Organic and Biological Chemistry

Exchange Reactions in the System Boron Trifluoride–Methanol[1]

J. Paasivirta[2] and S. Brownstein

Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Received April 10, 1965

Rates and the mechanism of exchange of free and complexed boron trifluoride have been determined by fluorine resonance spectroscopy on the system boron trifluoride–methanol. With excess boron trifluoride exchange rates of the hydroxyl proton were also measured. Excess methanol causes rapid proton exchange, but chemical shifts of the individual species were obtained.

Introduction

The boron trifluoride–methanol system is typical of Friedel–Crafts catalysts. It has been used for polymerization of olefins, and studies have been made on the mechanism of the polymerization.[3–5] Exchange of boron trifluoride with its amine and ether complexes has been reported to occur by displacement rather than dissociation of the complex.[6] The exchange of complexed boron trifluoride between different alcohols has also been investigated.[7] It was thought that n.m.r. techniques might give useful information on reactions occurring when the system contains an excess of the Lewis acid, as commonly occurs during catalysis of Friedel–Crafts reactions. The exchange of the hydroxyl proton in buffered methanol solutions has been measured, and mechanisms have been suggested for the exchange.[8,9] A similar procedure has been adopted with the methanol–BF_3 complex.

Experimental

Preparation of Samples. Anhydrous grade sulfur dioxide was used as solvent and kept over phosphorus pentoxide in a storage bulb of the vacuum system. Reagent grade methanol was distilled onto previously dried calcium sulfate and after several hours was distilled at room temperature into a storage flask of the vacuum system. All other reagents were distilled at low temperature into storage bulbs. The samples were prepared by condensing appropriate amounts of the constituents into an n.m.r. tube by standard, vacuum-line techniques. Concentrations are reported as molalities.

Spectral Measurements. A Varian spectrometer system was used to obtain the spectra. The operating frequencies were 56.4 and 94.1 Mc. for fluorine resonance spectra and 56.4 and 100.0 Mc. for proton resonance spectra. The data obtained at the two field strengths were in agreement. The spectrometer had been modified to operate by a "time division pulse scheme" and used a probe constructed in this laboratory.[10] Details of the internal arrangement of the probe are shown in Figure 1. Thin Dural plates screwed to the sides of the probe had the sweep coils cemented to them. The sweep coils, with a mean diameter of 1.25 in., consist of 40 turns of No. 32 insulated copper wire. They then match the electrical and magnetic characteristics of the Varian HR60 probe assembly. For operation at 56.4 Mc., the receiver coil is four turns of No. 30 insulated copper wire and the transmitter coil, which is wound concentric to the receiver coil, is one and a half turns of No. 30 wire. At 94.1 and 100.0 Mc. more satisfactory performance was obtained when the receiver coil consisted of three turns of wire. Since the transmitter and receiver coils are concentric it was necessary to pulse the preamplifier as well as the transmitter and receiver to completely decouple the transmitter and receiver coils. Total thickness of the probe assembly is 19 mm. It was operated repeatedly between $+180$ and $-130°$ with no ill effects. The temperature was obtained with a copper–constantan thermocouple located at the bend of the probe dewar insert. A calibration chart was obtained with a thermocouple in a dummy sample tube.

Calculation of Lifetimes. Since there is a large chemical shift between the two fluorine-containing species the approximations of slow and rapid exchange were used in the appropriate situations.[11] The calculation of rate constants for the exchange of free and complexed boron trifluoride from the lifetimes requires a knowledge of the concentration of free boron trifluoride in solution. For a constant amount of uncomplexed BF_3 in the sample tube the concentration in solution will increase with decreasing temperatures. The fraction of BF_3 in solution at any given temperature was determined by measuring the areas of the fluorine resonance peaks of BF_3 in solution and of $CFCl_3$ in a sealed capillary in the sample tube. A

(1) Issued as National Research Council Contribution No. 8598.
(2) National Research Council Postdoctoral Fellow, 1963–1964.
(3) French Patents 793,226 and 801,883 (1936); German Patent 704,038 (1941); British Patent 453,854 (1936).
(4) J. M. Clayton and A. M. Eastham, *Can. J. Chem.*, **39**, 138 (1961).
(5) H. R. Allcock and A. M. Eastham, *ibid.*, **41**, 932 (1963).
(6) S. Brownstein, A. M. Eastham, and G. A. Latremouille, *J. Phys. Chem.*, **67**, 1028 (1963).
(7) P. Diehl, *Helv. Phys. Acta*, **31**, 686 (1958).
(8) Z. Luz, D. Gill, and S. Meiboom, *J. Chem. Phys.*, **30**, 1540 (1959).
(9) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).

(10) The kindness of Dr. S. Meiboom in furnishing circuit diagrams prior to publication is gratefully acknowledged.
(11) 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, p. 221.
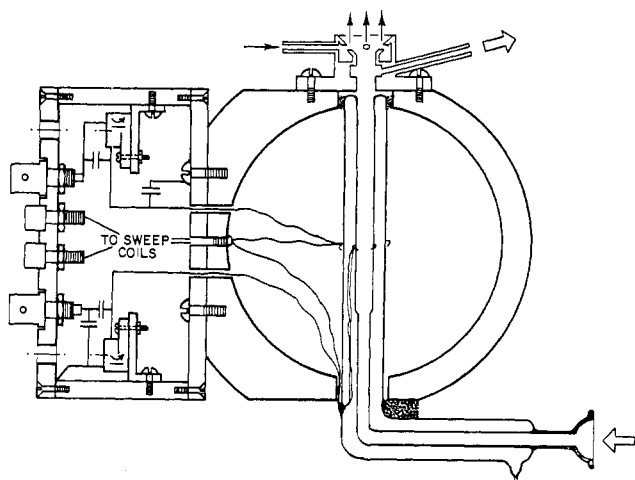
Figure 1. Internal arrangement of the probe assembly.

Figure 2. Exchange rates for collapsed doublet.

Figure 3. Exchange rates for a broadened doublet $M/M_0 = H/L$.

constant ratio of peak areas was obtained at the lowest temperatures. Assuming that this implied essentially complete solution of the BF_3 it was then possible to calculate the fraction of BF_3 in solution at the higher temperatures. This was done with methylene chloride and sulfur dioxide as solvents. The solubility of boron trifluoride in methylene chloride as a function of temperature was also obtained by a manometric technique.[12] The fraction of BF_3 in solution calculated from the manometric data agreed with the results obtained by the n.m.r. method.

The lifetime of the hydroxylic proton in the methanol–boron trifluoride complex was determined from the proton resonance signal of the methyl group. Ratios of peak to trough of the doublet were used for slow exchange and line widths were used for more rapid exchange. The equation relating line shape to exchange rate was used to calculate these parameters, and the results are shown in Figures 2 and 3. Since the spin coupling constant between the CH_3 and OH protons in $CH_3OH \cdot BF_3$ is only 4.11 c.p.s., it was necessary to extend the available tables for situations corresponding to lower resolution.[13–15] Measurements are in radians/second. It was found that tables of line shapes were not adequate due to errors inherent in interpolation. A computer was programed to give line widths and peak ratios directly.[16] It can be seen from Figures 2 and 3 that T (defined in Figure 2) has a large influence on the apparent rate. This appears to be the principal error in the rate determinations. Quantum corrections are not included since they will depend upon the chemical shift between the spin-coupled protons.[17] In the present work this correction would be a maximum of 2% at the fastest exchange rates measured and was therefore not included in the calculations.

All lines were fitted by least-square techniques and the errors listed are standard deviations.

(12) S. Brownstein and J. Paasivirta, *Can. J. Chem.*, **43**, 1645 (1965).
(13) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).
(14) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).
(15) "Tables of Exchange Broadened NMR Multiplets," Technical Note No. 2, Contract No. AF GI(052)–03 between the U. S. Air Force and the Weizmann Institute of Science, Rehovoth, Israel, 1958; ASTIA No. AD-213 032.
(16) The numerical data are available upon request.
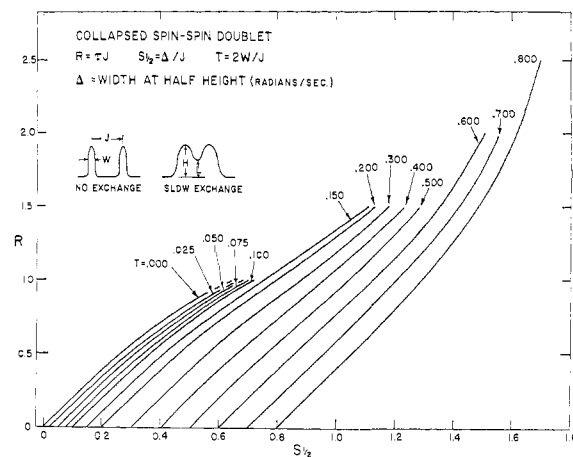(17) J. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958).
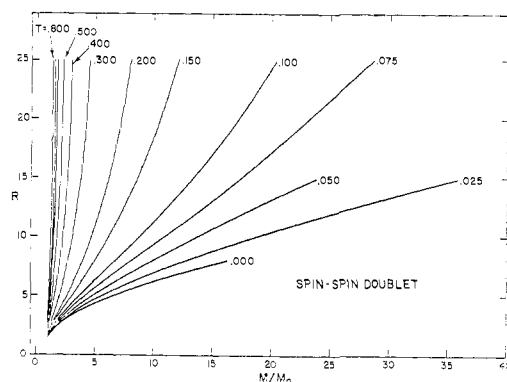
Results

Sulfur dioxide was the only adequate solvent found for methanol–boron trifluoride which did not itself complex with boron trifluoride. The concentration dependence of the exchange of free and complexed boron trifluoride is in better agreement with a displacement mechanism than one of dissociation.[6] This is shown in Table I where rate constants, calculated for

Table I. Concentration and Temperature Dependence of the Rate Constants for Exchange of BF_3 with $CH_3OH \cdot BF_3$

[Free BF_3]/ [complexed BF_3]	—200°K.—		—250°K.—		—297°K.—	
	$\log k_2$	$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$	$\log k_1$
1.0	2.31	2.22	3.45	3.26	4.34	3.92
0.62	2.40	2.04	3.59	2.98	4.44	3.61
0.34	2.24	1.74	3.56	2.86	4.50	3.61
0.25	2.30	1.72	3.38	2.62	4.28	3.32

both exchange mechanisms, are listed for three representative temperatures. It can be seen that k_1, the rate constant for exchange by dissociation, is concentration dependent while k_2, the rate constant for exchange by displacement, is not. There is a linear dependence of $\log k_2$ with the reciprocal of the absolute temperature. From this, the enthalpy of activation for boron trifluoride exchange was calculated to be 5.3
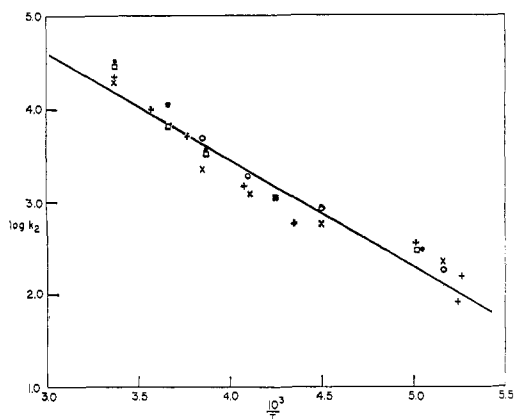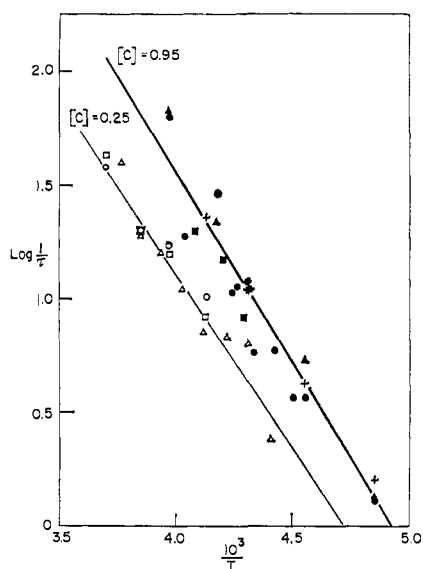
Figure 4. Temperature dependence of k_2.

Figure 5. Temperature dependence of the lifetime for proton exchange.

Figure 6. Chemical shift of the methyl group protons: a, $[CH_3OH]$ = 0.83 m and $[BF_3]$ = 0.48 m; b, $[CH_3OH]$ = 0.69 m and $[BF_3]$ = 0.29 m; and c, $[CH_3OH]$ = 0.70 m and $[BF_3]$ = 0.11 m.

$\pm$ 0.2 kcal./mole and the logarithm of the pre-exponential term was 8.1 $\pm$ 0.2. The results are plotted in Figure 4.

With an excess of boron trifluoride all the methanol is present as the 1:1 complex. At low temperatures spin coupling of 4.11 c.p.s. may be observed between the methyl and hydroxyl protons. This collapses at higher temperatures due to exchange of the hydroxyl proton. The lifetime for this exchange as a function of temperature is shown in Figure 5. The slopes of the lines for higher and lower concentrations are $-1.7 \pm$ 0.1 and $-1.5 \pm$ 0.1. This is not sufficient accuracy to calculate the reaction order with the concentration range experimentally available. For the expression $1/\tau = k[CH_3OH \cdot BF_3]^x$ it is possible to set limits of 0.5 and 1.0 for x. The enthalpy of activation for proton exchange is 7.3 $\pm$ 0.5 kcal./mole.

In the presence of an excess of methanol to boron trifluoride only one peak attributable to the hydroxyl proton is observed in the proton resonance spectrum. At low temperatures two peaks attributed to methyl groups may be observed. As the temperature is raised, these merge to a single peak. The positions of the individual methyl peaks are independent of temperature
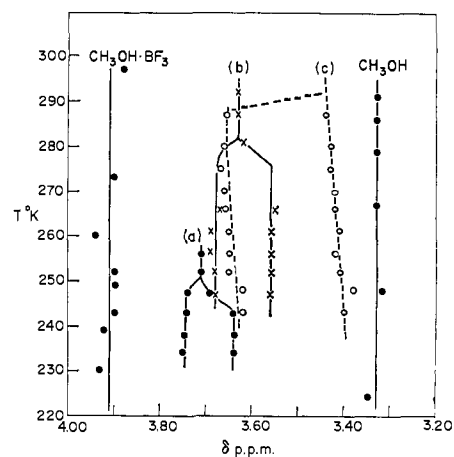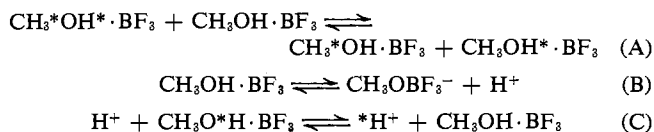
but vary with sample composition. This is shown in Figure 6 for some of the samples investigated. The relative areas of the separate methyl peaks were also determined and were found to be essentially independent of temperature.

Discussion

The concentration dependence of the lifetime of exchanging species is related to the conventional chemical rate constant, k, by the equation

$$\frac{1}{\tau_A} = k[A]^{m-1}$$

where m is the order of the reaction.[18] Therefore the exchange of the hydroxylic proton in the methanol–boron trifluoride complex is between three halves and second order in complex. Such a concentration dependence could be explained by exchange of two molecules of methanol–BF_3 (eq. A), or by exchange of a molecule with an ion formed by dissociation of the methanol–BF_3 complex (eq. B and C). Solvation of the ions in eq. B and C is assumed, but not specifically

$CH_3*OH* \cdot BF_3 + CH_3OH \cdot BF_3 \rightleftharpoons$

$\qquad\qquad CH_3*OH \cdot BF_3 + CH_3OH* \cdot BF_3$ (A)

$CH_3OH \cdot BF_3 \rightleftharpoons CH_3OBF_3^- + H^+$ (B)

$H^+ + CH_3O*H \cdot BF_3 \rightleftharpoons *H^+ + CH_3OH \cdot BF_3$ (C)

shown. If the exchange occurs as in eq. A, a second-order dependence on concentration is expected. The order will be $^3/_2$ if the exchange occurs as shown in eq. B and C. However it is unlikely that exchange could occur as in B and C. If there is sufficient dissociation, as in eq. B, recombination with ions originating from other molecules provides another mechanism for exchange. The rate of this exchange would be first order in methanol–boron fluoride, which is contrary to the experimental results. Therefore eq. A represents the most probable pathway for exchange of the hydroxylic protons.

The rate of exchange of the hydroxylic protons and the rate of exchange between free and complex boron trifluoride may be independently varied by appropriate

(18) A. Loewenstein and T. M. Connor, Ber. Bunsenges physik. Chem., 67, 280 (1963).

Sample composition[a]	Relative areas, 2:1/1:1	K 2:1	Chemical shift of averaged 1:1 peak		Chemical shift (2:1) Calcd.
			Obsd.	Calcd.	
[CH$_3$OH] = 0.83 [BF$_3$] = 0.48	0.68 ± 0.05	1.5	3.64	3.68	4.50
[CH$_3$OH] = 1.16 [BF$_3$] = 0.46	4.9 ± 0.3	6.9	3.40	3.50	3.76
[CH$_3$OH] = 0.69 [BF$_3$] = 0.29	1.54 ± 0.15	3.0	3.56	3.54	4.39
[CH$_3$OH] = 0.70 [BF$_3$] = 0.11	6.8 ± 0.9	2.3	3.40	3.38	Concentration too low

[a] Concentration given in molalities.

choice of reagent concentrations. With conditions such that the rate of BF$_3$ exchange is about 1000 sec.$^{-1}$ the individual multiplets arising from proton spin coupling may be observed. Therefore the process of exchanging one BF$_3$ for another in the methanol–boron fluoride complex does not seem to appreciably affect the proton–proton spin coupling.
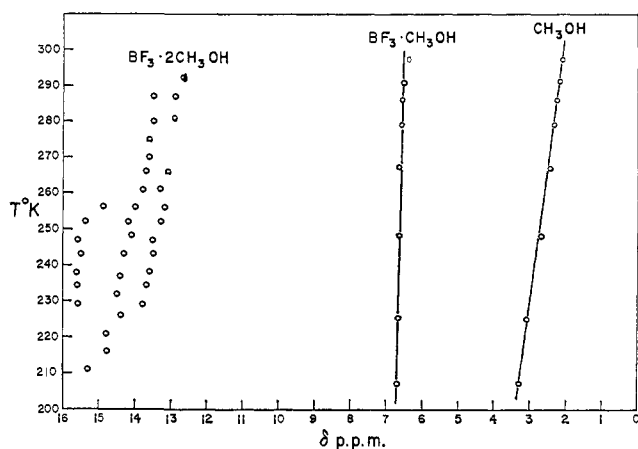

Figure 7. Chemical shift of the hydroxyl protons. These results may be summarized by the equations δOH free = $-0.0134T$ + 6.06 and δOH 1:1 = $-0.0046T$ + 7.78.

With an excess of methanol over boron fluoride the three species CH$_3$OH, BF$_3$·CH$_3$OH and BF$_3$·2CH$_3$OH are present.[19] At most only two peaks, attributable to the methyl groups of these species, are observed in the proton resonance spectra. Since the position of these peaks depends upon sample composition, but not upon temperature, the peaks must arise from an averaging of each of two species with the third, via a rapid exchange re-

(19) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 63.

action. Several assignments are possible for the species causing these peaks. From the relative areas of the peaks and the stoichiometry of the samples only two assignments give a consistent equilibrium constant for the reaction

$$CH_3OH \cdot BF_3 + CH_3OH \rightleftharpoons BF_3 \cdot 2CH_3OH$$

The independent requirement that the position of the averaged peaks be consistent with the chemical shifts of the pure components and the composition of the samples leaves only one possible assignment. The methyl peak at lower field is assigned as an average of the 1:1 complex and free methanol. The peak at higher field then arises from the averaged shift of the 2:1 complex and free methanol. In Table II are shown the results for calculations based on this assignment. The chemical shift of the methyl groups in the 2:1 complex appears as a difference between two larger numbers and is therefore not too accurate. The temperature at which the two methyl peaks merge, due to rapid exchange, is greater for a smaller concentration of boron trifluoride. However the complexity of a variety of exchange reactions and the narrow temperature interval in which line broadening and merging occurs prevents a discussion of this exchange.

Only a single peak attributable to the hydroxyl proton is observed at all temperatures when an excess of methanol is present. The chemical shift of this peak will be the weighted average of those for CH$_3$OH, BF$_3$·CH$_3$OH, and BF$_3$·2CH$_3$OH. Since all the concentrations and the chemical shifts of the hydroxyl proton in CH$_3$OH and BF$_3$·CH$_3$OH are available, the chemical shift for the hydroxyl protons in BF$_3$·2CH$_3$OH may be calculated. This is shown as a function of temperature in Figure 7. It is interesting to note that the chemical shift for the 2:1 complex is at lowest field rather than between the 1:1 complex and free methanol.