

HYPERCONJUGATION IN AROMATIC CATION COMPLEXES

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Abstract—Aromatic hydrocarbons react with the strong acid HF-BF_3 to form an aromatic cation plus the fluoroborate ion. The proton adds to a definite ring carbon atom and completely transfers its charge. The charge is distributed by resonance to positions *ortho* and *para* to the added proton. Alkyl groups on these positions stabilize the ion and distribute the charge further by hyperconjugation or induction. Thus, the mesitylene cation is more stable than the toluene cation by a factor of 280,000 and more stable than the other trimethylbenzenes by a factor of 70. Competition experiments among various 1, 3, 5-trialkylbenzenes show no change in basicity as the alkyl groups vary from methyl to ethyl to *isopropyl* to *tert.*-butyl. In this series, therefore, the loss in carbon-hydrogen hyperconjugation is balanced by an increase in the induction effect and in carbon-carbon hyperconjugation.

AROMATIC hydrocarbons, as is well known, form loose molecular complexes with many reagents, such as silver ion,¹ iodine² and hydrogen chloride.³ The acceptor molecule combines loosely with the π -electron cloud of the aromatic ring. We have found⁴ that alkylbenzenes also form mole-for-mole complexes with HF-BF_3 . But, with this strong acid, the complexes are of an altogether different type. A proton adds to a definite ring carbon atom, completely transfers its charge to the aromatic hydrocarbon and thus brings into play inductive and hyperconjugative effects that do not show up in the π complexes.

Relative stability of complexes

Evidence for the existence of these complexes was obtained by measuring the vapor pressure of various mixtures of HF-BF_3 and aromatic hydrocarbons. One mole of the aromatic was stirred with 10 moles of liquid anhydrous HF in a closed system; because the aromatic and HF are immiscible two separate phases co-existed. Small amounts of BF_3 were added at intervals, and the pressure was measured after each addition.

The measurements are plotted in Fig. 1. The straight-line curve for BF_3 in HF alone shows that BF_3 in HF obeys Henry's law. No detectable amounts of HBF_4 are formed. The curves for hexamethylbenzene and mesitylene break sharply at the point where the mol ratio of BF_3 to aromatic equals one. As BF_3 is added, it reacts mole-for-mole with the aromatic until the aromatic is used up. Also, as the BF_3 is added, the hydrocarbon gradually dissolves in the HF layer and the mixture becomes homogeneous. Then the pressure rises abruptly and follows a line roughly parallel to that for HF-BF_3 alone.

The complex formed by mesitylene is less stable than that by hexamethylbenzene:

¹ I. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* **71**, 3644 (1949).

² H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* **71**, 2703 (1949).

³ H. C. Brown and J. Brady, *J. Amer. Chem. Soc.* **71**, 3573 (1949).

⁴ D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.* **73**, 2013 (1951).

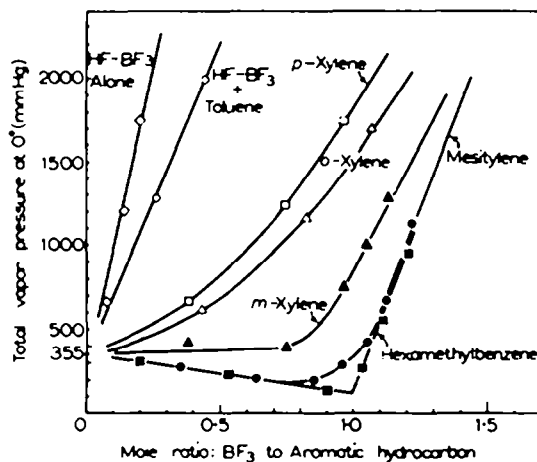


FIG. 1. Vapor pressures of mixtures of HF-BF₃ and aromatic hydrocarbons.

it exerts a slightly higher BF₃ pressure in the one-to-one region. The *m*-xylene complex is still less stable and approaches 100 per cent association only at relatively high BF₃ pressures. The complexes with *o*-xylene, *p*-xylene and toluene are progressively less stable.

The spread between the curve for the three xylene complexes permitted calculation of their relative stabilities. But, to get quantitative information for the other methylbenzenes required a series of batch extraction experiments in which the aromatics competed with each other for a limited amount of acid. In these experiments, two aromatics were dissolved in an inert paraffinic solvent, *n*-heptane, and were then shaken up with HF plus BF₃. The aromatic hydrocarbon that showed the greater tendency towards complex formation reacted preferentially and dissolved as a complex in the HF layer. A typical extraction run with mesitylene and *m*-xylene showed, in mol per cent:

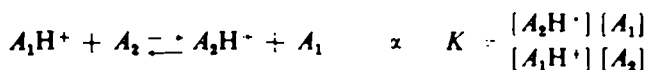
	Feed	Raffinate	Extract
<i>n</i> -Heptane	50.0	75.0	0
Mesitylene	16.5	0.1	49
<i>m</i> -Xylene	33.5	24.9	51

Mesitylene was preferentially taken into the acid layer.

To measure this selectivity, single-stage separation factors, called α 's, were calculated. They were defined as the mol ratios of the two components in the acid phase divided by the same mol ratio in the hydrocarbon phase. As a first approximation, we assumed that the ratio of the two aromatics in the hydrocarbon phase was equal to the ratio of free, uncomplexed aromatics in the acid layer. Then, the α value can be looked upon as the equilibrium constant for the reaction:

TABLE 1. RELATIVE BASICITIES OF THE METHYLBENZENES
p-Xylene . . . 1

Methylbenzene	α
Toluene	0.01
<i>p</i> -Xylene	1
<i>o</i> -Xylene	2
<i>m</i> -Xylene	20
Pseudocumene (1, 2, 4-)	40
Hemimellitene (1, 2, 3-)	(40)
Durene (1, 2, 4, 5-)	120
Prehnitene (1, 2, 3, 4-)	170
Mesitylene (1, 3, 5-)	2,800
<i>iso</i> Durene (1, 2, 3, 5-)	5,600
Pentamethylbenzene	8,700
Hexamethylbenzene	89,000



in which the two aromatics compete for a proton. For this reason, it is called the relative basicity of the two aromatics.

Experiments were carried out for all of the methylbenzenes, and the α values obtained were arranged in Table 1. Basicity increases with the addition of each methyl group. The xylenes are more basic than toluene; the trimethylbenzenes more basic than the xylene. But *meta* orientation contributes most to basic character. Thus, *m*-xylene is by far the most basic of the xylenes. Likewise, mesitylene with three *meta*-oriented groups, is far more basic than its isomers. In fact, it is more basic than two of the tetramethylbenzenes, which have only two *meta*-oriented groups.

TABLE 2. BASICITIES TOWARD VARIOUS REAGENTS

Methylbenzene	Ag ⁺ *	HCl [†]	I ₂ ‡	HF-BF ₃ §
Toluene	1.02	0.92	0.97	0.01
<i>p</i> -Xylene	1.00	1.00	1.00	1
<i>o</i> -Xylene	1.10	1.13	1.01	2
<i>m</i> -Xylene	1.15	1.26		20
Mesitylene	0.69	1.59	1.06	2800

* Solubility of arene in aqueous Ag⁺.¹

† Solubility of HCl in arene.³

‡ Light absorption.²

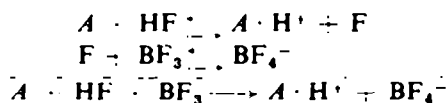
§ Competitive extraction.⁴

The relative basicity values obtained by use of this strong acid are compared in Table 2 with those obtained by others using weak electrophilic reagents. With the weak acids the spread from toluene through metitylene is small, in no case being greater than twofold. In contrast, the spread as measured by the strong acid, HF-BF₃, is about 280,000-fold. The strong acid completely transfers its charge to the aromatic

ring so that hyperconjugative and inductive effects are more important than they are in π complexes formed by the weaker acids.

Nature of the complexes

The best interpretation of the reaction of complex formation is:



When the aromatic is added to HF alone, the equilibrium for the top reaction lies far to the left, as shown by the fact that aromatics are only slightly soluble in HF. However, when BF_3 is present, the reaction goes to completion because the stable fluoroborate ion is formed. For this reason 1 mole of BF_3 interacts with 1 mole of aromatic, as was observed in the vapor-pressure and batch-extraction experiments.

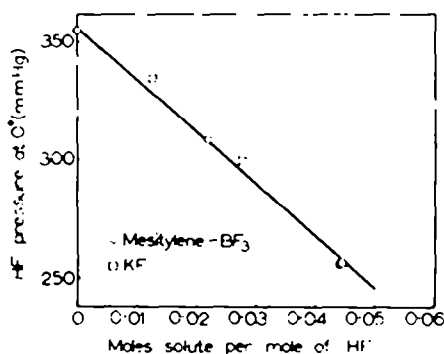


FIG. 2. Vapor-pressure lowering of HF by added KF or mesitylene- BF_3 .

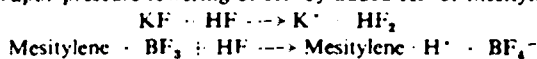


TABLE 3. COMPARISON OF CONDUCTIVITIES AND RELATIVE BASICITIES

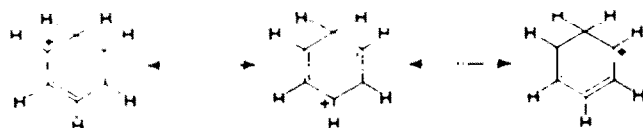
Methylbenzene	Relative conductivity in HF ^a	Relative basicity in HF-BF ₃ ^a
<i>p</i> -Xylene	1	1
<i>o</i> -Xylene	1.1	2
<i>m</i> -Xylene	26	20
Pseudocumene (1, 2, 4-)	63	40
Hemimellitene (1, 2, 3-)	69	40
Durene (1, 2, 4, 5-)	140	120
Prehnitene (1, 2, 3, 4-)	400	170
Mesitylene (1, 3, 5-)	13,000	2800
<i>iso</i> Durene (1, 2, 3, 5-)	16,000	6500
Pentamethylbenzene	29,000	8700
Hexamethylbenzene	97,000	89,000

^a M. Kilpatrick and F. E. Luborsky, *J. Amer. Chem. Soc.* **75**, 577 (1953).

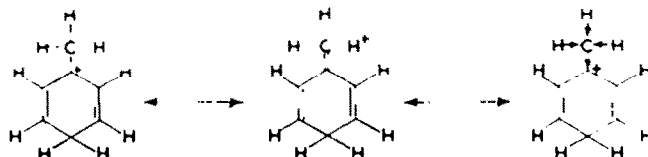
More evidence supporting the theory that one molecule of aromatic and one of BF_3 gives two ions instead of an ion pair or a single addition complex is shown in Fig. 2. Incremental amounts of a solute, either KF or an equimolar mesitylene- BF_3 mixture, were added to HF at 0°C , and the vapor pressure was measured. The points for both KF and for mesitylene- BF_3 fall along the same straight line, showing that they both give the same molal vapor-pressure lowering. If KF forms two particles in solution, then mesitylene- BF_3 must also do the same.

Conclusive evidence that these particles are charged was obtained from measurements of the conductivities of small amounts of the methylbenzenes dissolved in HF .⁶ From these measurements were calculated values proportional to the equilibrium constants for the acid-base reaction. These values are shown in the first column of Table 3; our values, in the second column. The two sets of figures are in good agreement, considering that in our work we used concentrations of aromatic in HF that were about fifty-fold greater than in the conductivity studies.

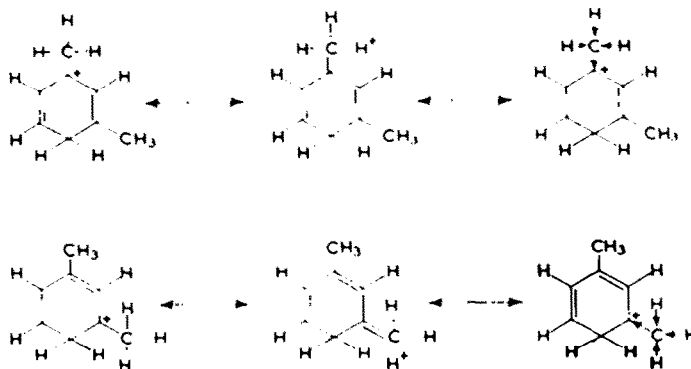
The probable structure of the aromatic cation is:



Presumably the proton adds directly to a ring carbon atom and the positive charge is distributed to the *ortho* and *para* positions by resonance. If one of these positions has an alkyl substituent, the positive charge can be further distributed and stabilized by hyperconjugation or induction, as shown for the toluene cation:



The arrows represent displacement of the bonding pair, under the influence of the positive charge, from their normal position in the neutral molecule. Also, if the aromatic has another alkyl group in the *meta* position, as does *m*-xylene, the charge can be further distributed, by induction and hyperconjugation, to both alkyl groups:



Mesitylene, with three *meta*-oriented groups, can stabilize and distribute the positive charge to all three alkyl groups.

Effect of change of alkyl group on basicity

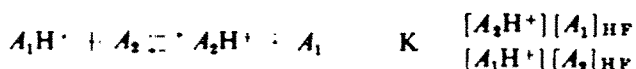
Some idea of the relative contributions of the inductive and hyperconjugative effect in stabilizing the cation could be obtained by comparing methyl substituents with ethyl, *isopropyl* and *tert.*-butyl groups. But a direct comparison has not previously been possible because alkyl groups larger than methyl migrate rapidly from one ring to another in the presence of HF-BF₃. We have recently found, however, that the 1,3,5-trialkylbenzenes are exceptionally stable in HF-BF₃ and that they maintain their configuration long enough for an extraction experiment to be made.

Therefore, a series of competitive extraction experiments was run with 1,3,5-trialkylbenzenes containing methyl, ethyl, *isopropyl* and *tert.*-butyl groups. Two 1,3,5-trialkylbenzenes dissolved in *n*-heptane were shaken up with HF plus enough BF₃ to complex with about one-half of the total aromatic present. The hydrocarbon phase and the acid layer were then separated and were analyzed by gas chromatography. A single-stage separation factor, α , was calculated for each pair.

TABLE 4. APPARENT BASICITY OF THE 1, 3, 5-TRIALKYL BENZENES

1, 3, 5-Trialkylbenzene	α
1, 3, 5-Tri- <i>tert.</i> -butylbenzene	1.0
1-Methyl-3, 5-di- <i>tert.</i> -butylbenzene	2.8
1, 3, 5-Triisopropylbenzene	4.8
1-Methyl-3, 5-diisopropylbenzene	6.0
1, 3, 5-Triethylbenzene	8.4
1, 3-Dimethyl-5- <i>tert.</i> -butylbenzene	15.5
1, 3-Diethyl-5-methylbenzene	16.8
1, 3-Dimethyl-5- <i>isopropyl</i> benzene	20.2
1, 3-Dimethyl-5-ethylbenzene	30.7
1, 3, 5-Trimethylbenzene	54.4

The α values obtained were arranged in order in Table 4. The basicity apparently increases with decreasing branching in the side-chain. As the methyl segments of the tertiary butyl groups are replaced by hydrogen atoms, the α values become larger. The effect on apparent basicity is in the order: methyl > ethyl > *isopropyl* > *tert.*-butyl. Carbon-hydrogen hyperconjugation, therefore, appears to contribute more than induction or carbon-carbon hyperconjugation. But before this conclusion can be accepted a correction must be made. The equilibrium constant for the acid-base reaction in the HF layer is:



But the single-phase separation factor, α , is:

$$\alpha = \frac{[A_2H^+][A_1]_{Heptane}}{[A_1H^+][A_2]_{Heptane}}$$

Therefore:

$$K = \alpha \frac{[A_1]_{\text{HF}}[A_2]_{\text{Heptane}}}{[A_2]_{\text{HF}}[A_1]_{\text{Heptane}}}$$

The ratio between the uncomplexed hydrocarbons, $[A_1]$ and $[A_2]$, in the acid phase can be estimated from the solubilities of the free uncomplexed hydrocarbons in HF:

$$\frac{[A_1]_{\text{HF}}}{[A_2]_{\text{HF}}} = \frac{[A_1]_{\text{Heptane}}}{[A_2]_{\text{Heptane}}} \times \frac{\text{Solubility of } A_1 \text{ in HF}}{\text{Solubility of } A_2 \text{ in HF}}$$

and, therefore:

$$K = \alpha \times \frac{\text{Solubility of } A_1 \text{ in HF}}{\text{Solubility of } A_2 \text{ in HF}}$$

Direct measurement of the physical solubility of these highly basic aromatics in HF is not possible because most of the aromatic that goes into the HF layer is in the protonated form:



Recently, however, Mackor *et al.*⁶ showed that a good estimate of the concentration of free uncomplexed aromatic in HF, $[A]_{\text{HF}}$, could be obtained from an extrapolation of the solubilities of less basic aromatics in HF. The logarithms of the solubilities of benzene, toluene and xylene in HF at 0° differ by a constant, 0.20, as shown by the following values:

Aromatic	Benzene	Toluene	<i>p</i> -Xylene	<i>m</i> -Xylene
Log (<i>A</i>)	1.35	1.55	1.76	1.72

Solubilities of the heavier alkylbenzenes were estimated by assuming that the value of log $[A]$ decreases by 0.2 for each additional methyl group on the ring. The values of 0.4, 0.6 and 0.8 were used for the corresponding ethyl, *isopropyl* and *tert.*-butyl groups.

TABLE 5. CORRECTED RELATIVE BASICITIES

1, 3, 5-Trialkylbenzene	α	$-\text{Log } (A)$	Corrected relative basicity, K
1, 3, 5-Tri- <i>tert.</i> -butylbenzene	1.0	3.75	1.0
1-Methyl-3, 5-di- <i>tert.</i> -butylbenzene	2.8	3.15	0.8
1, 3, 5-Triisopropylbenzene	4.8	3.15	1.4
1-Methyl-3, 5-diisopropylbenzene	6.0	2.75	1.2
1, 3, 5-Triethylbenzene	8.4	2.55	0.6
1, 3-Dimethyl-5- <i>tert.</i> -butylbenzene	15.5	2.55	1.1
1, 3-Diethyl-5-methylbenzene	16.8	2.35	0.7
1, 3-Dimethyl-5- <i>isopropyl</i> benzene	20.2	2.35	0.9
1, 3-Dimethyl-5-ethylbenzene	30.7	2.15	0.9
1, 3, 5-Trimethylbenzene	54.4	1.95	1.0

⁶ F. L. Mackor, A. Hofstra and J. H. Van Der Waals, *Trans. Faraday Soc.* **54**, 186 (1958).

Solubilities for all the 1,3,5-trialkylbenzenes in HF were calculated by this means and are shown in Table 5. These values were substituted in the equation relating α to K , the corrected relative basicity. The K values so calculated are shown in the last column. No trend is observed as the alkyl group changes. In going from methyl to ethyl to *isopropyl* to *tert.*-butyl, the loss in carbon-hydrogen hyperconjugation apparently is balanced by an increase in the inductive effect and in carbon-carbon hyperconjugation.

Carbon-hydrogen hyperconjugation, therefore, must be an important mode of electron release in the methyl-substituted cations. If only the inductive effect were involved, an increase in basicity would be expected with an increase in size and branching of the alkyl substituent.