[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Isomerization of *o*- and *p*-Xylenes and Some Related Alkylbenzenes Under the Influence of Hydrogen Bromide and Aluminum Bromide; the Relative Isomerization Aptitudes of Alkyl Groups[1,2]

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The isomerization of *o*- and *p*-xylenes in toluene solution under the influence of hydrogen bromide and aluminum bromide was examined. The reaction follows second-order kinetics, first order in the xylene and first order in hydrogen bromide–aluminum bromide. The second-order kinetics are attributed to the distribution of protons between the toluene used as solvent and the *o*- and *p*-xylenes which undergo isomerization. The rate constants obtained for *o*-xylene are 5.84×10^{-6} and 1.98×10^{-4} l. mole^{-1} sec.$^{-1}$ at 0 and 25°, respectively. *p*-Xylene isomerizes at a faster rate with k_2 3.25×10^{-5} and 8.78×10^{-4} l. mole^{-1} sec.$^{-1}$ at these temperatures. From these data, the activation energies are 22.8 kcal./mole for *o*-xylene and 21.3 kcal./mole for *p*-xylene. *o*-Xylene isomerizes to *m*-xylene without the concurrent formation of *p*-xylene. Similarly, no *o*-xylene appears to be formed in the isomerization of *p*-xylene. These results rule out an unlocalized π-complex (Dewar) as an intermediate in the isomerization. It is concluded that the isomerization must proceed either through a localized π-complex or through a mechanism involving a direct 1:2 shift of the methyl group. The rates of isomerizaton increase markedly in the series: *p*-xylene, *p*-ethyltoluene and *p*-isopropyltoluene. It is concluded that the ease of isomerization of alkyl groups increases sharply in the series: methyl < ethyl < isopropyl < (*t*-butyl). This order of rates is explained by postulating that the alkyl groups gain a positive charge during the transfer and that the rate is determined by the ability of the groups to stabilize the positive charge. Two possible mechanisms are considered: (1) an equilibrium between the σ-complex and a high energy localized π-complex prior to isomerization, and (2) a direct transfer from the σ-complex leading to a charged transition state. Either possibility will account for the facts. *p*-Xylene isomerizes faster than *o*-xylene by a factor greater than can be accounted for on the basis of statistical considerations. This higher rate for *p*-xylene is attributed to the higher concentration of the proper *p*-xylene σ-complex required for isomerization.

Qualitative observations on the isomerization of the xylenes under the influence of hydrogen bromide and aluminum bromide have been described previously by Baddeley and his co-workers.[4] A quantitative study of the isomerization of the xylenes in liquid hydrogen fluoride under the influence of boron fluoride has been reported by McCaulay and Lien.[5]

In connection with the study of the mechanism of the Friedel–Crafts reaction, we have been investigating the directive effects in the alkylation of toluene with alkyl halides under the influence of aluminum bromide. It was observed that, under the conditions of the alkylation experiments, the initial isomer distributions were altered significantly by subsequent isomerization. In order to circumvent this difficulty, it was necessary to study this isomerization in some detail. For this reason, we undertook to obtain quantitative data on the isomerization of *p*- and *o*-xylenes, *p*-ethyltoluene and *p*-isopropyltoluene.

Our alkylation experiments were carried out by adding one mole of alkyl bromide to a mixture of six moles of toluene and one mole of aluminum bromide (Al_2Br_6). Under these conditions, the reactions remain completely homogeneous.[6]

We were interested in applying the results of these isomerization studies to the problems arising in the alkylation experiments. For this reason, the isomerizations were carried out in a system identical with the alkylation system at the completion of alkylation.

Results

The isomerization of the xylenes was carried out in the following manner. Toluene and aluminum bromide (Al_2Br_6) were mixed in a mole ratio of 5 to 1, producing a clear orange-colored solution. The slow addition of one mole of hydrogen bromide caused the formation of a dark reddish-brown second layer, which increased in volume until the system became homogeneous again. The isomerization was initiated by the addition of one mole of the appropriate xylene. Samples were withdrawn at appropriate intervals of time and quenched in ice-water. The dried toluene–xylene mixture was analyzed by infrared absorption.

In this manner, the kinetics of isomerization of both *p*- and *o*-xylene were studied at both 0 and 25°. Under the same conditions, *m*-xylene did not isomerize or exhibit any other change.

Examination of the infrared spectra revealed that *o*-xylene isomerized to *m*-xylene without the formation of any detectable amounts of *p*-xylene. Likewise, the isomerization of *p*-xylene proceeded directly to the *m*-xylene without any observable formation of the *ortho* isomer.[7]

The rate data were found to fit the second-order rate equation $k_2t = x/a(a - x)$ (Fig. 1). The rate constants and derived data are summarized in Table I.

TABLE I

RATE CONSTANTS AND DERIVED DATA FOR THE ISOMERIZATION OF *o*- AND *p*-XYLENES

	o-Xylene	*p*-Xylene
k_2, 0°, l. mole^{-1} sec.$^{-1}$	5.84×10^{-6}	3.25×10^{-5}
k_2, 25°, l. mole^{-1} sec.$^{-1}$	1.94×10^{-4}	8.78×10^{-4}
E_{act}, kcal./mole	22.8	21.3
log A	14.86	14.36
$\Delta H^{\ddagger}$, kcal./mole	22.3	20.9
$\Delta S^{\ddagger}$, cal./deg.	−0.68	−2.41

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(1) The Catalytic Halides. XI.

(2) Based upon a thesis submitted by Hans Jungk 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) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

(5) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

(6) These conditions were suggested by studies previously reported, which showed that up to six moles of toluene could be added to a toluene–aluminum bromide–hydrogen bromide complex without separation of phases; H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6268 (1953).

(7) Similar results were obtained by J. F. Norris and D. Rubinstein (THIS JOURNAL, **61**, 1163 (1939)) in their observations of the isomerization of *o*- and *p*-xylenes at somewhat higher temperatures in the presence of aluminum chloride.

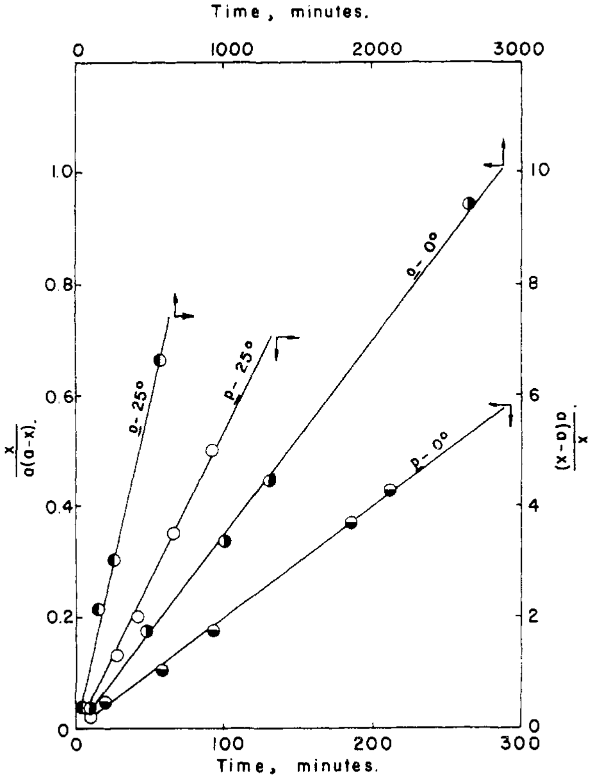


Fig. 1.—Rates of isomerization of *o*- and *p*-xylenes at 0 and 25°.

The isomerizations of *p*-ethyl- and *p*-isopropyltoluene are exceedingly rapid in this reaction system. It was necessary to resort to a flow technique to achieve a reaction time sufficiently short so that the reaction could be halted prior to complete isomerization. Because of these difficulties, we abandoned our attempts to follow the rates of isomerization of these compounds and were content to establish a qualitative comparison of the rates (Table II).

TABLE II

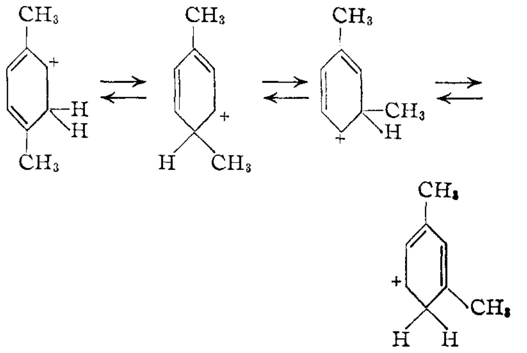
ISOMERIZATION OF *p*-ETHYL- AND *p*-ISOPROPYLTOLUENES WITH 0.005 SECOND REACTION TIME

Toluene		Isomer distribution, % *o*-	*m*-	*p*-
p-Ethyl-	Init.	7.6	5.0	87.4
	Final	12.1	7.7	80.2
p-Isopropyl-	Init.	0	0	100
	Final	0	52.0	48.0

With a reaction time of approximately 0.005 second, the extent of isomerization of *p*-ethyltoluene was 7% and that of *p*-isopropyltoluene was 52.0%. The results clearly establish that the order of ease of isomerization of alkyl groups under these conditions must be methyl < ethyl < isopropyl, with *t*-butyl presumably faster still.

Discussion

The second-order kinetics observed for the isomerization reaction were unexpected. Actually, were the *p*-xylene to be essentially completely converted to a σ-complex,[8] existing in equilibrium with a higher energy form which rearranges (1), the reaction would be expected to follow first-order kinetics.[4,5,9]

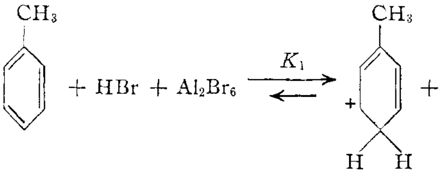


(1)

The small entropies of activation (Table I) are in accord with a unimolecular rearrangement and not with any bimolecular process as might be suggested by the second-order kinetics of the reaction. However, the rate data agree far better with the treatment as a second-order reaction than they do with analysis as a first order reaction.

It is our belief that the reaction is essentially a unimolecular rearrangement of the σ-complex, with the second-order kinetics arising from an equilibrium distribution of protons between the toluene used as solvent and the *o*- and *p*-xylene undergoing isomerization.

Consider the following reaction mechanism, with the reaction going to completion primarily because of the high stability of the σ-complex of *m*-xylene.[10] The process for *o*-xylene would be similar.



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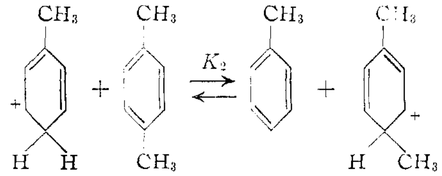

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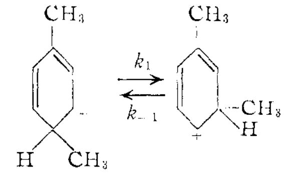

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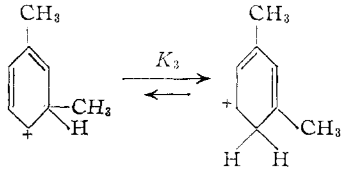

(5)

The addition of hydrogen bromide and aluminum bromide to toluene results in the formation of the

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[8] H. C. Brown and J. D. Brady, THIS JOURNAL, 74, 3570 (1952).

[9] G. Baddeley, *J. Chem. Soc.*, 944 (1950).

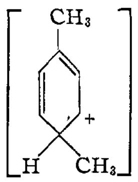
[10] D. A. McCaulay and A. P. Lien, THIS JOURNAL, 73, 2013 (1951).

σ-complex[6] (2). The added xylene in part abstracts a proton from this solvent σ-complex, forming a new σ-complex (3). There will exist an equilibrium distribution between the various isomeric σ-complexes of which that shown (3) will lead to isomerization (4). The stability of the σ-complex of *m*-xylene (5) prevents the reverse reaction (k_{-1}) from becoming significant.

According to the proposed reaction scheme, $S^{\ddagger}$ (measured) = ΔS (step 3) + $S^{\ddagger}$ (step 4). It is reasonable to expect the entropy change for a reaction such as step 3 to be near zero and the entropy of activation for a unimolecular rearrangement, such as step 4, to be small. Therefore the small entropies of activation obtained (Table I) are in accord with the values predicted from the proposed reaction scheme.

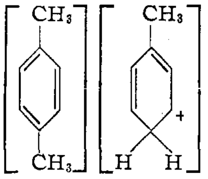
Assuming that the rearrangement of the σ-complex is the rate-determining stage, the kinetic expression is

rate = k_1



Using the equilibrium expression (3), this becomes

rate = k_1K_2



Under the experimental conditions (toluene in large excess and [HBr] = [Al_2Br_6]), this expression reduces to

$$\text{rate} = k_1K_1'K_2[p\text{-xylene}][Al_2Br_6, HBr]$$

in agreement with experimentally observed kinetics.

Unfortunately, there are no measurements available for the equilibrium between hydrogen bromide–aluminum bromide and various aromatics. Consequently, we cannot calculate directly the distribution of protons between the toluene used as solvent and the xylenes undergoing isomerization to provide a test for the explanation advanced to account for the second-order kinetics.

However, the relative basicities of toluene, *p*-xylene, *o*-xylene and *m*-xylene have been determined in the hydrogen fluoride–boron fluoride system.[11] It is possible to calculate the distribution of protons between the various aromatic species in our experiments, assuming these values for the relative basicities.[12]

On this basis, the addition of one mole of hydrogen bromide–aluminum bromide to a 5:1 molar mixture of toluene and each of the xylenes would result in the following distribution of σ-complexes

$$\frac{\text{Toluene}\cdot H^+}{o\text{-Xylene}\cdot H^+} = \frac{0.62}{0.38}$$

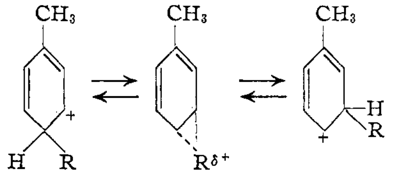
$$\frac{\text{Toluene}\cdot H^+}{p\text{-Xylene}\cdot H^+} = \frac{0.66}{0.34}$$

$$\frac{\text{Toluene}\cdot H^+}{m\text{-Xylene}\cdot H^+} = \frac{0.19}{0.81}$$

These considerations indicate that in the initial stages of the reaction the protons probably are attached predominantly to the toluene, present in excess. The formation of the more basic *m*-xylene, as the reaction proceeds, effectively removes hydrogen bromide–aluminum bromide from the system. Consequently, the distribution of protons between toluene and *o*- or *p*-xylene does not remain constant and first-order kinetics are not followed.

It is of interest to consider more closely the exact mechanism of alkyl group transfer.[4,5] The isomerizations proceed directly from the *o*- or *p*-xylene to *m*-xylene without the formation of the third possible isomer in detectable amounts. The result cannot be accounted for in terms of a mechanism[9] involving an "unlocalized" π-complex.[13] Such a π-complex with the alkyl group attached to the π-electron cloud would be expected to lead to the distribution of the migrating alkyl group to all available positions in the ring.

The results are in far better agreement with a mechanism involving a direct transfer of the alkyl group, *i.e.*, a 1,2-shift. Here we have two possibilities to consider. Either the alkyl group passes from the original carbon atom to its neighbor, passing through a transition state[4] as in (7), or there is formed a "localized" π-complex as a high energy intermediate (8).[15]



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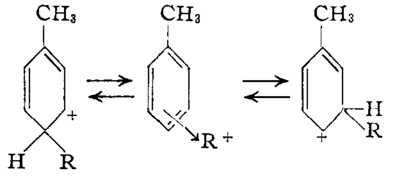

(8)

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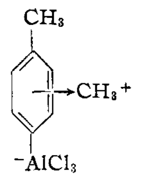
[11] D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

[12] Some uncertainty exists in the precise values of the basicities of the less basic aromatics. Consequently, we utilized the relative basicities as calculated by F. E. Condon [THIS JOURNAL, **74**, 2528 (1952)] from the experimental data of D. A. McCaulay and A. P. Lien [THIS JOURNAL, **73**, 2013 (1951)] for the more basic aromatics.

[13] M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 432. It should be pointed out that the actual structure proposed by Dewar, has been shown to be incorrect (ref. 14, 4), since it does not account for the need of halogen acid in the isomerization. This, in itself, does not rule out unlocalized π-complexes as intermediates. The term unlocalized π-complex is used here to designate a π-complex in which the electrophilic group is attached to the π-electron cloud with relatively free mobility around this cloud.



[14] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 813 (1943).

[15] See Fig. 4, ref. 5.

TABLE III

ISOMERIZATION DATA FOR *o*- AND *p*-XYLENE

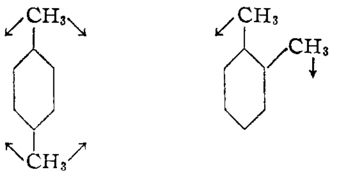
Reactants[a] Toluene	Reactants[a] Al_2Br_6	Reactants[a] Xylene	Temp., °C.	Time, min.	Products (xylene)[b] *o*-	Products (xylene)[b] *m*-	Products (xylene)[b] *p*-	Rate constants k_2, l. mole^{-1} sec.$^{-1}$
55.5	64.3	12.8	0	0	1.219			
				118	1.178	0.0408		4.01×10^{-6}
				478	1.004	.215		6.13
				1008	0.864	.354		5.56
				1307	.789	.430		5.70
				2633	.568	.651		5.95
							Ave.[c]	5.84 ± 0.29
47.1	54.6	10.9	25	0	1.221			
				33	0.828	0.393		1.96×10^{-4}
				143	.365	.856		2.50
				262	.263	.958		1.91
				566	.134	1.087		1.96
							Ave.[d]	1.94 ± 0.03
29.7	34.4	6.8	0	0			1.214	
				18		0.0660	1.110	4.77×10^{-5}
				57		.140	1.090	3.06
				92		.215	0.995	3.24
				185		.374	.838	3.32
				211		.407	.795	3.36
							Ave.[e]	3.25 ± 0.18
50.5	58.5	11.6	25	0			1.186	
				8		0.363	0.835	7.55×10^{-4}
				26		.760	.460	8.68
				42		.835	.346	8.12
				65		.950	.226	9.16
				91		.993	.173	9.16
				308		1.050	.045	11.49
							Ave.[f]	8.78 ± 0.66

[a] Grams. [b] Moles/liter. [c] Graphical value: 5.90×10^{-6}. [d] Graphical value: 1.96×10^{-4}. [e] Graphical value: 3.37×10^{-5}. [f] Graphical value: 9.03×10^{-4}.

Both in the transition state (7) and in the π-complex intermediate (8) the alkyl group R carries a positive charge. It is well recognized that the stability of carbonium ions increases markedly with increased branching, $CH_3^+ < C_2H_5^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$. Consequently, the activation energy should decrease and the rate should increase with increased branching of the alkyl group R.

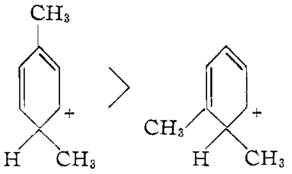
On the basis of present evidence, it is not possible to reach a decision as to whether the structure with the alkyl group midway between its initial and rearranged position represents a transition state or a high energy intermediate. The results, however, definitely exclude the participation of an "unlocalized" π-complex as an important intermediate in the reaction.

The relative rates of isomerization of *p*-xylene as compared to *o*-xylene are 4.53 at 25° and 5.57 at 0°. A factor of 2 might be accounted for on the basis of statistical considerations, since *p*-xylene possesses twice as many possibilities for isomerization as does *o*-xylene (9).



(9)

However, even this factor of 2 must be considered as an upper limit since isomerization of *o*-xylene should be facilitated slightly by relief of steric strain. Moreover, *o*-xylene is somewhat more basic than *p*-xylene, so that the equilibrium concentration of all of the σ-complexes must be smaller for the *para* isomer. We are, therefore, forced to the conclusion that the larger rate of isomerization of *p*-xylene, as compared to the *ortho* isomer, must be attributed to a higher equilibrium concentration of the particular σ-isomer responsible for the rearrangement (10).



(10)

In many aromatic substitution reactions in which steric effects are quite small, such as nitration, chlorination and protonation, it is observed that the partial rate or equilibrium factors are larger for the *para* position than for the *ortho*.[16] The larger *para* partial factors must be related to the greater stabilities of the *para* σ-complexes, presumably arising from more complete hyperconjugative interaction with the methyl group in

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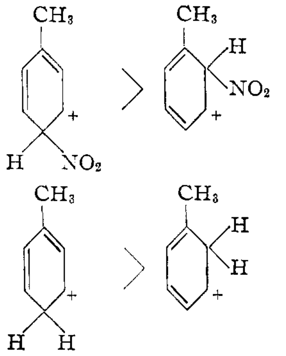
[16] H. C. Brown and C. W. McGary, THIS JOURNAL, **77**, 2300 (1955).

the *para* as compared to that in the *ortho* position (11).



(11)

On this basis, the proposed higher equilibrium concentration postulated to be responsible for the isomerization of *p*-xylene (10) is quite reasonable.

Experimental Part

Materials.—The highest purity, commercially available hydrocarbons were utilized. These were dried with calcium hydride and fractionated through a column rated at 70 theoretical plates. In each case, center fractions of constant boiling point and refractive index were taken and stored over calcium hydride. The physical constants of the materials used are: toluene, b.p. 110.0° at 742 mm., $n^{20}D$ 1.4985; *o*-xylene, b.p. 144.1° at 748 mm., $n^{20}D$ 1.5051; *p*-xylene, b.p. 137.9° at 745 mm., $n^{20}D$ 1.4954; *m*-xylene, b.p. 138.9° at 740 mm., $n^{20}D$ 1.4969; *p*-isopropyltoluene, b.p. 176.9° at 744 mm., $n^{20}D$ 1.4902.

p-Ethyltoluene was prepared by a procedure patterned after a synthesis of *p*-diethylbenzene reported by Fittig.[17]

A mixture of 69 g. of *p*-bromotoluene and 55 g. of ethyl bromide was added slowly (over 30 minutes) to a mixture of 28 g. of sodium in 300 ml. of anhydrous ether contained in a 1-l., 3-necked flask at 0°. After several hours at 0°, the ice-bath was removed and the reaction allowed to stand overnight at room temperature. The mixture was filtered and fractionated. The yield was 30% of theoretical; b.p. 161.7° at 743 mm., $n^{20}D$ 1.4985.[18]

In the original experiments, commercial aluminum bromide (Fisher Scientific Co.) was used after distillation. The material was transferred rapidly to a 500-ml., round-bottomed flask and distilled under nitrogen in an all-glass system to remove partially hydrated material and entrained hydrogen bromide. For use in the reactions, the purified catalyst then was distilled as needed directly into the reaction flask.

In subsequent work, the aluminum bromide was synthesized. The product thus obtained was superior in quality to the commercial material.

Into a 1-l., 3-necked flask was placed 150 g. of C.P. aluminum wire (Baker and Adamson), cut into short pieces. The flask was fitted with a condenser and an addition funnel. One pound of bromine (Mallinckrodt) was added through the dropping funnel at a rate sufficient to maintain the product in a liquid state. Following completion of the addition (5–6 hr.), the product was maintained as a liquid for an additional 8 hr. to permit the last traces of the dissolved bromine to react with the excess aluminum. At the end of this period, the product was distilled through a Claisen distilling head and West condenser into a 1-l., 3-necked flask immersed in an ice-bath. (Steam was passed through the jacket of the condenser to prevent solidification.) The clear white product was stored under dry nitrogen.

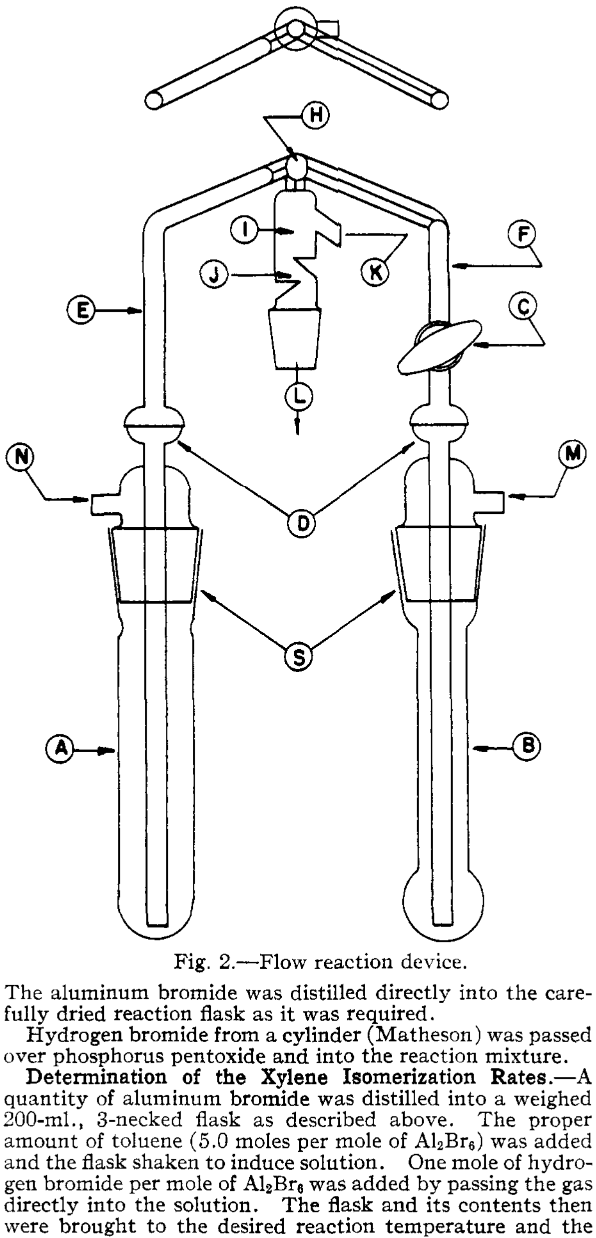


Fig. 2.—Flow reaction device.

The aluminum bromide was distilled directly into the carefully dried reaction flask as it was required.

Hydrogen bromide from a cylinder (Matheson) was passed over phosphorus pentoxide and into the reaction mixture.

Determination of the Xylene Isomerization Rates.—A quantity of aluminum bromide was distilled into a weighed 200-ml., 3-necked flask as described above. The proper amount of toluene (5.0 moles per mole of Al_2Br_6) was added and the flask shaken to induce solution. One mole of hydrogen bromide per mole of Al_2Br_6 was added by passing the gas directly into the solution. The flask and its contents then were brought to the desired reaction temperature and the reaction begun by rapid addition of the xylene isomer (one mole per mole of Al_2Br_6). At appropriate time intervals, 10- to 15-cc. samples were removed and drained into 250-ml. erlenmeyer flasks containing approximately 30 g. of crushed ice. The organic portion was separated, washed with water and dried with Drierite.

The compositions of the xylene fractions were determined directly from the toluene–xylene product mixtures. This was accomplished by infrared analysis using a Perkin–Elmer double beam instrument. In order to analyze for the xylenes without interference from the excess toluene, a technique was developed which made it possible to compensate for this excess toluene by using a suitable quantity of toluene as the reference.

In the isomerization of *p*-xylene, the concentrations of the *para* and *meta* isomers were determined directly from the respective infrared peaks. In the isomerization of *o*-xylene, the concentration of *m*-xylene was determined again from the infrared peak but it was not possible to use the *o*-xylene peak, because of some interference between it and the toluene peak. The concentration of *o*-xylene was determined by difference between the total xylene added and the *m*-xylene found.

The experimental results are summarized in Table III.

The Flow System.—The apparatus shown in Fig. 2 was

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[17] R. Fittig and J. Koenig, *Ann.*, **144**, 285 (1867).

[18] Infrared analysis indicated the presence of 12.6% of the *o*- and *m*-isomers. Unfortunately, this was not detected until after the isomerization studies had been completed. Moreover, we found that because of the width of the absorption bands, particularly for *m*-ethyltoluene, infrared analysis of the isomer distribution in the ethyltoluenes was far less satisfactory than in the case of the xylenes and the isopropyltoluenes. The results clearly establish the rate of isomerization to lie between that of *p*-xylene and *p*-isopropyltoluene. Consequently, a repetition of the synthesis and isomerization was not attempted.

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.

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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]

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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$_N$2, 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).