Proton Magnetic Resonance Spectrum of Termolecular, Oriented π Complex

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To give evidence of localization of an acceptor in an oriented π complex, the proton magnetic resonance (pmr) spectra of the yellow toluene–ethyl fluoride–boron fluoride complex are observed at −80°. The proton resonances of the CH_2F and CH_3 groups in ethyl fluoride are split into the respective doublets as a result of interaction with the single ^{19}F nucleus. The interaction shift of ethyl fluoride in a toluene solution of an un-ionized ethyl fluoride–boron fluoride complex is to lower field relative to ethyl fluoride in the pure un-ionized complex. Here an induced ring diamagnetism is absent. The observed shift is regarded as characteristic, not of a symmetrical π complex or a benzenonium ion complex, but of the oriented π complex.

Recently we observed the ultraviolet (uv) and infrared (ir) spectra of a yellow toluene–ethyl fluoride–boron fluoride complex at low temperatures. The uv spectrum of the complex[1] closely resembles the spectrum of a protonated benzenonium ion complex, but is quite different from the spectrum of toluene. The complex dissociates reversibly by dilution with liquid ethyl fluoride. The ir spectra[2] show that the C–H, C–F, and B–F force constants of the complex are only slightly different from the corresponding force constants of the respective components. In the complex, therefore, a C–F bond of ethyl fluoride is not broken, boron fluoride retains its planar structure, and the ethyl carbonium and tetrafluoroborate ions are absent. We concluded from these results that the complex is not an ethyl benzenonium tetrafluoroborate complex as suggested by Olah,[3] but a termolecular, oriented π complex, $CH_3C_6H_5\cdots C_2^{\delta+}H_5F\cdot B^{\delta-}F_3$, in which an un-ionized ethyl fluoride–boron fluoride complex is oriented near an *ortho* or *para* position in toluene.

In this work the proton magnetic resonance spectra have been observed for obtaining an additional evidence for the formation of the termolecular, oriented π complex at low temperatures.

Results

Elleman and coworkers[4] observed the pmr spectra of ethyl fluoride at 27°. The proton resonances of the CH_2F group show a doublet, each component of which is further split into a quartet. Similarly, the proton resonances of the CH_3 group show a doublet, each component of which is further split into a triplet. We observed the proton resonance spectra of pure liquid ethyl fluoride at −80° and obtained similar results. The spectra of a toluene solution of ethyl fluoride, in which a mole ratio of ethyl fluoride/toluene was 1:1, were also observed at −80°. A shift of the ethyl hydrogen resonance signals to high field was found. The chemical shifts and the spin–spin coupling constants for both pure liquid ethyl fluoride and dissolved ethyl fluoride are given in Table I.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE ETHYL FLUORIDE SYSTEM

	δ^a			J_{HF}^b	
Compound	CH_3	CH_2F	J_{HH}^b	CH_3	CH_2F
C_2H_5F	1.09	4.24	7	27	47
C_2H_5F in $C_6H_5CH_3$	0.81	3.94	7	27	47
$C_2H_5F\cdot BF_3$ complex	1.21	4.47	7	29	46
$C_6H_5CH_3\cdot C_2H_5F\cdot BF_3$ complex	1.43	4.62	7	29	46

[a] Chemical shifts are given in δ units with tetramethylsilane as external standard (δ 0). [b] Coupling constants are given in cycles per second.

Ethyl fluoride forms the un-ionized complex with boron fluoride at low temperatures. The pmr spectra of the un-ionized complex were observed at −80° and are shown in Figure 1. The chemical shifts and the spin–spin coupling constants for the ethyl group in the complex are given in Table I. The proton resonances of the CH_2F and CH_3 groups in ethyl fluoride were still split into the respective doublets by ^{19}F. An interaction shift of ethyl fluoride in the un-ionized complex was to lower field relative to pure liquid ethyl fluoride.

When boron fluoride is dissolved in the toluene solution of ethyl fluoride at low temperatures, the color of the solution becomes yellow and the toluene–ethyl fluoride–boron fluoride complex is formed. The pmr spectra of the liquid complex, in which a mole ratio of toluene/ethyl fluoride/boron fluoride was 1:1:1, were observed at −80° and are shown in Figure 1. The chemical shifts and the spin–spin coupling constants for the ethyl group in the complex are given in Table I. The proton resonances of the CH_2F and CH_3 groups in ethyl fluoride, which were split into the respective doublets by ^{19}F, were still found. These resonance signals displaced to low field and broadened. The broadening of the signals may result from a high viscosity of the liquid complex. A pmr signal of the aliphatic CH_2 group in the benzenonium ion complex[5] was found with difficulty. The proton resonances of the CH_3 group in ethyl fluoride were overlapped with the proton resonances which were probably attributable to the CH_3 protons of ethyl group in ethyltoluene.

When boron fluoride is withdrawn by evacuation from the complex, ethyltoluene is obtained.[2] The spectra of the solution, from which a portion of boron fluoride was withdrawn by evacuation, was observed at −80° and are shown in Figure 1. The intensities

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[1] R. Nakane, A. Natsubori, and O. Kurihara, *J. Amer. Chem. Soc.*, **87**, 3597 (1965).

[2] R. Nakane, T. Ōyama, and A. Natsubori, *J. Org. Chem.*, **33**, 275 (1968).

[3] G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **80**, 6541 (1958).

[4] D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectr.*, **7**, 307 (1961).

[5] G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).

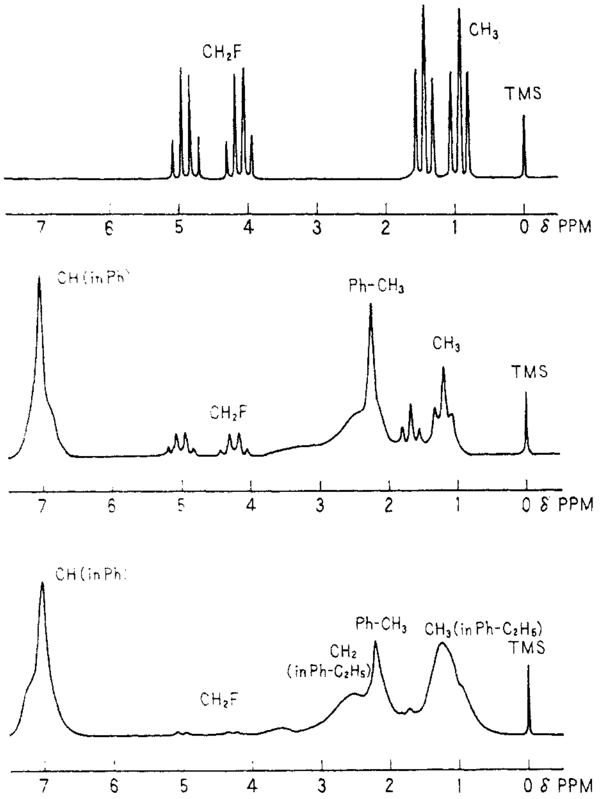

Figure 1.—Proton magnetic resonance spectra observed at −80°: (a) the un-ionized ethyl fluoride–boron fluoride complex; (b) the toluene–ethyl fluoride–boron fluoride complex; (c) the solution obtained when a portion of boron fluoride is withdrawn by evacuation from the termolecular complex.

of the proton resonances became lower in the CH_2F and CH_3 groups in ethyl fluoride, but became higher in the CH_2 and CH_3 groups in ethyltoluene. The chemical shifts for the CH_2 and CH_3 groups in ethyltoluene were observed to be 2.5 and 1.1 ppm (δ). These signals were broadened. The chemical shift for a very weak and broad signal which may be attributed to the aliphatic CH_2 group in the protonated benzenonium ion complex was approximately 3.3 ppm (δ). The shifts of the CH_2F and CH_3 signals of ethyl fluoride on the removal of boron fluoride were not observed. Hence the spectra shown in Figure 1b seems to be the additive spectra of the complex containing a small amount of protonated ethyltoluene.

The thermodynamic isotope effect shows that boron fluoride forms a very weak complex with methyl chloride or isopropyl chloride at low temperatures.[6] Hence boron fluoride can form the complex with ethyl chloride. The pmr spectra of the 1:1 ethyl chloride–boron fluoride complex and its toluene solution, in which the mole ratio of toluene/ethyl chloride/boron fluoride was 1:1:1, were observed at −80°. The chemical shifts and the spin–spin coupling constants are given in Table II. The solution is colorless. The ethylated products could not be obtained when the solution was allowed to warm to room temperature, while the ethylated products were obtained by warming the yellow toluene–ethyl fluoride–boron fluoride complex. No boron fluoride catalyzed ethylation with ethyl chloride proceeds at any temperature.

Table II

Chemical Shifts and Coupling Constants of the Ethyl Chloride System

Compound	δ^a CH_3	δ^a CH_2Cl	$J_{HH}{}^b$
$C_2H_5Cl \cdot BF_3$ complex	1.51	3.67	7
$C_2H_5Cl \cdot BF_3$ complex in $C_6H_5CH_3$	1.10	3.10	7

[a] Chemical shifts are given in δ units with tetramethylsilane as external standard (δ 0). [b] Coupling constants are given in cycles per second.

Discussion

In the pmr spectra of the toluene–ethyl fluoride–boron fluoride complex, the proton resonances of the CH_2F and CH_3 groups in ethyl fluoride, which are split into the respective doublets as a result of interaction with a single ^{19}F nucleus, are still found. Little variation of the coupling constants between ^1H and ^{19}F is found when the un-ionized complex is dissolved in toluene. The C–F bond of ethyl fluoride is not broken in the termolecular complex.[7] The pmr spectra support our previous conclusion[1,2] that the yellow complex is not the ethyl benzenonium tetrafluoroborate complex but the termolecular π complex.

When boron fluoride is dissolved in alkyl fluoride, the un-ionized complex is formed, causing (a) the force constant of BF_3 out-of-plane bend to become lower, (b) the B–F force constant to become slightly higher, (c) the C–F force constant to become slightly lower, and (d) the C–H force constant to become slightly higher.[8] When the un-ionized complex is dissolved in toluene, the termolecular π complex is formed and the force constant of BF_3 out-of-plane bend becomes further slightly lower, but the variations of the C–H and C–F force constants are not distinct.[2] The lowering of the force constant of BF_3 out-of-plane bend is much smaller in the termolecular π complex formation than in the un-ionized complex formation.[2] Therefore, the variations of the C–H and C–F force constants are probably smaller in the former case than in the latter case. The transformation of geometry of ethyl group and the weakening of the C–F bond seems to be negligible and, hence, the coupling constants between ^1H and ^1H and between ^1H and ^{19}F vary little when the termolecular π complex is formed with the un-ionized complex and toluene. On the other hand, a little variation of the coupling constants between ^1H and ^{19}F is found when ethyl fluoride forms the un-ionized complex with boron fluoride.

The interaction shift of ethyl fluoride in the un-ionized ethyl fluoride–boron fluoride complex is to lower field relative to pure ethyl fluoride. The shift to low field is attributable to a small transformation of geometry of ethyl group. Also when boron fluoride is dissolved in the toluene solution of ethyl fluoride, the ethyl hydrogen signals displace to low field. The solution becomes yellow and the termolecular π complex is formed. If the above shift of ethyl hydrogen signals

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(6) R. Nakane, O. Kurihara, and A. Natsubori, *J. Phys. Chem.*, **68**, 2876 (1964).

(7) Ethyl fluoride involved in the solution is not free ethyl fluoride obtained by dissociation of the un-ionized complex, for, if so, the shift to high field will be found. However, it is not so. When free ethyl fluoride is added to the complex, the pmr signals of ethyl group displace to high field. For example, in the pmr spectra of the solution in which a mole ratio of toluene/ethyl fluoride/boron fluoride is 1:1.5:1, the chemical shift for CH_2F group in ethyl fluoride was found to be 4.21 ppm (δ). The peaks became sharp.

(8) R. Nakane and T. Ōyama, *ibid.*, **70**, 1146 (1966).

is attributable only to the transformation of geometry of ethyl group, the interaction shift will not be so large in the termolecular π-complex formation than in the un-ionized complex formation, for the geometry of ethyl group in the termolecular π complex is little different from that in the un-ionized complex. However, the chemical shift for CH_2F group in ethyl fluoride displaces from 4.24 to 4.47 ppm (δ) when boron fluoride is dissolved in ethyl fluoride, while the chemical shift for CH_2F group in ethyl fluoride displaces from 3.94 to 4.62 ppm (δ) when boron fluoride is dissolved in the toluene solution of ethyl fluoride. The large shift of ethyl hydrogen signals to low field in the termolecular π complex formation must be attributed to another effect.

Reeves and Schneider[9] observed the pmr signal of chloroform in the aromatic solvents and found that a symmetrical π-complex formation results in the shift of chloroform resonance to high field, which can be attributed to a large induced diamagnetism resulting from the circulation of π electrons in the aromatic ring. It appears, therefore, that ethyl fluoride is located near the sixfold axis above the plane of the aromatic ring in the toluene solution of ethyl fluoride.

The electronic densities in toluene are larger at the *ortho* and *para* positions than at a *meta* position. When boron fluoride is dissolved in the toluene solution of ethyl fluoride, ethyl fluoride, which is located near the sixfold axis above the plane of the aromatic ring, first forms the un-ionized complex with boron fluoride. The pmr signals of ethyl fluoride displace to low field. Thereafter, the un-ionized complex is transfered to the position near the *ortho* or *para* position in toluene and is oriented or localized. Here the induced ring paramagnetism of the aromatic is operative. The pmr signals of ethyl fluoride further displace to low field.

The shift to low field can also be interpreted as follows: the chemical shifts of proton resonances of ethyl group are lower in the termolecular π complex than in the un-ionized complex; there is little transformation of geometry of ethyl group when the un-ionized complex is dissolved in toluene; if the un-ionized complex is located near the sixfold axis above the plane of the aromatic ring in the termolecular π complex, the proton signals of ethyl group in ethyl fluoride will displace to high field, for the induced ring diamagnetism is existent; however, it is not so; the un-ionized complex is located at such a position that the induced ring paramagnetism is operative.

The toluene solution of the un-ionized ethyl chloride–boron fluoride complex is colorless. When the absorption spectrum of the solution was measured at −95°, the fine structure of the benzenoid band of toluene was still observed, but a new strong absorption characteristic of the termolecular π complex was not observed.[10] This result suggests no formation of the toluene–ethyl chloride–boron fluoride complex at low temperatures. The interaction shift of ethyl chloride in the solution is to higher field than that of the pure ethyl chloride–boron fluoride complex. Here the induced ring diamagnetism is existent. In the solution, therefore, the un-ionized complex is located near the sixfold axis above the plane of the aromatic ring.

The shift of ethyl hydrogen signals to low field is observed when the un-ionized boron fluoride complex is dissolved in toluene at low temperatures and then the termolecular π complex is formed. However, the shift of ethyl hydrogen signals to high field is observed when the termolecular π complex can not be formed even at low temperatures. Thus, the shift to low field seems to be attributable to the localization of the un-ionized complex in the termolecular π complex. The pmr spectra confirm our previous suggestion[1,2] such that the yellow toluene–ethyl fluoride–boron fluoride complex, which is isolated at low temperatures, is the termolecular, oriented π complex.

Experimental Section

Materials.—Toluene, ethyl fluoride, and boron fluoride were prepared and purified by previously published methods.[1] Ethyl chloride was obtained from Tokyo Kasei Co. This was purified by low temperature fractional distillation.

Proton Magnetic Resonance Spectra.—All proton magnetic resonance spectra were observed on the JNM-C-60 high resolution nmr spectrometer, which was operated at 60 Mc at −80°. The spectra were not observed in the dilute solutions, for the termolecular π complex dissociates in other solvents than toluene and the liquid ethyl fluoride–boron fluoride complex. When tetramethylsilane was dissolved in the termolecular π complex, the shifts of ethyl hydrogen signals to high field increased with increasing mole ratio of tetramethylsilane to the complex. Consequently, tetramethylsilane could not be used as standard internal reference and was used as standard external reference contained in a sealed capillary tube centered in the middle of sample tubes. Line positions were accurate to ±0.03 ppm. In the observation of the toluene–ethyl fluoride–boron fluoride complex, *e.g.*, boron fluoride was condensed on the toluene solution of ethyl fluoride, which was introduced into the sample tube and then was solidified with liquid nitrogen. The sample tube was sealed, allowed to warm to −80°, and then measured. Five samples were prepared. The observed values were reproducible. In observations of other systems the similar procedures were used.

When a small amount of toluene was dissolved in the excess ethyl fluoride–boron fluoride complex at low temperatures, the solution, in which the termolecular π complex was a solute and the ethyl fluoride–boron fluoride complex was a solvent, was formed. The termolecular π complex was stable in the solution.[1] The spectra of the solution were observed at −80°. The chemical shift for CH proton of toluene was little different from that observed in the 1:1:1 complex. This showed that little shift of CH signal of toluene in the termolecular π complex occurred when the medium changed from the ethyl fluoride–boron fluoride complex to the toluene–ethyl fluoride–boron fluoride complex. There was little effect that bulk susceptability may have on the shifts of the CH_2F and CH_3 signals of ethyl fluoride, which were observed when the medium changed from ethyl fluoride–boron fluoride complex to the toluene–ethyl fluoride–boron fluoride complex.

Registry No.—Ethyl fluoride, 353-36-6; ethyl fluoride–boron fluoride, 373-60-4; toluene–ethyl fluoride–boron fluoride, 4601-90-5; ethyl chloride–boron fluoride, 19190-35-3.

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[9] L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

[10] Unpublished data.