

pendicular and radial ones may be rotated together toward or away from the ring axis.

On the basis of these assignments and with the reservation just made, we may examine the shielding elements one by one to determine the effects of complexation by comparison with previously published anisotropic shieldings in the parent molecules. The increases in shielding are denoted by  $\Delta\sigma_i$  in Table I. The results of the comparison are striking: the perpendicular element is unchanged by complexation and the tangential one only moderately. The change in liquid state chemical shifts observed in complexation is almost entirely accounted for by a very large change ( $>50$  ppm) in the shielding when the external field is in the radial direction. The very specificity of the change means that arguments based on gross electron density must be incomplete. If an "average excitation energy" picture is to be used, it must consider specifically the energies of excited states of appropriate symmetry. It is noteworthy that the lowest energy electronic spectral band in  $(C_6H_6)Cr(CO)_3$  has been calculated to be a  $5e \rightarrow 6e$  transition and to be  $xy$  polarized.<sup>20</sup> One might thus naively have anticipated that the in-plane elements would be more affected upon complexation than the perpendicular element. It is interesting that in the free arenes the radial element is almost insensitive to the identity of the substituent but this suffers the predominant change on  $\pi$  complexation. One could view this shielding, when the external field is directed radially, as requiring greatly enhanced circulation about an axis parallel to the C-H bond, and as a corollary the marked upfield shift of the aromatic protons upon complexation can also be rationalized. Hitherto, this latter result has been attributed solely to a quenching of the aromatic ring current.<sup>21</sup> A number of molecular orbital calculations on sandwich and half-sandwich compounds have used a Mulliken population analysis approach, although this has been criticized.<sup>22</sup> Clearly a detailed picture of the electron density distribution in the arene chromium tricarbonyls would be very valuable. However, not being experts in the field, we defer to our more knowledgeable colleagues for further exegesis.

Finally, one would hope that, as more data become available, theories relating substituent parameters to isotropic shifts of fluorine or carbon nuclei in free<sup>23</sup> or  $\pi$ -complexed<sup>24,25</sup> aromatic systems will be superseded by correlations with appropriate tensor elements.

## References and Notes

- (1) (a) Massachusetts Institute of Technology; (b) McMaster University.
- (2) (a) For a review, see M. H. Chisholm and S. Godleski, *Prog. Inorg. Chem.*, **20**, 299-420 (1976). (b) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972).
- (3) B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 2012 (1973).
- (4) L. A. Fedorov, Z. A. Stumbrevichyute, A. K. Prokofev, and E. I. Fedin, *Dokl. Akad. Nauk SSSR*, **209**, 134 (1973).
- (5) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972).
- (6) K. R. Aris, V. Aris, and J. M. Brown, *J. Organomet. Chem.*, **42**, 67 (1972).
- (7) R. G. Parker and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 743 (1970).
- (8) C. D. M. Beverwijk and J. P. C. M. van Dongen, *Tetrahedron Lett.*, 4291 (1972).
- (9) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **59**, 569 (1973).
- (10) E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature (London)*, **82**, 1659 (1958); J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc.*, **98**, 1031 (1976).
- (11) M. Maricq and J. S. Waugh, *Chem. Phys. Lett.*, **47**, 327 (1977).
- (12) J. S. Waugh, M. Maricq, and R. Cantor, *J. Magn. Reson.*, **29**, 183 (1978).
- (13) (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); (b) W. Strohmeier, *Z. Naturforsch. B*, **17**, 627 (1962).
- (14) S. Pausak, J. Tegenfeldt, and J. S. Waugh, *J. Chem. Phys.*, **61**, 1338 (1974).
- (15) (a) O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 1619 (1967); (b) J. Besançon and J. Tirouflet, *Bull. Soc. Chim. Fr.*, 861 (1969).
- (16) W. R. Jackson, C. F. Pincombe, I. D. Rae, and S. Thapabinkarn, *Aust. J. Chem.*, **28**, 1535 (1975).
- (17) M. A. Viswamitra and S. N. Vaidya, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **121**, 472 (1965).
- (18) G. Huttner and B. Krieg, *Chem. Ber.*, **105**, 3437 (1972).
- (19) B. Caro and G. Jaouen, *Tetrahedron Lett.*, 1229, 2061 (1974).
- (20) D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).
- (21) W. Strohmeier and H. Hellman, *Chem. Ber.*, **97**, 1877 (1964).
- (22) S. E. Anderson, Jr., and R. S. Drago, *Inorg. Chem.*, **11**, 1564 (1972).
- (23) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).
- (24) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 360 (1974).
- (25) J. L. Fletcher and M. J. McGlinchey, *Can. J. Chem.*, **53**, 1525 (1975).

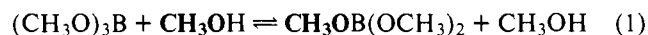
## Solvent Isotope Effect on the Rate of Methoxyl Exchange between Methyl Borate and Methanol

William C. Hutton and Thomas I. Crowell\*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received May 10, 1978

**Abstract:** NMR studies of methyl borate in methanol solution indicate fast methoxyl exchange with a large deuterium solvent isotope effect:  $k_{CH_3OH}/k_{CH_3OD} = 11.0$  at 25 °C. The temperature dependence of the first-order rate constants ( $s^{-1}$ ) is given by  $k_{CH_3OH} = 5.7 \times 10^3 e^{-2360/RT}$  and  $k_{CH_3OD} = 9.1 \times 10^3 e^{-4060/RT}$ . These constants refer to a pH-independent phase of the exchange. Catalysis by lyonium and lyate ions occurs with approximate rate constants ( $M^{-1} s^{-1}$ )  $k_{CH_3OH_2^+} = 1.4 \times 10^5$ ,  $k_{CH_3OD_2^+} = 1.0 \times 10^5$ , and  $k_{CH_3O^-} = 7 \times 10^{10}$ .

Alkyl transfer between borate esters and alcohols, a moderately fast reaction with secondary alkyl borates at room temperature, is too fast for conventional measurements at room temperature in the case of primary borates.<sup>1</sup> We have found the rate of the symmetrical exchange reaction (1) to be accessible by NMR line broadening and report rate constants and solvent isotope effects for the reaction.



## Results

Reaction 1 was observed in methanol solutions<sup>2</sup> of trimethyl borate (MB) sufficiently concentrated (4.4 M) to give equal concentrations of borate and alcohol methyl groups. The 100-MHz methyl proton resonance of such a solution is a broad singlet over the temperature range  $-23$  to  $+91$  °C. When  $CH_3OD$  is used, however, the methyl signal is a doublet. At 91 °C, this doublet is approaching coalescence. Below  $-23$  °C,

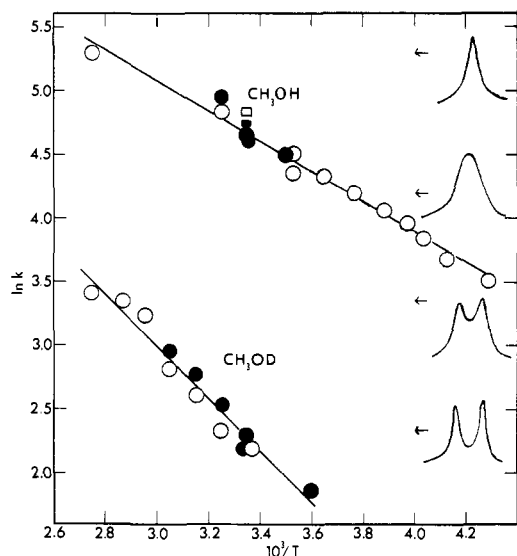


Figure 1. Arrhenius plots of rate constants for methoxyl exchange between methyl borate and methanol, from NMR data: (●)  $^1\text{H}$  60 MHz; (○)  $^1\text{H}$  100 MHz; (□)  $^{13}\text{C}$  25 MHz, from computer fit of line shape; (■)  $^{13}\text{C}$  25 MHz, from chemical shift. Typical signal shapes are shown for 100 MHz at the four rates indicated. Lines represent eq 2 and 3.

$(\text{CH}_3\text{O})_3\text{B}-\text{CH}_3\text{OH}$  and  $(\text{CH}_3\text{O})_3\text{B}-\text{CH}_3\text{OD}$  both show doublets (Figure 1).

While the proton NMR line widths of certain boron compounds are caused by conformational changes or  $^{11}\text{B}$  relaxation phenomena,<sup>3</sup> our results are consistent with chemical exchange which is subject to a kinetic isotope effect. Reaction 1 apparently averages the two methyl frequencies while in  $\text{CH}_3\text{OD}$  it is slow enough to allow the separate signals to appear. If 0.1 M hydrochloric acid, sulfuric acid, or sodium methoxide is added to either system, an exchange-narrowed singlet, line width 2.5 Hz, is observed. This is expected, since the ethanolysis of 2-butyl borate is quite sensitive to acid-base catalysis.<sup>1</sup> Catalysis of the hydrolysis of other borate esters has been carefully studied.<sup>4</sup>

By comparing observed with computed signal shapes at 60 and 100 MHz for exchange between the two nonequivalent sites, values of  $\tau$  and  $k$  ( $\text{s}^{-1}$ ) =  $1/\tau$  were obtained. Several examples of spectra (100 MHz) are shown in Figure 1. The Arrhenius plots in Figure 1 are

$$k_{\text{CH}_3\text{OH}} = 5.7 \times 10^3 e^{-2360/RT} \quad (2)$$

$$k_{\text{CH}_3\text{OD}} = 9.1 \times 10^3 e^{-4060/RT} \quad (3)$$

Figure 2 shows the 25-MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the systems. The larger chemical shift difference between borate and methanol carbon, as compared with the  $^1\text{H}$  shift, causes the  $\text{CH}_3\text{OD}$  system to be nearly a slow-exchange case while in  $\text{CH}_3\text{OH}$  the signals are not quite coalesced at 25 °C. The computer fit shown corresponds to the rate constant plotted as the open square in Figure 1. If the rate constant is calculated from the frequencies, without considering line widths, the deviation from the Arrhenius plot is halved (solid square).

The 32-MHz  $^{11}\text{B}\{^1\text{H}\}$  spectrum, identical for MB- $\text{CH}_3\text{OH}$ , MB- $\text{CH}_3\text{OD}$ , and MB- $\text{CH}_3\text{OH}$ -0.1 M HCl, is the singlet expected for MB.

The effect of acid and base on  $k_{\text{CH}_3\text{OH}}$  and  $k_{\text{CH}_3\text{OD}}$  in buffered hydrochloric acid and sodium methoxide solutions,  $10^{-5}$ – $10^{-2}$  M, was studied through a series of spectra at 90 MHz, examples of which are shown in Figure 3. The results are plotted in Figure 4. The actual methoxide ion concentration,  $[\text{OCH}_3^-]$ , is far lower than the stoichiometric concentration of sodium methoxide  $[\text{NaOCH}_3]_{\text{T}}$  due to association with MB as shown in eq 4.<sup>5</sup> Although Gut's value<sup>5</sup> of  $-5.64$

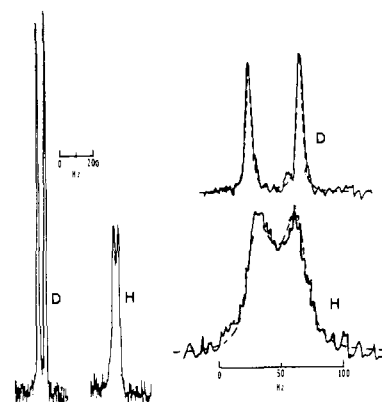


Figure 2.  $^{13}\text{C}$  NMR spectra (25 MHz, 25 °C, proton decoupled) of methyl borate in methanol (H) and in methanol- $d_1$  (D). The dashed lines show computed spectra.

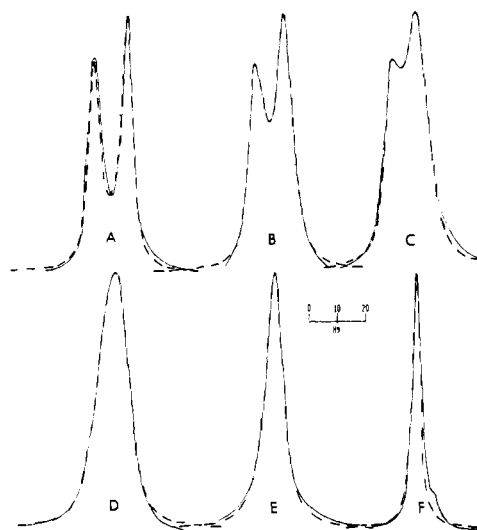
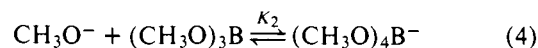


Figure 3. Typical  $^1\text{H}$  NMR spectra (90 MHz, 33 °C) of methyl borate in methanol- $d_1$ , showing the effect of acid and base. Dashed lines are computed for each  $\tau$  value, given: A, no added reagent, 0.105 s; B,  $2.5 \times 10^{-4}$  M HCl, 0.045 s; C,  $3 \times 10^{-4}$  M  $\text{NaOCH}_3$ , 0.031 s; D,  $2 \times 10^{-3}$  M  $\text{NaOCH}_3$ , 0.0177 s; E,  $1.0 \times 10^{-3}$  M HCl, 0.0086 s; F, 0.1 M  $\text{H}_2\text{SO}_4$ , 0.0003 s.



for  $\text{p}K_2$  in dilute solution, ionic strength 1.0, would be subject to a considerable medium effect in our concentrated MB solutions, we nevertheless used it in eq 5 to calculate the methoxide ion concentration in MB- $\text{NaOCH}_3$  solutions. Equation 5 is a special case of the more general expression 6 which is the

$$\begin{aligned} [\text{OCH}_3^-] &= [(\text{CH}_3\text{O})_4\text{B}^-]/10^{5.64}[\text{MB}] \\ &= [(\text{CH}_3\text{O})_4\text{B}^-]/4.4 \times 10^{5.64} \\ [\text{OCH}_3^-] &= 5.2 \times 10^{-7}[\text{NaOCH}_3]_{\text{T}} \quad (5) \end{aligned}$$

result of combining the definitions of  $K_2$ ,  $K_w$ , and electrical neutrality.  $C$  is defined as  $[\text{NaOCH}_3]_{\text{T}} - [\text{HCl}]_{\text{T}}$ . Eq 6 is well approximated by eq 5 when  $[\text{NaOCH}_3]_{\text{T}} > 10^{-5}$  M.

$$[\text{OCH}_3^-] = \frac{C + [C^2 + 4K_w(K_2[\text{MB}] + 1)]^{1/2}}{2(K_2[\text{MB}] + 1)} \quad (6)$$

The  $\text{pH}^6$  of 4.4 M MB without added acid or base (the experimental conditions of Figures 1 and 2) was estimated by glass-electrode potentials to be greater than 5.0 and is plotted as 6.0 in Figure 4.

The symmetrical transesterification of methyl benzoate by

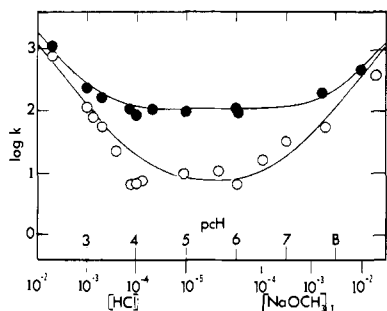
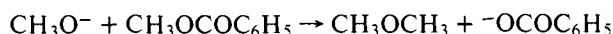
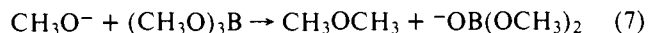


Figure 4. Rate as a function of pCH for methoxyl exchange of methyl borate with methanol (●) or methanol- $d_1$  (○). Curves represent eq 10 and 11.

sodium methoxide is accompanied by slow nucleophilic attack on the methyl carbon, forming dimethyl ether.<sup>7</sup>



However, since we detected no pressure increase over a refluxing solution of MB and sodium methoxide, we have no evidence for the analogous displacement, reaction 7, at 60 °C.



### Experimental Section

Methyl borate (Aldrich) was fractionated, bp 69.1 °C (757 mmHg). Reagent grade methanol and methanol- $d_1$  (Aldrich 99.5%) were dried by fractionation from magnesium through a 120-cm packed column or were used untreated. NMR samples were prepared by two procedures: (1) by successive distillation of MB, methanol, and (when required)  $\text{Me}_4\text{Si}$ , in a vacuum system, from storage bulbs into an NMR tube immersed in liquid nitrogen (the sample was degassed and the tube sealed off while pumping); (2) by a standard volumetric technique using an apparatus filled with dry air. The exchange rate showed moderate sensitivity to water; 1%  $\text{D}_2\text{O}$  in MB- $\text{D}_2\text{O}$  caused the doublet nearly to coalesce, and use of MB without fractionation produced only a singlet.

The NMR spectra were recorded using a variety of instruments. The 60-, 90-, and 100-MHz spectra were recorded on Varian EM-360, EM-390, and HA-100 spectrometers, respectively. The spectra were recorded under conditions such that saturation was avoided. The  $^{11}\text{B}$  and  $^{13}\text{C}$  spectra were measured at 32 and 25 MHz in the Fourier transform mode using a JEOL PS-100 P/EC-100 spectrometer. Full proton decoupling was applied for both nuclei. Some probe temperatures were measured with the standard Varian ethylene glycol/methanol samples and their corresponding temperature-chemical shift correlation graphs. Most probe temperatures were measured using a thermistor temperature probe (Yellow Spring Instruments #44115) in conjunction with a digital ohmmeter. Probe temperatures were measured before and after each separate spectrum, and sufficient time was allowed for probe temperatures to reequilibrate between spectra. The temperature range studied was limited by the freezing and boiling points of the MB- $\text{CH}_3\text{OH}$  system.

The line shapes were plotted by computer from the Gutowsky-Holm equation for two nonequivalent sites with chemical shifts 13.4, 12.0, and 8.0 Hz at 100, 90, and 60 MHz, respectively. The methyl line width used was 2.2 Hz except at 90 MHz, where a line width of 3.2 Hz not only resulted in the best fit to the signals of exchanging methyl groups but in fact was the observed value for fast exchange. The chemical shifts, from  $\text{Me}_4\text{Si}$ , of  $\text{CH}_3\text{OD}$ , MB, and their coalesced peaks are 202, 208, and 205 Hz at 60 MHz. For computation of the exchange rate from  $^{13}\text{C}$  signals, the difference of the separate methyl frequencies, 41.5 Hz, from the spectrum of MB- $\text{CH}_3\text{OD}$  was used as the chemical shift difference, together with a line width of 3.3 Hz selected for the best fit of the data. The calculation of  $\tau$  from frequencies alone was made using eq 8<sup>8</sup> where 32.4 is the difference in the methyl frequencies in the nearly coalesced spectrum of MB- $\text{CH}_3\text{OH}$  (Figure 2).

$$\begin{aligned} 1/2\tau &= (\pi/\sqrt{2})[(41.5)^2 - (32.4)^2]^{1/2} \quad (8) \\ \tau &= 0.00868 \text{ s} \end{aligned}$$

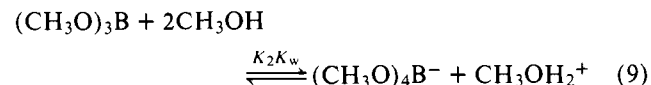
A Radiometer 26 pH meter was used to determine the approximate pCH of 4.4 M MB- $\text{CH}_3\text{OH}$  solutions. The glass electrode, which attained a constant potential in methanol within a few minutes,<sup>9</sup> was calibrated with  $10^{-3}$ - $10^{-4}$  M hydrochloric acid and with benzoate and saccharin buffers, giving the relationship  $\text{pCH} = 1.1\text{pH}_{\text{obsd}} + 2.0$ . Titration of 0.087 M MB with 0.139 M sodium methoxide then yielded, for example, a  $\text{pH}_{\text{obsd}}$  of 8.1 with total borate and methoxide concentrations of 0.0796 and 0.0121 M. Use of eq 6 leads to a value of  $1.5 \times 10^5$  for  $K_2$ , which we consider satisfactory confirmation of Gut's value<sup>5</sup> obtained with the hydrogen electrode. The  $\text{pH}_{\text{obsd}}$  of 4.4 M MB varied between 4.6 and 5.2, which would imply a pCH of 7.1-7.7 if the methanol scale were unchanged by the high MB concentration. However, hydrochloric acid ( $10^{-4}$  M) in 4.4 M MB- $\text{CH}_3\text{OH}$  gives the pH meter reading,  $\text{pH}_{\text{obsd}} = 0.0$ , expected of  $10^{-2}$  M acid. The conclusion that the hydrogen ion concentration in 4.4 M MB is much less than  $10^{-5}$  M is essential to the discussion of the pCH-rate function.

A test for the formation of dimethyl ether (bp -138 °C) in refluxing 2 M sodium methoxide plus 0.7 M MB was carried out in a sealed-glass system with a water-cooled condenser and mercury manometer, under 740 mmHg of air pressure. No significant pressure increase was observed in 3 weeks.

### Discussion

The solvent isotope effect is large for the "solvent-catalyzed" or pCH-independent part of the exchange. The ratio  $k_{\text{H}}/k_{\text{D}}$  from Figure 1 is 11.0 at 25 °C, and  $\Delta H_{\text{D}}^\ddagger - \Delta H_{\text{H}}^\ddagger = 1.7$  kcal/mol. Both of these values are close to the respective theoretical estimates of 11.5 and 1.4 kcal/mol for OH vs. OD.<sup>10</sup> The ratio of frequency factors,  $A_{\text{D}}/A_{\text{H}}$ , is 1.6, a normal figure which does not indicate tunnelling.<sup>11</sup> This isotope effect is particularly interesting because most known solvent isotope effects,  $k_{\text{H}}/k_{\text{D}}$ , are about 2 and seldom above 3, far below the theoretical maximum. In an extensive summary of kinetic solvent isotope effects,<sup>12a</sup> some of the highest are found in the neutral hydrolysis of esters and anhydrides.<sup>12b</sup> Five reactions show  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  between 3.5 and 3.9, with  $\Delta S^\ddagger = -32$  to  $-50$  cal/(deg mol). In two examples, the hydrolysis of ethyl dichloroacetate and of catechol sulfite, the isotope effects reach 5.0 and 6.0. Our methoxyl exchange resembles these reactions both in the high isotope effect and in the low entropy of activation; the low preexponential factors in Arrhenius equations 2 and 3 correspond to entropies of activation  $\Delta S_{\text{H}}^\ddagger = -41.3$  and  $\Delta S_{\text{D}}^\ddagger = -40.4$  cal/(deg mol). The exchange of 2-butyl borate with methanol,<sup>1</sup> measured in dilute solution by a dilatometer, shows a comparable entropy of activation,  $-38.2$  cal/(deg mol), but a higher enthalpy of activation, 7.1 kcal/mol. The low activation enthalpy of methyl borate is comparable to that found by Heyes and Lockhart, 2-4 kcal/mol, for methoxyl exchange between methyl borate and dimethyl phenylboronate in toluene.<sup>13</sup>

The determination of exchange rate as a function of hydrogen and methoxide ion concentration (Figure 4), although limited in scope and accuracy, supports the assertion that the reaction showing the large isotope effect is solvent-catalyzed only. Solutions of MB are acidic, due to the interaction of the Lewis acid with methanol:



The extent of this ionization may be calculated by eq 6 with  $C = 0$  and  $K_w = 1.58 \times 10^{-17}$ <sup>14</sup> predicting a pCH of 5.2. If the reduction in the methanol concentration by the high proportion of MB is taken into account, 5.8 is obtained and this pCH would be further raised by the decrease in dielectric constant, compared with pure methanol. Although these manipulations of high concentrations cannot be very accurate, it is likely that the pCH of 4.4 M MB is above 5.5. This expectation is borne out by the pH meter reading, which shows the acidity to be greatly increased by  $10^{-4}$  M HCl while  $k_{\text{CH}_3\text{OH}}$  and  $k_{\text{CH}_3\text{OD}}$

show no increase. This is an important observation; if the pcH of the MB solution itself were 4, the concentration axis of Figure 4 between  $[\text{NaOCH}_3]_{\text{T}} = 10^{-4}$  and  $\text{pcH} = 4$  would be condensed, and the inference of a pcH-independent region of the rates would be questionable.

The rate constants in Figure 4 were fitted by the following equations, representing the curves drawn:

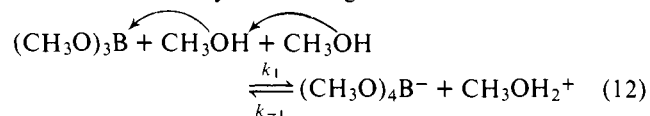
$$k_{\text{H}} (\text{s}^{-1}) = 105 + 1.4 \times 10^5 [\text{CH}_3\text{OH}_2^+] + 7 \times 10^{10} [\text{OCH}_3^-] \quad (10)$$

$$k_{\text{D}} (\text{s}^{-1}) = 7 + 1.0 \times 10^5 [\text{CH}_3\text{OD}_2^+] + 7 \times 10^{10} [\text{OCH}_3^-] \quad (11)$$

Because of uncertainties in temperature, the values 100 and  $7 \text{ s}^{-1}$  for  $k_{\text{CH}_3\text{OH}}$  and  $k_{\text{CH}_3\text{OD}}$  are considered less accurate than those calculated for  $34^\circ\text{C}$  from eq 2 and 3, 119 and  $11.7 \text{ s}^{-1}$ . Linearity in  $[\text{CH}_3\text{OH}_2^+]$  and  $[\text{OCH}_3^-]$  is assumed, not proven, and the accuracy is insufficient to give the isotope effect on the catalytic constants. The analysis does, however, show that the large isotope effect is on  $k_{\text{solvent}}$  and also that the catalytic constant for methoxide ion,  $7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , is so high as to suggest a diffusion-controlled reaction.

The fact that pcH independence of the rate extends to hydrogen ion concentrations as high as  $10^{-4} \text{ M}$ , where exchange of the hydroxyl protons in methanol is very fast,<sup>15</sup> eliminates any possible effect of methyl line broadening by spin coupling with hydroxyl. This possibility of course does not exist in  $\text{CH}_3\text{OD}$ .

The high solvent isotope effect, low entropy of activation, and (for 2-butyl borate) the observation of general base catalysis are consistent with the involvement of two methanol molecules, one acting as a nucleophile and the other as a base in the solvent-catalyzed exchange:



If, however, the equilibrium constant  $K_2K_w$  for the ionization (9) or (12) is  $10^{-11.2} \text{ M}$  and the first-order rate constant  $k_1$  is set equal to  $10^2 \text{ s}^{-1}$ , the observed specific rate of exchange, then the reverse rate constant  $k_{-1}$  for the recombination of the oppositely charged ions must be on the order of  $10^{13} \text{ M}^{-1} \text{ s}^{-1}$ . Since this exceeds the value for a bimolecular, diffusion-controlled reaction, mechanism 12 is inadmissible unless it is modified to mean ionization rather than dissociation,<sup>16</sup> so that

exchange takes place via an ion pair. But high isotope effects can be caused by a variety of mechanisms<sup>17</sup> and the possibility of a cyclic one is not ruled out.

Methoxide ion may take the place of one methanol molecule in eq 12 or, in view of its high nucleophilicity,<sup>18</sup> may attack the Lewis acid directly. An alternative interpretation of methoxide catalysis is direct donation of methoxide ion by  $(\text{CH}_3\text{O})_4\text{B}^-$  to  $(\text{CH}_3\text{O})_3\text{B}$ , as proposed by Bell<sup>19</sup> for  $\text{B}(\text{OH})_4^-$ . Since the concentration of  $(\text{CH}_3\text{O})_4\text{B}^-$  is higher than that of  $\text{CH}_3\text{O}^-$  by a factor of  $10^6$ , the corresponding rate constant would be about  $10^5 \text{ M}^{-1} \text{ s}^{-1}$  as compared with  $7 \times 10^{10}$  for methoxide ion. Further consideration of this mechanism would require observation of the reaction order with respect to MB and therefore the use of more dilute solutions than our experimental method permitted.

**Acknowledgment.** We thank Ms. Barbara Erwine of Varian Associates, Palo Alto, Calif., for some of the 60-MHz variable-temperature spectra and Dr. William Espersen for the use of his computer program.

## References and Notes

- (1) G. T. Perkins and T. I. Crowell, *J. Am. Chem. Soc.*, **78**, 6013 (1956); C. L. Denson and T. I. Crowell, *ibid.*, **79**, 5656 (1957).
- (2) Methanol is the solvent throughout this article.
- (3) H. Beall and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973); R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 1401 (1978).
- (4) D. W. Tanner and T. C. Bruice, *J. Am. Chem. Soc.*, **89**, 6954 (1967).
- (5) R. Gut, *Helv. Chim. Acta*, **47**, 2262 (1964).
- (6) pcH is defined as  $-\log [\text{CH}_3\text{OH}_2^+]$ .
- (7) J. F. Bunnett, M. M. Robison, and F. C. Pennington, *J. Am. Chem. Soc.*, **72**, 2378 (1950).
- (8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
- (9) C. D. Ritchie and P. D. Heffley, *J. Am. Chem. Soc.*, **87**, 5402 (1965).
- (10) J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 2nd ed, 1962, p 72.
- (11) R. P. Bell, "The Proton in Chemistry", Chapman and Hall, London, 2nd ed, 1973, p 281.
- (12) (a) P. M. Laughton and R. E. Robertson, in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 7; (b) p 486.
- (13) R. Heyes and J. C. Lockhart, *J. Chem. Soc. A*, 326 (1968).
- (14) J. F. Coetzee and C. D. Ritchie, Ed., "Solute-Solvent Interactions", Marcel Dekker, New York, N.Y., 1969, pp 52, 199.
- (15) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **84**, 4664 (1962).
- (16) E. Grunwald, in "Proton-Transfer Reactions", E. Caldin and V. Gold, Ed., Wiley, New York, N.Y., 1975, p 114.
- (17) R. L. Schowen, *Prog. Phys. Org. Chem.*, **9**, 326 (1972).
- (18) J. Murto, *Acta Chem. Scand.*, **18**, 1043 (1964).
- (19) R. P. Bell, J. O. Edwards, and R. B. Jones, "The Chemistry of Boron and its Compounds", E. L. Muetterties, Ed., Wiley, New York, N.Y., 1966, p 219.