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Kinetic and Equilibrium Isotope Effects of Proton Exchange and Autoprotolysis of Pure Methanol Studied by Dynamic NMR Spectroscopy

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Ionisation / Isotopeneffekte / Katalyse / Magnetische Kernresonanz / Reaktionskinetik

The rate constants of the intermolecular proton exchange in pure methanol, i.e. the reciprocal proton lifetimes, τ_0^{-1} , have been determined as a function of the temperature by total lineshape analysis of the ^1H -NMR spectra. Since CH_3OH is an AB_3 spin system of high order the quantum mechanical density matrix formalism was employed for the simulation of the spectra. The neglect of high order effects as well as the presence of impurities had led to inconsistencies in previous studies. For the first time, the primary kinetic isotope effects were determined indirectly by simulation of the ^1H -NMR spectra of CH_3OD samples containing 1 vol-% CH_3OH . The results are given by

$$\tau_0^{-1} = 10^{6.1 \pm 0.3} \exp(-28.5 \pm 1 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}, 290 < T < 340 \text{ K},$$

for CH_3OH , and

$$\tau_0^{-1} = 10^{5.7 \pm 0.4} \exp(-29.3 \pm 2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}, 298 < T < 345 \text{ K},$$

for CH_3OD , with a kinetic isotope effect of 3.2 ± 0.4 at 298 K. — The data cannot be explained by a cyclic exchange mechanism. However, they can be quantitatively related to the autoprotolysis constant of methanol and to Grunwald's kinetic data on proton transfer in buffered methanol solutions. It is concluded that the proton lifetimes in pure methanol are determined by the natural amount of free solvated CH_3OH_2^+ and CH_3O^- ions generated by autoprotolysis. The observed energy of activation is then the sum of two terms, namely the energy of activation of the proton jumps between the ions and a methanol molecule, and half the enthalpy of methanol selfdissociation. In the presence of acid or basic impurities the second term becomes negligible. We propose a method for the quantitative determination of these impurities in the 10^{-9} to 10^{-7} mol l^{-1} range. From our results we derive an equilibrium isotope effect of $(K^{\text{H}}/K^{\text{D}})_{298 \text{ K}} = 6 \pm 3$ for the autoprotolysis of pure methanol, which has not been reported before. It is shown that the literature data on proton exchange in pure water and other protic systems can be explained in a similar way. The mechanism of the neutralisation in water and methanol is discussed. For the neutralisation of solutions containing 1 mol of each ion it is found that the mean number of proton transfer steps necessary is 5.3 for water and 2.5 for methanol. These data correlate well with the molar solvent density.

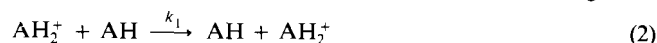
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1. Introduction

The mechanism of the intermolecular proton exchange in pure protic liquids such as water, alcohols, or amines is an old question. It was recognized early [1–3] that the exchange, written formally as



is catalyzed by the conjugated acids and bases according to



and

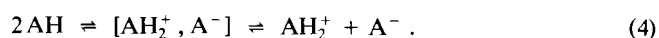


Because of the difficulty in preparing solvents which are free from acid or basic impurities, i.e. solvents which are characterized by intrinsic proton lifetimes τ_0 , information on proton exchange in protic systems was largely derived from salt or buffer containing solutions [3–13]. The magnitude of the rate constants k_1 and k_2 of the fast single proton transfer processes Eqs. (2) and (3) were first estimated for water by Eigen and De Maeyer [4] from the neutralisation rate constant measured by kinetic relaxation spectroscopy. The results were later confirmed for pure water by Ertl and Gerischer [5], and recently by Holzwarth, Goodall et al. [6]. Conductivity measurements of proton and deuteron mobility in ice and liquid water by Eigen and De Maeyer [7] revealed that in the liquid state the rate determining step of Eqs. (2) and (3) is not the proton transfer in the hydrogen bonded chain but the “structural diffusion” of the hydrogen bonded structure, i.e. the addition of the AH molecules to the ion containing associates and their separation.

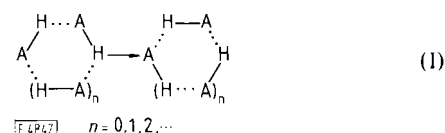
Using dynamic NMR spectroscopy, values of k_1 and k_2 were then derived directly by Meiboom [8], later by Tewari and Glick [9] and Rabideau and Hecht [10]. For this purpose the proton lifetimes in ^{17}O enriched water were measured as a function of the pH [8–10] and the temperature [9]. The energies of activation [9] of k_1 and k_2 were found to be 10.9 and 11.3 kJ mol $^{-1}$ respectively and are, thus, equal to the activation energy of the neutralisation [6]. k_1 and k_2 were measured for buffered methanol solutions by Grunwald et al. [11–13]. The energy of activation of k_1 was found to be about 8 kJ mol $^{-1}$. Consistent values were obtained by extrapolating to zero buffer concentrations.

Attempts to measure the intrinsic proton lifetimes of pure protic systems have been made by several authors. However, the kinetic data and especially the energies of activation showed a considerable scattering from between 8 and 12 kJ mol $^{-1}$ for water [13, 14] and methanol [15] to 42 kJ mol $^{-1}$ for ethanol/water [16] and isopropanol/water [17, 18]. A thorough study of Vermold and Yoon [19] revealed very slow exchange rates for methanol after adding small traces of sodium methoxide. The activation energy was found to be 13 kJ mol $^{-1}$. All these results are, thus, consistent with an exchange catalyzed by added acids and bases.

Several exchange mechanisms have been discussed for pure protic systems. As suggested by Grunwald in Ref. [17] the exchange could be catalyzed according to Eqs. (2) and (3) by the free solvated ions which are generated by the autoprotolysis of the solvents:



The activation parameters of this exchange catalyzed by the intrinsic ions should then be affected by the enthalpy and the entropy of the autoprotolysis. The dissociation Eq. (4) represents an additional exchange mechanism. However, the exchange is not complete if the ions in the ion pair formed in the first reaction step recombine before they dissociate into free ions, i.e. before the hydrogen bond structure has changed. Proton exchange in the same hydrogen bonded cluster is possible only if the associates have a cyclic structure as shown in scheme 1. Evidence for cyclic proton exchange between carb-



oxylic acids and alcohols was obtained by Grunwald et al. [11, 12, 20] as side reaction of catalyzed exchange in buffered protic mixtures. Very little is known about these non-dissociative proton transfer processes, though they are assumed to be key steps of bifunctional catalysis [21], especially in enzymatic reactions. Therefore, we have studied appropriate model reactions in this laboratory: the cyclic proton and deuteron exchange between acetic acid and methanol in tetrahydrofuran [22–25], selfexchange of 1-amino-3-iminopropene in CS $_2$ [26], and, as an intramolecular reference, double hydrogen tunneling in porphines [27–29]. Early evidence for a cyclic proton exchange in buffered methanol obtained by Luz et al. [3] was later shown by Grunwald et al. [11] to be caused by experimental imperfections. Therefore, the cyclic exchange mechanism is also improbable for pure methanol, although its postulation is very tempting because there is evidence for cyclic hydrogen bonded associates, especially tetramers [30–32] in methanol. Formulations of cyclic exchange in methanol are still found in many textbooks on NMR-spectroscopy.

In order to contribute to answering the question whether the intrinsic proton lifetimes of pure protic systems are a measure of the autoprotolysis constant, a problem which has been recently treated theoretically by Hertz [33], or whether they represent cyclic processes, we have reinvestigated the kinetics of proton exchange in pure methanol using total ^1H -NMR line-shape analysis. Imperfections in previous studies were excluded by using the quantum mechanical density matrix formalism developed by Kaplan [34], Alexander [35], and Binsch [36]. Recently [22] we adapted the theory for the general case of superposed different intermolecular exchange mechanisms. A special effort was made in preparing samples of high purity leading for the first time to the consistent results reported in this paper. It is shown that the lifetimes of the protons in very pure methanol are determined by the presence of the free solvated ions CH_3OH_2^+ and CH_3O^- generated by the autoprotolysis of methanol. For the first time, we also present the kinetic isotope effects of the intrinsic proton exchange in pure methanol, detected indirectly from the ^1H -NMR lineshape of CH_3OD samples containing 1 vol-% CH_3OH . These effects are interpreted in terms of the equilibrium isotope effects of the autoprotolysis which have not yet been reported for methanol [37]. A method for the quantitative determination of CH_3OH_2^+ and CH_3O^- in methanol is given. Our analysis explains in a quantitative way all the scattering of the kinetic data of proton ex-

change [14–19] in unbuffered protic systems. Finally, from the discussion of the neutralisation rate constants and the rate constants k_1 and k_2 the number of proton transfer steps necessary for the neutralisation for a given number of ions is obtained for water and methanol.

2. Experimental

2.1. Preparation of Samples

The NMR samples had to be prepared very carefully in order to exclude air and moisture or other impurities that might catalyze the proton exchange. The following procedure was, therefore, adopted. CH_3OH (Uvasol, Merck, Darmstadt) and CH_3OD containing 1 vol-% CH_3OH (ICN-Chemikalien, München) were dried over molecular sieve (Merck, 3 Å) in glass vessels which were attached to a vacuum line described previously [23, 24]. In the meantime additional molecular sieve was regenerated in a second glass vessel at 360°K and 10^{-6} mbar. The pre-dried methanol was then condensed into this vessel for further drying. This procedure was repeated once. Part of the purified liquid was then condensed into the NMR sample bulb, also attached to the vacuum line in order to clean the inner glass surface. After evaporation the bulb was refilled by condensation and sealed off. For the NMR measurements the bulbs were placed in an outer 5 mm sample tube of a microcell assembly (No. 529, Wilmad, Buena, New Jersey). The result was a homogeneous temperature over the samples which prevented refluxing of the liquid at elevated temperatures. The CH_3OD samples, cylindrical bulbs of 4 mm diameter and 30 mm length provided the necessary deuterium lock signal for stabilizing the static magnetic field. In the case of the CH_3OH samples benzene- d_6 was used as field locking compound and was filled into the space between the inner and the outer tube. In the case of the cylindrical bulbs this space was too restricted and the lock signal too weak. Therefore, spherical bulbs of 4 mm diameter were used for most of the CH_3OH samples.

2.2. Determination of the Kinetic Data

The ^1H -NMR spectra were measured with a Bruker CXP-100 Fourier Transform pulse NMR spectrometer. The temperature was measured from the temperature dependent distance $\Delta\nu = \nu_{\text{CH}_3\text{OH}} - \nu_{\text{CH}_3\text{OD}}$ between the two methanol signals according to van Geet [38]. The NMR spectra, stored in digital form in the Bruker computer Aspect 2000 were transferred to the Univac 1108 of the Rechenzentrum der Universität Freiburg by means of a direct data line and a computer terminal, with a floppy disk (Comm-Stor, Sykes, Rochester) as data buffer. Since the proton spin system of CH_3OH is an AB_3 spin system of high order the lineshape calculations i.e. the determination of the proton lifetimes had to be based on the quantum mechanical density matrix formalism developed by Kaplan [34], Alexander [35], and Binsch [36]. We have recently proposed a kinetic formulation of this lineshape theory for the general case of superposed intermolecular exchange. Using this formulation it is no longer necessary to assume reaction mechanisms at the stage of the lineshape simulations. The computer program used for the calculations has been described in detail [22]. The calculated spectra were fitted to the experimental spectra by minimizing the standard deviation. The parameters varied during the simulation of the spectra were the pseudo first order methanol self-exchange rate constants, i.e. the inverse proton lifetimes, τ_0^{-1} , the coupling constant $J_{\text{CH}_3\text{OH}}$, and the chemical shift difference $\Delta\nu$. The static line width, W_0 , was given by the inhomogeneity of the static magnetic field and was taken from the line width of reference samples measured at each temperature. The reference for the CH_3OD samples was a cylindrical bulb containing C_6D_6 with 5 vol-% C_6H_6 . As reference for the CH_3OH samples a spherical bulb containing C_6H_6 was placed in the microcell assembly using C_6D_6 as locking compound in the outer tube. For this arrangement W_0 turned out to be greater as compared to the cylindrical assembly. Therefore, for the CH_3OD samples, lower values of τ_0^{-1} could be obtained as compared for the CH_3OH samples. The methyl group signal of the CH_3OD samples did not contain sufficient information on the deuterium lifetimes. Hence, after baseline correction, only the CH_3OH signals of these samples were simulated.

3. Results

A typical set of superposed experimental and calculated ^1H -NMR spectra of a sample of pure methanol at 90 MHz is shown in Fig. 1. The high order effects of the AB_3 spin system are clearly seen as a distortion of the signals especially at higher temperatures where the chemical shift difference $\Delta\nu$ between the two signals decreases due to the breaking of hydrogen bonds [38]. In Fig. 2 a typical set of signals of the residual CH_3OH protons in CH_3OD is shown. Tab. 1 contains all the static and dynamic parameters used for the simulation of the spectra. Fig. 3 shows the corresponding Arrhenius curves constructed from the results of four CH_3OH and three CH_3OD samples which were prepared independently from different lots. The two curves are represented by the equations:

$$(\tau_0^{\text{H}})^{-1} = 10^{6.1 \pm 0.3} \exp(-28.5 \pm 1 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}, \quad 290 < T < 340 \text{ K}, \quad (5a)$$

and

$$(\tau_0^{\text{HD}})^{-1} = 10^{5.7 \pm 0.4} \exp(-29.3 \pm 2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}, \quad 298 < T < 345 \text{ K}, \quad (5b)$$

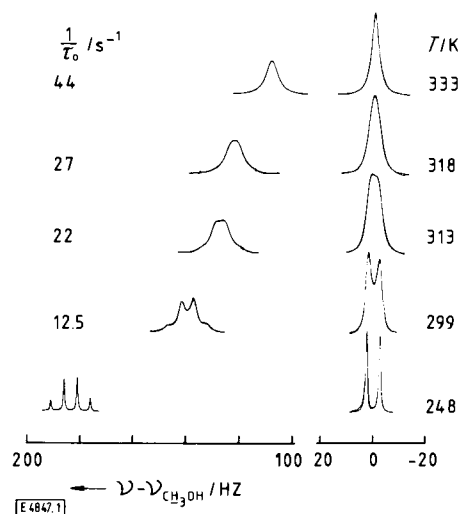


Fig. 1
Superposed experimental and calculated ^1H 90 MHz NMR signals of pure methanol as a function of the temperature. Left: CH_3OH signal, right: CH_3OD signal. The intensities of the two signals are not normalized to the corresponding number of protons (100 scans, 90° -pulses, repetition time 10 s)

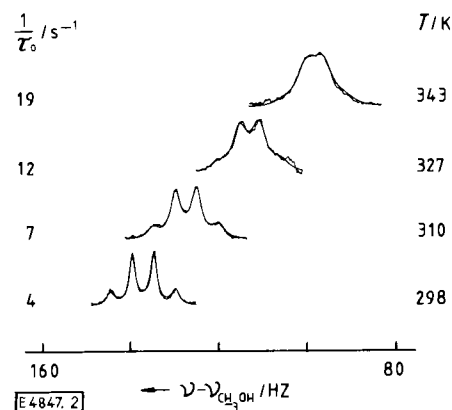


Fig. 2
Superposed experimental and calculated ^1H 90 MHz NMR signals of the residual CH_3OH protons (1 vol-%) in CH_3OD as a function of the temperature (1000 scans, 90° pulses, 10 s repetition time)

Table 1

Static and dynamic parameters describing the ^1H -90 MHz NMR spectra of pure methanol as a function of the temperature T . τ_0 : proton lifetime, $\Delta\nu$: difference of the chemical shifts of the methyl group and the hydroxyl group, J : coupling constant, W_0 : static line width, K : molal autoprotolysis constant determined from Eq. (10), $k_1 + k_2$: sum of rate constants given by Eq. (20)

T/K	τ_0^{-1}	$\Delta\nu/\text{Hz}$	W_0/Hz	J/Hz	$K/\text{mol}^2 \text{ kg}^{-2}$	$k_1 + k_2/\text{s}^{-1}$
a) CH_3CH						
339.5	50.0	103.7	1.5	5.2	.147–15	.129+12
335.5	48.0	107.3	1.5	5.2	.125–15	.134+12
333.0	44.0	108.6	1.4	5.1	.112–15	.130+12
332.0	43.0	110.4	1.5	5.2	.108–15	.129+12
330.5	41.5	111.2	1.5	5.2	.101–15	.129+12
327.0	35.0	113.3	1.6	5.2	.865–16	.118+12
327.0	33.5	114.6	1.6	5.2	.865–16	.112+12
325.0	35.0	116.1	0.5	5.1	.790–16	.123+12
324.0	32.5	117.3	1.4	5.2	.755–16	.117+12
323.5	30.0	117.9	2.5	5.2	.737–16	.109+12
321.5	30.0	119.5	1.8	5.1	.672–16	.114+12
319.5	29.0	121.5	2.6	5.2	.611–16	.116+12
318.0	27.0	122.6	0.6	5.1	.568–16	.112+12
317.0	26.0	123.6	0.7	5.1	.541–16	.110+12
316.0	26.0	125.9	2.6	5.2	.515–16	.113+12
315.5	24.0	125.6	1.7	5.2	.502–16	.106+12
315.0	24.0	125.2	1.8	5.2	.490–16	.107+12
312.5	22.0	127.6	0.7	5.1	.432–16	.104+12
312.5	21.0	128.5	2.6	5.2	.432–16	.998+11
310.0	19.5	129.6	1.5	5.2	.379–16	.988+11
309.0	19.0	130.3	1.8	5.2	.360–16	.989+11
308.0	18.0	133.0	3.0	5.2	.341–16	.962+11
306.5	17.5	132.6	1.5	5.2	.315–16	.974+11
305.0	16.7	134.1	1.7	5.2	.290–16	.972+11
304.0	17.0	134.3	1.3	5.2	.274–16	.101+12
304.0	16.0	134.7	0.7	5.2	.274–16	.953+11
303.0	15.0	136.5	3.4	5.2	.259–16	.919+11
301.0	16.0	138.0	1.7	5.2	.232–16	.104+12
301.0	13.5	137.4	0.8	5.2	.232–16	.876+11
300.0	14.0	139.9	3.0	5.2	.219–16	.935+11
299.5	12.0	138.8	0.8	5.2	.212–16	.813+11
299.0	12.0	139.4	1.3	5.2	.206–16	.825+11
298.0	13.0	139.6	2.4	5.2	.195–16	.920+11
298.0	14.0	140.1	1.6	5.2	.195–16	.991+11
293.0	12.0	144.4	1.1	5.2	.144–16	.988+11
291.5	10.0	145.8	0.8	5.2	.131–16	.863+11

T/K	$\tau_0^{-1}/\text{s}^{-1}$	$\Delta\nu/\text{Hz}$	W_0/Hz	J/Hz
b) $\text{CH}_3\text{OD} + 1 \text{ vol.-% } \text{CH}_3\text{OH}$				
345.5	20.0	95.1	1.5	5.2
343.0	19.0	97.9	1.5	5.1
339.0	15.0	101.1	1.5	5.2
337.0	15.0	102.8	1.3	5.2
333.5	14.0	106.5	1.2	5.1
330.5	13.0	109.1	1.3	5.1
327.5	12.0	112.8	1.5	5.1
323.5	11.0	115.5	1.0	5.1
319.5	10.0	119.6	1.2	5.1
316.5	9.0	121.3	0.8	5.2
313.5	7.0	124.5	1.1	5.1
310.0	7.0	127.2	1.3	5.1
304.0	5.0	132.2	1.2	5.2
304.0	5.0	132.8	1.0	5.2
298.5	4.0	137.0	1.0	5.0
297.0	3.5	138.9	1.3	5.1

with a kinetic isotope effect of

$$(\tau_0^{\text{H}}/\tau_0^{\text{HD}})_{298\text{K}} = 3.2 \pm 0.4. \quad (5c)$$

The index HD signifies the proton lifetimes in the CH_3OD samples.

4. Discussion

These results exhibit several features which are unexpected at first sight. The energy of activation of the proton exchange, $E_a^{\text{H}} = 28.5 \text{ kJ mol}^{-1}$ is much higher than the values of 8 to 13 kJ

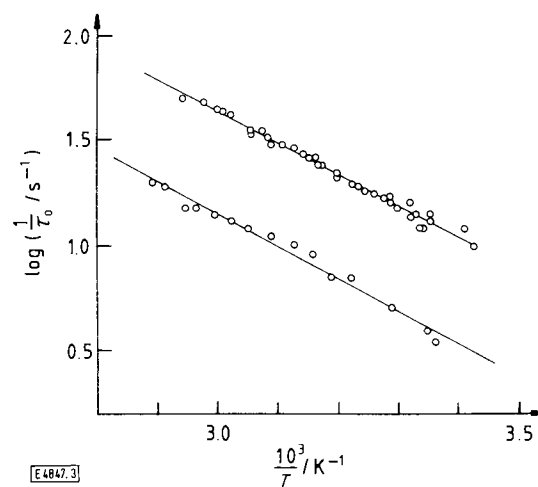


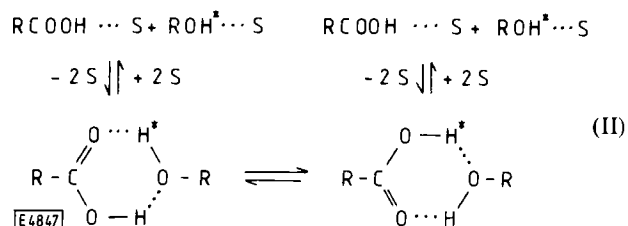
Fig. 3

Arrhenius diagram of the proton exchange in pure CH_3OH and (upper curve) and CH_3OD (lower curve)

mol^{-1} reported previously [16, 19]. The kinetic isotope effect is high although E_a^{H} is equal to E_a^{HD} , the energy of activation of proton exchange in the CH_3OD samples. Usually [39], kinetic isotope effects arise from different values for the energies of activation. Notice that for water the relation between proton and deuteron conductivity [7] and the kinetic isotope effect of the neutralisation [5] were of the order of $2^{1/2}$, as expected from the reduced masses. Our findings can, therefore, not be explained by an exchange catalyzed by added acid or basic impurities but must be intrinsic to methanol. This interpretation is supported by the fact that the results could be reproduced. As shown below they can only be explained by the mechanism in which the exchange is catalyzed by the intrinsic free solvated ions CH_3OH_2^+ and CH_3O^- generated by autoprotolysis.

4.1. Rejection of the Cyclic Exchange Mechanism

The cyclic exchange mechanism has to be excluded for the following reasons. First, ethanol and other alcohols should show intrinsic proton lifetimes of the same order as methanol which is obviously not the case [1, 2]. The slow proton exchange limit in ethanol is easily reached by purifying, which indicates that the proton lifetimes are at least 10 times greater than in methanol. A second argument results from our kinetic studies on double proton transfer and hydrogen bonding [23–25] between methanol and acetic acid in tetrahydrofuran, S, which takes place according to scheme II. It was shown that the



central exchange step is characterized by an activation energy of about 27 kJ mol^{-1} and a pre-exponential factor of about $\log A = 10$. For a cyclic process involving only methanol mole-

cules we should, therefore, expect a much higher energy of activation than the observed value given in Eq. (5). The observed value of $\log A = 6$ in Eq. (5) is, similarly, far too low for a cyclic process in a hydrogen bonded intermediate. In consequence, the cyclic exchange mechanism must be rejected.

4.2. Intrinsic Ion Catalyzed Exchange Mechanism in Pure Methanol and Water

In this section we examine the ion catalyzed mechanism. It will be treated in a form valid for any pure protic system AH. Its extension to binary and ternary systems is straightforward.

By consideration of the kinetic results for buffered protic systems [8–13] the total rate v of proton exchange is given by

$$v = \frac{C_{AH}^0}{\tau} = k_1^* C_{AH}^0 C_{AH_2^+} + k_2^* C_{AH}^0 C_{A^-} + k_d^* C_{AH}^0{}^2 \\ = k_1 C_{AH_2^+} + k_2 C_{A^-} + k_d. \quad (6)$$

$C_{AH_2^+}$ and C_{A^-} are the concentrations of the ions, C_{AH}^0 is the solvent concentration in the pure liquid given by

$$C_{AH}^0 = \frac{\rho}{M}, \quad (7)$$

where M is the molar mass of AH and ρ the density.

For the sake of generality, at this stage we shall leave open the question whether the ions are added to the solvent or whether they have been created by autoprotolysis, as represented by the last term in Eq. (6). At 298 K, k_1 and k_2 are given for methanol according to Grunwald et al. [11] by

$$k_1 = 8.8 \cdot 10^{10} \text{ s}^{-1}, \quad k_2 = 1.85 \cdot 10^{10} \text{ s}^{-1}. \quad (8)$$

k_d is the dissociation rate constant. The intrinsic concentrations of AH_2^+ and A^- are given by the molar autoprotolysis constant, K' :

$$K' = \frac{k_d}{k_n} = \rho^2 K = C_{AH_2^+} \cdot C_{A^-}. \quad (9)$$

k_n is the neutralisation rate constant and K the molal autoprotolysis constant. For methanol, several authors have reported values for K as a function of the temperature [37]. We will refer here to the data of Leung and Grunwald [40] which may be expressed by the equation:

$$K = (4.039 \cdot 10^{-15} - 6.686 \cdot 10^{-17} T/K + 4.161 \cdot 10^{-19} (T/K)^2 \\ - 1.154 \cdot 10^{-21} (T/K)^3 + 1.204 \cdot 10^{-24} (T/K)^4) \text{ mol}^2 \text{ kg}^{-2}, \\ 183 < T < 306 \text{ K}. \quad (10)$$

Using Eqs. (9) and (10) the third term in Eq. (6) can be estimated for methanol from the diffusion controlled rate constant $k_n = 4.3 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ for the ion recombination between AH_2^+ and the picrate ion in methanol measured by Strobusch et al. [41]. We obtain a value of the order of $10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$ for the last term in Eq. (6); this can be safely neglected. For water, one obtains a similar result. We shall now follow a very useful definition of Hertz [33] and introduce the difference Δx of the molal ion concentrations

$$\Delta x = x_{AH_2^+} - x_{A^-} = \frac{1}{\rho} (C_{AH_2^+} - C_{A^-}). \quad (11)$$

Positive Δx represent the molal concentrations of an added acid HX, negative Δx the molal concentrations of a base MA added to the pure solvent HA. MX is a salt. The pure solvent is characterized by $\Delta x = 0$. It is useful to define the quantity

$$f = k_2/k_1 \quad (12)$$

which has the value of 0.21 for methanol as calculated from Eq. (8). By combination of the Eqs. (6), (7), (9), (11), and (12) we obtain

$$\tau^{-1} = k_1(1+f)M \left[\left(K + \frac{\Delta x^2}{4} \right)^{1/2} + \frac{\Delta x}{2} \frac{1-f}{1+f} \right]. \quad (13)$$

For $|\Delta x| \gg K^{1/2}$ this equation reduces to

$$\tau^{-1} = k_1 M \Delta x \approx k_1 M x_{AH_2^+} = M x_{AH_2^+} A_1 \exp(-E_1/RT) \quad (14)$$

if $\Delta x > 0$ and to

$$\tau^{-1} = k_2 M \Delta x \approx k_2 M x_{A^-} = M x_{A^-} A_2 \exp(-E_2/RT) \quad (15)$$

if $\Delta x < 0$. For water E_1 and E_2 were found to be equal [9] within the margin of error and, therefore, we can assume temperature independent values for f . For $|\Delta x| \ll K^{1/2}$, i.e. for $\Delta x \rightarrow 0$ Eq. (13) reduces to

$$\tau_0^{-1} = k_1(1+f)MK^{1/2} = (k_1 + k_2)K^{1/2}/C_{AH}^0. \quad (16)$$

By introducing the van't Hoff law of autoprotolysis into Eq. (16) one obtains

$$\tau_0^{-1} = M(1+f)A_1 \exp(\Delta S/2R) \exp(-(E_1 + \Delta H/2)/RT), \quad (17)$$

from which we deduce

$$E_a = E_1 + \frac{\Delta H}{2}. \quad (18)$$

A useful combination of Eqs. (13) and (16) is

$$\tau^{-1} = \tau_0^{-1} K^{-1/2} \left[\left(K + \frac{\Delta x^2}{4} \right)^{1/2} + \frac{\Delta x}{2} \frac{1-f}{1+f} \right]. \quad (19)$$

Using Eqs. (5a) and (9) we are able to calculate τ^{-1} as a function of the temperature for different values of Δx . The resulting Arrhenius curves are shown in Fig. 4. Curve a represents our

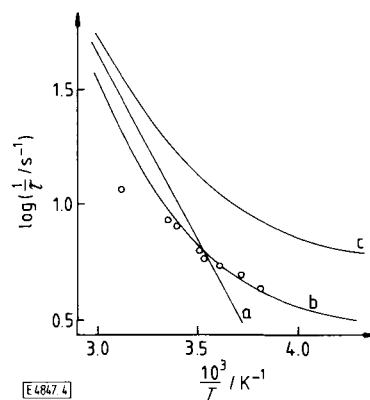


Fig. 4

Calculated Arrhenius curves of proton exchange in methanol according to Eq. (19). a) Pure methanol with $\Delta x = 0$ as defined in Eq. (13); b) basic methanol solution with $\Delta x = -1.2 \cdot 10^{-8} \text{ mol kg}^{-1}$; c) acid solution with $\Delta x = 5 \cdot 10^{-9} \text{ mol kg}^{-1}$; the circles represent values obtained by Versmold and Yoon [19] for slightly basic solutions

experimental values for pure methanol with $\Delta x = 0$, given in Eq. (5a). Curve c is calculated from Eq. (19) for an acidic solution with $\Delta x = 5 \cdot 10^{-9} \text{ mol kg}^{-1}$, curve b represents a basic solution with $\Delta x = -1.2 \cdot 10^{-8} \text{ mol kg}^{-1}$. At low temperatures the curves b and c are well represented by Eqs. (14) and (15), respectively, i.e. low energies of activation are found in the presence of added HX or MA. At high temperatures the consequence of the enhanced autoprotolysis is $x_{\text{AH}_2^+} \approx x_{\text{A}^-} \gg \Delta x$ and all curves are well represented by Eq. (17). The observed energy of activation now increases by the half of the dissociation enthalpy ΔH , as shown in Eq. (18). With $E_1 = 8 \text{ kJ mol}^{-1}$ according to Ref. [11], and $\Delta H = 45 \text{ kJ mol}^{-1}$, calculated from eq. (10) (see also Ref. [37]), we obtain $E_0^{\text{H}} = 30 \text{ kJ mol}^{-1}$ which fits our experiments very well as shown in Eq. (5a). At intermediate temperatures the curves in Fig. 4 are concave. Curve b shows a particularly interesting behaviour which arises from the fact that $k_1 \neq k_2$. The lifetimes τ for the slightly basic solutions are longer than the lifetimes for pure methanol. By differentiating Eq. (13) vs. Δx we obtain the conditions for $(\tau^{-1})_{\min}$

$$\Delta x = (f - 1) \left(\frac{K}{f} \right)^{1/2}$$

with

$$(\tau^{-1})_{\min} = \tau_0^{-1} \frac{2\sqrt{f}}{1+f} = 2(k_1^* k_2^* K')^{1/2}.$$

The right side of this equation is equivalent to an expression derived by Hertz [33c]. Though in the basic solution the proton exchange is predicted to be slower than in the pure solvent, the energy of activation is still lower for the basic solution than for the pure solvent at the section point of the corresponding curves a and b as shown in Fig. 4. This result is understandable only with the ansatz of Eq. (6) in which intrinsic ions and added are treated equally. If the intrinsic proton exchange were not catalyzed by the free solvated ions generated by autoprotolysis but took place in a neutral hydrogen bonded cluster the addition of slight traces of bases MA would *never* decrease but *always* increase the total proton exchange rate. This prediction is supported by the findings of Versmold and Yoon [19]. Their experimental proton lifetimes for very weak basic solutions, which were obtained by adding small quantities of 10^{-6} molar solutions of NaOCH_3 in methanol to pure methanol are indicated in Fig. 4 as circles. The values are well represented by curve b except for one point at high temperatures which could, however, arise from a combination of slight systematic and random errors.

From our experimental data given in Eq. (5a) and the autoprotolysis constants of Eq. (9) we are now able to determine $k_1 + k_2$ as a function of the temperature using Eq. (16). The data are given in Table 1 and the corresponding Arrhenius curve in Fig. 5. We obtain

$$k_1 + k_2 = 10^{12.3 \pm 0.3} \exp(-7.7 \pm 0.5 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}, \quad 290 < T < 340 \text{ K}. \quad (20)$$

with

$$(k_1 + k_2)_{298 \text{ K}} = 9.3 \cdot 10^{10} \text{ s}^{-1}.$$

This value compares well with the corresponding value of $10.6 \cdot 10^{10} \text{ s}^{-1}$ found by Grunwald et al. [11] for buffered methanol

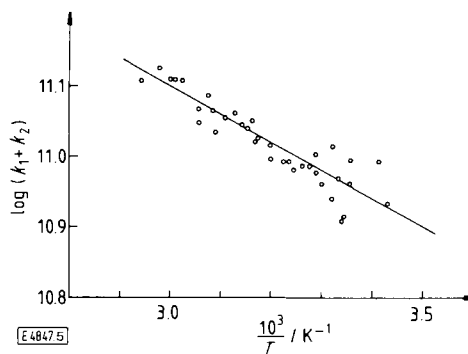


Fig. 5

Arrhenius diagram (Eq. (20)) of the elementary proton transfer in methanol according to Eqs. (2) and (3)

solutions at different pH's expressed by Eq. (8). The energy of activation agrees equally well with the value of $E_1 = 8 \text{ kJ mol}^{-1}$ given by the same authors [11]. It follows that it is possible to predict the intrinsic proton lifetimes for any protic system using Eq. (16) if the autoprotolysis constant and the values of k_1 and k_2 are known from the study of buffered solutions. For water these values were measured by Tewari and Glick [9], and may be expressed in the form

$$(k_1 + k_2)/\text{C}_{\text{H}_2\text{O}} = 10^{12.0} \exp(-11 \text{ kJ mol}^{-1}/RT) \text{ l mol}^{-1} \text{ s}^{-1}. \quad (21)$$

The dependence of the molar autoprotolysis constant of water [37] is given by

$$K' = 10^{-4.23} \exp(-56 \text{ kJ mol}^{-1}/RT) \text{ mol}^2 \text{ l}^{-2}. \quad (22)$$

Substituting Eqs. (21) and (22) in Eq. (16) one obtains

$$\tau_0^{-1} = 10^{9.9} \exp(-39 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}. \quad (23)$$

In Fig. 6 the Arrhenius curve Eq. (23) is shown as a straight line and compared with the experimental values from Refs. [13] and [14]. There is a close agreement between the experimental values and the predicted curve especially at high temperatures as expected from Eq. (19). At lower temperatures positive deviations are observed which can be explained by the presence of very small traces of basic or acid impurities in the samples. However, as pointed out by Hertz [33] and Graf et al. [14], it is

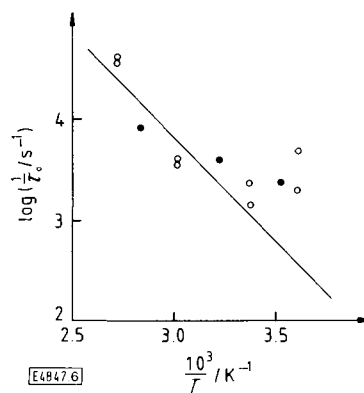


Fig. 6

Arrhenius diagram of proton exchange in pure water. The straight line was calculated from Eq. (23). ○: Experimental values of Knispel and Pintar [13], ●: experimental values of Graf et al. [14]

possible that the scattering of the data of Pintar and Knispel [13] arises from systematic errors. The high energies of activation of about 42 kJ mol⁻¹ for proton exchange in ethanol/water [16] and isopropanol/water [17, 18] can be interpreted in a similar way. The slow exchange in ethanol seems then to be the consequence of the low dielectric constant, which leads to large negative dissociation entropies [37].

4.3. Relation between $k_1 + k_2$ and the Neutralization Rate Constant

Since the kinetic isotope effects of k_1 and k_2 have not been measured directly but can only be estimated for water from the conductivity data of Eigen et al. [7] it is useful for the discussion of our experimental data given in Eq. (5) to establish a relation between k_1 , k_2 and the neutralisation rate constant, k_n , for k_n^H/k_n^D was measured directly at least for pure water [5]. As was pointed out by Eigen et al. [4, 7], k_n , k_1 , and k_2 must be of the same order because the rate determining step of the neutralisation, i.e. the backward reaction in Eq. (4) is the formation of the ion pair via diffusion steps characterized by Eqs. (2) and (3). In fact, the energies of activation of these processes are equal for water [6, 9] as mentioned in section 1. In addition, k_n was shown to be related to the ion diffusion coefficients as evaluated from conductivity measurements via the Debye-Smoluchowsky theory of diffusion controlled ionic reactions [4, 5], and the diffusion coefficients are related to k_1 and k_2 . However, to our knowledge, k_n and $k_1 + k_2$ have not yet been interrelated. This can be done as follows.

The rate law of the neutralisation is given by [4]:

$$v_n = k_n \cdot C_{AH_2^+} \cdot C_{A^-}.$$

The total lifetime τ_i of the ion i depends on the concentration of the ion j :

$$\tau_i^{-1} = \frac{v_n}{C_i} = k_n C_j, \quad i, j = A^-, AH_2^+. \quad (24)$$

Consider now an initial state with $C_i = C_j$, which implies a final state without ions. For the neutralisation m proton transfer steps are necessary:



The mean time τ_s required for one step is given by

$$\tau_s^{-1} = k_1 + k_2 \quad (25)$$

because k_1^{-1} and k_2^{-1} are the mean times characterizing the proton transfer steps described by Eqs. (2) and (3). The neutralisation time τ_i is then m times the time τ_s of a single step. One obtains

$$m = \frac{\tau_i}{\tau_s} = \frac{k_1 + k_2}{k_n C_i}. \quad (26)$$

Since $E_n = E_1 = E_2$, m must be independent on the temperature in approximation. From the literature data we are able to compute m for water and for methanol at a given ion concentration. Since the rate constants used were derived from very dilute solutions where the attractive forces between the ions can be neglected i.e. where the activity coefficients are 1, low values of C_i should be chosen when applying Eq. (26). However, our approach here is to set $C_i = 1 \text{ mol l}^{-1}$ and to ignore the ionic

interactions. With the values of $k_n = 1.3 \cdot 10^{11} \text{ l mol s}^{-1}$, taken from Refs. [4–6], $k_1 + k_2 = 6.9 \cdot 10^{11} \text{ s}^{-1}$ for water according to Ref. [9], and using $k_n = 4.3 \cdot 10^{10} \text{ mol l}^{-1} \text{ s}^{-1}$ as obtained by Strobusch et al. [41] as a lower limit for methanol we obtain with Grunwald's [11] data (Eq. (8)) the values of $m(H_2O) = 5.3$ and $m(CH_3OH) = 2.5$. These values seem to correlate with the numbers of solvent molecules per volume, $C^0(H_2O) = 55 \text{ mol l}^{-1}$ and $C^0(CH_3OH) = 25 \text{ mol l}^{-1}$. However, the absolute values depend in a complicated way on the solvent structure. Since the neutralisation of A^- and AH_2^+ is controlled by the diffusion each encounter leads to the products. If for sterical or energetical reasons more encounters are necessary the mean number of proton transfer steps also increases. For example, proton transfer from $CH_3OH_2^+$ to pyridine in methanol is characterized by the rate constant $k_n = 1.57 \cdot 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ according to Marshall et al. [42]. The mean number of proton transfer steps is then about 7 as calculated from Eq. (26).

4.4. Interpretation of the Kinetic Isotope Effects in Terms of Equilibrium Autoprotolysis Isotope Effects

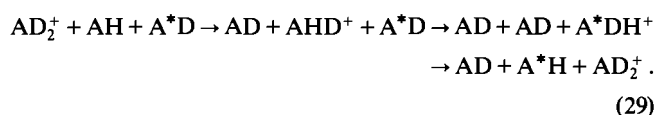
The deuteron lifetimes in CH_3OD are given in analogy to Eq. (6) by

$$\begin{aligned} v &= \frac{C_{AD}^0}{\tau^D} = k_1^{*D} C_{AD}^0 C_{AD_2^+} + k_2^{*D} C_{AD}^0 C_{A^-} \\ &= k_1^D C_{AD_2^+} + k_2^D C_{A^-} \end{aligned}$$

which leads for the pure solvent according to Eq. (16) in section 4.2 to

$$(\tau_0^D)^{-1} = \frac{k_1^D + k_2^D}{C_{AD}^0} \sqrt{K'^D}. \quad (27)$$

However, we have measured the lifetimes τ_0^{HD} of the residual CH_3OH protons in CH_3OD and not the lifetimes τ_0^D . We have then to establish the relation between these two quantities. It is obvious that the lifetimes τ_0^{HD} are determined by the following reactions:



The corresponding rate law of proton exchange in CH_3OD is then given by

$$\begin{aligned} v &= \frac{C_{AH}}{\tau^{HD}} = k_1^{*HD} C_{AH} C_{AD_2^+} + k_2^{*HD} C_{AH} C_{A^-} \\ &= k_1^{HD} \frac{C_{AH}}{C_{AD}^0} C_{AD_2^+} + k_2^{HD} \frac{C_{AH}}{C_{AD}^0} C_{A^-} \end{aligned} \quad (30)$$

from which it follows that

$$(\tau_0^{HD})^{-1} = \frac{k_1^{HD} + k_2^{HD}}{C_{AD}^0} \sqrt{K'^D}. \quad (31)$$

The relations between k_i^H , k_i^{HD} , and k_i^D depend on the mechanism of the proton transfer process. If the proton transfer were the rate determining step then $k_2^{HD} = k_2^H$. k_1^{HD} should lie somewhere between k_1^H and k_1^D because the exchange step in Eq. (29) is characterized by the jump of one proton and two deuterons.

For the structural diffusion mechanism as proposed by Eigen et al. [4, 7], however, $k_1^{\text{HD}} = k_1^{\text{D}}$ and $k_2^{\text{HD}} = k_2^{\text{D}}$ because the proton exchange rate constant is determined by the time constant of the change in the hydrogen bonded structure of CH_3OD and not of CH_3OH . The lifetime of the residual protons, τ_0^{HD} , equals then the intrinsic deuteron lifetimes, τ_0^{D} , as shown by comparison of Eqs. (27) and (31). The kinetic isotope effect of the neutralisation in water was found by Ertl and Gerischer [5] to have a value of about 1.7. By combining Eqs. (26), (27), and (31) we obtain with $C_{\text{AH}}^0 = C_{\text{AD}}^0$

$$1 \leq \frac{k_1^{\text{H}} + k_2^{\text{H}}}{k_1^{\text{HD}} + k_2^{\text{HD}}} \leq \frac{k_1^{\text{H}} + k_2^{\text{H}}}{k_1^{\text{D}} + k_2^{\text{D}}} = \frac{k_n^{\text{H}}}{k_n^{\text{D}}} \approx 1.7$$

or

$$\left(\frac{\tau_0^{\text{HD}}}{\tau_0^{\text{H}}}\right)^2 \geq \frac{K'^{\text{H}}}{K'^{\text{D}}} \geq \left(\frac{1}{1.7} \frac{\tau_0^{\text{HD}}}{\tau_0^{\text{H}}}\right)^2.$$

Using our experimental value given in Eq. (5c) we obtain

$$9 \geq \frac{K'^{\text{H}}}{K'^{\text{D}}} \geq 3.5$$

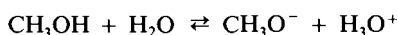
for methanol at 298 K. With a normal kinetic isotope effect of

$$\frac{k_1^{\text{HD}} + k_2^{\text{HD}}}{k_1^{\text{D}} + k_2^{\text{D}}} = \sqrt{2},$$

as expected from the reduced masses and as deduced by Eigen et al. [4, 7] from the isotope effect of the proton mobility and from the isotope effect of the water reorientation measured by the ultrasonic technique [43], we obtain for the most probable structural diffusion mechanism a value of

$$\frac{K'^{\text{H}}}{K'^{\text{D}}} = 5 \pm 0.5.$$

The corresponding value for water [37] is about 5. For methanol no data have yet been reported. For the reaction



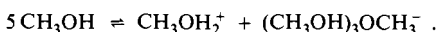
in mixtures of water and methanol George and Woolley [44] gave value of 6 ± 3 which is of the same order as our result.

5. Conclusions

It has been shown that it is possible to purify methanol to such an extent that the proton lifetimes as observed by dynamic NMR spectroscopy become the intrinsic proton lifetimes characteristic for the pure solvent. In pure methanol and, probably, also in other protic systems such as water, alcohols, amines or mixtures of these, the intrinsic exchange arises from free solvated ions generated by dissociation. From the change in the energy of activation of the proton exchange resulting from the addition of basic or acid impurities to the pure solvent the enthalpy and the entropy of the autoprotolysis can be obtained in a quite convenient way. The measurement of the lifetimes of the residual protons in the deuterated solvents leads then to the equilibrium isotope effects of the autoprotolysis. The method may be particularly applicable in binary or ternary systems and may be, by the same, taken for the determination of acid and basic impurities in the solvents.

Note added in proof:

Prof. V. Gold, London, has brought into our attention on NMR study with S. Grist [45] on CH_3OH chemical shifts in acidic and basic methanol solutions at different deuterium atom fractions. Mainly due to zero point energy differences of the OL stretching vibration [46] where L = H, D the hydrogen content of CH_3OL_2^+ and of the solvation shell of CH_3O^- is higher as expected for a statistical distribution. Assuming that CH_3O^- is hydrogen bonded to three solvent molecules because of its three electron lone pairs the autoprotolysis reaction can be written as



With this assumption Gold and Grist predicted an equilibrium isotope effect of $(K'_{\text{H}}/K'_{\text{D}})_{306.5\text{K}} = 6.3$ for the autoprotolysis of pure methanol. This value derived from salt containing solution agrees very well with our value of 5 at 298 K derived directly for pure methanol.

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