

Intermediate Complex of Boron Fluoride Catalyzed Alkylation

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It is found by measurement of absorption spectra and thermodynamic isotope effect that the intermediate complex in boron fluoride catalyzed alkylation, formed when an alkylbenzene is dissolved in a liquid nonionized alkyl halide-boron fluoride complex at low temperatures, is not a σ -complex but an oriented π -complex such as IV.

Introduction

Olah and Kuhn¹ have isolated intermediate 1:1:1 complexes in Friedel-Crafts alkylations, by low temperature interaction of alkylbenzenes, alkyl fluorides, and boron fluoride; they conclude that the complexes, which were colored and had high specific conductivity, are σ -complexes. However, there was only a small kinetic hydrogen isotope effect in such alkylations, and the relative stability of σ -complexes did not show any correlation with the obtained relative rates of several alkylbenzenes, whereas the relative stability of π -complex did.² Hence they assumed that an oriented π -complex formation and not a σ -complex formation was involved in the main rate-determining step.

By measuring the equilibrium constant of boron isotope exchange between gaseous boron fluoride and liquid boron fluoride complexes at low temperatures, we have shown in our previous work³ that the value of the equilibrium constant which represents the thermodynamic isotope effect is related to the polarity, stability, and catalytic activity of the complex. Moreover, we find that *t*-butyl chloride can *t*-butylate toluene in the presence of boron fluoride. In the present work, the absorption spectra of the intermediate complexes of boron fluoride catalyzed alkylations and the thermodynamic isotope effect for these complex systems were measured at low temperatures. From the results obtained, the structure of the complexes is discussed.

Results

The Absorption Spectra. Prior to the measurements of absorption spectra of alkylbenzene-alkyl halide-boron fluoride complexes, the low temperature absorption spectra of toluene, *m*-xylene, and mesitylene in liquid boron fluoride were measured. With mesitylene, however, no positive result was obtained because of its extremely small solubility. The benzenoid bands of these alkylbenzenes were still found as shown in Figure 1, but new absorption bands were not observed in the visible and near-ultraviolet regions. Therefore it appears that boron fluoride cannot form stable complexes with alkylbenzenes. Reid⁴ considered that the absorption band found at 318 $m\mu$ in the spectrum of

the toluene-hydrogen fluoride-boron fluoride system is due to the presence of $C_6H_5CH_2BF_3$ complex, and Mackor⁵ asserted that boron fluoride can form covalent complexes with aromatic hydrocarbons in 1,2-dichloroethane, the spectra of the complexes being similar to those of benzenium ions.⁶ The absorption spectra of boron fluoride-methyl fluoride, -ethyl fluoride, -isopropyl fluoride, -isopropyl chloride, and -*t*-butyl chloride complexes were observed also, but no absorption bands were found in the region of wave length longer than 220 $m\mu$. Rosenbaum and Symons⁷ reported that solutions of both *t*-butyl alcohol and isobutylene give in concentrated sulfuric acid a single measurable absorption band with λ_{max} 291 \pm 2 $m\mu$, and Olah, *et al.*,⁸ found that alkyl fluoride-antimony pentafluoride complexes in antimony pentafluoride give absorption bands around 290 $m\mu$.

Olah¹ asserted that a toluene-methyl fluoride-boron fluoride complex is formed at low temperatures though he could not characterize it because of the low boiling point of methyl fluoride and consequential difficulty of preparation. However, we found that, at -95° , a mixture of toluene, methyl fluoride, and boron fluoride of mole ratio of 1:1:1 become merely a two-phase colorless liquid. The solubility of toluene or *m*-xylene in liquid methyl fluoride-boron fluoride complex is very small, but very small amounts of these alkylbenzenes could be dissolved in the liquid complex. The absorption spectra of these solutions at the freezing point (approximately -110°) and near the boiling point (approximately -66°) of the solutions are not different from the absorption spectra of these alkylbenzenes dissolved in liquid methyl fluoride, as shown in Figures 2 and 3. However, when the absorption spectrum of mesitylene dissolved in excess liquid methyl fluoride-boron fluoride 1:1 addition complex was measured at the freezing point of the solution, strong absorption bands were observed around 257 and 356 $m\mu$ (Figure 4). Thus it appears that methyl fluoride-boron fluoride complex does not form a 1:1:1 addition complex with toluene or *m*-xylene, but does with mesitylene at low temperatures. The spectrum of the mesitylene-methyl fluoride-boron fluoride complex resembles that of benzenium ion. When the solution with dissolved mesitylene-methyl fluoride-boron fluoride complex is allowed to warm up to its boiling point, the peaks become faint, and the fine structure of the benzenoid band of mesitylene, which is observed at the same position as that of mesitylene in liquid methyl

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(6) Aromatic hydrocarbon-boron fluoride-1,2-dichloroethane complexes would be formed.

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(8) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, 86, 1360 (1964).

(1) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, 80, 6541 (1958).
(2) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, 83, 4571 (1961); 84, 1688 (1962).
(3) R. Nakane, O. Kurihara, and A. Natsubori, *J. Phys. Chem.*, 68, 2876 (1964).
(4) C. Reid, *J. Am. Chem. Soc.*, 76, 3264 (1954).

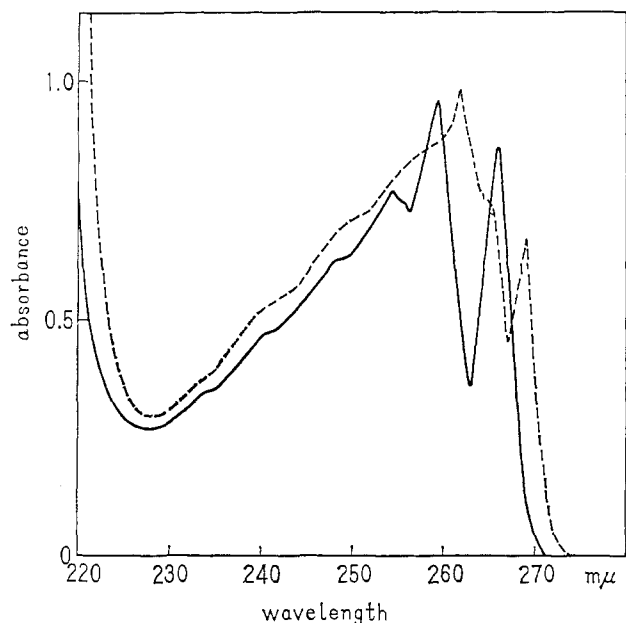


Figure 1. Absorption spectra of toluene and *m*-xylene dissolved in liquid boron fluoride. Mole ratios: —, $C_6H_5CH_3:BF_3 = ca. 0.001:1$ at approximately -127° ; ---, $m-C_6H_4(CH_3)_2:BF_3 = ca. 0.001:1$ at approximately -127° .

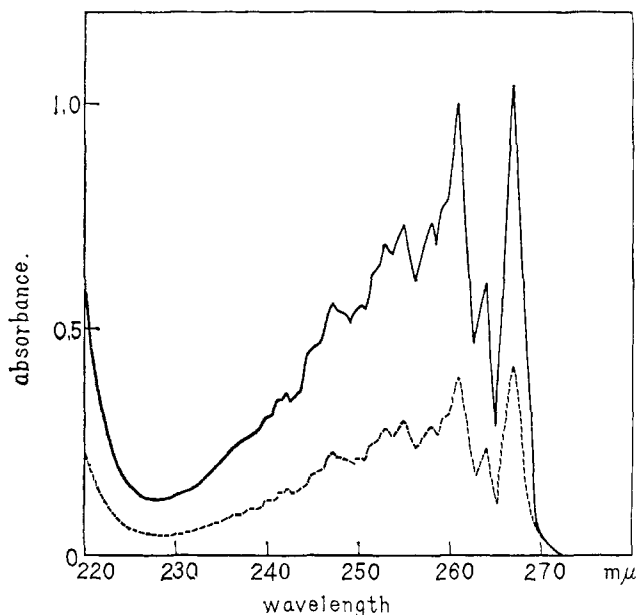
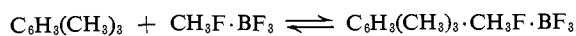


Figure 2. Absorption spectra of toluene dissolved in liquid methyl fluoride and in liquid methyl fluoride-boron fluoride complex. Mole ratios: —, $C_6H_5CH_3:CH_3F = ca. 0.001:1$ at approximately -142° ; ---, $C_6H_5CH_3:CH_3F:BF_3 = ca. 0.001:1:1$ at approximately -110° .

fluoride, appears overlapped upon the above peaks. This spectrum shows that in the solution mesitylene coexists with a small amount of the 1:1:1 addition complex. When the solution was again allowed to cool, the intensity of the peaks became higher reversibly. Therefore, it follows that in dilute solution the re-



versible dissociation equilibrium is established between the 1:1:1 addition complex and its original components. At the freezing point of the solution the equilib-

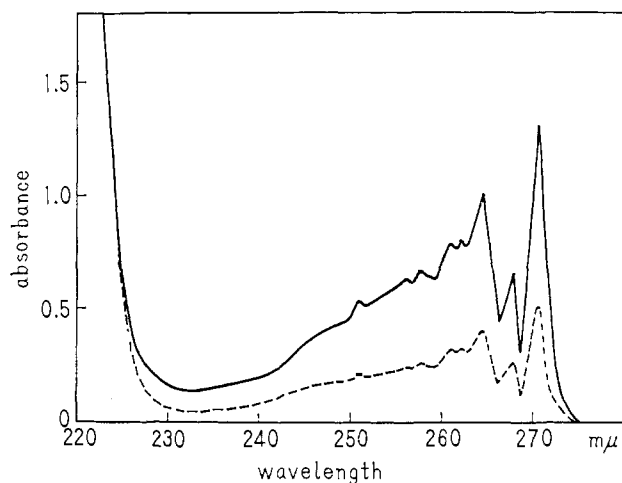


Figure 3. Absorption spectra of *m*-xylene dissolved in liquid methyl fluoride and in liquid methyl fluoride-boron fluoride complex. Mole ratios: —, $m-C_6H_4(CH_3)_2:CH_3F = ca. 0.001:1$ at approximately -142° ; ---, $m-C_6H_4(CH_3)_2:CH_3F:BF_3 = ca. 0.001:1:1$ at approximately -110° .

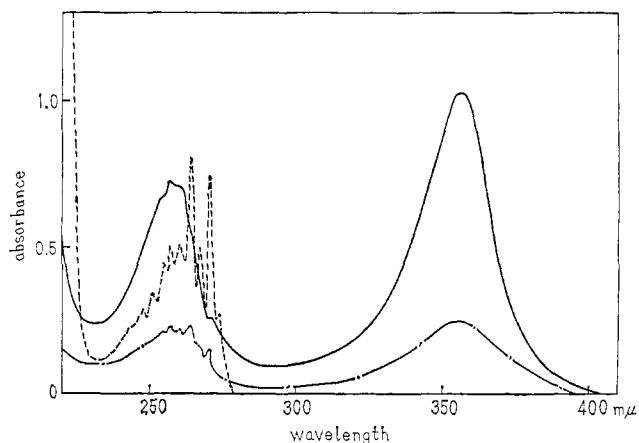


Figure 4. Absorption spectra of the mesitylene-methyl fluoride-boron fluoride complex dissolved in liquid methyl fluoride-boron fluoride complex. Mole ratios: —, $C_6H_3(CH_3)_3:CH_3F:BF_3 = ca. 0.0001:1:1$ at approximately -110° ; - · - · - ·, $C_6H_3(CH_3)_3:CH_3F:BF_3 = ca. 0.0001:1:1$ at approximately -66° ; ---, $C_6H_3(CH_3)_3:CH_3F = ca. 0.001:1$ at approximately -142° .

rium lies to the right and at the boiling point to the left, and this complex never decomposes irreversibly into alkylating products in this dilute solution.

When alkylbenzenes were dissolved in excess liquid ethyl fluoride-boron fluoride 1:1 addition complex and the absorption spectrum of the solution was measured at the freezing point of the solution (approximately -105°), strong absorption bands, which were due to the 1:1:1 addition complexes, were observed near 270 and 370 $m\mu$ as shown in Figures 5, 6, and 7. When these solutions were allowed to warm up to the boiling point of the solutions (approximately -60°), the intensity of the peaks scarcely changed. Therefore, the alkylbenzene-ethyl fluoride-boron fluoride complexes formed, the spectra of which resemble the spectrum of mesitylene-methyl fluoride-boron fluoride complex, scarcely dissociate in the ethyl fluoride-boron fluoride 1:1 addition complex solution, and hence the former 1:1:1 addition complexes are more stable than the latter 1:1:1 addition complex. However, when the

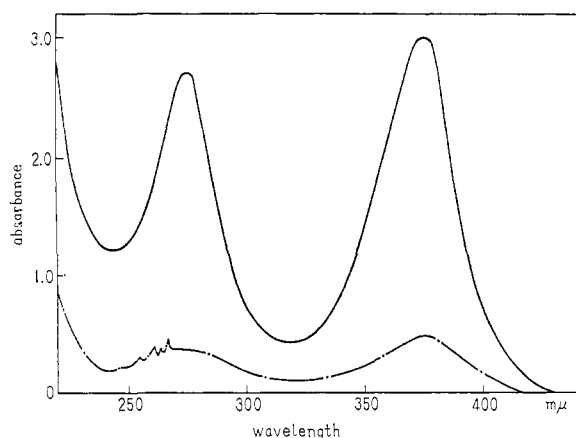


Figure 5. Absorption spectra of the toluene-ethyl fluoride-boron fluoride complex dissolved in liquid ethyl fluoride-boron fluoride complex. Mole ratios: —, $C_6H_5CH_3:C_2H_5F:BF_3 = ca. 0.0001:1:1$ at approximately -105° ; - - - - , $C_6H_5CH_3:C_2H_5F:BF_3 = ca. 0.0001:1:0.1$ at approximately -140° .

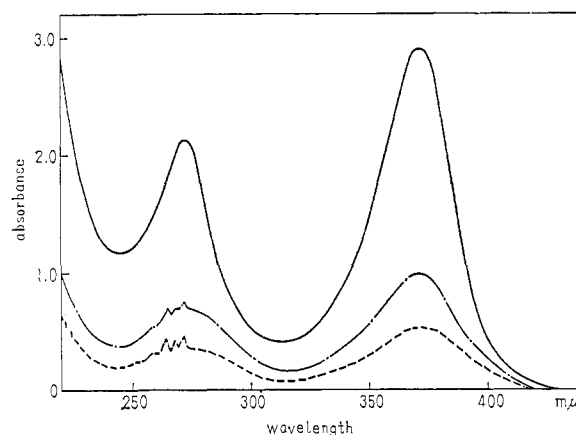


Figure 6. Absorption spectra of the *m*-xylene-ethyl fluoride-boron fluoride complex dissolved in liquid ethyl fluoride-boron fluoride complex. Mole ratios: —, $m-C_6H_4(CH_3)_2:C_2H_5F:BF_3 = ca. 0.0001:1:1$ at approximately -105° ; - - - - , $m-C_6H_4(CH_3)_2:C_2H_5F:BF_3 = ca. 0.0001:1:0.1$ at approximately -140° ; - · - · - , $m-C_6H_4(CH_3)_2:C_2H_5F:BF_3 = ca. 0.0001:1:0.1$ at approximately -100° .

above solutions were diluted with liquid ethyl fluoride at approximately -140° , the strong peaks became faint, overlapping the fine structure of the benzenoid band of the original alkylbenzenes which then appeared. When the above dilute solutions were allowed to warm up, the peaks near $370 m\mu$ became fainter, but when these solutions were again cooled, they returned reversibly to their original intensity observed at approximately -140° , as shown in Figures 5, 6, and 7. The effect of dilution for the toluene complex was larger than that for the mesitylene complex. Therefore, the latter complex is more stable than the former complex, but the stability difference between the two complexes is much smaller than that between the toluene-hydrogen fluoride-boron fluoride complex and mesitylene-hydrogen fluoride-boron fluoride complex.⁹ When small quantities of alkylbenzene and boron fluoride were dissolved in liquid ethyl fluoride, most of the alkylbenzene remained without forming the complex. Thus, in

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

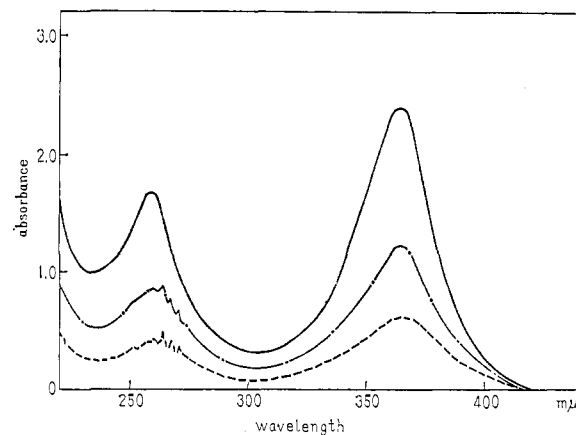


Figure 7. Absorption spectra of the mesitylene-ethyl fluoride-boron fluoride complex dissolved in liquid ethyl fluoride-boron fluoride complex. Mole ratios: —, $C_6H_3(CH_3)_3:C_2H_5F:BF_3 = ca. 0.0001:1:1$ at approximately -105° ; - - - - , $C_6H_3(CH_3)_3:C_2H_5F:BF_3 = ca. 0.0001:1:0.1$ at approximately -140° ; - · - · - , $C_6H_3(CH_3)_3:C_2H_5F:BF_3 = ca. 0.0001:1:0.1$ at approximately -100° .

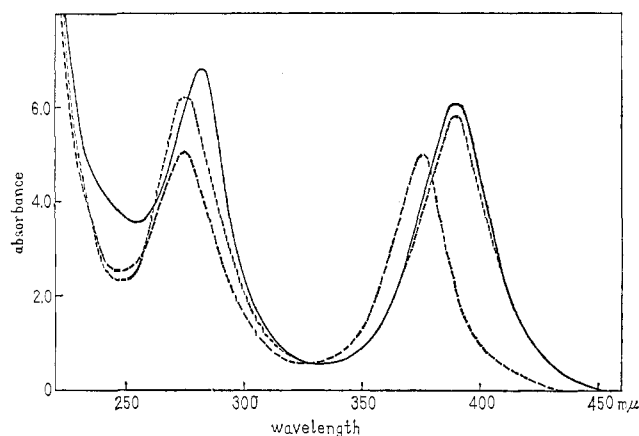


Figure 8. Absorption spectra of alkylbenzene-isopropyl fluoride-boron fluoride complexes dissolved in liquid isopropyl fluoride. Mole ratios: —, $C_6H_5CH_3:i-C_3H_7F:BF_3 = ca. 0.0001:1:0.01$ at approximately -135° ; - - - - , $m-C_6H_4(CH_3)_2:i-C_3H_7F:BF_3 = ca. 0.0001:1:0.01$ at approximately -135° ; - · - · - , $C_6H_3(CH_3)_3:i-C_3H_7F:BF_3 = ca. 0.0001:1:0.01$ at approximately -135° .

dilute solutions reversible dissociation equilibria occur also between alkylbenzene-ethyl fluoride-boron fluoride 1:1:1 addition complexes and their original components, and, in ethyl fluoride-boron fluoride 1:1 addition complex solution, the equilibria must lie far to the right, in ethyl fluoride solution to the left. These complexes also never decompose irreversibly in these dilute solutions.

When alkylbenzenes were dissolved in excess liquid isopropyl fluoride-boron fluoride 1:1 addition complex, the absorption spectra of alkylbenzene-isopropyl fluoride-boron fluoride complexes were observed at the freezing point of the solution (approximately -118°). The spectra of these complexes resembled those of other 1:1:1 addition complexes. When the solutions were allowed to warm up, isopropyl fluoride decomposed and other absorption bands, which were seemingly due to the polymer, appeared in the ultraviolet and visible regions, and since the intensity of these absorption bands was very strong, the change of the absorption

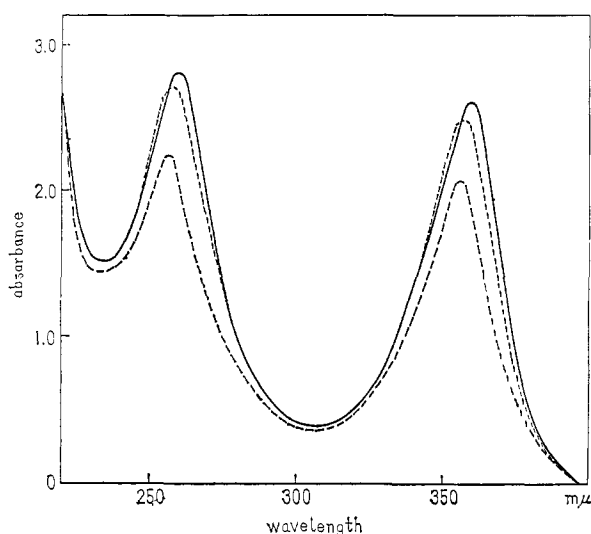


Figure 9. Absorption spectra of alkylbenzene-*t*-butyl chloride-boron fluoride complexes dissolved in liquid *t*-butyl chloride-boron fluoride complex. Mole ratios: —, $C_6H_5CH_3:t-C_4H_9Cl:BF_3 = ca. 0.0001:0.7:1$ at approximately -95° ; - - - - - , $m-C_6H_4(CH_3)_2:t-C_4H_9Cl:BF_3 = ca. 0.0001:0.7:1$ at approximately -95° ; - · - · - · , $C_6H_5(CH_3)_3:t-C_4H_9Cl:BF_3 = ca. 0.0001:0.7:1$ at approximately -95° .

bands of the complexes could not be traced. When the solutions were diluted by liquid isopropyl fluoride, no change was observed in the absorption spectra. Also, even when small amounts of alkylbenzene and boron fluoride were dissolved in liquid isopropyl fluoride, the fine structures of the benzenoid bands of the alkylbenzenes disappeared and strong peaks were observed, as shown in Figure 8. Therefore, alkylbenzene-isopropyl fluoride-boron fluoride complexes are more stable than alkylbenzene-ethyl fluoride-boron fluoride complexes which are more stable than the mesitylene-methyl fluoride-boron fluoride complex. However, in dilute solutions of dissolved alkylbenzene-isopropyl fluoride-boron fluoride 1:1:1 addition complex, too, reversible dissociation equilibria will be established between the complexes and their original components, and in either isopropyl fluoride-boron fluoride 1:1 addition complex solution or isopropyl fluoride solution, the equilibria will lie far to the right.

t-Butyl chloride-boron fluoride solutions of alkylbenzenes, solidified by liquid nitrogen, were allowed to warm up to their freezing point (approximately -95°), and their absorption spectra were measured. Two strong peaks of absorption bands were observed, as in the cases of dilute solutions of alkylbenzene-alkyl fluoride-boron fluoride complexes. When the solutions were further heated, the vapor pressure became higher than 1 atm. Boron fluoride was then drawn out from the cell and the solutions solidified immediately. At the time when this solid reached its melting point, the boron fluoride was completely withdrawn, and the absorption spectra of the melted solutions were then measured. In the toluene system, the presence of *t*-butylmethylbenzene was observed, but in the *m*-xylene or mesitylene systems, *m*-xylene or mesitylene appeared again. Moreover, the gases, which evolved when the 1:1:1 addition complexes were allowed to warm up, were analyzed with a mass spectrometer. Hydrogen chloride was observed⁸ in the

toluene system, but not in the *m*-xylene or mesitylene system. Thus, it appears that at low temperatures a polar *t*-butyl chloride-boron fluoride complex forms with the toluene 1:1:1 addition complex, which decomposes irreversibly into *t*-butylmethylbenzene when boron fluoride is withdrawn from this complex in the low-temperature region; but with *m*-xylene or mesitylene, 1:1:1 addition complexes, which dissociate reversibly into their original components, do not decompose irreversibly. Olah, *et al.*,¹⁰ found that toluene, *o*-xylene, or *m*-xylene was *t*-butylated with *t*-butyl bromide and isobutylene in nitromethane solution at 25° by the use of stannic chloride or aluminum chloride as catalyst, while *p*-xylene or mesitylene was not.

Small quantities of alkylbenzene and boron fluoride were dissolved in liquid mixture of *t*-butyl chloride and isopropyl fluoride. Such mixtures were used because the melting point of *t*-butyl chloride is too high for boron fluoride to be dissolved. As in the case of ethyl fluoride solutions of alkylbenzene-ethyl fluoride-boron fluoride complexes, most of the alkylbenzenes remained in the solution at -95° . Thus, reversible dissociation equilibria occur also between alkylbenzene-*t*-butyl chloride-boron fluoride 1:1:1 addition complexes and their original components in dilute alkyl chloride solution.

The positions of peaks of absorption bands of alkylbenzene-alkyl halide-boron fluoride complexes are summarized in Table I.

Table I. Positions of Absorption Maxima ($m\mu$)^a of Alkylbenzene-Alkyl Halide-Boron Fluoride Complexes

$i-C_3H_7F \cdot BF_3$	275, 376	275, 390	282, 390
$C_2H_5F \cdot BF_3$	259, 364	272, 371	275, 375
$t-C_4H_9Cl \cdot BF_3$	257, 357	258, 358	260, 361
$CH_3F \cdot BF_3$	257, 356

^a All values $\pm 2 m\mu$.

Thermodynamic Isotope Effect. In the previous work⁸ the equilibrium constants of boron isotope exchange between gaseous boron fluoride and some liquid boron fluoride-alkyl halide complexes were measured at low temperatures. The equilibrium constants between gaseous boron fluoride and liquid boron fluoride-ethyl fluoride or -isopropyl fluoride complexes at -68 and -95° were measured in this work by a similar method. All values obtained are summarized in Table II.

As shown in the previous report, the density of localized electrons on the vacant orbital of the boron atom in the boron fluoride complex, and hence the polarity of the complex, becomes higher as the equilibrium constant becomes larger. Thus the polarity of alkyl halide-boron fluoride complexes, and hence the electron deficiency of polar cations in the complexes, decreases in the following order: $(CH_3)_2^{\delta+}CHF \dots$

(10) G. A. Olah, S. H. Flood, and M. E. Moffatt, *J. Am. Chem. Soc.*, 86, 1060 (1964).

Table II. Equilibrium Constant of Boron Isotope Exchange between Boron Fluoride and Boron Fluoride Complexes

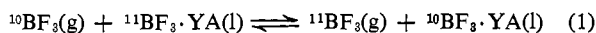
Complex	+70°	+20°	+0°	-23°	-32°	-68°	-95°	-112°	Ref.
BF ₃ ·O(CH ₃) ₂	(1.030) ^a	1.029	1.034	1.041					e
BF ₃ ·O(C ₂ H ₅) ₂	1.028	1.034	1.040 ^b	1.040 ^c	1.053				e
BF ₃ ·OC ₄ H ₉	(1.029) ^a	(1.035) ^a	(1.038) ^a	(1.041) ^a					e
BF ₄ ⁻	(1.037) ^a	(1.044) ^a	(1.048) ^a	(1.053) ^a					e
BF ₃ ·i-C ₃ H ₇ F·C ₆ H ₅ CH ₃	(1.059) ^a	(1.062) ^a	(1.066) ^a	(1.071) ^a		(1.085) ^a	(1.096) ^a	(1.105) ^a	f
BF ₃ ·C ₂ H ₅ F·C ₆ H ₅ CH ₃						1.037			f
BF ₃ ·C ₂ H ₅ F·m-C ₆ H ₄ (CH ₃) ₂						1.034			f
BF ₃ ·C ₂ H ₅ F·p-C ₆ H ₄ (CH ₃) ₂						1.043			f
BF ₃ ·t-C ₄ H ₉ Cl·C ₆ H ₅ CH ₃							1.015	1.020	f
BF ₃ ·CH ₃ F + C ₆ H ₅ CH ₃							1.020		f
BF ₃ ·i-C ₃ H ₇ F						1.025	1.035		f
BF ₃ ·C ₂ H ₅ F						1.021	1.030		f
BF ₃ ·CH ₃ F							1.020	~1.026	g
							(1.020) ^a	(1.022) ^a	h
BF ₃ ·t-C ₄ H ₉ Cl							~1.023	~1.033	f, g
BF ₃ ·i-C ₃ H ₇ Cl							1.016	1.021	g
BF ₃ ·CH ₃ Cl							1.016	1.021	i
BF ₃							1.006	1.011	i, j

^a Calculated from infrared and Raman spectra. ^b -3°. ^c -22°. ^d +25°. ^e See ref. 16. ^f Present report. ^g See ref. 3. ^h See ref. 17. ⁱ R. Nakane and O. Kurihara, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **56**, 161 (1962). ^j See ref. 22.

$\delta^- \text{F}_8 > \text{CH}_3\delta^+\text{CH}_2\text{F} \dots \delta^- \text{BF}_3 > (\text{CH}_3)_3\delta^+\text{CCl} \dots \delta^- \text{BF}_3 > \delta^+\text{CH}_3\text{F} \dots \delta^- \text{BF}_3 > (\text{CH}_3)_2\delta^+\text{CHCl} \dots \delta^- \text{BF}_3, \delta^+\text{CH}_3\text{Cl} \dots \delta^- \text{BF}_3$. These results agree partly with the results obtained by Olah¹¹ from measurements of specific conductivity.

Next, the equilibrium constants of boron isotope exchange between gaseous boron fluoride and alkylbenzene solutions of alkyl halide-boron fluoride complexes were measured at -68 and -95°. The obtained results are also summarized in Table II. From these results it appears that the equilibrium constants for alkyl halide-boron fluoride complex systems vary by the coexistence of alkylbenzene when the 1:1:1 addition complex is formed at low temperatures, but they do not vary when the addition complex is not formed even at low temperatures. The equilibrium constant was not measured when the complex was solid at -68°.

Now, when the following isotopic exchange occurs between gaseous boron fluoride and the liquid boron fluoride complex which is formed with the donor molecule YA



the equilibrium constant is given by

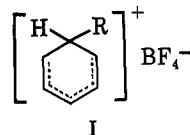
$$K = \frac{[Q_{^{10}\text{BF}_3 \cdot \text{YA}(\text{l})}]}{[Q_{^{11}\text{BF}_3 \cdot \text{YA}(\text{l})}]} \bigg/ \frac{[Q_{^{10}\text{BF}_3(\text{g})}]}{[Q_{^{11}\text{BF}_3(\text{g})}]} \quad (2)$$

Here, the ratio of one to the other of the partition functions of isotopic molecules is

$$\frac{Q_2}{Q_1} = \frac{s_1}{s_2} \prod_i \frac{u_{2i} \exp(-u_{2i}/2)[1 - \exp(-u_{1i})]}{u_{1i} \exp(-u_{1i}/2)[1 - \exp(-u_{2i})]} \quad (3)$$

where 1 and 2 refer to the different isotopic molecules, s_1 and s_2 are the symmetry numbers, $u_i = hc\omega_i/kT$, and ω_i is the i th normal vibrational frequency.¹² Thus, when the normal vibrational frequencies of gas-

eous boron fluoride and liquid boron fluoride complexes are obtained, the equilibrium constants can be calculated from eq. 2 and 3. The presence of the BF₄⁻ anion revealed by the absorption bands near 1050 cm⁻¹ due to the asymmetric B-F stretch proves the ionic structures of CH₃COBF₄¹³ and NO₂BF₄¹⁴ for similar absorption bands are observed in tetrafluoroborates such as NaBF₄, KBF₄, or NH₄BF₄.¹⁵ Therefore, if alkylbenzene-alkyl fluoride-boron fluoride 1:1:1 addition complexes have ionic structures such as I for one, similar absorption bands should reveal the presence of the BF₄⁻ anion. Since the isotopic shifts of normal vibrational frequencies of tetrafluoroborates are known, the equilibrium constant between



gaseous boron fluoride and the BF₄⁻ anion can be calculated by eq. 2 and 3. The calculated value is 1.085 at -68°. In general, the calculated value agrees fairly well with the observed value whenever the isotopic shifts of normal vibrational frequencies are known. For example, in the isotopic exchange between gaseous boron fluoride and boron fluoride-methyl ether, -ethyl ether, or -tetrahydrofuran complexes, Palko, *et al.*,¹⁶ compared the observed equilibrium constants with the values calculated by eq. 2 and 3 from infrared and Raman spectral data and found a good agreement between the two. Recently, Nakane and Oyama¹⁷ observed the infrared spectra of liquid ¹⁰BF₃·CH₃F

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 H. C. Urey, *J. Chem. Soc.*, 562 (1947); J. Bigeleisen and M. G. Mayer,
J. Chem. Phys., **15**, 261 (1947).

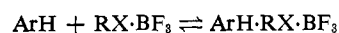
and $^{11}\text{BF}_3\text{CH}_3\text{F}$ complexes at approximately -110° and used the isotopic data to calculate the theoretical equilibrium constant for isotopic exchange between gaseous boron fluoride and its methyl fluoride complex. It was found that in this complex the BF_4^- anion is not present and the C-F bond is only slightly weakened and, moreover, as shown in Table II, the calculated values agree fairly well with the observed values. Therefore, all values of the equilibrium constants for the complexes, in which BF_4^- anion is contained, should be nearly equal to the calculated values. Similarly, the value of the equilibrium constant for a complex, in which the BF_3Cl^- anion is contained, will be nearly equal to that for methyl ether-boron fluoride complex as shown in the previous report.³ If the obtained alkylbenzene-alkyl halide-boron fluoride complex is the σ -complex and has the ionic structure I, the observed values of equilibrium constant should show a fairly good agreement with the calculated values. However, all observed values were much smaller than the calculated values for tetrafluoroborates and were not much different from the values for the polar complexes such as alkyl halide-boron fluoride complexes containing no anion. Thus it follows that alkylbenzene-alkyl halide-boron fluoride complexes do not contain anions such as BF_4^- or BF_3Cl^- , but polar anions such as $-\text{F}\cdots^{\delta-}\text{BF}_3$ or $-\text{Cl}\cdots^{\delta-}\text{BF}_3$. On the other hand, if the solution were no more than an alkylbenzene solution of alkyl halide-boron fluoride complexes, the presence or absence of alkylbenzene would, as in the case of a mixture of toluene and boron fluoride-methyl fluoride complex, not affect the value of the equilibrium constant, for the normal vibrational frequencies of polarized alkyl halide-boron fluoride complexes are not at all affected by the addition of alkylbenzene. However, when alkyl halide-boron fluoride complexes such as the ethyl fluoride-boron fluoride complex are mixed with alkylbenzene at low temperatures, the equilibrium constants become different from those of original alkyl halide-boron fluoride complex systems. This result shows that the density of localized electrons on the vacant orbital of the boron atom changes and hence some normal vibrational frequencies in the BF_3 molecule change as the result of the reaction in which a partially electron-deficient carbon atom in the alkyl halide becomes bound to the π -electron cloud of the alkylbenzene where electron density is the highest. Thus it follows from the viewpoint of anion formation that nonionized alkyl halide-boron fluoride complexes, the equilibrium constants of which are larger than a certain value, form with alkylbenzenes not the complexes of ionic structures but the polar complexes at low temperatures.

Discussion

The absorption spectra and the thermodynamic isotope effects studied in this investigation have provided us with the following results: methyl fluoride-boron fluoride complexes, in which the electron deficiency of the polar cation is small, can form 1:1:1 addition complexes with mesitylene but not with toluene or *m*-xylene at low temperatures; alkyl halide-boron fluoride complexes such as boron fluoride-ethyl fluoride, -isopropyl fluoride, or -*t*-butyl chloride, in which the electron deficiency of polar cations becomes larger

than that in the methyl fluoride-boron fluoride complex, can form 1:1:1 addition complexes with all alkylbenzenes at low temperatures; the mesitylene-isopropyl fluoride-boron fluoride complex is more stable than the mesitylene-ethyl fluoride-boron fluoride complexes which is more stable than the mesitylene-methyl fluoride-boron fluoride complex; the mesitylene-ethyl fluoride-boron fluoride complex is more stable than the toluene-ethyl fluoride-boron fluoride complex, but the stability difference between the two complexes is much smaller than that between the toluene-hydrogen fluoride-boron fluoride complex and the mesitylene-hydrogen fluoride-boron fluoride complex; all alkylbenzene-alkyl halide-boron fluoride 1:1:1 addition complexes are weak complexes which exist only at low temperatures, and in dilute solution the reversible dissociation equilibrium is established between the 1:1:1 addition complex and its original components; all these complexes show respectively two characteristic peaks of absorption bands which resemble those of benzenium ions; when boron fluoride is removed completely from alkylbenzene-*t*-butyl chloride-boron fluoride complexes at low temperatures, the toluene complex decomposes irreversibly into *t*-butylmethylbenzene, but the mesitylene or *m*-xylene complexes dissociate reversibly into mesitylene or *m*-xylene.

The 1:1:1 addition complex which is formed when alkylbenzene is dissolved in the liquid nonionized polar alkyl halide-boron fluoride complex at low temperatures seems to be the intermediate complex of the boron fluoride catalyzed alkylation, for the alkylation can proceed when boron fluoride is removed completely from the 1:1:1 addition complex. Now, if this intermediate complex is the σ -complex suggested by Olah,¹ the activation energy required to break the carbon-carbon bond should be larger than that required to break the carbon-hydrogen bond, for no kinetic hydrogen isotope effect was observed in Friedel-Crafts alkylation.² However, in a dilute solution at low temperatures, the reversible dissociation equilibrium



is established between the isolable intermediate 1:1:1 addition complex and its original components, and the complex does not decompose irreversibly into alkylating products even if allowed to warm up in dilute solution. It is customary to consider π -complexes weak and reversible interactions of aromatics with neutral or slightly polarized reagents or with ions, not capable of effecting irreversible changes. Therefore, the intermediate 1:1:1 addition complex isolated at low temperatures is probably a π -complex which can only be a loose association near the beginning of the reaction path of alkylation.

In Olah's work,¹ alkyl fluorides were dissolved in aromatics, and boron fluoride was then introduced until the increase of weight ceased in the cooled solutions. Therefore, Olah's σ -complexes were prepared under different conditions from our systems. The nature of the complexes can depend very much on the way they were prepared. Hence the intermediate complexes we obtained may have been different from Olah's σ -complexes.

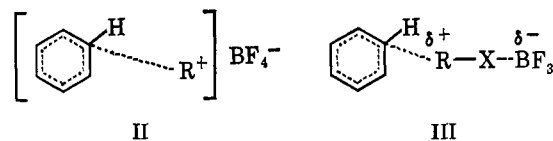
This conclusion is supported also by the fact that the toluene-*t*-butyl chloride-boron fluoride complex decomposes into *t*-butylmethylbenzene, but the mesitylene-*t*-butyl chloride-boron fluoride complex dissociates only reversibly into mesitylene. As a result of steric hindrance it will be impossible for *t*-butyl cation to approach mesitylene so closely as to form a carbon-carbon bond and hence to form the σ -complex as an intermediate. This can explain why *t*-butylation of mesitylene does not proceed. Therefore, it is evident that the mesitylene-*t*-butyl chloride-boron fluoride 1:1:1 complex isolated at low temperatures is not a σ -complex and the aromatic interacts only weakly with the *t*-butyl chloride-boron fluoride complex; hence the distance between the aromatic and *t*-butyl chloride-boron fluoride complex is long. Since the spectra of this complex and the corresponding toluene or *m*-xylene complexes are closely similar, the latter complexes too do not seem to be σ -complexes.

The *m*-xylene-*t*-butyl chloride-boron fluoride complex also does not decompose irreversibly, but dissociates reversibly in the low temperature region. Olah, *et al.*,¹⁰ found that *t*-butylation of *m*-xylene with stannic chloride or aluminum chloride catalyst gives only 5-*t*-butyl-1,3-dimethylbenzene at room temperature with a reaction rate only one-twentieth of that of the *t*-butylation of *o*-xylene, while the relative isopropylation rates of *m*-xylene and *o*-xylene are not so different from unity.¹⁸ They suggested that the activated transition state leading to the σ -complex formation is composed of separate transition states corresponding to the *meta*-, *para*-, and *ortho*-positions, the *meta*-position representing the highest energy barrier. The *m*-xylene-*t*-butyl halide-acidic halide 1:1:1 addition complexes which are formed at low temperatures are not σ -complexes. They do not seem transformable into *ortho* or *para* isomers of σ -complexes because of the steric hindrance. It also seems impossible for the *m*-xylene-*t*-butyl chloride-boron fluoride complex to transform into the *meta* isomer of the σ -complex over the energy barrier which is too high. Therefore, when boron fluoride is removed from the *m*-xylene-*t*-butyl chloride-boron fluoride complex in the low temperature region, the complex will dissociate reversibly. However, when the reaction temperature becomes higher, the 1:1:1 addition complex will barely pass over the transition state leading to the *meta* isomer of the σ -complex.

The thermodynamic isotope effect also shows that the intermediate complex is not a σ -complex which has an ionic structure such as I, for the alkylbenzene-boron fluoride-ethyl fluoride, -isopropyl fluoride, or -*t*-butyl chloride 1:1:1 addition complexes do not contain anions such as BF_4^- or BF_3Cl^- but polar anions such as $-\text{F}\cdots\delta^-\text{BF}_3$ or $-\text{Cl}\cdots\delta^-\text{BF}_3$.

Thus, it is evident that the intermediate complexes which are formed when aromatics are dissolved in liquid nonionized alkyl halide-boron fluoride complexes at low temperatures are not σ -complexes but π -complexes. However, they cannot be the symmetrical π -complexes suggested by Dewar,¹⁹ for they show two

strong peaks of absorption bands around 260 and 360 μm , respectively, and the intensity of these peaks is much higher than that of benzenoid bands of the original alkylbenzenes. They must thus be unsymmetrical charge-transfer complexes of the oriented π -complex types. However, they cannot be oriented π -complexes such as II which was suggested by Brown²⁰ as high-energy intermediates and assumed by Olah² as



nonisolable intermediate complexes formed at first in the whole process of alkylation, for they do not contain anions. Thus, it seems likely that the alkylbenzene-alkyl halide-boron fluoride 1:1:1 addition complex is an oriented π -complex (III) containing a carbon-hydrogen bond, a carbon-halogen bond, and a partially formed carbon-carbon bond which is comparatively long and weak, and that the partially formed carbon-carbon bond becomes stronger as either the electron deficiency of the alkyl halide-boron fluoride complex or the basicity of alkylbenzene becomes larger, causing the oriented π -complex to become more stable.

Mesitylene can form a stable ionic complex with boron fluoride in hydrogen fluoride solution, whereas the only evidence that toluene may form a complex with boron fluoride in hydrogen fluoride solution is that the observed Henry's law constant is lower for the toluene-hydrogen fluoride-boron fluoride system than for the hydrogen fluoride-boron fluoride system.⁹ Both mesitylene and toluene can form oriented π -complexes with boron fluoride in ethyl fluoride solution. The two ethyl fluoride complexes are not very different in stability, whereas the mesitylene-hydrogen fluoride-boron fluoride complex is far more stable than the toluene-hydrogen fluoride-boron fluoride complex. Thus, the change of stability of oriented π -complexes such as the alkylbenzene-alkyl halide-boron fluoride complexes with increasing basicity of alkylbenzenes seems to be similar to that of symmetrical π -complexes,² but not to that of σ -complexes. However, this change of stability of oriented π -complexes may become larger as the electron deficiency of attacked polarized complexes becomes larger.

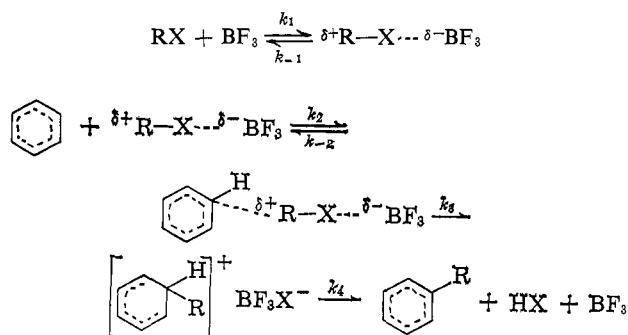
When alkylbenzenes attack nonionized alkyl halide-boron fluoride complexes at low temperatures, an isolable intermediate oriented π -complex such as III is formed at first, and the transformation from this complex into the intermediate σ -complex seems to be involved in the rate-determining step, for at low temperatures the intermediate oriented π -complex dissociates reversibly in a dilute solution and decomposes irreversibly into an alkylating product only when boron fluoride is removed from this complex and, moreover, it is known that the proton loss is not rate determining in Friedel-Crafts alkylation.² In this case, breaking of the carbon-halogen bond in the isolable oriented π -complex will require high activation energy. Thus,

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boron fluoride catalyzed alkylation in a low temperature region seemingly proceeds as



where $k_1, k_{-1}, k_2, k_{-2}, k_4 \gg k_3$.

Experimental

Materials. Methyl fluoride, ethyl fluoride, and isopropyl fluoride were prepared from methyl, ethyl, and isopropyl tosylates by reaction with potassium fluoride.²¹ Highly pure *t*-butyl chloride was commercially available. Boron fluoride was obtained from the Harshaw Chemical Co. All materials were purified by low-temperature fractional distillation before use.³ Toluene and *m*-xylene were Matheson Coleman and Bell spectral grade reagents. Mesitylene was obtained from Tokyo Kasei Co.

The Measurement of Absorption Spectra. The absorption spectra were measured with a Cary recording spectrophotometer, Model 14 M. The cell used in this measurement is of quartz of the same type as the one that served in the previous work to measure the ultraviolet absorption spectra of boron fluoride-monoolefin complexes at low temperatures.²² The double-wall container was evacuated after the fashion of dewar vessels in order to obtain thermal insulation. The path length, through which the beams of ultraviolet and visible lights were passed, was found to be approximately 0.5 mm. by comparison with a 1-cm. quartz standard cell by the use of a standard aqueous solution of copper-amine complex.

For the measurement of absorption spectrum, alkyl halide gas or boron fluoride gas and a mixture of both gases and then a small amount of alkylbenzene vapor were introduced, one following another, into the cell maintained cold by liquid nitrogen. The condensed solid mixture was allowed to warm up and melt, and the absorption spectrum was measured. The fine structure of the benzenoid band of toluene dissolved in liquid boron fluoride showed maxima at 254, 2595 (main), 266 $m\mu$, etc., and that of *m*-xylene showed maxima at 262 (main), 269 $m\mu$, etc. The fine structure of the benzenoid band of toluene dissolved in liquid methyl fluoride showed maxima at 247, 255, 258, 261, 264, 267 (main) $m\mu$, etc.; that of *m*-xylene showed maxima at 251, 258, 2625, 2645, 268, 2715 (main) $m\mu$, etc.; and that of mesitylene showed maxima at 255,

257, 260, 264 (main), 267, 2705, 2735 $m\mu$, etc. In other alkyl fluoride solutions similar spectra were observed. The fine structures of the benzenoid bands of alkylbenzenes dissolved in liquid *t*-butyl chloride showed maxima at the following positions: 249, 253, 256, 260, 262, 2645, 2685 (main) $m\mu$, etc., for toluene; 259, 266 (main), 269, 273 $m\mu$, etc. for *m*-xylene; 256, 2585, 2625, 2655, 268, 272 (main) $m\mu$, etc. for mesitylene. The fine structure of the benzenoid band of *t*-butylmethylbenzene dissolved in liquid *t*-butyl chloride showed maxima at 252, 259, 2645, 2665, 2725 (main) $m\mu$, etc. The positions and relative intensities of these fine structures were different from those of absorption bands of these alkylbenzenes dissolved in cyclohexane at room temperature.

The Measurement of the Thermodynamic Isotope Effect. The methods were the same as those in the preceding work.^{3,22} Constant low temperature baths at the melting points of *p*-cymene (-68°), toluene (-95°), and carbon disulfide (-112°) were used.

When the separation factors of boron isotope exchange between boron fluoride gas and liquid solutions of the mole ratios of boron fluoride to isopropyl fluoride of 1:1.5 and 1:1.8 were measured at -95° , the values were found always to be 1.035 ± 0.002 . In these cases the liquid became yellow and propane was observed in the gas phase, but it could be inferred that the impurities, the by-products of the reaction, did not affect the separation factor, for the values showed no correlation with amounts of impurities. For the reason given in the preceding work,³ the equilibrium constant is equal to the separation factor obtained. In a similar way, the values of equilibrium constants for other complex systems and at other temperatures were also measured. The equilibrium constant of the exchange reaction between gaseous boron fluoride and the boron fluoride-*t*-butyl chloride complex was obtained by extrapolation.

Toluene-isopropyl fluoride-boron fluoride, toluene-ethyl fluoride-boron fluoride, and *m*-xylene-ethyl fluoride-boron fluoride complexes were yellow liquids of vapor pressures of approximately 50, 80, or 40 mm. at -68° , respectively. The toluene-*t*-butyl chloride-boron fluoride complex melted at -122° and had a vapor pressure of approximately 760 mm. at -95° . The equilibrium constant of the exchange reaction between boron fluoride gas and a two-phase liquid composed of the liquid methyl fluoride-boron fluoride complex and liquid toluene was found to be equal to that for the boron fluoride-methyl fluoride complex system. The equilibrium constants for other alkyl halide-boron fluoride-alkylbenzene complexes, which are solid at -68° , were not measured in the present work. The error in the equilibrium constants for alkylbenzene-alkyl fluoride-boron fluoride complexes was ± 0.003 and that for the toluene-*t*-butyl chloride-boron fluoride complex was ± 0.002 .

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