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Association of Mineral Acids with Water in Dioxan-Water Mixtures

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Mineral acids were found by cryoscopic measurements to be associated with water to a varying degree in dioxan-water mixtures of low-water content. Each perchloric acid molecule is associated with two water molecules even at the lowest concentrations studied whereas association between water and sulphuric or hydrochloric acid was observed only at somewhat higher water concentrations. The following equilibrium constants were evaluated: $K = [2H_2O{\cdot}2HCl]/[H_2O]^2 \cdot [HCl]^2 = 2.33\ M^{-3}$ and $K = [H_2O{\cdot}H_2SO_4]/[H_2O] \cdot [H_2SO_4] = 22\ M^{-1}$. Association to higher associates also takes place depending on the water concentration. Association of water molecules occurs also and the equilibrium constant for the formation of the n-mer from the monomer and an $(n - 1)$-mer is approximately constant, $K = 0.7\ M^{-1}$. Values of K_{BH^+} of 2,4-dichloroaniline extrapolated to zero acid concentration were derived for the whole range of solvent mixtures at 25°C. At low water concentrations the two water molecules associated with the perchloric acid molecule are liberated in the proton transfer reaction. The second order rate constant of the hydrolysis of 1,1-dimethoxyethane catalysed by perchloric acid changes in a similar manner as K_{BH^+} of the dichloroaniline in dioxan-water mixtures. It is concluded that no water is involved in the transition state and that the mechanism is unimolecular in agreement with previous results. It is proposed that kinetic experiments combined with studies of protolytic equilibria can be used to determine the order of an acid-catalysed solvolysis reaction with respect to the hydroxylic reagent.

Previous work[1–7] has shown that kinetic measurements of acid catalysed reactions in dioxan-water mixtures at low water concentrations are useful when studying reaction mechanisms. The present investigation was undertaken in order to obtain more information about the state of mineral acids in dioxan-water mixtures.

EXPERIMENTAL

Materials. Dioxan (Fluka AG, purified by the method of Hess and Frahm) was retreated by the method of Hess and Frahm.[8] The water used had been freshly distilled and purified with ion-exchange resins. Sodium chloride, hydrochloric acid 30 %, perchloric acid 70 % and sulphuric acid 98 % (all guaranteed reagents from E. Merck AG) were used as received. 2,4-Dichloroaniline (Fluka AG) was recrystallised from methanol; m.p. 61.5—62°C. 1,1-Dimethoxyethane (Fluka AG) was distilled before use.

Cryoscopic measurements. The experiments were performed in a glass tube to which a Beckman thermometer was fitted. In each series of measurements either known volumes of the acids were added from a micro syringe or weighed amounts of solvent were transferred to the solution in the tube. The solution was cooled slowly in an ice bath while being stirred with a magnetic stirrer. The degree of supercooling was taken into account in the calculation of the concentrations at the freezing point. Each measurement was repeated until a constant freezing point was recorded.

Calculations. Solutions of water in dioxan. Previous investigations of Virtanen [9] and others (for references, see Ref. 9) have shown that association of water occurs when water is dissolved in dioxan. The equation

$$\Delta t^\circ = 4.83\, y - 3.4\, y^2 + 3.5\, y^3 - 1.6\, y^4 \tag{1}$$

where Δt° is the freezing point depression and y the analytical concentration of water, was derived from the experimental data. The sum a of the concentrations of the monomer and various associates of water is given by $a = \Delta t^\circ/4.83$ where 4.83 is the molal freezing point depression of dioxan.[8] When Δt° is substituted in eqn. (1), it is found that

$$a = y - 0.704\, y^2 + 0.724\, y^3 - 0.331\, y^4 \tag{2}$$

The association of water to dimers, trimers, *etc.*, is defined by the equilibrium constants

$$\begin{aligned} K_2 &= [(H_2O)_2]/[H_2O]^2 \\ K_3 &= [(H_2O)_3]/[H_2O]^3 \end{aligned} \tag{3}$$

The sum a of the concentrations of the monomer and various associates of water is then

$$a = x + K_2x^2 + K_3x^3 + K_4x^4 + \ldots \tag{4}$$

where x is the concentration of monomeric water and K_2, K_3, etc., equilibrium constants for the formation of dimers, trimers, *etc.* The analytical concentration y of water is

$$y = x + 2K_2x^2 + 3K_3x_3 + 4\,K_4x^4 + \ldots \tag{5}$$

These values of y are substituted into eqn. (2) and the terms containing x^5 and higher powers are neglected. The coefficients of this equation are compared with the respective coefficients of eqn. (4). Values of the equilibrium constants obtained on solving these equations are $K_2 = 0.704$ M^{-1}, $K_3 = 0.620$ M^{-2}, and $K_4 = 0.404$ M^{-3}(M = moles/kg). The values obtained show that in the concentration range from 0.1 M to 0.8 M water in dioxan higher terms than those containing x^5 are not needed. These equilibrium constants yield freezing point depressions that are in satisfactory agreement with the experimental results. Some of the results are shown in Table 1.

Somewhat different values for the equilibrium constants of the various associates have been obtained by other authors; *e.g.* Virtanen [9] reported $K_2 = 0.385$ M^{-1} and $K_3 = 0.440$ M^{-1}. However, he used another method of calculation and neglected the possible formation of tetramers and higher polymers of water. It is not possible to decide whether the formation of these higher polymers should be taken into account in the calculations, but there seems to be no reason why the association of water should not proceed to higher polymers.

The activities of water in dioxan were measured by Niini.[10] These values can be used to calculate the equilibrium constants of the association of water by a method similar to that used above. The values $K_2 = 0.136$ M^{-1}, $K_3 = 0.050$ M^{-2}, and $K_4 = 0.025$ M^{-3}

Table 1.

y	0.1161	0.2738	0.4901	0.5626
a	0.1076	0.2338	0.3834	0.7855
Δt°exptl.	0.517	1.123	1.890	2.749
Δt°calc.	0.520	1.129	1.852	2.717
Difference	0.003	0.006	−0.042	−0.032

Table 2.

[HCl] anal.	0.197	0.226	0.263	0.315	0.394	0.524
[HCl] exptl.	0.199	0.224	0.253	0.301	0.476	0.500
Difference	−0.002	0.002	0.010	0.014	0.018	0.024

at 25°C are obtained. These values are smaller than the values obtained from freezing point data, the differences being possibly due to the different temperatures. A large temperature effect also leads to an error in the values calculated from freezing point data because the temperature is not constant in a series of measurements.

Solutions of hydrogen chloride in dioxan. In dioxan containing small amounts of water, mineral acids are associated with water to varying degrees and the tendency to form associates decreases in the order $HClO_4 > H_2SO_4 > HCl$. Hydrogen chloride is present as the monomer in dry dioxan, at least up to a concentration of 0.5 M.

Equation [HCl] exp. $= \Delta t^\circ/4.83$ was used to obtain the values in Table 2. The results are in agreement with the results of Virtanen.[9]

The tendency of hydrogen chloride to associate with water increases with increasing concentration of water in dioxan. When $[HCl] + [H_2O]$ is less than about 0.2 M in dioxan, the association of water and hydrogen chloride occurs to an extent of less than about 1 % as determined by cryoscopic measurements on solutions in which the ratio $[HCl]/[H_2O]$ varied from 0.3 to 3. Cryoscopic measurements indicate an association of hydrogen chloride and water in more concentrated solutions. Two equilibria were considered:

$$H_2O + HCl = H_2O{\cdot}HCl \qquad K_3 = [H_2O{\cdot}HCl]/[H_2O]{\cdot}[HCl] \tag{6}$$

$$2H_2O + 2HCl = 2H_2O{\cdot}2HCl \qquad K_2 = [2H_2O{\cdot}2HCl]/[H_2O]^2{\cdot}[HCl]^2 \tag{7}$$

Values of K_1 and K_2 were calculated from the cryoscopic data assuming that either reaction (6) or reaction (7) takes place. The association of water was taken into account in the calculations.

The values of K_1 increase but the values of K_2 remain approximately constant when the concentrations of water and hydrogen chloride in dioxan are increased. Reaction (7) then describes better than reaction (6) the association of water and hydrogen chloride in the concentration range studied. The associates first formed are probably highly polar and resemble an ion pair ($H_3O^+Cl^-$). They are therefore dimerised to a large extent in a solvent of low dielectric constant such as dioxan. Values of K_2 calculated from several experiments with $[HCl]/[H_2O]$ varying from 0.6 to 1.4 gave similar results as shown in Table 3; the mean values varied between 2.2 and 2.6. The mean of all experimental values is $K_2 = 2.33$ M^{-3}. It is likely that with increasing acid and water concentrations even higher associates and also the free ions occur to an increasing extent.

Table 3.

[HCl] anal.	0.197	0.223	0.263	0.318	0.387	0.513
$[H_2O]$ anal.	0.160	0.182	0.214	0.259	0.315	0.418
$[HCl] + [H_2O]$ anal.	0.357	0.405	0.477	0.577	0.702	0.931
$\Delta t^0/4.83$ M^{-1}	0.297	0.332	0.372	0.420	0.479	0.574
Difference	0.060	0.073	0.105	0.157	0.223	0.357
K_1 M^{-1}	1.80	1.78	2.45	3.70	4.38	9.70
K_2 M^{-3}	2.48	2.20	2.28	2.50	2.46	2.75

Solutions of sulphuric acid in dioxan. The extent of association of sulphuric acid and water increases with increasing water concentration. At low water concentrations sulphuric acid is more strongly associated with water than hydrogen chloride is. When the sum of the concentrations of the acid and water $[H_2SO_4] + [H_2O]$ is less than about 0.05 M, less than 5 % of the acid is associated with water. At higher concentrations association occurs to an increasing extent and the following reaction may occur.

$$H_2O + H_2SO_4 = H_2O{\cdot}H_2SO_4,\ K = [H_2O{\cdot}H_2SO_4]/[H_2O]{\cdot}[H_2SO_4] \tag{8}$$

Table 4.

$[H_2SO_4]$ anal.	0.006	0.023	0.075	0.115	0.172	0.229
$[H_2O]$ anal.	0.007	0.028	0.093	0.142	0.213	0.284
$[H_2SO_4] + [H_2O]$ anal.	0.013	0.051	0.168	0.257	0.385	0.513
$\Delta t^0/4.83$ M^{-1}	0.011	0.047	0.119	0.116	0.226	0.280
Difference	0.002	0.004	0.049	0.091	0.159	0.233
K M^{-1}			29.1	25.2	27.9	22.2

When the total concentration of $[H_2O] + [H_2SO_4]$ varies from about 0.2 M to about 0.5 M, the association occurs according to eqn. (8), but at higher concentrations, higher associates are formed. Values of K similar to those given in Table 4 were obtained from data for solutions with $[H_2SO_4]/[H_2O]$ ratios from 1.4 to 0.4; the mean value of K was 22 M^{-1}.

Solutions of perchloric acid in dioxan. Solutions of perchloric acid in dioxan containing more than two moles of water per mole of perchloric acid are sufficiently stable for cryoscopic measurements. Perchloric acid is much more strongly associated with water than the other acids studied. Already at the lowest acid and water concentrations, $[H_2O] + [HClO_4]$ varying from 0.01 to 0.03 M and $[H_2O]/[HClO_4]$ from 2.6 to 6.5, each perchloric acid molecule is associated with two water molecules. At higher concentrations association proceeds to higher complexes.

Table 5.

$[HClO_4]$ anal.	0.009	0.017	0.026	0.002	0.0048	0.010
$[H_2O]$ anal.	0.022	0.045	0.067	0.015	0.031	0.062
$[2H_2O{\cdot}HClO_4] + [H_2O]$	0.014	0.028	0.041	0.013	0.026	0.052
$\Delta t^0/4.83$ M^{-1}	0.016	0.027	0.037	0.013	0.024	0.046
Difference	−0.002	0.001	0.004	0.000	0.002	0.006

Only part of the experimental results are shown in Table 5. These results already show that the cryoscopic measurements are in agreement with the values calculated assuming the perchloric acid to be completely in the form of associates $2H_2O{\cdot}HClO_4$. Attempts to calculate equilibrium constants for various possible higher associates were unsuccessful, as satisfactorily constant equilibrium constants were not obtained. This is probably due to simultaneous formation of several higher associates together with the formation of associates of water. An approximate value of about $K = 40$ M^{-1} was obtained for the equilibrium constant $K = [3H_2O{\cdot}HClO_4]/[2H_2O{\cdot}HClO_4]_2[H_2O]$.

Acid-base equilibrium measurements. Optical densities of 0.002 M solutions of 2,4-dichloroaniline in dioxan-water mixtures containing weighed amounts of perchloric acid and those of solutions containing equal amounts of the acid but no 2,4-dichloroaniline were measured at the wavelengths of maximum absorbance with a Beckman DU spectrometer using 1 cm cells. The wavelength of maximum absorbance varied from 3000 Å to 3070 Å in the range of solvent mixtures used in the present work. Several measurements were made on solvent mixtures of constant water concentration in which the acid concentration was varied more than 20-fold. The acid constant of 2,4-dichloroaniline was calculated by fitting the equation

$$K_{BH^+} = I\left([HClO_4] - \frac{[B]}{I+1}\right) \qquad (9)$$

where I is the ratio $I = (E - E_{BH^+})/(E_B - E)$ and [B] the concentration of 2,4-dichloroaniline. The term in brackets is the concentration of unreacted perchloric acid in the solution. The absorbance of the base E_B and the conjugate acid E_{BH^+} were obtained by measuring the absorbances of solutions containing no and a large excess of perchloric acid, respectively.

The values of K_{BH^+} were satisfactorily constant in both water-rich or dioxan-rich solvent mixtures over the whole range of perchloric acid concentrations used in the

Table 6. Acid constants K_{BH^+} of 2,4-dichloroaniline in dioxan-water mixtures extrapolated to zero perchloric acid concentration at 25°C.

H_2O wt. %	$[H_2O]$ M	K_{BH^+} M	pK_{BH^+}	$2\log[H_2O] + pK_{BH^+}$	$-\frac{dK_{BH^+}}{d[HClO_4]}$
0.093	0.053	0.000054	4.27	1.72	0
0.194	0.111	0.00025	3.60	1.69	0
0.394	0.225	0.00083	3.08	1.78	0.06
0.832	0.475	0.00475	2.33	1.68	0.12
1.65	0.941	0.0240	1.62	1.57	0.31
3.26	1.86	0.090	1.05	1.59	0.48
6.26	3.58	0.200	0.70	1.81	0.55
16.67	9.56	0.73	0.14	2.10	1.44
33.50	19.26	0.365	0.44		0.40
60.00	34.23	0.083	1.08		0.12
80.01	45.95	0.0203	1.69		0
100	55.33	0.0080	2.10		0

experiments. The values of K_{BH^+} in the intermediate solvent mixtures decreased approximately linearly with increasing perchloric acid concentration. Values of K_{BH^+} obtained by extrapolation to zero acid concentration are shown together with the values of the slope $dK_{BH^+}/d[HClO_4]$ in Table 6. The changes in the values of K_{BH^+} are probably due to variations in the degree of dissociation of the ion pairs and to a possible association of the ion pairs to higher associates. Free ions are dominate in water-rich solvent mixtures and ions pairs in dioxan-rich solvent mixtures and K_{BH^+} is constant over a wide range of perchloric acid concentrations. The change of the values of K_{BH^+} observed in the intermediate range of solvent mixtures is also partly due to a decrease in the concentration of free water with increasing perchloric acid concentration due to $HClO_4-H_2O$ association. The values of K_{BH^+} decrease rapidly with water concentration.

Kinetic measurements. The kinetic measurements were performed in vapour-free reaction vessels as described previously.[1] Acetaldehyde produced in the reaction was analysed by the bisulphite method.[7] The final value was taken after at least 10 times the half-life of the reaction. The rate constants were calculated from the first-order rate equation except for the reactions in dioxan containing only small amounts of water in which case the reverse reaction had to be taken into account.

Table 7. Rate constants of the hydrolysis 1,1-dimethoxyethane in dioxan-water mixtures at 20°C. Initial acetal concentration 0.05 M.

$[H_2O]$ M	$[HClO_4]$ M	$10^2k_{H^+}$ $M^{-1}s^{-1}$	pK_{BH^+}	$pK_{BH^+} - \log k_{H^+}$	K
55.5	0.00051	17.4	2.09	0.89	
44.4	0.00051	9.70	1.69	0.70	
33.3	0.00051	4.46	0.98	0.33	
22.2	0.00051	1.66	0.52	0.30	
11.1	0.00051	0.69	0.14	0.30	
5.55	0.00051	1.10	0.36	0.32	
2.22	0.00021	2.84	0.92	0.47	
1.11	0.00010	10.1	1.48	0.48	
0.55	0.000051	46.9	2.20	0.53	
0.22	0.000021	458	3.04	0.43	0.56
0.11	0.000010	1650	3.61	0.40	0.34

$$\frac{dx}{dt} = k_1 (a - x) - k_{-1} x^2 \tag{10}$$

The equation was integrated and rearranged to

$$k_1 = \frac{1}{t'} \ln \frac{a}{a - x} \tag{11}$$

where

$$t' = t - K' \int \frac{x^2}{a - x} dt \tag{12}$$

and

$$K' = \frac{k_{-1}}{k_1} = \frac{[\text{acetaldehyde}] [\text{ROH}]}{[\text{acetal}]} \tag{13}$$

Values of K' were calculated from the final values of the kinetic experiments and the values of t' were evaluated graphically. The calculated values of k_1 were satisfactorily constant in each run. The second-order rate constants k_{H+} were calculated by dividing the first-order rate constant by the perchloric acid concentration. Values of k_{H+} together with those of $K = K'/[H_2O]$ are given in Table 7.

DISCUSSION

Cryoscopic measurements. The acid strengths of mineral acids in dioxan containing low concentrations of water as measured[5] by their ability to protonate 2-chloroaniline increase in the order $HCl < H_2SO_4 < HClO_4$. The presented cryoscopic data for the same solvent mixtures show that the extent of association of mineral acids with water increases in the same order, perchloric acid being the acid most strongly associated with water in dioxan. Already at very low concentrations (0.002 to 0.01 M) of water in dioxan, each perchloric acid molecule is associated with two water molecules. It is possible that perchloric acid is fully ionised in dioxan of low water content, the proton being attached to two water molecules in the ion pair $H_5O_2^+ \cdot ClO_4^-$. At higher water concentrations additional water molecules are associated with the ion pair, and this leads to an increased degree of dissociation of the ion pairs. When the amount of water present is less than two moles per mole of perchloric acid, associates with two or more water molecules cannot be formed and the high oxidizing power of perchloric acid in anhydrous media is probably due to an increased degree of protonation of organic molecules in the absence of water.

The acid strength of sulphuric acid in dioxan containing low concentrations of water is much weaker than that of perchloric acid.[5] The formation of sulphuric acid-water associates in dioxan occurs to a much smaller extent than the formation of perchloric acid-water associates. In dioxan containing 0.01 to 0.05 M H_2O and 0.002 to 0.02 M H_2SO_4, only sulphuric acid and water monomers are found to exist cryoscopically. It is therefore concluded that sulphuric acid is present mainly as unionised molecules in dioxan containing low concentrations of water. With increasing water concentration $H_2O \cdot H_2SO_4$ associates and also higher ones are formed. The equilibrium constant K for the dimer formation is 22 M^{-1} at about 11°C. It is not possible to decide whether a charge distribution corresponding to a hydrogen bond or an ion pair structure dominates in the $H_2O \cdot H_2SO_4$ associate.

Hydrogen chloride is even weaker an acid than sulphuric acid in dioxan containing low concentrations of water and cryoscopic measurements show that it is associated with water to even a lesser extent than sulphuric acid. Association of hydrogen chloride occurs to a very small extent, if at all, at concentrations from 0.1 to 0.4 M in anhydrous dioxan and at least 95 % of the acid is present as monomers as already observed by Virtanen.[9] When the concentration of water in dioxan exceeds 0.1 M, a marked association of water and hydrogen chloride occurs. The main product seems to be the tetramer $2H_2O{\cdot}2HCl$. The equilibrium constant of the formation of this associate is 2.43 M^{-3} (eqn. (7)). At water concentrations higher than about 0.4 M, higher associates are also present. The associate is possibly a dimer of an intimate ion pair $H_3O^+{\cdot}Cl^-$. Such associates would be expected to be formed by two highly polar dipoles in solvents of low dielectric constant when their concentrations are fairly high as in the present case.

When water is dissolved in dioxan, water-dioxan associates dominate in dilute solutions. At higher water concentrations water polymers are also formed. No associate seems to be specially favoured and several polymers seem to be present simultaneously. An analysis of the cryoscopic data gave the values $K_2 = 0.70\ M^{-1}$, $K_3 = 0.62\ M^{-2}$, and $K_4 = 0.40\ M^{-3}$ for the equilibrium constants of the formation of water dimers, trimers and tetramers from the monomer in dioxan. Also higher associates may be formed, but the present results do not allow a calculation of the equilibrium constants of these associates.

Equilibrium constants $K_{n-1,n}$ for the formation of n-mers from $(n - 1)$-mers and the water monomer calculated from the given equilibrium constants are $K_{12} = K_2 = 0.70$, $K_{23} = K_3/K_2 = 0.88$, and $K_{34} = K_4/K_3 = 0.65\ M^{-1}$. These are approximately constant and show that no associate is favoured more than any other. The fraction of hydrogen atoms in the water molecules that is not involved in hydrogen bonding would be expected to be small. Reaction (3) should then be written

$$2\ \mathrm{ORO\cdots HOH\cdots ORO = ORO\cdots HOH\cdots ORO\cdots HOH\cdots ORO + ORO} \tag{14}$$

$$\text{or } 2\ \mathrm{ORO\cdots HOH\cdots ORO = ORO\cdots \underset{\underset{\displaystyle HOH\cdots ORO}{\vdots}}{HOH}\cdots ORO + ORO} \tag{15}$$

The equilibrium constants K_2' of these reactions obtained by multiplying K_2 by the concentration of dioxan (ORO) is $11.7 \times 0.70 = 8.2$. If the reaction occurs according to eqn. (14), a value of about 1 is expected for K_2' because similar hydrogen bonds are involved in both the monomer and dimer. A statistical correction of $8.2/2 = 4.1$ does not either explain the difference. The large value obtained for K_2' can be explained if the bond uniting a hydrogen atom to a water oxygen is more stable than the bond uniting a hydrogen atom to the oxygen atom in dioxan. Both reactions (14) and (15) occur simultaneously, but reaction (14) is favoured over reaction (15) by a factor of about 4.

Acid-base equilibria. In a previous study [5] the acid constants of 2-chloroaniline in dioxan-water mixtures at 20°C were measured. The experimental method was somewhat different from that used in the present work. The water concentration was not kept constant, but increased with increasing acid concentration, whereas in the present study the water concentration was kept constant and the acid concentration was varied. This difference may explain why constant values of K_{BH^+} were obtained in the previous work but not in the present work when the acid concentration was varied. It was necessary to extrapolate the values obtained in the present study to zero acid concentration.

The values given in Table 6 show that the value of pK_{BH^+} of 2,4-dichloroaniline is a minimum in the dioxan-water mixture in which the water concentration is about 10 M. The pK_{BH^+} value increases linearly with decreasing log $[H_2O]$ at low water concentrations. The slope is approximately -2.0 as indicated by the approximately constant values of the expression $2 \cdot \log [H_2O] + pK_{BH^+}$ given in Table 6. A value of the slope was found to be -1.9 for 2-chloroaniline [5] and -1.7 for acetamide and N,N-dimethylacetamide.[6] These values show that two water molecules are liberated when a proton is transferred from perchloric acid to a base in dioxan-water mixtures from 0.05 to 3 M in water. Cryoscopic measurements showed that two water molecules are associated with one perchloric acid molecule in dioxan containing less water than about 0.05 M. These two water molecules are then liberated in the proton transfer reaction. As it is not likely that a base is associated with water molecules at these low concentrations of water in dioxan, the protonated base is not either associated with water molecules. At higher water concentrations perchloric acid would be expected to be associated with more than two water molecules as indicated by the cryoscopic measurements, but only two water molecules are liberated in the proton transfer reaction. It then seems that the proton is associated with two water molecules which are liberated when the proton is transferred to the base.

Kinetic measurements. The second-order rate constants of hydrolysis of 1,1-dimethoxyethane catalysed by perchloric acid in dioxan-water mixtures at 20°C show a deep minimum when the water concentration is about 10 M. A similar minimum value is also observed for the acid constant K_{BH^+} of 2,4-dichloroaniline. Values of log k_{B^+} — pK_{BH^+} remain almost constant over the whole range of solvent mixtures in spite of the large changes observed in k_{H^+} and K_{BH^+} in these mixtures. The large changes in the rate of acid hydrolysis of dimethoxyethane are then due mainly to changes in the protonation equilibria of dimethoxyethane; the rate constant of protonated dimethoxyethane remains almost constant in dioxan-water mixtures. This is to be expected for a reaction taking place by the unimolecular A1 mechanism. The unimolecular mechanism has been confirmed for dimethoxyethane also in previous studies.[7] As has been shown already by previous work,[1-7] comparison of the variation of the rate constant of the acid hydrolysis with the variation of the acid constant of base in the same solvent mixtures offers a useful tool for determining the mechanisms of acid-catalysed solvolysis reactions.

Values of log k_{H^+} — pK_{BH^+} for reactions in dioxan-water mixtures of high water concentration, *i.e.* higher than about 10 M, need not necessarily be constant and they may change depending on the reaction and the base used for comparison because of specific solvent effects. However, these effects become negligible at low water concentrations and log $k_{H^+} - pK_{BH^+}$ is either constant for A1 reactions or varies linearly with the logarithm of the water concentration of the solvent mixture for reactions occurring by mechanisms in which water molecules are involved in the transition state.

As shown by the two values given in Table 7, the equilibrium constant of the hydrolysis of the acetal does not remain constant. Its value depends on whether acetaldehyde, acetaldehyde hydrate or acetaldehyde monoacetal is assumed to be the major product of the hydrolysis reaction. As the equilibrium constants for the reactions giving these products cannot be calculated separately from the present data, the value of about 0.4 calculated for K is not of any great value. The value $K = 7$ was obtained for diethoxymethane in dioxan-water mixtures at 40°C in previous work.[1]

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