*Fig. 2.* Comparison of the experimental and calculated molecular intensity curves $M(q)$. The experimental data are shown in dots, a: $NH_4Cl$, b: $NH_3$ and $HCl$.

the distance 3.26 Å found in crystals of the NaCl type [8] and is also shorter than ordinary $NH\cdots Cl$ hydrogen-bonded distances which range from 2.91 to 3.41 Å.[9] This shortening seems to be due to the covalent character occurring from the change of phase as seen in the cases of alkali halides,[10] and also due to the presence of a strong hydrogen bond in the gaseous $NH_4Cl$ molecule. With respect to this point, it is of interest to note that the bond length obtained for $H-Cl$ in an $NH_4Cl$ molecule is longer than that in $HCl$ molecule, 1.29 Å, by about 0.2 Å. The amplitude of vibration for $N\cdots Cl$ was found to be 0.17 Å. A simple calculation gives 0.26 md/Å for the force constant of the $NH\cdots Cl$ hydrogen bond.

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# A Reinvestigation of the General Acid Catalysis Reported for the Hydrolysis of Ethyl Orthoformate in Dioxane-Water Solvents

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In recent papers [1-3] we showed that the hydrolysis of ethyl orthoformate proceeds in water and in 65/35 w/w dioxane-water by the $A$-1 mechanism. First, the structural effects in the hydrolysis of a series of orthoformates in water and in 65 wt. % dioxane-water were in accordance with this mechanism. Second, the solvent deuterium isotope effect, $k_{D_3O^+}/k_{H_3O^+} = 2.98$, in water point to a proton transfer pre-equilibrium. The ratio was of the same magnitude in 65/35 w/w dioxane-water. Third, the lack of general acid catalysis in water excluded the alternative mechanism, a rate-determining proton transfer reaction. Thus it is surprising that DeWolfe and coworkers [4,5] have presented experimental evidence for general acid catalysis in the hydrolysis of ethyl orthoformate in 50−70 % dioxane-water solutions although the reaction is subject to specific hydronium ion catalysis in water. On the basis of the

kinetic data for the hydrolysis of 2-methoxyethyl orthoformate, opposite solvent effects would be expected; the change from water to 65/35 w/w dioxane-water resulted in a change from the $A$-$S_E2$ mechanism to the $A$-1 mechanism.[6] Thi s mechanistic change could be explained on the basis of differences in the stabilization of the transition states of the proton transfer reaction and the subsequent heterolysis.

To clarify the above-mentioned controversy in the hydrolysis of ethyl orthoformate in dioxane-water, the hydrolysis of this ester was subjected to a thorough kinetic study in acetate buffers.

*Experimental.* Ethyl orthoformate was the preparation used in previous studies.[7] The used dioxane was purified by the standard method.[8]

The rate coefficients of hydrolysis were determined spectrophotometrically by following the appearance of ethyl formate. The performance of the kinetic measurements has been described previously.[1]

To show that the hydrolysis of ethyl orthoformate has features typical of general acid catalysis, we repeated some of the measurements of DeWolfe and co-workers.[4],[5] The data in Table 1 (expt. A) reveal that the rate coefficients increase linearly with the concentration of the undissociated acid in buffer solutions of constant acid-base molar ratio (see Fig. 1). The ionic strength was adjusted to about
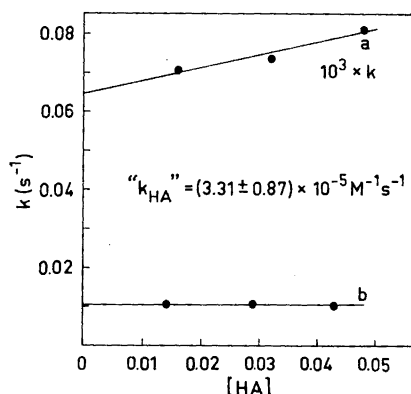


*Fig. 1.* First-order rate coefficients for the hydrolysis of ethyl orthoformate in acetate buffers in 65/35 w/w dioxane-water at 25°C against the concentration of acetic acid. Notation: a, ionic strength 0.05 (NaCl+NaAc) and b, ionic strength 2.00 (LiClO$_4$).
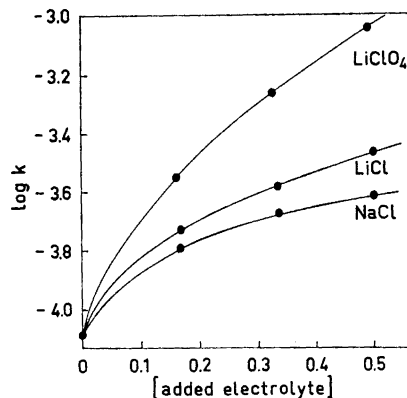
*Fig. 2.* The logarithms of the rate coefficients for the hydrolysis of ethyl orthoformate in acetate buffers in 65/35 w/w dioxane-water at 25°C against the concentration of added electrolyte.

0.05 M by addition of sodium chloride. The consistency with the data of DeWolfe *et al.*[4],[5] is evident. To study whether these effects are really due to general acid catalysis, further experiments were run in acetate buffer solutions containing various electrolytes with dioxane-water as the solvent.

First, we studied the effect of the concentration of added electrolyte on the rate of hydrolysis of ethyl orthoformate in acetate buffers. The data in Table 1 (expts. B−D) show a remarkable increase in the rate coefficient with increasing ionic strength of the solution. For instance, the addition of 0.5 mole of lithium perchlorate per liter led to a tenfold increase in the rate. The logarithms of the rate coefficients are plotted against the concentration of the added electrolyte in Fig. 2; marked differences are seen in the effects of various electrolytes. The greatest salt effect is that of lithium perchlorate. The salt effects of lithium chloride and sodium chloride are almost equal. To get a picture of the salt effect of sodium acetate, the hydrolysis of ethyl orthoformate was studied in two acetate buffers (expt. E). The rate increased with the concentration of the undissociated acid much more than in experiment A in which the ionic strength was kept constant by addition of sodium chloride. The plots in Fig. 2. reveal also that at high electrolyte concentrations the rate increase is smaller.

*Table 1.* First-order rate coefficients of the hydrolysis of ethyl orthoformate in acetate buffers in 65/35 w/w dioxane-water at 25°C. The constant molar ratio of acid to base is about 1.

| Experiment | Buffer solution [HA] (M) | Added electrolyte E | [E] (M) | Ionic strength (M) | $10^5 k$ (s$^{-1}$) |
|---|---|---|---|---|---|
| A | 0.048 | NaCl | 0 | 0.05 | 8.11 |
|   | 0.032 | ,, | 0.0167 | 0.05 | 7.34 |
|   | 0.016 | ,, | 0.0333 | 0.05 | 7.05 |
| B | 0.043 | LiClO$_4$ | 1.95 | 2.00 | 1020 |
|   | 0.044 | ,, | 1.46 | 1.51 | 544 |
|   | 0.046 | ,, | 0.976 | 1.02 | 266 |
|   | 0.047 | ,, | 0.488 | 0.54 | 92.2 |
|   | 0.047 | ,, | 0.325 | 0.38 | 54.3 |
|   | 0.047 | ,, | 0.163 | 0.21 | 27.8 |
| C | 0.047 | LiCl | 0.500 | 0.55 | 34.1 |
|   | 0.047 | ,, | 0.333 | 0.38 | 26.3 |
|   | 0.048 | ,, | 0.167 | 0.22 | 18.5 |
| D | 0.047 | NaCl | 0.500 | 0.55 | 24.2 |
|   | 0.047 | ,, | 0.333 | 0.38 | 21.1 |
|   | 0.048 | ,, | 0.167 | 0.22 | 15.9 |
| E | 0.048 |  |  | 0.051 | 8.11 |
|   | 0.032 |  |  | 0.034 | 6.13 |
|   | 0.016 |  |  | 0.017 | 4.15 |
| F | 0.043 | LiClO$_4$ | 1.95 | 2.00 | 1020 |
|   | 0.029 | ,, | 1.97 | 2.00 | 1080 |
|   | 0.014 | ,, | 1.98 | 2.00 | 1040 |

Although the nature of the salt effects is unknown, we can conclude that the observed rate variations are largely due to changes in the dissociation constants of the catalyst acids due to salt effects in the used solvent system.

The kinetic results discussed above show that one must be cautious when suggesting general acid catalysis only on the basis of data for reactions in buffer solutions in dioxane-water mixtures. For instance, the apparent general acid catalysis of the hydrolysis of ethyl orthoformate in acetate buffers (expt. A) may be only the result of a difference in the salt effects of sodium acetate and sodium chloride as we can conclude on the basis of the data in Table 1. To get further experimental evidence for the lack of general acid catalysis, possible differences in salt effects must be eliminated. The plots in Fig. 2 illustrate that this situation can be approached if the reactions take place in solutions of high electrolyte concentration and constant ionic strength. Therefore, the hydrolysis of ethyl orthoformate was studied in about 2 M lithium perchlorate solutions (expt. F). General acid catalysis was not detected

(see Fig. 1). Thus it is evident that the hydrolysis of ethyl orthoformate proceeds in 65/35 w/w dioxane-water by way of a protonation pre-equilibrium.

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