The Complex Formation of Boron Fluoride with Lower Olefins at Low Temperatures. II. Isotope Effects and Absorption Spectra of Boron Fluoride-Butene Systems

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(Received July 5, 1963)

By measuring the isotope effects and absorption spectra of boron fluoride-ethylene and -propyrene systems, the authors predicted in a preceding paper[1] that only polar mono-olefins would form σ-complexes with boron fluoride at low temperatures. In the present report similar measurements for boron fluoride-1-butene, -*cis*-2-butene and -*trans*-2-butene systems will be reported and the prediction confirmed. The relation between the values of the equilibrium constant of isotopic exchange and the catalytic ability of boron fluoride complexes will also be discussed.

Experimental

Except for a low temperature bath prepared by the use of the melting point of −95°C of toluene, the experimental methods were exactly the same as those used in the preceding work.

Results and Discussion

Isotope Effects. — Findings concerning the isotope effect are shown in Table I. The values of the equilibrium constants of isotopic exchange with polar mono-olefins, 1-butene and *cis*-2-butene, were found to be appreciably larger than 1.011 while that with a non-polar *trans*-2-butene was 1.011 at −112°C.

TABLE I. EQUILIBRIUM CONSTANT OF BORON ISOTOPE EXCHANGE FOR BORON FLUORIDE-BUTENE SYSTEMS AT LOW TEMPERATURE

System	Equilibrium constant $[^{10}B/^{11}B]_{liq}/[^{10}B/^{11}B]_{gas}$	
	−95°C	−112°C
BF_3-1-C_4H_8	1.012±0.002	1.017±0.002
BF_3-*cis*-2-C_4H_8	1.015±0.002	1.020±0.002
BF_3-*trans*-2-C_4H_8	1.006±0.002	1.011±0.002

These findings indicate again that boron fluoride can form σ-complexes with polar mono-olefins at low temperatures, but not with non-polar mono-olefins. Thus, the conclusion drawn in the preceding work was confirmed to be correct.

The values of the equilibrium constants of isotopic exchange between boron fluoride gas and many liquid boron fluoride complexes at various temperatures are summarized in Table II, and the values for very strong complexes with an *n*-donor, such as methyl ether, are compared with the values for weak complexes found by us. The equilibrium constants for systems of boron fluoride-*n*-donor complexes or of tetrafluoborate ions are the largest, while those for systems of liquid boron fluoride or of solutions of boron fluoride in non-polar mono-olefins are the smallest. The equilibrium constant for the system of tetrafluoborate ions, the structure of which is completely tetrahedral, is 1.028±0.008 at temperatures from 20 to 30°C.[2] The equilibrium constant for the boron fluoride-methyl ether complex system is also 1.028±0.002 at 25°C,[3] and the value calculated from the experimental equation given by Palko et al.[3] is 1.082 at −112°C. In the boron fluoride-methyl ether complex, every boron atom is situated at the top of the pyramidal structure.[4] On the other hand, the equilibrium constant for the system of liquid boron fluoride, the molecule of which has a structure of a planar form, is 1.011±0.002 at −112°C.[1] The methyl fluoride-boron fluoride complex has been considered to be a weak complex, $^{\delta+}CH_3\cdot F \rightarrow {}^{\delta-}BF_3$, for its conductivity is poor.[5] The equilibrium constant for the methyl fluoride-boron fluoride complex system is 1.020±0.002 at −95°C,[6] appreciably smaller than that for the boron fluoride-methyl ether complex system and larger than that for the liquid boron fluoride system. Though the boron fluoride-sulfur dioxide complex has been considered to be a weak complex because of the shape of its

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[1] R. Nakane, T. Watanabe, O. Kurihara and T. Ōyama, This Bulletin, 36, 1376 (1963).

[2] B. Kiselev, "Kernenergie," 4 Jahrgang, 421 (1961).

[3] A. Palko, G. Begun and L. Landau, *J. Chem. Phys.*, 37, 552 (1962).

[4] S. Bauer, G. Finlay and A. Laubengeyer, *J. Am. Chem. Soc.*, 65, 889 (1943).

[5] G. Olah, S. Kuhn and J. Olah, *J. Chem. Soc.*, 1957, 2174.

[6] R. Nakane and O. Kurihara, unpublished.

TABLE II. EQUILIBRIUM CONSTANT OF BORON ISOTOPE EXCHANGE BETWEEN BORON FLUORIDE GAS AND LIQUID BORON FLUORIDE COMPLEXES

Liquid complex	Equilibrium constant, $[^{10}B/^{11}B]_{liq}/[^{10}B/^{11}B]_{gas}$				Ref.
	+25°C	−95°C	−96.5°C	−112°C	
BF_3-CH_3OCH_3	1.028	(1.071)[a,b]		(1.082)[a,b]	3
BF_4^-	1.028	—[a]		—[a]	2
BF_3-$C_6H_5OCH_3$	1.032	—[a]		—[a]	9
BF_3-$(C_4H_9)_2S$	1.033	—[a]		—[a]	9
BF_3-C_6H_5OH	1.027	—[a]		—[a]	9
BF_3-$(C_2H_5)_3N$	1.023	—[a]		—[a]	10
BF_3-C_4H_8O	1.036	—[a]		—[a]	10
BF_3-SO_2			1.022	—[a]	8
BF_3-CH_3F		1.020			6
BF_3-CH_3Cl			1.016	1.021	8
BF_3-*cis*-2-C_4H_8		1.015		1.020	present report
BF_3-C_3H_6		1.013[c]		1.018	1
BF_3-1-C_4H_8		1.012		1.017	present report
BF_3-$CHClF_2$			1.011	1.017	8
BF_3, C_2H_4				1.011	1
BF_3, *trans*-2-C_4H_8		1.006		1.011	present report
BF_3		(1.006)[d]		1.011	1

a) solid ; b) calculated from experimental equation ; c) measured newly ; d) estimated

fusion curve,[7] its equilibrium constant is nearly equal to that for the boron fluoride-methyl chloride complex system.[8] These results show that the value of the equilibrium constant is proportional to the stability of the complex.

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

$$^{10}BF_{3(gas)} + {}^{11}BF_3\cdot YA_{(liq)} \overset{k}{\rightleftharpoons} {}^{11}BF_{3(gas)} + {}^{10}BF_3\cdot YA_{(liq)} \qquad (1)$$

the equilibrium constant is given by

$$K = \frac{[Q_{^{10}BF_3\cdot YA\,(liq)}]}{[Q_{^{11}BF_3\cdot YA\,(liq)}]} \Bigg/ \frac{[Q_{^{10}BF_3\,(gas)}]}{[Q_{^{11}BF_3\,(gas)}]} \qquad (2)$$

Here, the ratio between the partition functions of isotopic molecules is

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_i \frac{u_{2i}\exp(-u_{2i}/2)\,[1-\exp(-u_{1i})]}{u_{1i}\exp(-u_{1i}/2)\,[1-\exp(-u_{2i})]} \qquad (3)$$

where 1 and 2 refer to the different isotopic molecules, σ_1 and σ_2 are the symmetric numbers, $u_i = hc\omega_i/kT$, and ω_i is the ith normal vibrational frequency.[9] Thus, when the normal vibrational frequencies of gaseous boronfluoride and liquid boron fluoride complexes are obtained, the equilibrium constants can be calculated from Eqs. 2 and 3.

In the isotopic exchange between boron fluoride gas and the boron fluoride-methyl ether complex, Palko et al.[3] compared the observed equilibrium constants with the values calculated by Eqs. 2 and 3 from infra and Raman spectra data and found that, when the transformation of boron fluoride from planar to pyramidal resulted in an increase in the B—F distance and a weakening of the B—F force constant, the isotope effect caused by the B—F bond was so marked that it overbalanced the formation of the B—O bond, which had the opposite effect upon the partition function ratio. This suggests the possibility that the equilibrium constants of the isotopic exchange between gaseous boron fluoride and all boron fluoride complexes may depend mostly on the B—F force contants and scarcely at all on the force constant of the bond formed between boron and donor atoms. This possibility is supported by the observation of many strong boron fluoride complexes other than the boron fluoride-methyl ether complex, for example, boron fluoride-anisole,[10] -thioether,[10] -phenole,[10] -triethyl amine[11] and -furan[11] complexes. That is, the equilibrium constants between gaseous boron fluoride and these complexes, in which every boron atom will be situated at the top of the pyramidal structure and the vacant orbital of the boron atom will

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7) H. Booth and D. Martin, *J. Am. Chem. Soc.*, **64**, 2198 (1942).

8) R. Nakane and O. Kurihara, *Papers Inst. Phys. Chem. Research (Tokyo)*, **56**, 161 (1962).

9) H. Urey, *J. Chem. Soc.*, **1947**, 562.

10) R. Healy and A. Palko, *J. Chem. Phys.*, **28**, 211 (1958).

11) S. Ribnikar and G. Bootsma, *Bull. Inst. Nucl. Sci.*, "Boris Kidrich," **9**, 91 (1959).

be completely filled with electrons from donor atoms, as in the cases of the boron fluoride-methyl ether complex and tetra-fluoborate ions, are also approximately 1.03 at room temperature, as is shown in Table II.

Therefore, the equilibrium constants for these strong complex systems may always be expected to be approximately 1.08 at $-112^\circ C$, for the value calculated for the boron fluoride-methyl ether system is 1.082 at $-112^\circ C$.

Liquid boron fluoride, the equilibrium constant of which is 1.011 at $-112^\circ C$, has the planar structure and vacant orbitals of the boron atom. The weak complexes which have intermediate values between 1.011 and 1.08 at $-112^\circ C$ have slightly-dissociated polar covalent bonds such as are found in $^{\delta+}CH_3\cdot F \rightarrow {}^{\delta-}BF_3$, but the boron fluoride in these complexes has not yet been completely transformed to a pyramidal structure and only small parts of the electrons from donor atoms may be located on the vacant orbitals of boron atoms.

Thus, it seems very likely that the equilibrium constants of isotopic exchange for boron fluoride complex systems depend mostly on the density of electrons coming from donor atoms and locating on the vacant orbitals of boron atoms, or on the B—F force constant, which becomes weaker in proportion to the transformation of boron fluoride from planar to pyramadial; the equilibrium constants seem to depend scarcely at all on the force constant of the bond formed between boron and donor atoms. Accordingly, they indicate the possibility of complex formation and the degree of the transformation of boron fluoride. Therefore, the larger the equilibrium constant, the larger the degree of deformation, and, hence, the more stable the complex.

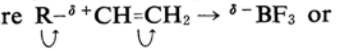
If, in the complex, the pyramidal form is the dative structure and the planar form is the no-bond structure, the equilibrium constant of isotopic exchange may be assumed to represent the abundance ratio of both structures in the complex, as does the dipole moment.

When the structure of complex is completely dative, the equilibrium constant will be approximately 1.08 at $-112^\circ C$, as in the case of the boron fluoride-methyl ether complex system, while when it is completely no-bond, the constant will be 1.011 at $-112^\circ C$, as in the case of the liquid boron fluoride system. In a complex in which the constant has intermediate values, the ratio of dative to no-bond structures will have values between one and zero.

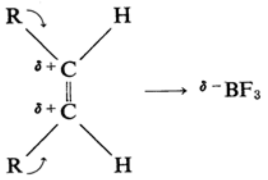
Thus, it seems certain, from the observed values of the equilibrium constants, that boron fluoride can form weak σ-complexes with polar mono-olefins only at low temperatures, but that boron fluoride dissolved in liquid non-polar mono-olefins has the same planar structure as liquid boron fluoride molecule and that, therefore, no σ-bond can be formed between boron and carbon atoms, even at low temperatures.

In boron fluoride-polar mono-olefin-σ-complexes, the dative structure may be ($R-{}^{+}CH-CH_2-{}^{-}BF_3$), in which π-electrons of the double bond are transferred completely to vacant orbitals of the boron atoms and the boron fluoride molecule becomes deformed completely to the pyramidal structure, while the no-bond structure remains ($R-CH=CH_2, BF_3$). The ratio of dative to no-bond structures may be far smaller than one, for the equilibrium constants observed at $-112^\circ C$ are far smaller than 1.08. Hence, it seems clear that σ-complexes have not the ultimate structure of $R-{}^{+}CH-CH_2-{}^{-}BF_3$, as was formerly believed of intermediate products in the polymerization of olefins by a boron fluoride catalyst.[12]

As has been shown in the preceding work and as will also be shown in the next section, V←N absorption bands, indicating the presence of a double bond, were still observed in the measurements of the absorption spectra of boron fluoride-mono-olefin complexes. Therefore, it seems very likely that the σ-complexes are



$R-{}^{\delta+}CH=CH_2 \rightarrow {}^{\delta-}BF_3$ or



It is also interesting to consider the relation between the equilibrium constants and the dipole moments of mono-olefins. The following values of the dipole moments of gaseous mono-olefins are known: 0.35 D,[13] 0.37 D[14] or 0.35±0.01 D[15] for propylene; 0.30 D[16] or 0.37 D[17] for 1-butene; 0.00 D[16] for *trans*-2-butene, and 0.33 D[18] for *cis*-2-butene. The values for liquid mono-olefins at low temperatures are not known, but they may not be very different from the above values.

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[12] C. Price and J. Ciskowski, *J. Am. Chem. Soc.*, **60**, 2499 (1938).

[13] K. McAlpine and C. Smith, ibid., **55**, 459 (1933).

[14] H. Watson, G. Rao and K. Ramaswamy, *Proc. Roy. Soc.*, **A143**, 582 (1934).

[15] A. Mariott and F. Buckley, "Table of Dielectric Constants and Dipole Moments of Substances in the Gaseous State," Natl. Bur. Stand. Circ., No. 537, Washington, D. C. (1953).

[16] H. Watson and K. Ramaswamy, *Proc. Roy. Soc.*, **A156**, 142 (1936).

[17] C. Smith and C. Zahn, *J. Am. Chem. Soc.*, **47**, 2501 (1925).

[18] J. Boggs, C. Crain and J. Whiteford, *J. Phys. Chem.*, **61**, 482 (1957).

Propylene and 1-butene are both mono-substituted terminal mono-olefins, although their electron-releasing substituents are different. *cis*-2-Butene is a di-substituted internal mono-olefin. Now, mono-olefin must polarize in order to form σ-complexes with boron fluoride. When polar, the larger the dipole moment of mono-olefin, the larger the deformation of boron fluoride, and therefore, the larger will the equilibrium constant be expected to become. To infer from the values of the dipole moments of gaseous propylene and 1-butene, liquid propylene and 1-butene may be expected to have nearly the same dipole moment value. Therefore, it is no wonder that boron fluoride-propylene and boron fluoride-1-butene systems have nearly the same equilibrium constant of the isotope. However exchange the equilibrium constant for boron fluoride-*cis*-2-butene system is larger than that for the boron fluoride-propylene and -1-butene systems even though the value of the dipole moment of liquid *cis*-2-butene is supposed to be nearly the same or a little smaller than that of propylene or 1-butene. This may be attributed to the fact that there are two electron-releasing groups in one molecule of *cis*-2-butene, while there is only one electron-releasing group in one molecule of propylene or 1-butene. Thus, it seems certain that equilibrium constant relates not only to the dipole moment but also to the steric structure of mono-olefin or the number of electron-releasing groups existing in a molecule of mono-olefin.

The boron fluoride-methyl ether complex is a very active catalyst. The methyl fluoride-boron fluoride complex, which is a less reactive catalyst, can alkylate benzene readily, since alkylation needs the presence of only such incipient carbonium as is found in the $^{\delta+}CH_3\cdot F \rightarrow {}^{\delta-}BF_3$ complex, for example; such free carbonium ions as CH_3^+ are not required.[19] Polar mono-olefin-boron fluoride complexes do exist at low temperatures, but they do not partake in the polymerization of mono-olefin, and methyl chloride or mono-chlorodifluoro methane-boron fluoride complexes have no catalytic ability. Therefore, there should also be the following relation between the equilibrium constant and the catalytic ability of a Friedel-Crafts catalyst: the larger the former, the more active will the latter become.

Absorption Spectra.—No $T_R \leftarrow N$ absorption band of 1-butene, *cis*- and *trans*-2-butenes could be observed at the temperatures of their melting points, for the band was obscured by the long-wavelength tail of strong $V \leftarrow N$ absorption bands. Therefore, the effects of boron fluoride upon the $T_R \leftarrow N$ bands of 1-butene, *cis*- and *trans*-2-butene have been left unexamined.

In the present work, the effects of boron fluoride upon the fine structure of the long-wavelength tail of $V \leftarrow N$ bands have been examined, because the band peaks that lie in the region of wavelengths shorter than 190 mμ could not be traced by the Type 14 M Cary recording spectrophotometer used. The fine structure of the $V \leftarrow N$ bands of 1-butene dissolved in a large amount of methane at a temperature near the freezing point of the solution (approximately $-170°C$) is shown in Fig. 1. Since the fine structure of the $V \leftarrow N$ bands of *trans*-2-butene was indistinct, a measurement similar to the above was made on ethylene instead; the results are shown in Fig. 2.

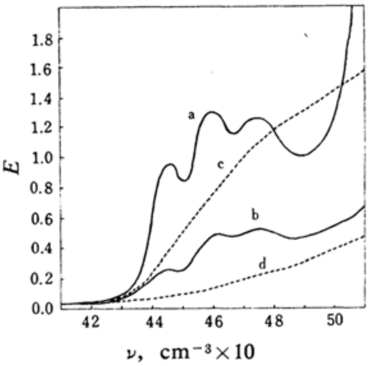

Fig. 1. Absorption spectra of 1-butene in liquid methane and boron fluoride.
Solvent: —— methane ---- boron fluoride
mole fraction of 1-butene in solution: (a) 0.33×10^{-2} (b) 0.2×10^{-2}, (c) $<1.89\times10^{-2}$ (d) $<0.13\times10^{-2}$

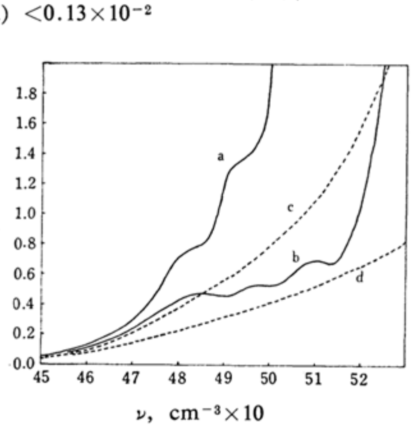

Fig. 2. Absorption spectra of ethylene in liquid methane and boron fluoride.
Solvent: —— methane, ---- boron fluoride
mole fraction of ethylene in solution: (a) 10.0×10^{-2}, (b) 0.72×10^{-2} (c) 7.7×10^{-2} (d) 3.8×10^{-2}

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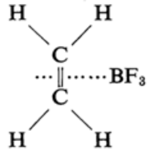
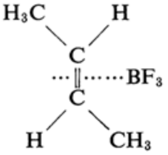
[19] H. Brown, H. Pearsall, L. Eddy, W. Wallace, M. Grayson and K. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

Similar measurements were also made on the absorption spectra of 1-butene and ethylene in large amounts of boron fluoride at temperatures near the freezing points of the solutions (approximately $-130°C$) ; these results are also shown in Figs. 1 and 2. Although the $V \leftarrow N$ bands were still observed in both cases, two points are noticeable. First, in order to obtain the same values of intensity for $V \leftarrow N$ bands at the same wavelengths, the concentration of mono-olefin must be larger in a boron fluoride solution than in a methane solution. Second, the fine structures of $V \leftarrow N$ bands, which were observed in a methane solution, disappeared in a boron fluoride solution. As for the first point, it cannot yet be determined whether the intensity of $V \leftarrow N$ bands really decreases or whether the peaks of these bands shift towards shorter wavelengths, for these peaks were not measured. At any rate, the fact is that boron fluoride influenced. the intensity or the wave number of $V \leftarrow N$ bands. As for the second point, it must be remembered that the fine structures of the absorption bands in benzene at 267 $m\mu$ disappeared when benzene formed a π-complex with hydrogen fluoride.[20] Therefore, the above two points seem to suggest the complex formation of boron fluoride with 1-butene and ethylene.

However, in the preceding work, experiments on isotope effects showed that ethylene cannot form a σ-complex with boron fluoride. Hence, the complex formed with ethylene is concluded to be an unstable π-complex :



trans-2-Butene may also form a π-complex :



On the other hand, 1-butene, and perhaps propylene and *cis*-2-butene too, may form both σ-complexes and π-complexes.

In the polymerization isomerization and other reaction of olefins by boron fluoride catalysts, the σ-complexes found by us are not the intermediate products, and the σ-complex formation proceeds parallel with these reactions, as has been explained in the preceding work. No doubt these reactions occur through the actual transfer of protons to mono-olefins to form such ions as $R-{}^{+}CH-CH_3$, and the rates of the reactions are proportional to the stability of the ion. No doubt, it can be taken for granted that these reactions proceed through π-complexes, yet needless to say, the rate-determining step in these reactions does not involve the initial formation of π-complexes as is in the case of aromatic substitution.[21]

Summary

The equilibrium constants of isotopic exchange between boron fluoride gas and boron fluoride in 1-butene and *cis*-2-butene solutions have been found to be 1.017 ± 0.002 and 1.020 ± 0.002 at $-112°C$, and 1.012 ± 0.002 and 1.015 ± 0.002 at $-95°C$. In boron fluoride-*trans*-2-butene system, the equilibrium constant is 1.011 ± 0.002 at $-112°C$ and 1.006 ± 0.002 at $-95°C$.

When 1-butene and ethylene are dissolved in liquid boron fluoride, the intensity or the wave number of the $V \leftarrow N$ absorption bands in mono-olefins is changed and the fine structure of these bands disappear.

Thus, the following conclusion, more decisive than that of the preceding work, has been obtained :

Boron fluoride can form liquid σ-complexes with polar mono-olefins with electron-releasing substituents. On the other hand, with nonpolar mono-olefins it cannot form σ-complexes but only unstable π-complexes. Although σ-complexes are not the intermediate products in reactions by boron fluoride catalysts, it is possible that these reactions proceed through π-complexs. However, the rate-determining step does not involve the initial formation of π-complexes.

It has also been suggeted that the equilibrium constant may be proportional to the ratio of dative to no-bond structure in the complex, and it has been found that the larger the equilibrium constant, the higher become the stability and the catalytic activity of the complexes.

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[20] M. Kilpatrick and H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).

[21] H. Brown and J. Brady, ibid., **74**, 3570 (1952).