

Schiff bases, the 3-methyl and the acetomethyl groups interact quite strongly, whereas in the *trans* form no large steric interactions are observable and a planar configuration of maximum orbital overlap may easily be maintained. When the methyl group is placed in the 4-position, as in acetylacetone Schiff bases, the reverse situation occurs. In a planar *cis* configuration, no important steric interactions are noted; however, in the *trans* arrangement, the 4-methyl and the carbonyl groups interact to such a degree that it is difficult to obtain a planar backbone for maximum overlap.

The variation in the *cis-trans* equilibrium as the group on the nitrogen is changed from a methyl to a benzyl or a hydrogen may also be attributed to steric factors. Either the ability of the solvent to solvate the nitrogen or the ease of forming dimers and *n*-mers between the *trans* forms of the molecule may be involved.

The NH-CH spin-spin coupling of 13 c.p.s. in these systems of fixed *trans* geometry is larger than the value of 6 c.p.s. for the coupling between an amino hydrogen and a freely rotating alkyl group, similar to the constants for hydrocarbon systems. Of course the coupling constants involving amine hydrogens are in error to the extent that proton exchange on the nitrogen is sig-

nificant. Since the observed couplings vary only a small amount between compounds and between solvents, exchange probably is not a serious problem.

The paramagnetic shift of the vinyl hydrogens between the *cis* and *trans* forms can be attributed to the carbonyl group which is closer to these protons in the extended form than in the chelated form. The large amount of negative charge calculated for the 3-carbon is reflected in the relatively diamagnetic location of the vinyl proton H_a in these compounds.

The increase in the amount of the *trans* species with increasing concentrations of the compounds in solution is indicative of a weak intermolecular association through the NH and C=O groups. Apparently, the entropy of intramolecular hydrogen bonding is counterbalanced by dipole repulsions and a larger *trans* conjugation energy.²⁰ Thus solvent and substituent effects²¹ can readily swing the *cis-trans* equilibrium in one direction or the other.

Acknowledgment.—We wish to thank Robert Freund for his assistance in programming and operating the IBM 1620 computer.

(21) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN.]

Nuclear Magnetic Resonance Studies of BF₃ Addition Compounds. I. The Exchange of BF₃ between (CH₃)₂O·BF₃ and (C₂H₅)₂O·BF₃¹

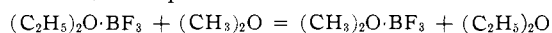
BY A. C. RUTENBERG, A. A. PALKO, AND J. S. DRURY

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Kinetic data for the exchange of BF₃ between (C₂H₅)₂O·BF₃ and (CH₃)₂O·BF₃ were obtained from the ¹⁹F n.m.r. spectra of eight mixtures of (C₂H₅)₂O, (CH₃)₂O, and BF₃. The rate of exchange decreased as a larger portion of the ether was complexed, and the activation energies rose from 11 kcal. for mixtures having >20% free ether to 16 kcal. for the mixture having no free ether. Two exchange mechanisms are indicated. The equilibrium constant for the reaction (C₂H₅)₂O·BF₃ + (CH₃)₂O = (CH₃)₂O·BF₃ + (C₂H₅)₂O was ~2.5 at 26°.

Introduction

Boron trifluoride forms stable 1:1 molecular addition compounds with methyl and ethyl ethers. In systems containing BF₃ and mixtures of these ethers, exchange of BF₃ occurs between the ether species. Although this exchange is too rapid to be observed by conventional techniques, it may be measured conveniently with a nuclear magnetic resonance spectrometer. This paper reports the results of kinetic studies made in this manner on the (CH₃)₂O-(C₂H₅)₂O-BF₃ system. Eight compositions containing varying BF₃/ether and methyl/ethyl ether ratios were examined over a temperature range of approximately 100° using the ¹⁹F resonance. In addition, the equilibrium constant for the reaction



was measured at several temperatures for six of these mixtures.

The ¹⁹F resonance for BF₃ addition compounds offers the combination of a strong signal, which is fairly narrow in the absence of chemical exchange, plus large chemical shifts between different BF₃ addition compounds. It is, therefore, suitable for quantitative kinetic studies. The spectra for two ether-BF₃ complexes are very simple, consisting at low temperatures of a pair of peaks which, as the temperature is raised, broaden, merge, and fuse to a single peak. The ¹⁹F resonance for BF₃ complexed with (CH₃)₂O appears at a field strength 5.3 p.p.m. above the corresponding (C₂H₅)₂O·BF₃ complex. This large chemical shift

permits very rapid exchanges to be observed; under the most favorable conditions, mean lifetimes (τ) as short as 1.5×10^{-6} sec. were measured. However, at low temperatures, mean lifetimes longer than 10^{-2} sec. were generally inaccurate. The observable range of τ varied from sample to sample. The temperature range for which accurate τ values could be measured also varied considerably. The usable temperature range for the sample containing the least BF₃ was -12 to -59°, while the range covered in the completely complexed system was +1 to +67°.

Experimental

The samples used in these experiments consisted of eight mixtures of BF₃, (CH₃)₂O, and (C₂H₅)₂O. The amount of uncomplexed (CH₃)₂O was limited to allow the samples to be heated without subjecting the glass sample tubes to high pressures.

The BF₃ and (CH₃)₂O used for these experiments were Matheson reagent grade chemicals; the (C₂H₅)₂O was Mallinckrodt anhydrous analytical grade material. High vacuum techniques were used for all preparations. The BF₃ was freed from noncondensable gas by a series of condensations and expansions at reduced temperature. The ethers were vacuum distilled, the middle portion being used to prepare the BF₃ complex. Great care was used to eliminate water from the system. Even traces of water cause the BF₃-ether complexes to decompose.

The procedure for preparing a given mixture of (C₂H₅)₂O, (CH₃)₂O, and BF₃ was as follows. After the all-glass vacuum apparatus was assembled, it was pretreated with BF₃ to remove traces of water. Approximately 5 ml. of (C₂H₅)₂O and (CH₃)₂O were separately distilled into calibrated receiving vessels, then were transferred to the reaction flask. The ethers were frozen and a measured quantity of purified BF₃ was added. After the mixture was warmed and thoroughly mixed, 0.5 ml. was sealed in an n.m.r. sample tube which had previously been fused to the reaction vessel.

(1) This paper is based on work performed for the U. S. Atomic Energy Commission by Union Carbide Nuclear Co.

TABLE I
 CHARACTERISTICS OF THE BF₃-ETHER EXCHANGE SYSTEMS

	A	B	C	D	E	F	G	H
Initial composition								
(C ₂ H ₅) ₂ O, moles	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
(CH ₃) ₂ O, moles	0.30	0.34	0.51	0.69	0.34	1.01	1.00	1.00
BF ₃ , moles	0.41	0.67	0.78	1.06	0.89	1.61	1.91	2.00
Equil. composition at 26°								
(C ₂ H ₅) ₂ O·BF ₃ , moles/l.	1.78	3.17	2.79	3.56	4.17	3.52	4.46	4.59
(CH ₃) ₂ O·BF ₃ , moles/l.	1.28	1.56	2.18	2.56	1.92	4.15	4.55	4.59
(C ₂ H ₅) ₂ O, moles/l.	5.73	3.87	3.63	2.21	2.63	1.27	0.13	0.00
(CH ₃) ₂ O, moles/l.	0.99	0.86	1.09	1.42	0.42	0.67	0.06	0.00
K _{eq} (exptl.) ^a	4.2	2.2	2.6	1.1	2.9	2.2	2.2 ^b	
τ × 10 ⁶ at 0°, sec.	3.1	3.6	6.7	10	17	28	260	670
95% confidence limits on τ	0.4	0.8	0.3	1	2	1	10	64
ΔE, kcal. mole ⁻¹	11.1	11.1	11.4	11.7	11.0	10.1	14.0	16.1
95% confidence limits on ΔE	0.8	0.7	0.7	0.5	0.8	0.2	0.3	0.7
Peak coalescing temp., °C.	-37.6	-34.5	-28.0	-23.0	-20.5	-14.5	+13.8	+22.0

^a $K_{eq} = \frac{[(CH_3)_2O \cdot BF_3][(C_2H_5)_2O]}{[(C_2H_5)_2O \cdot BF_3][(CH_3)_2O]}$. ^b Assumed and used to compute composition.

When not in actual use, the samples were stored at about -10°. Under these conditions, they remained colorless and showed no signs of decomposition after many months. Heating the samples in the course of the n.m.r. measurements caused a very small amount of decomposition. The higher temperature measurements were, therefore, usually made last.

The n.m.r. measurements were made using a Varian Associates high resolution spectrometer operating at a frequency of 56.4 Mc. The probe was equipped with a V-4340 variable temperature n.m.r. probe accessory and a V-4331-THR dewar probe insert. Cooling of the samples was achieved using dried air or nitrogen passed through a coil immersed in ice-water, Dry Ice-acetone, or liquid nitrogen. The samples were heated with air from a small electric heating coil. The temperature was adjusted by varying the heater voltage and the rate of flow of gas. Gas pressure was varied with a Matheson No. 70 regulator. The temperature of the gas stream just above the sample volume was monitored with a copper-constantan thermocouple connected to a 0-1 mv. Brown recorder. Samples were maintained at the desired temperature for at least 15 min. to ensure the attainment of thermal equilibrium before any measurements were made. The average temperature during a series of repeated measurements was estimated from the recorder trace. Measurements of line widths and the distance between peaks were made by modulating the peaks with a convenient frequency using a Hewlett-Packard model 200CD oscillator.

The equilibrium constants

$$K_{eq} = \frac{[(CH_3)_2O \cdot BF_3][(C_2H_5)_2O]}{[(C_2H_5)_2O \cdot BF_3][(CH_3)_2O]}$$

were determined in the following manner. At low temperatures, the relative areas of the (CH₃)₂O·BF₃ and (C₂H₅)₂O·BF₃ peaks were measured. The traces were cut out and weighed, or the areas were measured using the Varian V-3521 integrator. In favorable cases the width of the peaks, the relative area of both peaks, and the distance between the peaks were obtained from the same n.m.r. recorder trace. The fraction of BF₃ in either form at room temperature was estimated from the location of the single peak. Since the amounts of the three compounds used to prepare the mixture were known, sufficient information was available to compute the four concentrations comprising the equilibrium constant.

Calculations.—The major portion of this study was concerned with the calculation of τ, the mean lifetime in seconds of an ether·BF₃ addition compound, as a function of temperature and mixture composition. At those temperatures for which the exchange rate was slow enough to have two well defined separated peaks or fast enough to have a single peak, τ was calculated from the width of the line at half its maximum height. The calculations are described by Pople, Schneider, and Bernstein² and involve the assumptions: (1) the absorption line was Lorentzian and (2) relaxation contributions to the line broadening were negligible. An attempt was made to meet the first condition by careful spectrometer operation and the second requirement by using only line width data from the portion of the temperature range in which this condition appeared to be met. Since most of the measurements were made on fairly broad lines, slow passage conditions were easily achieved.

(2) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

The composition of the mixtures at room temperature was approximated by measuring the displacement of the single peak of the combined complexes (ν_e) from the (C₂H₅)₂O·BF₃ peak (ν_b) in a mixture of (C₂H₅)₂O and (C₂H₅)₂O·BF₃. The mole fraction of (CH₃)₂O·BF₃ (p_a) was calculated from the expression

$$p_a \cong \frac{\nu_e - \nu_b}{\nu_a - \nu_b}$$

where $\nu_a - \nu_b$ is the separation between the peaks of the combined complexes at large τ.

In the range in which the a and b peaks approached each other and were separated by $\nu_a' - \nu_b'$, τ was computed from the relationship

$$\tau = \frac{1}{2\pi} [(\nu_a - \nu_b)^2 - (\nu_a' - \nu_b')^2]^{-1/2}$$

The τ-values and corresponding temperatures were used to calculate the slope (*m*) of the least squares line

$$\log \tau = (m/T) + C$$

from which the activation energy for the exchange was obtained

Results and Discussion

The initial and equilibrium compositions of the eight mixtures studied are presented in Table I.

For mixtures A through F, the quantities of the four species at equilibrium were calculated from the known amounts of the three components used to prepare the mixture and the measured location of the single peak at 26°. Mixture G had too little uncomplexed ether to be analyzed by this technique; its composition was estimated, assuming the equilibrium constant was the same as in F. Mixture H was completely complexed. Equilibrium constants computed from these compositions are shown for 26°. The data indicate a preference of the BF₃ for (CH₃)₂O. Values of these constants based on peak area measurements in the temperature range -40 to -60° differed only slightly from the 26° results.

The mean lifetimes of the BF₃ addition compounds are shown in Table I. The τ-values at 0° for the various mixtures were obtained from the least squares line. The 0° temperature was near the center of the temperature range of this study and was arbitrarily chosen for discussion purposes. The temperatures at which the n.m.r. peaks for the two addition compounds merge to give a single peak are also presented. The mean lifetime at these temperatures is 7.6 × 10⁻⁴ sec. Figure 1 shows the experimentally determined τ-values plotted as a function of reciprocal temperature. The lines shown are the least squares straight lines.

In the temperature range of this study, the rate of exchange decreased as a larger portion of the ethers was complexed. The 0° τ-value increased 215-fold on going from 31 to 100% complexed ether.

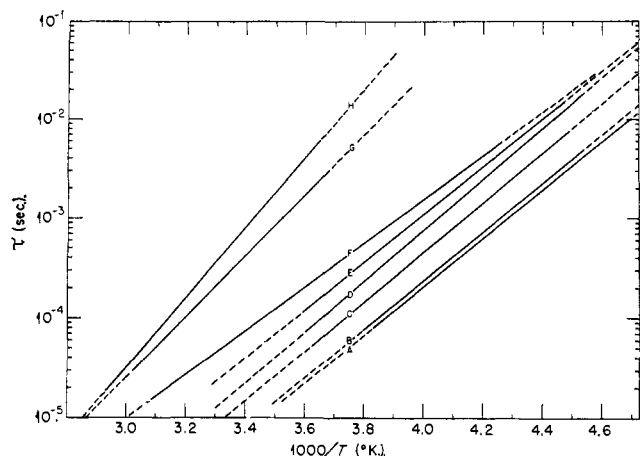
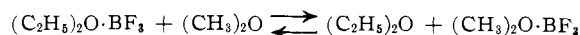
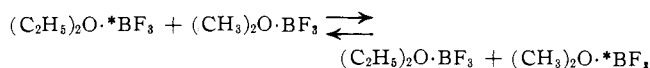


Fig. 1.—Temperature dependence of τ for various mixtures of BF_3 , $(\text{CH}_3)_2\text{O}$, and $(\text{C}_2\text{H}_5)_2\text{O}$. Solid portion of lines indicates range over which data were taken. Compositions of mixtures are listed in Table I.

The activation energy for exchange of BF_3 varied from 11 kcal. in those mixtures which contained a significant excess of uncomplexed ether to 16.1 kcal. for mixtures in which the ether was completely complexed. (Mixture F, which exhibited a slightly lower ΔE , was overheated during a malfunction of the equipment and, as a result, contained several per cent of the mixed ether $\text{C}_2\text{H}_5\text{OCH}_3$.) The data thus indicated the existence of two modes of exchange. The prevailing mechanism when little free ether was present was associated with a higher activation energy and a much slower rate of exchange (large τ) than was the process which predominated when an appreciable quantity of free ether was present. In the presence of uncomplexed ether, the exchange mechanism undoubtedly involved the transfer of a BF_3 molecule from the complexed ether to the free ether; thus



This exchange appears to proceed by the way of a displacement mechanism since the activation energy of exchange is somewhat less than the heats of formation of the BF_3 -ether complexes.³ Such an exchange should require less rearrangement of the solution, and hence be characterized by a smaller activation energy than the exchange of BF_3 between two species of complex



Accordingly, the completely complexed mixture displays a greater activation energy and a slower rate of exchange than the other mixtures.

It is of interest to compare the results of this study with the ^{19}F data of Diehl⁴ for the system BF_3 - CH_3OH - $\text{C}_2\text{H}_5\text{OH}$. His values of $\tau \times 10^5$ at 0° , estimated from a graph in his paper, were 87 at $\text{BF}_3/\Sigma \text{ alcohol} = 0.8$ and 1000 at $\text{BF}_3/\Sigma \text{ alcohol} = 0.4$. The activation energies for the corresponding systems were reported, respectively, as 7.3 ± 1 kcal.; and "about the same within greater limits of error." The rate of exchange in the alcohol system increased rapidly with BF_3 content for mixtures of $\text{BF}_3/\text{alcohol} > 0.5$. The effect of changing the BF_3 content thus was opposite in direction to that observed in the present study.

This divergent behavior of the alcohol system appears to result from a hydrogen bonding effect which has no counterpart in the ether system. Thus, for $\text{BF}_3/\text{alcohol}$ ratios less than 0.5, dialcohol complexes of BF_3 are formed in which two alcohol molecules are associated through hydrogen bonding. With increasing $\text{BF}_3/\text{alcohol}$ ratios, progressively smaller mole fractions of the more stable BF_3 -dicomplex are to be found in the system, qualitatively accounting for the increase in exchange rate.

(3) D. E. McLaughlin and M. Tamres, *J. Am. Chem. Soc.*, **82**, 5618 (1960).

(4) P. Diehl, *Helv. Phys. Acta*, **31**, 685 (1958).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Long-Range Coupling in the Nuclear Magnetic Resonance Spectra of Acenaphthene Derivatives¹

BY MICHAEL J. S. DEWAR AND ROBERT C. FAHEY²

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Partial analysis of the proton n.m.r. spectrum of 1-bromoacenaphthene and complete analyses for 5,6-dichloroacenaphthene, acenaphthene, and acenaphthylene are reported. Long-range couplings ($|J_{13}| = 1.5$, $J_{17} = 0$, $|J_{16}| = 0.5$ c.p.s.) are found in acenaphthene but not in acenaphthylene. The results are compared with π -electron coupling constants calculated from equations derived by McConnell.

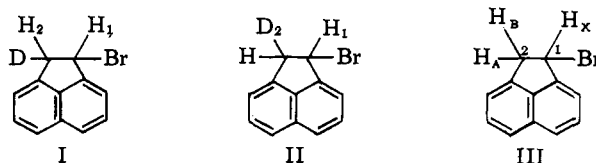
Introduction

In the course of other work,³ n.m.r. analysis was used to establish the stereochemistry of the products obtained in the polar addition of deuterium bromide to acenaphthylene. The products of addition, *cis*-1-bromoacenaphthene-2-*d*₁ (I) and *trans*-1-bromoacenaphthene-2-*d*₁ (II), were identified on the basis that the coupling J_{12} would be largest for the *cis* isomer. Analysis of the ABX portion of the n.m.r. spectrum of 1-bromoacenaphthene (III) is reported here and is consistent with this assignment. In the course of these studies we found that the C_1 and C_2 proton lines in these and other acenaphthene derivatives were split by long-range coupling with the aromatic protons.

(1) This work has been supported by a grant from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow.

(3) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245 (1963).



In the past few years long-range coupling has been a subject of special interest.⁴ Although considerable attention has been focused on olefins, acetylenes, and five-membered heterocyclic rings, relatively little is known about the details of long-range coupling in benzene derivatives. It has been shown that the splitting of the formyl proton resonance line in 2,4-disubstituted benzaldehydes is due to a coupling with a ring proton in either the 3- or 5-position rather than the nearest 6-position.⁵ Hoffman⁶

(4) See E. O. Bishop, *Ann. Reports*, **58**, 55 (1961).