylation by methyl iodide at 0° was carried out similarly.

The product distributions resulting from these reactions were determined by fractionating a portion of the reaction product. The yields of the various methylbenzene fractions, corrected to the initial reaction charge, are included in Table IV.

Competitive relative rates ordinarily can be calculated using the equation of Ingold.[16] As applied to benzene and toluene, their expression is

$$\text{relative rate} = \log \frac{T_0}{T} \Big/ \log \frac{B_0}{B}$$

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[16] C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931).

TABLE IV

REACTANTS AND PRODUCT DISTRIBUTIONS IN METHYLATION OF BENZENE AND TOLUENE

Reactants[a]					Temp., °C.	Products[a, b]			Relative rate
C_6H_6	$CH_3C_6H_5$	Al_2Br_6	CH_3Br	CH_3I		C_6H_6	$CH_3C_6H_5$	$(CH_3)_2C_6H_4$	
0.620	0.620	0.207	0.207		0–5	0.569	0.495	0.176	3.64
.564	.564	.188	.188		0–5	.523	.466	.139	3.55
.423	.121	.0909	.0909		0–5	.386	.144	.0396	4.10[c]
.381	.381	.127	.130		27–32	.352	.327	.0838	2.95
.246	.246	.0820	.0818		43–47	.224	.214	.0534	2.51
.430	.430	.143		0.143	0–1	.411	.366	.0844	4.57
.238	.238	.0793		.0796	0–1	.226	.200	.0489	4.38
.410	.410	.137		.137	0–1	.395	.349	.076	5.39
.626	.626	.209		.208	0–1	.589	.507	.157	4.60

[a] Moles. [b] Corrected to total molar charge from fractionation results. [c] Re-analysis gives relative rate = 4.11.

where T_0 and B_0 represent the initial concentrations of toluene and benzene, respectively, and T and B are the corresponding final concentrations.

In the methylation of benzene and toluene, this equation must be modified to allow for the formation of additional toluene from the methylation of benzene. The equation

$$(B_0/B)^{k_T/k_B} = \frac{(k_T/k_B)T_0 - (T_0 + B_0)}{(k_T/k_B)T - (T + B)}$$

was derived for this purpose.[17] The symbols are as above. The relative reactivity is represented by k_T/k_B. The relative rates calculated with this equation are given in Table IV. Considering both the precision realized in duplicate experiments and the uncertainties in the analytical procedure, we believe that the relative rates cannot be considered to be more accurate than ±0.5 unit.

A greater spread in the precision of the relative rate values was obtained in methylation with methyl iodide. This resulted from the presence of some methyl iodide in the benzene fraction obtained from fractionation, with a resultant uncertainty in estimating the precise amount of benzene present. The actual quantity of benzene in this fraction was determined by difference between the total fraction weight and the weight of methyl iodide present, the latter being calculated from the weight of silver iodide precipitated on treatment with alcoholic silver nitrate.

Discussion

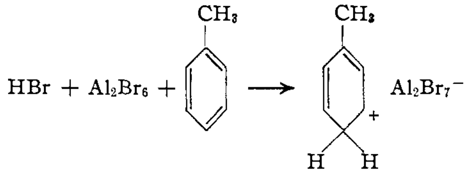
The speed of the reaction of benzene and toluene with methyl bromide was unexpected in view of the relatively rigorous reaction conditions which have been utilized for such reactions in the past, even in cases where molar amounts of the metal halide were present.[5]

The large difference in the reactivity of methyl bromide and iodide (k_{MeBr}/k_{MeI} 200) is also surprising. In both typical SN1 and SN2 reactions of alkyl halides, it is observed that the reaction rate increases in the order: RF < RCl < RBr < RI.[18]

It was observed previously that the addition compound of methyl iodide with aluminum bromide is much less stable than the corresponding derivative of methyl bromide.[11] This difference in stability was attributed to the decreased donor properties of iodine as compared to bromine. Consequently, it appears that the decreased pull by the aluminum bromide on the halogen is sufficiently important to overcome the lower strength of the carbon–iodine bond and result in a considerable decrease in reaction rate.

The high yield of the monomethylated derivative is also an unexpected characteristic of the system. The presence of alkyl groups on an aromatic ring results in an increase in the activity of the nucleus toward further attack by electrophilic reagents. With the susceptibility toward attack increasing in the order, benzene < toluene < xylenes, considerable amounts of higher methylated products might have been expected. Indeed, the literature is replete with numerous references to the formation of large amounts of polyalkyl derivatives as by-products of aromatic alkylation.[5,19]

The low yield of higher methylated derivatives in the present experiments must be attributed to the fact that the product is not present as such in the reaction mixture. The monomethylated product, as the more basic component of the reaction mixture, must be essentially in the form of the σ-complex and, therefore, not susceptible to further reaction.



Approximate calculations of the proton distribution in the toluene–xylene–aluminum bromide–hydrogen bromide system[15] using the equilibrium constants for toluene and xylenes in hydrogen fluoride–boron trifluoride[20,21] support this conclusion. Furthermore, both the observation that hydrogen bromide is not evolved from the reaction mixture and the observation that methyl bromide does not react with the toluene–aluminum bromide–hydrogen bromide reaction mixture argue that the σ-complex must be quite stable under the reaction conditions.

In this experiment, the three components were present in the mole ratio of 6 toluene:Al_2Br_6:HBr.

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[17] The derivation for this equation is given in the Experimental Part.

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

[19] A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

[20] D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[21] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

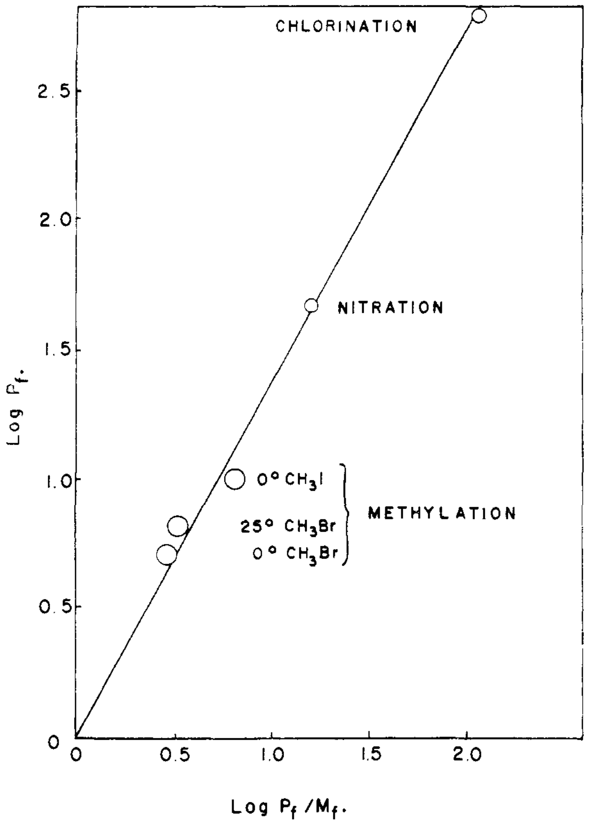


Fig. 2.—Partial rate factors.

The failure of methyl bromide to react with the excess toluene must mean that no free catalyst is present. Therefore, the negative ion of the σ-complex must have the composition $Al_2Br_7^-$ and not $AlBr_4^-$. It was previously concluded from vapor pressure studies of these systems that the $Al_2Br_7^-$ derivatives were considerably more stable than the corresponding complexes of $AlBr_4^-$.[13]

It is well known that catalytic amounts of the aluminum halides suffice to bring about the alkylation of large amounts of aromatic and to produce high yields of the higher alkylated derivatives. As was pointed out by Francis[19] the high yields of polyalkylated derivatives must be ascribed to the formation of a lower catalyst layer which serves to concentrate the catalyst, the alkyl halide and the more basic partially alkylated aromatics. Under the experimental conditions used in such reactions the σ-complexes must be partially dissociated so that some free aluminum halide is present in this layer together with some free partially alkylated aromatic.

It was pointed out earlier in this paper that were the reaction to involve a free methylcarbonium ion, then both isomer distributions and relative reactivities should be independent of the particular methyl halide used for the methylation. However, neither the isomer distribution nor the relative reactivities are independent of the halide.

For convenience in following the discussion, the average relative rate values and the derived partial rate factors are summarized in Table V.

TABLE V

RELATIVE RATES, ISOMER DISTRIBUTIONS AND PARTIAL RATE FACTORS IN METHYLATION OF BENZENE AND TOLUENE

Methyl halide	Temp., °C.	Isomer distribution, %			Relative rates	Partial rate factors[a]		
		p-	*m*-	*o*-		*pf*	*mf*	*of*
Bromide	0 to 5	28.9	17.3	53.7	3.77	6.56	1.96	6.07
Bromide	25 to 32	29.3	20.9	49.8	2.95	5.19	1.85	4.41
Iodide	−1 to 2	39.8	11.9	48.3	4.84	11.05	1.73	7.02

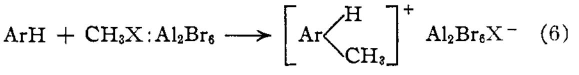
[a] Partial rate factor = 1.2 × (% obsd./% stat.) × relative rate.

Thus, in the methylation of toluene at 0°, methyl iodide yields 11.9% of *m*-xylene and 39.8% of *p*-xylene, a *para* to *meta* ratio of 3.3, whereas methyl bromide yields 17.3% *m*- and 28.9% *p*-, a *para* to *meta* ratio of 1.7. This difference in ratio appears to be well beyond the limits of the precision of the experimental techniques and to represent a significant difference in the selectivity of the two halides in the methylation reaction.

The data on the relative rate of methylation of toluene and benzene indicate a ratio at 0° of 3.8 for methyl bromide and a value of 4.8 for methyl iodide. Thus, here also, it appears that methyl iodide is the more selective of the two halides.

The results are, therefore, incompatible with a mechanism involving the formation and reaction of a free carbonium ion. They are consistent with the mechanism previously proposed for primary halides in which the aromatic participates in a nucleophilic attack (6) on a partially polarized alkyl halide–metal halide addition compound.[8]

$$CH_3X + Al_2Br_6 \rightleftarrows CH_3X:Al_2Br_6 \qquad (5)$$



$$ArH + CH_3X:Al_2Br_6 \longrightarrow \left[Ar\begin{matrix} H \\ CH_3 \end{matrix}\right]^+ Al_2Br_6X^- \qquad (6)$$

A quantitative relationship was proposed recently between the "activity" of a reagent, as measured by the relative rate of substitution of toluene and benzene and the "selectivity," as measured by the ratio of *para* to *meta* substitution in toluene.[22] Within the relatively large uncertainty of the present experimental data, the results appear to correspond to the proposed relationship (Fig. 2).

The difference in the "activity" and "selectivity" of the methyl bromide–aluminum bromide and methyl iodide–aluminum bromide addition compounds may be correlated with the difference in the relative tendencies of the two halogens to form a dative bond with the Lewis acid. The stronger bond formed by methyl bromide with the metal halide will result in a more highly polarized carbon–bromine bond. Consequently, the aromatic is required to contribute less in attaining the transition state and hyperconjugative contributions of the methyl group will be less important.

The weaker bond in the methyl iodide–aluminum bromide complex means that the metal halide exerts a smaller pull. Consequently, a greater push by the aromatic component is required in this case and hyperconjugative contributions of the methyl group are important, resulting in a greater selectivity of the reagent, both between toluene and benzene and between the *para* and *meta* positions of toluene.

In conclusion, the present results definitely

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[22] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

exclude a simple carbonium ion mechanism for Friedel–Crafts alkylations involving the methyl halides. The results are consistent with the displacement mechanism previously proposed for primary halides in which the aromatic component participates in a nucleophilic attack on a polarized alkyl halide–metal halide addition compound.

Experimental Part

Materials.—Benzene and toluene were purified as previously described[15] for toluene: tlouene, b.p. 110.0° at 744 mm., $n^{20}\text{D}$ 1.4985; benzene, b.p. 79.8° at 744 mm., $n^{20}\text{D}$ 1.5009.

Methyl bromide (Matheson Co.) was passed through a tube containing glass beads coated with phosphorus pentoxide and then condensed in a weighed vessel for addition to the reaction mixture.

Methyl iodide was washed with aqueous sodium bisulfite, separated and dried over Drierite. The material was then fractionated through a Todd column packed with $^1/_{16}''$ glass helices. A constant boiling fraction, b.p. 42.4° at 745 mm., $n^{20}\text{D}$ 1.5292, was utilized.

Purification and transfer procedures for the aluminum bromide have been described previously.[15]

Methylation Procedures.—Two different procedures were utilized. In one, the methyl halide was rapidly added as a liquid to effect reaction in as short a time as possible. In the second, the methyl halide was added slowly to permit temperature control of the reaction mixture.

A.—After the desired quantity of aluminum bromide had been transferred to a 200-ml., three-necked flask, the proper amount of aromatic (six moles per mole of Al_2Br_6) was added and the mixture shaken to facilitate solution. The methyl bromide (one mole per mole of Al_2Br_6) was added rapidly as a liquid at −80° to the solution cooled approximately 5° below the reaction temperature. The resultant temperature rise bracketed the desired reaction temperature. Methyl iodide could be added rapidly, utilizing this procedure without major heat effects.

B.—After the aromatic–aluminum bromide solution had been made up as in A, the methyl bromide was allowed to vaporize slowly into the reaction flask through an inlet tube which dipped into the reaction solution. The flask and its contents were maintained at the desired reaction temperature by immersion in a cooling bath.

Determination of the Extent of Methylation.—Methylation procedure A was followed for the reaction of benzene and toluene with methyl bromide. The quantities of reagents used are shown in Table I. Samples of 15 ml. were removed at the time intervals shown in the table and quenched by draining each sample into a 250-ml. erlenmeyer flask containing approximately 30 g. of crushed ice. The extent of the reaction was determined by titration of the hydrogen bromide in the water solution. The titration method is described below.

The methylation of toluene with methyl iodide followed procedure A. The reactants are listed in Table I. The progress of the reaction was followed by removing periodic samples (17 and 29 minutes). These were quenched as described above. After separating the organic portion and drying over Drierite, the quantity of xylene in the samples was determined by quantitative infrared analysis.

Determination of Methylation Products.—These experiments were carried out using methylation procedure A. Sufficient reactants were mixed to yield approximately 50 g. of material for fractionation. Reactions were run with contact times of 30, 60 and 120 min. The products were analyzed by fractionation in a Todd column packed with $^1/_{16}''$ steel helices and rated at 40 theoretical plates.

Attempted Methylation of Toluene–Aluminum Bromide–Hydrogen Bromide.—A mixture of 16.0 g. (0.174 mole) of toluene, 15.5 g. (0.0291 mole) of aluminum bromide and 0.0291 mole of hydrogen bromide was made up, as described previously.[15] With the solution at 25°, 2.76 g. (0.0291 mole) of methyl bromide was added rapidly. After 3 min., the reaction was quenched in ice-water. After separating and drying with Drierite, the organic portion was subjected to infrared analysis.

Determination of Isomer Distribution.—For these reactions, methylation procedure A was used. Toluene served as the aromatic component. Samples from methylation with methyl bromide were removed at 1 min. for the reaction at 25° and at the times indicated in Table II for the reaction at 0°. Samples were removed at 11 and 19 min. from the methylation reaction with methyl iodide. After quenching the samples, as described above, the dried (Drierite) toluene–xylene mixtures were analyzed directly by infrared to establish the composition of the xylene component. The samples resulting from reaction with methyl iodide contained some unreacted methyl iodide. Before infrared analysis, this was taken off in a Todd column containing a stainless steel spiral.

A compensating technique was used to analyze these samples. In this manner, a suitable amount of toluene, placed in the reference of the Perkin–Elmer double beam infrared absorption spectrophotometer, compensated for the excess toluene present in the sample.

Relative Rate Determination.—Methylation procedure B was used. The aromatic consisted of a mixture of benzene and toluene (usually equimolar). Addition of methyl bromide required 30 to 60 min. The reaction was then quenched. It required only 10 min. to add the methyl iodide but the reaction was allowed to proceed for 1–2 hr. The reactions were quenched on crushed ice. The organic portion was separated and dried with Drierite. The product distributions for the relative rate calculations were determined by fractionation in a Todd column with a stainless steel spiral. No unreacted methyl bromide was recovered by this technique. The unreacted methyl iodide was collected with the benzene. The method of analysis has been described in the Results section.

Equation for Relative Rate Calculation.—The equation used for the relative calculations is derived as follows.

The disappearance of toluene may be written as

$$-\,\mathrm{d[T]}/\mathrm{d}t = k_\mathrm{T}[\mathrm{T}] - k_\mathrm{B}[\mathrm{B}]$$

The disappearance of benzene may be expressed as

$$-\,\mathrm{d[B]}/\mathrm{d}t = k_\mathrm{B}[\mathrm{B}]$$

Combining and integrating these expressions

$$T - \frac{k_\mathrm{B}[\mathrm{B}]}{k_\mathrm{T} - k_\mathrm{B}}\, e^{k_\mathrm{T}t} = [\mathrm{T}_0] - \frac{k_\mathrm{B}[\mathrm{B}_0]}{k_\mathrm{T} - k_\mathrm{B}}$$

substituting

$$t = \ln\, [\mathrm{B}_0]/[\mathrm{B}]/k_\mathrm{B}$$

the final expression is

$$(\mathrm{B}_0/\mathrm{B})^{k_\mathrm{T}k_\mathrm{B}} = \frac{(k_\mathrm{T}/k_\mathrm{B})T_0 - (T_0 + B_0)}{(k_\mathrm{T}/k_\mathrm{B})\, T - (T + B)}$$

It is best to solve this equation graphically by plotting the function on each side of the equation against $k_\mathrm{T}/k_\mathrm{B}$. The relative rate is determined by the value of $k_\mathrm{T}/k_\mathrm{B}$ where the lines intersect.

Titration Technique—This titration method is a development of an analytical procedure reported by Snyder[23] which allows the separate determination of hydrogen bromide due to the catalyst and that resulting from the reaction. To the aqueous portion from the quenched mixture was added 10 cc. of 30% sodium potassium tartrate solution. This was then titrated to a phenolphthalein end-point with 0.1 *N* barium hydroxide, giving the total hydrogen bromide present. Next, 10 cc. of 30% potassium fluoride solution (previously neutralized) was added, making the solution basic. Sufficient 0.3 *N* hydrochloric acid was added to turn the indicator colorless. The solution was again titrated to the end-point with the base. The acid, corrected for the base used in the back titration, is equivalent to the hydrogen bromide coming from the aluminum bromide. The difference in the two titers corresponds to hydrogen bromide formed in the alkylation reaction.

From the titration, the quantities of catalyst in the sample were calculated. The extent of the reaction was calculated by multiplying the quantity of hydrogen bromide due to reaction by the ratio of catalyst charged to the reaction to that found in the sample.

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[23] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).