[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Isomerization of the Methylbenzenes

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RECEIVED AUGUST 8, 1952

Isomerization experiments and rate studies made on the xylenes, trimethylbenzenes and tetramethylbenzenes and catalyzed with hydrogen fluoride and boron trifluoride show that the amount of catalyst used has a pronounced effect on the composition of the isomerized equilibrium mixture. At low boron trifluoride concentrations the *m*-xylene content of 60% is in agreement with the thermodynamically calculated value of 57%, while at high concentrations the *m*-xylene content approaches 100%. Similarly, the predominant nine-carbon and ten-carbon isomers produced with minor amounts of boron trifluoride are pseudocumene (66%) and durene (70%), while with excess boron trifluoride the isomerized products are 100% mesitylene and 100% isodurene, respectively. This variation in equilibrium composition is attributed to the formation of stable complexes of hydrogen fluoride and boron trifluoride with *m*-xylene, mesitylene and isodurene.

The orientation of alkyl groups in the polyalkylbenzenes formed by alkylating benzene or its homologs is difficult to explain. With mild catalysts such as phosphoric acid, sulfuric acid and ferric chloride, the chief dialkylbenzene products are the ortho and para isomers,[1,2] which are the "normal" products predicted from the ortho- and para-directing effects of an alkyl group. Likewise, at low temperatures (−40 to 0°), methylation with active catalysts such as aluminum chloride yields normal products. Thus, Norris and Rubenstein[3] found *o*- and *p*-xylene to be the principal xylene isomers and pseudocumene the principal trimethylbenzene isomer formed by treating benzene or toluene with methyl chloride. However, at higher temperatures (50 to 100°) the *m*-xylene content of the xylene fraction and the mesitylene content of the trimethylbenzene fraction were both close to 90%. Also, at all temperatures and in the presence of excess aluminum chloride, 1,3,5-triethylbenzene was the predominant triethylbenzene produced by the ethylation of benzene.[3] The literature is generally in agreement that mild conditions give normal products and vigorous conditions lead to "abnormal" products.

The presence of 1,3-derivatives has been attributed to either dealkylation of the 1,2,4-product[4] or to isomerization of the 1,2- and 1,4-forms by an excess of catalyst.[3] Moderately high temperatures are required to isomerize the methylbenzenes; isomerization of the other alkylbenzenes proceeds even at low temperatures.[3] The dealkylation mechanism is open to the objection that intermolecular transfer of alkyl groups occurs only under conditions which will also effect intramolecular transfer, *i.e.*, isomerization. The isomerization mechanism, in itself, is also unsatisfactory, because it does not explain why many reported xylene and trimethylbenzene alkylates[4,5] contain *m*-xylene and mesitylene greatly in excess of the equilibrium percentages as calculated by Taylor, *et al.*,[6] or as determined experimentally by Norris and Vaala[7] and Pitzer and Scott.[8]

Recent studies in our laboratories of the acid-catalyzed isomerization of the methylbenzenes demonstrate the importance of catalyst concentration not only on rate of isomerization but also on equilibrium product distributions; these studies provide a mechanism to explain the abnormally high yields of 1,3- and 1,3,5-oriented products in Friedel–Crafts alkylation. The catalyst used, $HF-BF_3$, was especially suited for the investigation, inasmuch as the hydrogen halide component, hydrogen fluoride, was a liquid and could be used in excess to ensure a near constant activity and to serve as a high dielectric reaction solvent. Other Friedel–Crafts catalysts, such as $HCl-AlCl_3$ and $HBr-AlBr_3$, suffer from the disadvantage that their hydrogen halide components are gases, cannot act as reaction solvents, and cannot, except with extreme difficulty, be maintained at constant activity to allow attention to be focused on changes in metal halide concentration.

Experimental

The three xylenes were Eastman Kodak Company White Label grade and, after analysis, were used without further purification. The mesitylene, Eastman Kodak Company White Label grade, was found by infrared analysis to contain 3% impurities, which were mostly close-boiling nonaromatic hydrocarbons. The pseudocumene was obtained by fractionation of a sample of Eastman Kodak Company mixed trimethylbenzenes through a Hypercal distillation column and selection of a 167–171° cut, which infrared analysis showed to contain about 95% pseudocumene, 3% mesitylene, 0.5% hemimellitene and 1.5% mixed ethyltoluenes. The hydrogen fluoride and boron trifluoride were commercial grades of 99.6 and about 99% purity, respectively, obtained from the Harshaw Chemical Company.

The isomerization experiments were carried out in the same equipment and in the same manner as the earlier xylene-extraction studies.[9] The hydrocarbon was charged to a 1570-ml. carbon–steel autoclave, and then hydrogen fluoride and boron trifluoride were added. The mixture was stirred at the desired temperature and, after a predetermined time, the entire product was withdrawn into a polyethylene flask partly filled with crushed ice. The flask was then shaken until all the ice had melted. The supernatant hydrocarbon layer was then separated and fractionated through a column of thirty theoretical plates. Fractions of individual carbon numbers were analyzed by either infrared or ultraviolet absorption.

Results and Discussion

Whereas aromatic hydrocarbons are not appreciably soluble in hydrogen fluoride alone, they become completely miscible with the latter in the presence of excess boron trifluoride.[9,10] An ionized complex

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[1] F. W. Melpolder, J. E. Woodbridge and C. E. Headington, THIS JOURNAL, **70**, 935 (1948).

[2] L. J. Slanina, F. J. Sowa and J. A. Nieuwland, *ibid.*, **57**, 1547 (1935).

[3] J. F. Norris and D. Rubenstein, *ibid.*, **61**, 1163 (1939).

[4] C. C. Price, *Chem. Revs.*, **29**, 44, 64 (1941).

[5] A. W. Francis, *ibid.*, **43**, 257 (1948).

[6] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

[7] J. F. Norris and G. T. Vaala, THIS JOURNAL, **61**, 2131 (1939).

[8] K. S. Pitzer and D. W. Scott, *ibid.*, **65**, 813 (1943).

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

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

TABLE I

ISOMERIZATION OF XYLENES AT 82 TO 121°

6 moles HF per mole of xylene

Xylene	Meta-	Meta-	Ortho-	Meta-	Meta-	Ortho-	Para-
BF_3, moles/mole xylene	0.09	0.06	0.10	0.13	0.65	0.72	3.0
Temperature, °C.	82	100	100	121	82	82	3
Contact time, min.	30	30	30	3	30	30	1380
Yield of C_8 product, %	98	91	83	91	94	84	100
Composition of C_8 product, %							
o-Xylene	15	19	19	18	11	11	0
m-Xylene	64	60	61	60	74	75	100
p-Xylene	22	21	20	22	15	14	0

—containing one mole each of aromatic hydrocarbon, boron trifluoride and hydrogen fluoride—is formed in the acid layer. The fraction of the total aromatic hydrocarbon dissolved in the acid phase is therefore approximately equal to the mole ratio of boron trifluoride to hydrocarbon. The remaining hydrocarbon forms a separate phase. In some of the present experiments differing amounts of boron trifluoride were used to demonstrate the effect of varying concentration on product distribution. In other experiments a large excess of boron trifluoride was used to ensure the complete solution of the xylene in the acid phase. The latter studies were suitable for calculation of the reaction rate constants, because the homogeneous phase eliminated the complicating factors of a two-phase system.

Xylene Isomerization.—The results of experiments in which a pure xylene was isomerized with a large excess of hydrogen fluoride plus differing amounts of boron trifluoride are given in Table I. Separate experiments at 100° with *m*- and *o*-xylene gave products of the same composition and showed that isomerization equilibrium had been attained in 30 minutes. The equilibrium composition varied little with temperature; the experiments at 82, 100 and 121°, with small amounts of boron trifluoride, gave the same xylene product. The compositions of all four products agree closely with the equilibrium compositions as calculated by Taylor[6]:

	80°	120°
o-Xylene, %	18	19
m-Xylene, %	58	57
p-Xylene, %	24	24
	100	100

The *m*-xylene contents of the products of the three remaining runs were much greater than the equilibrium composition. These experiments differed from the others in that the boron trifluoride to xylene ratio was much higher. In these runs a large portion of the xylenes was present in the form of $HF–BF_3$–xylene complexes.[9] Two equilibria are in force: a virtual equilibrium in the hydrocarbon phase which has the composition calculated by Taylor,[6] and an actual equilibrium among the $HF–BF_3$–xylene complexes in the acid layer. This relationship may be depicted as shown in Fig. 1. The complex of *m*-xylene with $HF–BF_3$ is much more stable than the other xylene complexes[9,10] and, therefore, the *m*-xylene content in equilibrium in the acid phase is much higher than that in equilibrium in the hydrocarbon phase.

In these experiments the yield of xylene product ranged from 80 to 100%. The other products were toluene and trimethylbenzene formed by the disproportionation of xylene. At 30°, the lowest temperature studied, there was no detectable disproportionation, even though isomerization to *m*-xylene was complete. The activation energy required for isomerization therefore is much less than that required for disproportionation.

Trimethylbenzene Isomerization.—The results of experiments in which trimethylbenzenes were isomerized with a large excess of hydrogen fluoride (7 moles per mole of hydrocarbon) plus differing amounts of boron trifluoride are given in Fig. 2, wherein the mesitylene content of the C_9 product is plotted against the mole ratio of boron trifluoride to trimethylbenzene. All the points in the range of 0.0 to 1.0 mole of boron trifluoride per mole of trimethylbenzene fall along the straight line extending from 34% mesitylene to about 100% mesitylene; in all runs in which the boron trifluoride concentration was greater than 1.0 mole, the product was 100% mesitylene. Because these values were approached from both sides, equilibrium—*i.e.*, between the 1,2,4- and 1,3,5-isomers—had been achieved. The mesitylene content of 34% at 0.0 mole of boron trifluoride agrees well with the equilibrium trimethylbenzene composition at 100° as calculated by Taylor[6]:

Hemimellitene (1,2,3-), %	9
Pseudocumene (1,2,4-), %	60
Mesitylene (1,3,5-), %	31
	100

No hemimellitene was detected among the products. Apparently the interconversion of pseudocumene and mesitylene is much faster than that of pseudocumene and hemimellitene.

The mesitylene content increases with boron trifluoride concentration until, at 1.0 mole, mesitylene comprises almost 100% of the trimethylbenzene fraction. This variation in equilibrium composition with boron trifluoride concentration is due to the very high relative stability of the $HF–BF_3$–mesitylene complex.[10]

Tetramethylbenzene Isomerization.—The results of tetramethylbenzene isomerization are presented in Table II. When less than one mole of boron trifluoride was used, the predominant tetramethylbenzene isomer was durene; with more than one mole of boron trifluoride, isodurene was the only tetramethylbenzene isomer detected. The equilib-

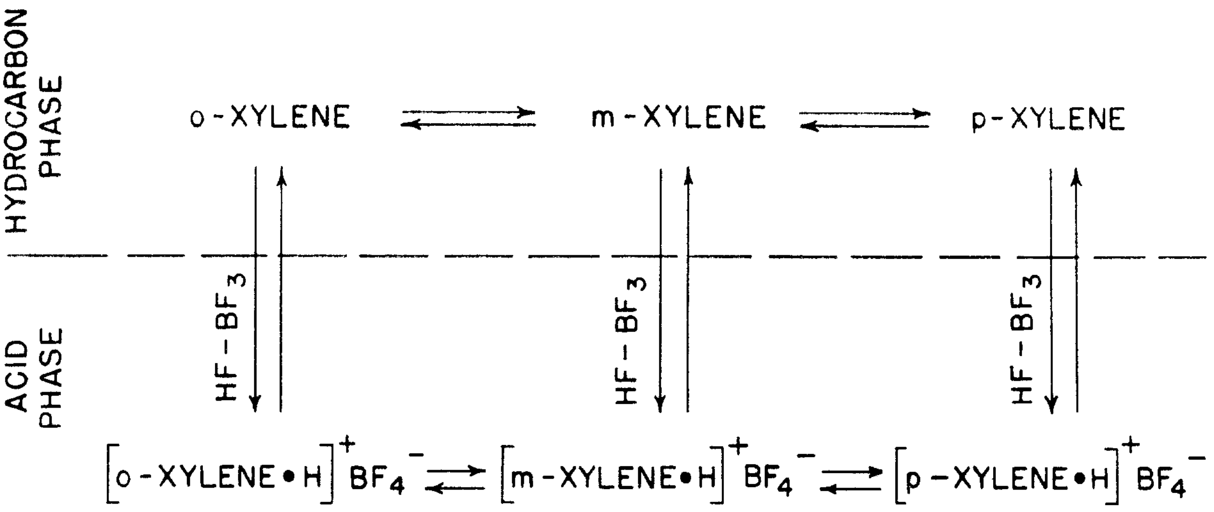


Fig. 1.—Equilibria among the xylenes.

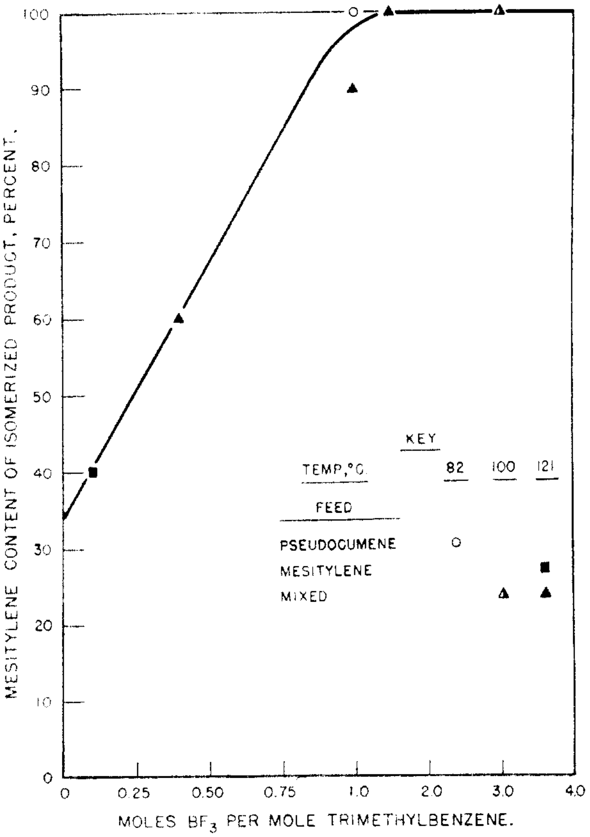


Fig. 2.—Composition of isomerized trimethylbenzenes.

Table II

Isomerization of Tetramethylbenzenes

6 to 12 moles HF per mole of tetramethylbenzene; a, mixture of tetramethylbenzenes from disproportionation of mesitylene; b, mixture of tetramethylbenzenes from disproportionation of pseudocumene; c, mixture of tetramethylbenzenes from disproportionation of pentamethylbenzene.

Tetramethylbenzene	a	b	c	Durene	Durene
Temperature, °C.	100	82	66	60	0
BF_3, moles per mole of tetramethylbenzene	0.1	1.0	1.0	1.3	1.4
Contact time, min.	30	30	30	30	60
Composition of the tetramethylbenzene product, %					
Prehnitene (1,2,3,4-)	0	0	0	0	0
Durene (1,2,4,5-)	70	0	0	0	96
Isodurene (1,2,3,5-)	30	100	100	100	4

rium composition of the tetramethylbenzenes once again depends upon the boron trifluoride concentration. The $HF-BF_3$–isodurene complex is stronger by several kilocalories than the complexes of its isomers,[10] and thereby is able to raise the equilibrium concentration of isodurenes from about 30% to an acid phase value of almost 100%.

Rates of Isomerization.—The experiments used for measuring rate constants were carried out with excess boron trifluoride to ensure homogeneous phase conditions, and at moderate temperatures (0 to 30°) to avoid disproportionation. The results with xylene are shown in Table III. In all cases, isomerization occurred with no detectable disproportionation to toluene and trimethylbenzene.

The products from *p*-xylene contained little *o*-xylene, and the products from *o*-xylene contained

Table III

Rates of Isomerization of the Xylenes

12 moles HF per mole xylene

Xylene	BF_3, moles per mole xylene	Temp., °C.	Time, min.	Composition of product, % *o*-Xylene	*m*-Xylene	*p*-Xylene
Ortho-	1.6	8	25	93	7	0
Ortho-	1.6	8	100	75	24	1
Ortho-	1.6	8	230	59	41	0
Ortho-	1.6	8	400	43	57	0
Para-	1.6	3	14	1	13	86
Para-	1.6	3	45	0	27	73
Para-	1.6	3	105	3	41	56
Para-	3.0	3	15	1	19	80
Para-	3.0	3	75	0	46	53
Para-	3.0	3	200	1	76	23
Para-	3.0	3	380	0	93	7
Para-	3.0	3	1380	0	100	0
Para-	3.2	3	340	2	85	13
Para-	3.2	3	1070	2	98	0
Para-	3.2	3	1415	1	99	0
Para-	1.6	30	25	3	78	19
Para-	1.6	30	55	3	87	10

no *p*-xylene. There must have been no direct conversion of the para isomer to the ortho isomer or *vice versa*. Also, the rate of isomerization of *m*-xylene to either the ortho isomer or the para isomer must be extremely low. The equilibrium concentration of *m*-xylene in the presence of excess boron trifluoride is very high; even when *p*-xylene was completely isomerized, the product consisted almost entirely of *m*-xylene.

The data of Table III are correlated in Fig. 3, wherein the per cent. xylene isomerized at each temperature is plotted on a semi-log scale against the reaction time. The points at each temperature lie along a straight line passing through the origin. Under these homogeneous conditions isomerization is a first-order reaction. The rate constants calculated from the slopes of these lines are given in Table IV. Also included is a value for durene calculated from the homogeneous phase run made at 0° (Table II).

TABLE IV

RATES OF ISOMERIZATION

	Temp., °C.	k, min.$^{-1}$	Half-time, min.
p-Xylene	3	0.0069	100
	30	.053	13
o-Xylene	8	.0023	300
Durene	0	.00096	1000

From the values for *p*-xylene at 3° and 30° the following equation was derived

$$2.303 \log k\,(p\text{-xylene}) = -\frac{12{,}700}{1.988T} + 18.2$$

The activation energy for *p*-xylene isomerization is therefore 12.7 kcal. The constants calculated by this equation for *p*-xylene at 0° (0.0055 min.$^{-1}$) and at 8° (0.0108 min.$^{-1}$) show that *p*-xylene isomerizes about 8 times as fast as durene and 5 times as fast as *o*-xylene.

Mechanism of Isomerization

The foregoing discussion has indicated that isomer distribution in polyalkylbenzene isomerization is dependent on boron trifluoride concentration and that variations in equilibrium composition are dependent on the relative stabilities of the hydrogen fluoride–boron trifluoride–aromatic complexes. A satisfactory mechanism not only must be consistent with these observations but also must provide an explanation of observed differences in reaction rates. In the present treatment, which is speculative, the fundamental theory of complex formation and alkyl group shift is similar to that proposed by Baddeley,[11,12] but the structures of the initial complexes and transition states are given more attention, in keeping with the observed experimental facts.

The first step is the rapid and reversible addition of a proton, furnished by the acid catalyst, to the alkylbenzene at the ring carbon holding the alkyl group to form an aromatic cation, as exemplified with *p*-xylene

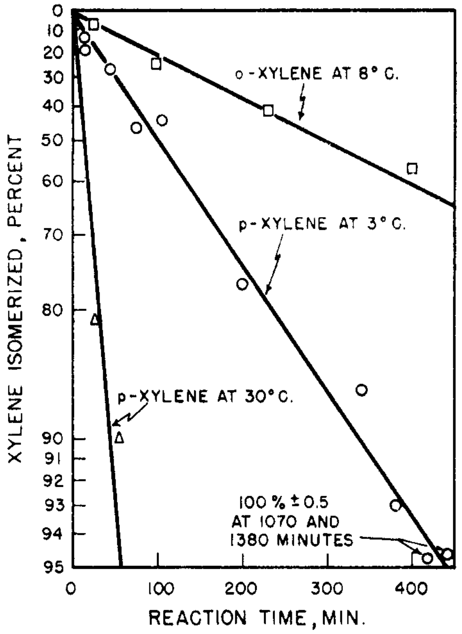
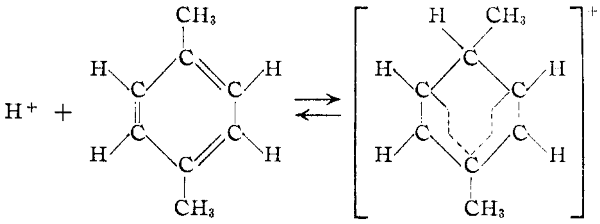
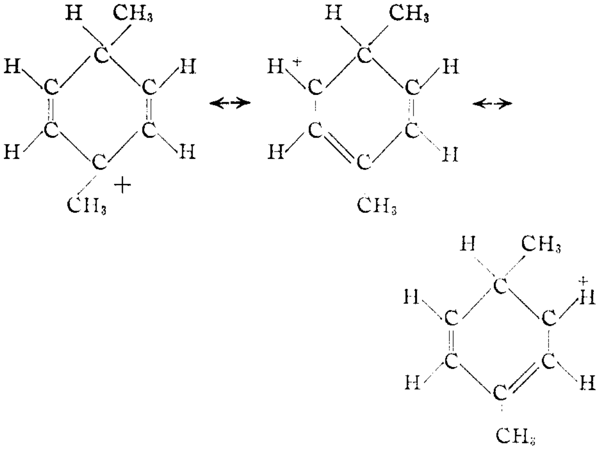


Fig. 3.—Homogeneous phase isomerization of *o*- and *p*-xylene.



The cation is a resonance hybrid of forms similar to



and, therefore, is a sigma-complex.[13] The stability of the cation is increased by alkyl substituents ortho and para to the added proton.[10] The catalyst functions as an ionizing solvent as well as a proton reservoir. The next step is the formation of a structure (complex AB) in which the transferring alkyl group is shared by the two ring carbon atoms.

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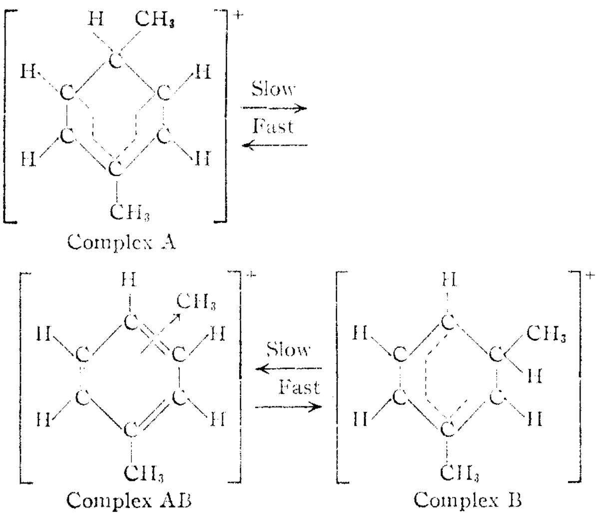
(11) G. Baddeley, *J. Chem. Soc.*, 994 (1950).

(12) G. Baddeley, G. Holt and D. Voss, *ibid.*, 100 (1952).

(13) H. C. Brown and J. D. Brody, THIS JOURNAL, **74**, 3570 (1952).



Complex A

Complex AB

Complex B

In Fig. 4 is presented a qualitative estimation of the energy changes involved in the conversion of complex A to complex B. If complex AB is a transition state, the potential energy curve will have form I. If it is an intermediate, the potential energy curve will have two peaks as in form II. In either case the activation energy can be approximated as $E_{AB} - E_A$ and $E_{AB} - E_B$ for the isomerization of complex A and complex B, respectively. The greater the number of alkyl groups ortho and para to the added proton, the greater the stability of the initial complex and the greater the activation energy $E_{AB} - E_A$. Complex A, with one group para to the added proton, therefore isomerizes at a much slower rate than complex B, with no ortho or para groups.

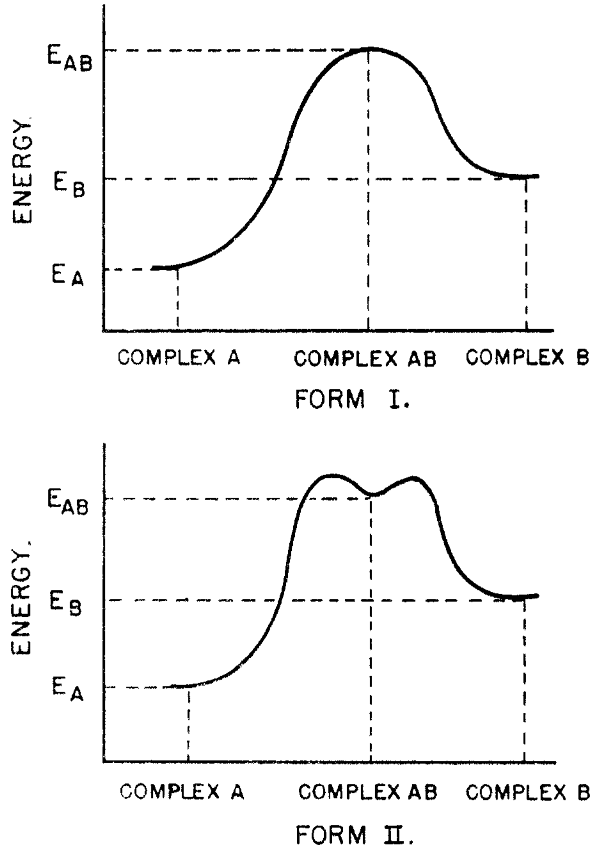
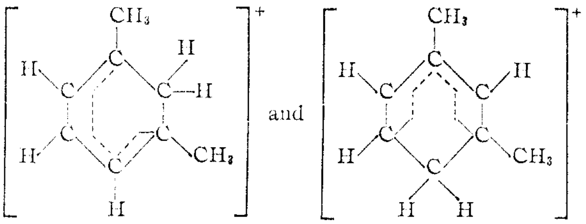


Fig. 4.—Energy diagrams for interconversion of complexes.

The relative concentrations of the two complexes must also be considered. Substantially all complexed *m*-xylene would have structures in which the added proton is ortho or ortho and para to both methyl groups



Only a minute portion would have the structure of complex B, which is relatively unstable because of no methyl groups ortho or para to the added proton. In this case the concentration effect predominates and the over-all rate of isomerization of *p*-xylene is much greater than that of *m*-xylene. Two opposing factors, therefore, must be evaluated in any attempt to predict the relative rates of methylbenzene isomerization.

The observation that durene isomerized at a slower rate than *p*-xylene may be explained on the basis that the two methyl groups in durene ortho and para to the added proton stabilize the initial complex more than they do the intermediate complex. The activation energy, $E_{AB} - E_A$, is greater for durene than for *p*-xylene. When both aromatics are completely complexed by a large excess of boron trifluoride, *p*-xylene isomerizes at the faster rate. However, when both aromatics compete for a limited amount of boron trifluoride, the concentration of complexed durene will be much greater than that of *p*-xylene[10]; and therefore the durene will isomerize much faster than *p*-xylene.

The presence of 1,3- and 1,3,5-oriented products in benzene alkylates had previously been accounted for by isomerization of the first-formed normal products.[3] The present results, which demonstrate that an acid catalyst can completely isomerize without disproportionating an alkylbenzene, not only are in agreement with this theory but permit its extension to the many cases in which the concentrations of meta-oriented products are greatly in excess of the thermodynamic equilibrium percentages.

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