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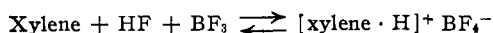
Relative Basicity of the Methylbenzenes*

BY D. A. McCAULAY AND A. P. LIEN

The relative basicities of all the methylbenzenes were measured. The techniques employed consisted of both batch extraction experiments, in which methylbenzene mixtures were treated with hydrogen fluoride and controlled amounts of boron trifluoride, and of vapor pressure measurements of mixtures of various methylbenzenes with hydrogen fluoride and boron trifluoride. The results show that the degree of basicity increases with the addition of each successive methyl group in going from toluene to hexamethylbenzene. Basicity is also influenced by position of methyl substituents; the 1,3-orientation contributes most to basic character. The complex formed by the interaction of a methylbenzene molecule with boron trifluoride in the presence of hydrogen fluoride contains one mole of boron trifluoride per mole of aromatic and probably consists of the two ions $\text{Ar}\cdot\text{H}^+$ and BF_4^- . It is suggested that the cation is a resonance hybrid of structures commonly assigned to intermediates in aromatic substitution reactions, and this postulate is used to explain the increasing stability of the complex with increasing number and with 1,3-orientation of methyl groups.

It has been recognized that aromatic hydrocarbons are weak bases,¹ and several methods have been developed recently for measuring this property. Andrews and Keefer² used the reaction of complex formation between silver ion and an aromatic nucleus as a measure of aromatic base strength. Fairbrother³ related the change in dipole moments of iodine in solution in various hydrocarbons with the basic character of each hydrocarbon solvent. Benesi and Hildebrand⁴ employed a spectrophotometric study of solutions of iodine in aromatic hydrocarbons to correlate the strength of iodine-aromatic complexes with the basicity of the aromatic hydrocarbons. Brown and Brady⁵ found that the solubility of hydrogen chloride in aromatic solvents at low temperatures serves as a measure of the basic property of the aromatic hydrocarbons. These methods have been used to compare the relative basicity of benzene with the basicities of its methyl-substituted homologs up to and including the trimethylbenzenes. In general, it has been found that the basic character of the benzene ring increases with the number of methyl substituents.^{2,3,4,5} Brown and Brady⁵ were also able to differentiate among the isomeric xylenes and the isomeric trimethylbenzenes.

Recently it was reported by this Laboratory⁶ that the individual xylene isomers could be separated by selective extraction with hydrogen fluoride containing a controlled amount of boron trifluoride. It was postulated that the reaction occurred



The extent to which this reaction proceeds is a direct measure of basicity, because the reaction represents the addition of a proton to an aromatic hydrocarbon. Since it was much more direct than the methods previously used, this extraction technique was employed to measure the basicities of all the methylbenzenes.

The object of the present work, therefore, was to determine the relative basicity of aromatic hydro-

carbons by using the reagent $\text{HF}\text{-BF}_3$. It was also desired to investigate the possibility of $\text{HF}\text{-BF}_3$ serving as a useful tool for separating otherwise difficultly-separable aromatic hydrocarbons. The procedures used were similar to those employed previously⁶ and consisted of both batch-extraction experiments and vapor-pressure measurements. In the batch-extraction experiments, two methylbenzenes dissolved in *n*-heptane were allowed to compete for a limited amount of boron trifluoride in the presence of excess hydrogen fluoride. The more basic hydrocarbon reacted preferentially with the boron trifluoride and dissolved as a complex in the hydrogen fluoride layer. The compositions of the extract and raffinate phases provided a quantitative measure of the basicity difference between the two methylbenzenes. The distribution of various aromatic hydrocarbons between *n*-heptane and hydrogen fluoride in the absence of boron trifluoride was also measured.

In the vapor-pressure study, the partial pressure of boron trifluoride was measured as it was added incrementally to a constant quantity of aromatic hydrocarbon in the presence of an excess of hydrogen fluoride. The shapes of the resulting vapor-pressure *vs.* composition curves give a qualitative picture of the basicity differences among the aromatic hydrocarbons and help to elucidate the nature of the acid-base reaction.

Experimental

Reagents.—The hydrogen fluoride, boron trifluoride and the xylenes used were described previously.⁶ Toluene was obtained from the J. T. Baker Co. (C.P. grade; n_D^{20} 1.4962); the impurities were estimated to be less than 1% and to consist of close-boiling non-aromatic hydrocarbons which would not interfere in this study. Durene (Edcan Laboratories, m.p. 79°) and pentamethylbenzene (Eastman Kodak Co., m.p. 54°) were estimated to be about 99% pure. Mesitylene (Eastman Kodak Co., White Label grade, b.p. 163–165°, n_D^{20} 1.4985) was found by infrared analysis to contain about 3% impurities which were mostly close-boiling non-aromatic hydrocarbons.

Prehnitene (b.p. 205°, n_D^{20} 1.5200) and hexamethylbenzene (m.p. 165°) were prepared from pentamethylbenzene by the Jacobsen migration reaction.⁷ Isodurene (b.p. 198°, n_D^{20} 1.5130) obtained by extracting a tetramethylbenzene mixture with $\text{HF}\text{-BF}_3$, was shown by infrared analysis to be 99+% pure. Pseudocumene was obtained by fractionating a sample of mixed trimethylbenzenes (Eastman Kodak Co.) through a Podbielniak Hypercal distillation column and selecting a 167–171° cut. Infrared absorption analysis showed this cut to contain about 95% pseudocumene, 3% mesitylene, 0.5% hemimellitene and 1.5% mixed ethyltoluenes.

* Presented before the Division of Physical and Inorganic Chemistry at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April, 1950.

(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

(2) Andrews and Keefer, *THIS JOURNAL*, **71**, 3644 (1949).

(3) Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(4) Benesi and Hildebrand, *THIS JOURNAL*, **71**, 2703 (1949).

(5) Brown and Brady, *ibid.*, **71**, 3573 (1949).

(6) McCaulay, Shoemaker and Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

(7) Smith and Lux, *THIS JOURNAL*, **51**, 2994 (1929).

Extraction Experiments.—The runs made on mixtures of *m*-xylene with trimethylbenzenes (Table I) were carried out in the same equipment and in the same manner as were the xylene extraction studies.⁸ The remaining extraction runs were made in the apparatus shown in Fig. 1. This apparatus was better adapted to handling smaller samples of hydrocarbon. It consisted of a 500-ml. magnetically stirred copper flask, a 1200-ml. copper vessel for metering the boron trifluoride and an open-end mercury manometer, connected to a copper manifold with lines leading to a vacuum pump and to hydrogen fluoride and boron trifluoride storage cylinders.

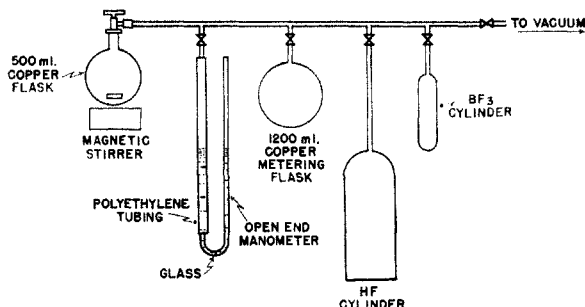


Fig. 1.—Batch extraction and vapor pressure apparatus.

A mixture of the two aromatic hydrocarbons to be compared was dissolved in *n*-heptane (except for Run A, Table I, in which no countersolvent was used), and the solution was added to the system which was immersed in a Dry Ice-acetone-bath. Hydrogen fluoride was distilled into the mixture from the cylinder, after which the flask was removed, weighed to determine the amount of hydrogen fluoride condensed, and reconnected. After the flask was cooled in a liquid nitrogen-bath, a volume of boron trifluoride equivalent to one-half mole per mole of total aromatic hydrocarbon was condensed into it from the calibrated metering vessel. The hydrocarbon-HF-BF₃ mixture was stirred as it was allowed to warm to about 20°. The flask was disconnected from the system, placed in an inverted position on a stand and its contents were allowed to settle 15 minutes. The lower acid phase was then withdrawn through the valve into a Dry Ice-cooled copper receiver, containing 200 g. of ice. A clean-cut separation of the two phases was readily obtained because of marked differences in color and viscosity. The hydrocarbon phase was finally removed and washed with ammonium hydroxide to remove traces of hydrogen fluoride and boron trifluoride.

To recover the hydrocarbons extracted into the acid layer, 300 ml. of *n*-pentane was added to the aqueous acid phase and the mixture was shaken vigorously as it warmed to room temperature. The mixture was transferred to a copper separatory funnel, where the lower aqueous acid phase was separated from the supernatant hydrocarbon.

The hydrocarbon products of all runs were fractionated through a column of 30 theoretical plates to obtain an analysis by carbon number. All isomeric mixtures were analyzed by either infrared or ultraviolet absorption.

Distribution Experiments.—The distribution experiments were carried out in the same apparatus and in the same manner as were the extraction runs, except that no boron trifluoride was used. An aromatic hydrocarbon dissolved in *n*-heptane was treated with an equal volume of liquid hydrogen fluoride at room temperature. After a 15-minute agitation period and a 30-minute settling period, the two phases were separated. The weight of aromatic hydrocarbon extracted into the acid layer was calculated from the change in refractive index of the hydrocarbon phase.

Vapor-Pressure Measurements.—The apparatus shown in Fig. 1 was also used for the vapor-pressure determinations, all of which were made at 0°. In each case, the partial pressure of boron trifluoride was measured as it was added incrementally to a constant quantity of aromatic hydrocarbon in the presence of an excess of hydrogen fluoride. The techniques employed were the same as those previously described,⁹ except that the vapor-pressure flask was magnetically stirred instead of manually shaken and the pressures were read on the more accurate mercury manometer instead of on a Bourdon-tube pressure gage.

Results and Discussion

Vapor-Pressure Studies.—The results of the vapor-pressure measurements are presented in Fig. 2, where the total vapor pressure is plotted against the mole ratio of boron trifluoride to aromatic hydrocarbon. The mole ratio of hydrogen fluoride to aromatic hydrocarbon was constant at 10 to 1. Also included in this figure are values taken from the work of Cady⁸ for the vapor pressure of hydrogen fluoride over HF-KF mixtures. The upper abscissa is used to represent the mole ratio of KF to HF.

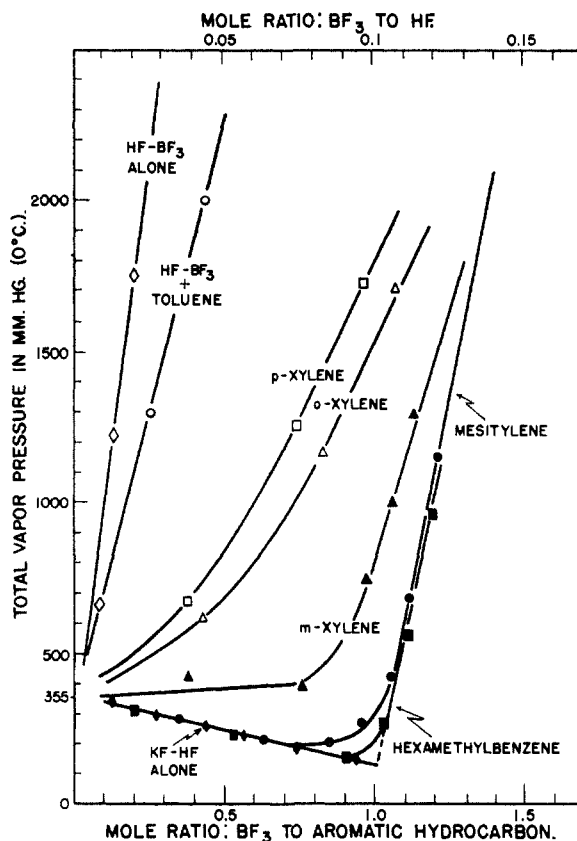


Fig. 2.—Vapor pressures of various HF-BF₃ methylbenzene systems at 0°: \diamond , HF-BF₃ alone; \circ , HF-BF₃ + toluene; \square , HF-BF₃ + *p*-xylene; \triangle , HF-BF₃ + *o*-xylene; \blacktriangle , HF-BF₃ + *m*-xylene; \bullet , HF-BF₃ + mesitylene; \blacksquare , HF-BF₃ + hexamethylbenzene; \blacklozenge , KF-HF alone, for the KF-HF system the upper abscissa denotes the mole ratio of KF to HF.

The curves for mesitylene and hexamethylbenzene coincide with the KF-HF curve approximately to the point where the mole ratio of boron trifluoride to aromatic hydrocarbon equals one. At this composition the curves break sharply and follow along a line which is roughly parallel to the curve for the system HF-BF₃ alone. It is evident, therefore, that these aromatic hydrocarbons form complexes containing one mole of boron trifluoride per mole of hydrocarbon. Also, the identical molar lowering of the vapor pressure of hydrogen fluoride by the complex and by KF is good evidence that the complex consists of two ions, which are probably Ar·H⁺ and BF₄⁻.

(8) Cady, THIS JOURNAL, 56, 1431 (1934).

TABLE I
 HF-BF₃ EXTRACTION OF ALKYL BENZENE MIXTURES

Run	A ^a	B	C ^b	D	E	F	G	H	J
Aromatic components	<i>m</i> -Xylene	<i>m</i> -Xylene	<i>m</i> -Xylene	Durene	Prehnitene	Iso-durene	Mesitylene	Iso-durene	Hexaethylbenzene
Component a	Mesitylene	Mesitylene	Pseudocumene	Mesitylene	Mesitylene	Mesitylene	Hexamethylbenzene	Pentamethylbenzene	Hexamethylbenzene
Moles extract per mole BF ₃ used	1.6	1.1	1.1	1.2	1.1	0.8	1.0	1.0	1.1
Composition of products, mole %									
Feed { Component a	67	67	52	50	50	50	50	50	50
Component b	33	33	48	50	50	50	50	50	50
Raffinate { Component a	99.2	99.4	60	91	87	45	88	55	62
Component b	0.8	0.6	40	9	13	55	12	45	38
Extract { Component a	61	51	43	30	30	62	19	44	33
Component b	39	49	57	70	70	38	81	56	67
Single stage separation factor, α _{b/a}	80	160	2	24	16	0.5	31	1.6	3.3

^a In run A no counter-solvent was used; in runs B and C the aromatic hydrocarbons were diluted with an equal volume of *n*-heptane; in the remaining runs about 5 vols. of *n*-heptane per vol. of aromatic hydrocarbon were used. ^b Feed contained 0.2% hemimellitene; its distribution between the two phases indicated the single plate separation between it and *m*-xylene to be about 2.

The complex formed by mesitylene is less stable than the hexamethylbenzene complex, as shown by the higher vapor pressure in the region of one mole of boron fluoride per mole of aromatic hydrocarbon. The *m*-xylene complex is still less stable. The fact that the *m*-xylene curve approaches the curves for the other two hydrocarbons at relatively high pressures indicates that complex formation is complete only when excess boron trifluoride is present. The complexes with *o*- and *p*-xylene are less stable than the *m*-xylene complex, while the complex formed by toluene is even less stable than the *p*-xylene complex. In fact, the only evidence that toluene forms a complex with HF-BF₃ is that the observed Henry's law constant (slope of the corresponding curve in Fig. 2) is lower for the system HF-BF₃-toluene than for the system HF-BF₃ alone.

Extraction Studies.—The results of the extraction experiments are given in Table I. In Runs A and B the concentration of mesitylene in the acid phase was much greater than its concentration in the raffinate phase, while the reverse was true for *m*-xylene. This shows that mesitylene is much more basic than *m*-xylene. It is likewise evident from the results of the remaining runs that pseudocumene and hemimellitene are more basic than *m*-xylene, that mesitylene is more basic than durene and prehnitene but less basic than hexamethylbenzene and isodurene, and that pentamethylbenzene is more basic than isodurene.

A quantitative measure of these basicity differences was obtained from a calculation of single-stage separation factors. These were defined as

$$\text{Separation factor} = \alpha \frac{b}{a} = \frac{N_b}{N_a} \frac{N_b'}{N_a'}$$

where N_b and N_a are the mole fractions of component b and component a in the extract phase, and N_b' and N_a' are the corresponding mole fractions in the raffinate phase. The alphas given in the table express quantitatively the basicity difference between the designated pairs. An approximate separation factor between any two compounds in the table may be calculated by multiplying or dividing the appropriate alphas.

The previous work on xylene isomer separation⁶ had shown that, in the presence of hydrogen fluoride, boron trifluoride forms with an aromatic hydrocarbon a mole-for-mole complex which is soluble in the acid phase. In some cases, however, considerably more aromatic hydrocarbon dissolved in the acid layer than could be accounted for by the mole-for-mole reaction. In these cases it was shown that the aromatic-HF-BF₃ complex acted as a mutual solvent to bring about the non-selective physical solution of additional amounts of uncomplexed xylene.⁶ Comparison of Runs A and B of Table I also illustrates this mutual solvent action. These runs were identical except that in Run B an inert counter-solvent (*n*-heptane) was used. The counter-solvent extracted most of the uncomplexed aromatic from the acid phase, and an extract yield approaching the theoretical (one mole of extract per mole of boron trifluoride) was obtained; consequently, the alpha was much higher than the alpha of Run A.

The previous work on xylene isomer separation⁶ had also shown that ethyl groups migrate from ring to ring very readily under extraction conditions. Hence, it was concluded that the HF-BF₃ method could not be used to measure the relative basicities of alkylbenzenes containing side chains greater than methyl. However, Run J (Table I), involving a mixture of hexaethyl- and hexamethylbenzene, was an experiment designed to avoid this limitation; all possibility of ethyl group migration was eliminated by the use of aromatic hydrocarbons containing no replaceable hydrogen. The results show that migration did not occur and that the hexamethylbenzene was selectively extracted into the acid layer. Assuming that the extraction results are not affected by the difference in molecular weight between the two hydrocarbons, it may be concluded that hexamethylbenzene is more basic than hexaethylbenzene. This leads to the generalization that lengthening of the alkyl side chain decreases the basicity of an alkylbenzene.

The extraction runs, besides providing results of theoretical interest concerning aromatic basicity, also have practical importance. For example, it

has been shown that HF-BF₃ may be used as a selective solvent for extracting mesitylene from a trimethylbenzene mixture or for extracting isodurene from a tetramethylbenzene mixture. These compounds are so much more basic than their isomers that a substantially complete separation could be made in a single batch extraction.

Series of Basicity of Methylbenzenes.—From the single-stage separation factors among the methylbenzenes determined by selective-extraction experiments in the present work (Table I) and previously,⁶ the basicity series shown in Table II was constructed.

TABLE II
SERIES OF BASICITY OF THE METHYLBENZENES

Benzene		Alpha relative to <i>p</i> -xylene ^a
Methyl-	(Toluene)	(ca. 0.01) ^b
1,4-Dimethyl-	(<i>p</i> -Xylene)	1
1,2-Dimethyl-	(<i>o</i> -Xylene)	3
1,3-Dimethyl-	(<i>m</i> -Xylene)	9
1,2,4-Trimethyl-	(Pseudocumene)	18
1,2,3-Trimethyl-	(Hemimellitene)	(ca. 18)
1,2,4,5-Tetramethyl-	(Durene)	60
1,2,3,4-Tetramethyl-	(Prehnitene)	85
1,3,5-Trimethyl-	(Mesitylene)	1400
1,2,3,5-Tetramethyl-	(Isodurene)	2800
Pentamethyl-		4350
Hexamethyl-	(Mellitene)	44500

^a *p*-Xylene adopted as standard because it is the first member of this homologous series to evidence appreciable basicity toward HF-BF₃. ^b Estimated from the vapor pressure measurements.

In general, the basicity of the aromatic ring increases with the number of methyl substituents. The basicity relationships in this series are shown diagrammatically in Fig. 3. The 1,3-orientation contributes most to basic character. Thus, *m*-

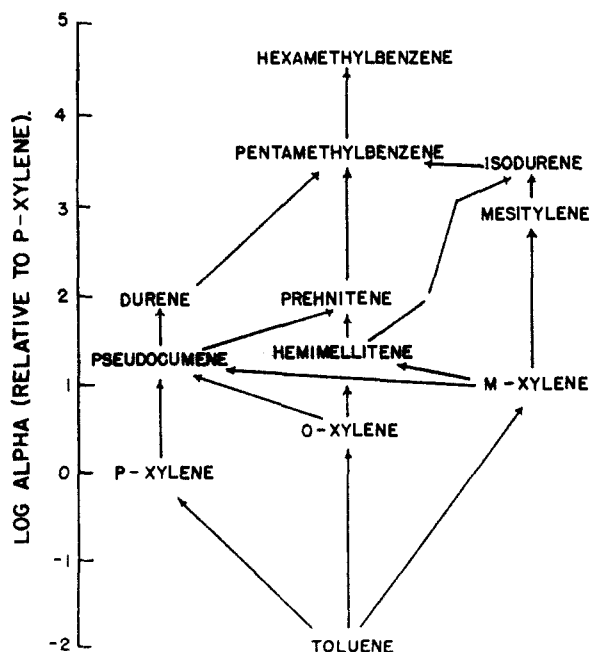


Fig. 3.—Increase in basicity of the aromatic ring with increase in number of methyl substituents.

xylene is the most basic of the xylenes and mesitylene is more basic than the other trimethylbenzenes as well as being more basic than two of the tetramethylbenzenes, durene and prehnitene. Hexamethylbenzene is the most basic, by far, of all the methylbenzenes. This fact was surprising because it was thought that perhaps an unsubstituted position on the benzene ring would be a requisite for complex formation. The extremely large difference in basicity between hexamethylbenzene and the other methylbenzenes was also unexpected.

Benzene is too weak a base for a determination of its relative basicity by this method. Other investigators^{2,3,4,5} using other methods, have shown benzene to have much less basic character than toluene.

Distribution Experiments.—The results obtained in the study on the distribution of various alkylbenzenes between *n*-heptane and hydrogen fluoride are presented in Table III. The distribution coefficients—defined as the mole fractions of aromatic hydrocarbon in hydrogen fluoride divided by the mole fraction in *n*-heptane—show that the solubility in hydrogen fluoride of all the aromatic hydrocarbons studied increases with increasing basicity of the hydrocarbon. When corrected to the same vapor pressure,⁹ as is done in the last column of Table III, the increase in the distribution coefficient with basicity becomes even larger. This is in agreement with the hypothesis suggested by Hammett¹ that aromatic hydrocarbons dissolve in hydrogen fluoride because of the occurrence of the reaction

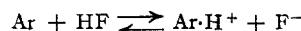
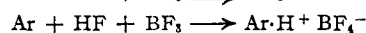
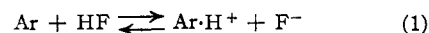


TABLE III
DISTRIBUTION OF VARIOUS AROMATIC HYDROCARBONS BETWEEN HYDROGEN FLUORIDE AND *n*-HEPTANE AT 25°

Aromatic hydrocarbon	<i>N</i> _{HF}	<i>N</i> _{Heptane}	$\frac{D \times 10^4}{N_{\text{HF}}/N_{\text{Heptane}}}$	$\frac{P_{\text{mm.}}}{\text{v.p. of arom. at 25}^\circ}$	$\frac{D/P_{\text{mm.}}}{\times 10^4}$
<i>p</i> -Xylene	0.00013	0.30	4	8.6	0.5
<i>m</i> -Xylene	.00036	.30	12	8.6	1.4
Mesitylene	.0027	.28	100	2.6	38
Hexaethylbenzene	.0019	.033	600	0.015	40,000
Hexamethylbenzene	.0025	.002	1100	.025	44,000

Structure of the Complex.—From the above evidence that the solubility of an aromatic hydrocarbon in hydrogen fluoride increases with its basicity, and from the facts learned in the vapor-pressure experiments (namely, that the complex contains one mole of boron trifluoride per mole of aromatic hydrocarbon and probably consists of two ions) it may be inferred that the reaction of complex formation is the sum of the two steps

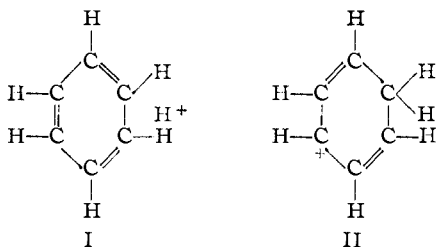


The structure of the cation postulated above will be discussed later. Because both reactions are ionic and rapid, and require little or no activation energy, it is not necessary to specify whether they

(9) Hildebrand, *J. Phys. Colloid Chem.*, **53**, 973 (1949).

occur simultaneously or in either sequence. When the aromatic is added to hydrogen fluoride alone, the equilibrium for reaction (1) lies far to the left, as shown by the fact that aromatic hydrocarbons are only slightly soluble in hydrogen fluoride. Boron trifluoride shows little tendency to react with hydrogen fluoride in the absence of a base⁶ because the concentration of fluoride ion in liquid hydrogen fluoride is very low. However, when both the aromatic hydrocarbon and boron trifluoride are simultaneously present in hydrogen fluoride solution, both reactions proceed much further to the right, because the fluoride ion produced in equation (1) is taken up by the BF_3 present. A mechanism similar to the above was proposed by Brown and Pearsall¹⁰ to account for the interaction between toluene, aluminum chloride and hydrogen chloride.

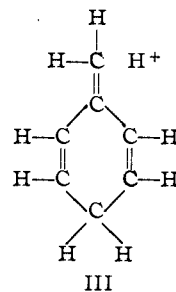
The present work shows that the stability of the methylbenzene cation formed in an HF-BF_3 medium varies greatly with the number and orientation of the methyl substituents. These differences in stability could be accounted for by postulating structures for the cation similar to those commonly assigned to intermediates in aromatic substitution reactions.¹¹ For example, the benzene cation formed by an acid-base reaction may be thought of as a resonance hybrid of four structures similar to I (no-bond forms) and three structures similar to II (*ortho*- and *para*-quinoid forms). A methyl



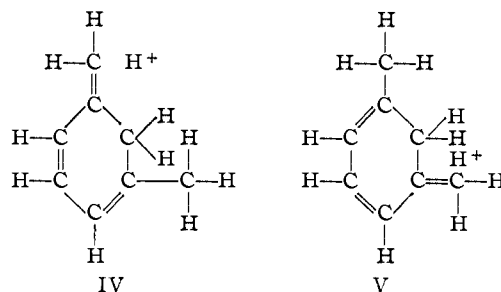
substituent enhances the basicity of the ring because the inductive effect makes all the ring carbon atoms more negative and strengthens the bond between a ring carbon and the added proton. Also, the bond between an added proton and a ring carbon atom which is *ortho* or *para* to the methyl substituent is strengthened to a greater degree by hyperconjugation of the methyl group with the benzene ring. Thus, a toluene cation, in addition to all the forms possible for a benzene cation, may also have structure III.

(10) Brown and Pearsall, Abstracts of Papers Presented to the Division of Physical and Inorganic Chemistry at the 112th Meeting of the American Chemical Society, New York, 1947, p. 19.

(11) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 259.



In a similar manner, as methyl groups are added, the inductive effect becomes larger and, if the methyl group is placed *meta* to a methyl group already present, the possibilities for resonance increase. Thus, for a *m*-xylene cation, in addition to all the forms possible for a toluene cation, there can be postulated the additional structures IV and V, which contribute to the resonance hybrid.



The increasing relative basicities of all the remaining methylbenzenes may be correlated with their structures in an analogous manner.

The results of the extraction experiment in which it was found that hexamethylbenzene is more basic than hexaethylbenzene indicate that replacement of an alpha hydrogen atom of an alkyl substituent by a methyl (or higher) group tends to decrease the basicity of an aromatic hydrocarbon. Since the electron-releasing capabilities of an alkyl group due to the inductive effect are in the order methyl < ethyl < isopropyl, etc., and those due to hyperconjugation (*i. e.*, the Baker-Nathan effect^{12,13}) are in the order methyl > ethyl > isopropyl, etc., it appears that the latter effect contributes more to the basicity of an aromatic hydrocarbon than does the inductive effect.

Acknowledgment.—The authors are indebted to P. J. Launer of this Laboratory for carrying out the infrared absorption analyses.

WHITING, INDIANA

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(12) Baker and Nathan, *J. Chem. Soc.*, 1844 (1935).

(13) Deasy, *Chem. Revs.*, **36**, 145 (1945).