

Effect of Quaternary Ammonium Ions on the Hydrolysis of Esters Catalyzed by a Cation Exchange Resin

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n-Propyl acetate and ethyl *n*-hexanoate have been hydrolyzed by a cation exchange resin catalyst, where the active H⁺ ions have been partially substituted by PhCH₂N⁺Me₂(CH₂)₁₆CH₃ and PhCH₂N⁺Me₃ ions. Modification of the environment of the transition state by the presence of the replacing ion on the resin skeleton is discussed. The nature of solvent has been varied in the *n*-propyl acetate hydrolysis.

The effect of partial replacement of the hydrogen ions in cation exchange resin by cations (magnesium and quaternary ammonium ions) has been investigated by Hammett *et al.* in the catalyzed hydrolysis of esters in 70% aqueous acetone (1, 2). The remaining hydrogen ions of the resin were unchanged, improved or reduced in catalytic properties, depending on the nature both of the replacing ion and of the ester being hydrolyzed. From the specifically favorable effect of the replacement of hydrogen ions by cetyltrimethyl and methyltribenzylammonium ions on the hydrolysis of ethyl *n*-hexanoate and methyl phenylacetate respectively, it was advanced that a quaternary ammonium ion alters the environment of the transition state for the reaction in such a way to produce an especially low value of the standard free energy of the transition state when the quaternary ammonium ion and the ester have some prominent structural feature in common.

An alternative approach to this problem follows from the Helfferich's standpoint (3), by which the pore liquid of the resin, where reaction occurs, is treated as a homogeneous system and the ester is distributed between pore liquid and supernatant solution according to a distribution coefficient.

More recently, Gates and Johanson (4),

studying the vapor-phase dehydration of alcohols to ethers, used a hydrogen-form resin catalyst partially neutralized by lithium and sodium ions. Specific interactions of these last with the catalytically active hydrogen sites were revealed and attributed either to the participation of the replacing ions in the reaction or to a heterogeneity in the resin.

Ion exchange resins, where hydrogen ions were partially substituted by cations, have been used in the catalyzed vapor phase dehydration of formic acid (5).

The present work includes the hydrolysis of *n*-propyl acetate and ethyl *n*-hexanoate catalyzed by a cation exchange resin where hydrogen ions have been partially replaced by benzyldimethylhexadecyl and trimethylbenzylammonium ions. The polarity of the solvent has been varied in the hydrolysis of *n*-propyl acetate. With the reaction rate, the distribution coefficient of esters has been measured because modifications of the ester partition between resin and supernatant solution, due to the replacement of the hydrogen ions by different cations, may be expected. The last occurrence may contribute to the overall effect of the replacing ion on the reaction rate.

EXPERIMENTAL

Materials. Commercial *n*-propyl acetate (RP Carlo Erba), ethyl *n*-hexanoate

(Schuchardt), 32-48 and 150-250 mesh Dowex 50W X2 resin, benzyldimethylhexadecylammonium (Fluka) and trimethylbenzylammonium chloride (RP Carlo Erba) have been employed.

H⁺ Replacement. The hydrogen form resin has been contacted with 0.1 M quaternary ammonium chloride solution in amount suitable for the desired degree of neutralization. The last has been determined by titrating with 0.1N NaOH solution the residual H⁺ ions in the resin in the presence of dissolved NaCl (6).

Porosity. The resin porosity has been determined as ratio between the volumes of both sorbed and structurally bound water and the fully water-swollen resin. The water was eliminated by drying the resin samples at 40-50°C under vacuum through 4 hr and successively over P₂O₅ at room temperature up to constant weight.

The porosity of the catalyst decreases with the fraction of H⁺ substituted (Fig. 1).

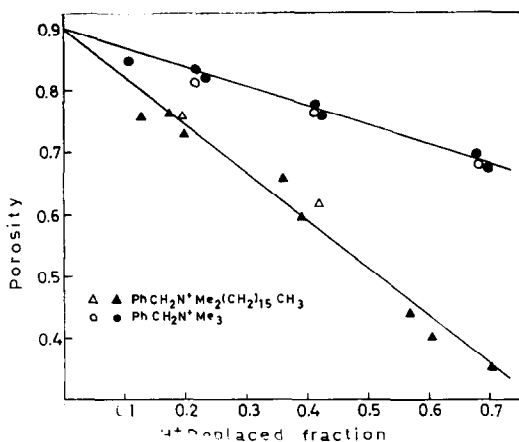


FIG. 1. Influence of partial neutralization of resin by quaternary ammonium ions upon its porosity. Resin size: \blacktriangle , \bullet 32-48 mesh; \triangle , \circ 150-250 mesh

Because the valence of the counter ions is constant, this effect may be attributed to the different size and solvation tendency of the quaternary ammonium ions compared with H⁺. Although generally the less polar the solvent, the weaker is the solvation tendency of the ions, it was found that the porosity was not appreciably

varied when the resin had been contacted with 50 and 70% aqueous acetone.

Sorption equilibrium. The distribution coefficient of the esters, defined as ratio of concentrations of solute in the sorbent and in the solution, has been obtained by contacting at 30°C the resin and the solution, containing 0.05 moles of ester per liter, in the volumetric ratio of 1:3 and 1:6 for *n*-propyl acetate and ethyl *n*-hexanoate respectively. The contact time was sufficient for establishment of sorption equilibrium, but too short for significant conversion. The residual amount of ester in solution has

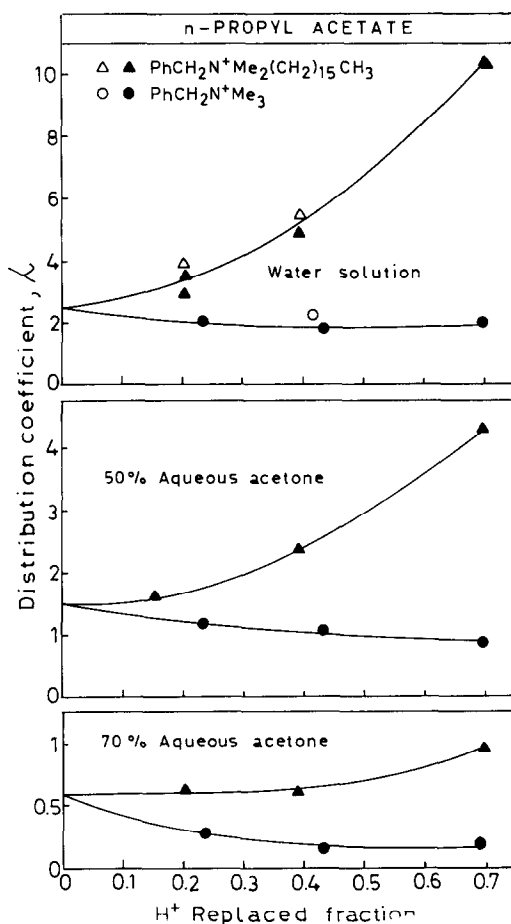


FIG. 2. Influence of partial neutralization of resin by quaternary ammonium ions upon distribution coefficient of *n*-propyl acetate in water solution and aqueous acetone. Resin size: \blacktriangle , \bullet 32-48 mesh; \triangle , \circ 150-250 mesh

been determined by chromatographic analysis (6).

The effect of the replacing ions on the sorption equilibrium is shown in Figs. 2 and 3 where the distribution coefficient is reported against the fraction of H^+ substituted. The sorption of the esters is enhanced when H^+ is replaced by $PhCH_2N^+Me_2(CH_2)_{15}CH_3$; on the contrary the distribution coefficient decreases with increasing the neutralization of resin by $PhCH_2N^+Me_3$. A high affinity and thus strong sorption may be expected when the chemical configurations of the solute and the matrix are similar. Therefore, because *n*-propyl acetate and ethyl *n*-hexanoate are aliphatic compounds, the above behavior could be attributed to the prevailing aliphatic and aromatic nature of the $PhCH_2N^+Me_2(CH_2)_{15}CH_3$ and $PhCH_2N^+Me_3$ groups respectively. The effect of the nature of solvent on the distribution coefficient of *n*-propyl acetate is shown in Fig. 2.

Hydrolysis. The reaction has been car-

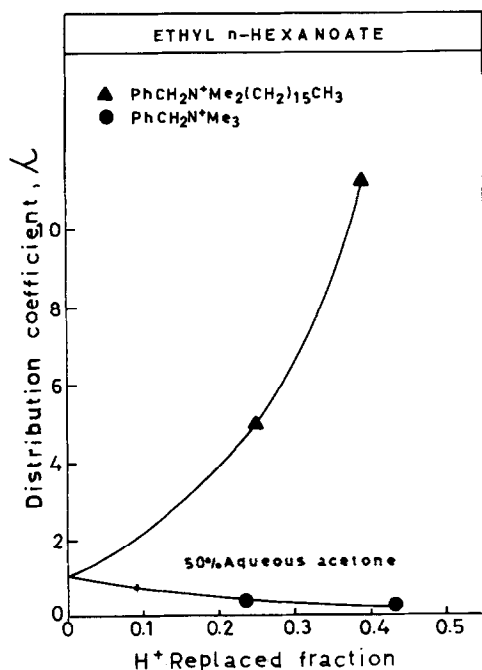


Fig. 3. Influence of partial neutralization of resin by quaternary ammonium ions upon distribution coefficient of ethyl *n*-hexanoate in 50% aqueous acetone. Resin size: 32-48 mesh

ried out with samples of catalyst and reacting solution in sealed tubes; the ester concentration and the ratio (resin volume)/(solution volume) were 0.05 mole/liter and about 0.045 respectively. Continuous agitation has been obtained by fixing the tubes to a rotating disk placed in a thermostatic bath at $30 \pm 0.1^\circ C$.

The catalyzed hydrolysis of the esters in excess water is a pseudofirst order reaction and the values of k' , the hydrolysis rate constant, is obtained from the slope of the plot of $-\ln(1 - X)$ against t , where X is the conversion and t is the reaction time. The k' values are very closely proportional to the ratio of quantity of resin to volume of solution; therefore the specific rate constant, k , calculated by dividing k' by the ratio of the number of moles of hydrogen ions in the resin to the volume of solution, is introduced.

Experiments have been made to reveal the presence of mass transfer resistance outside or within the resin; by varying the rate of shaking and the size of particles, it was deduced that inter- or intraparticle

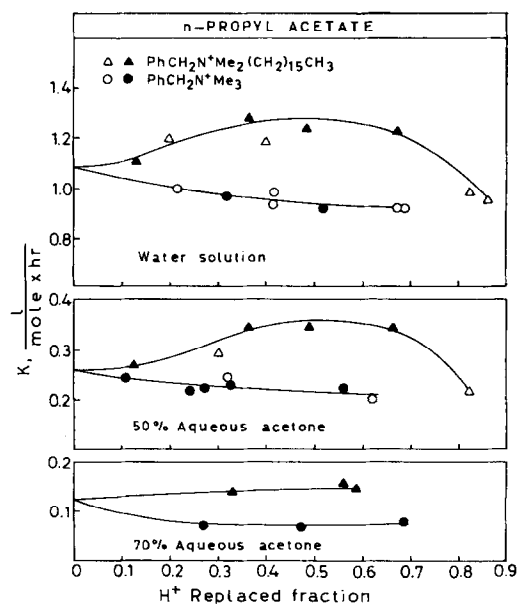


Fig. 4. Influence of partial neutralization of resin by quaternary ammonium ions upon specific rate constant of hydrolysis of *n*-propyl acetate in water solution and aqueous acetone. Resin size: ▲, ● 32-48 mesh; △, ○ 150-250 mesh

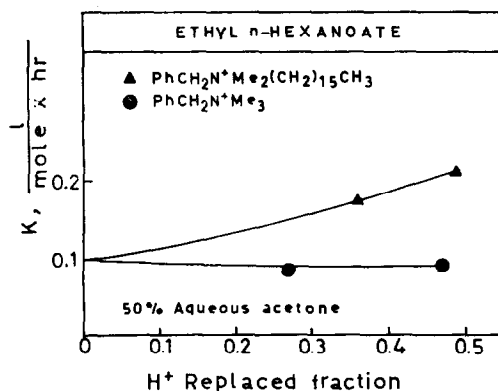


FIG. 5. Influence of partial neutralization of resin by quaternary ammonium ions upon specific rate constant of hydrolysis of ethyl *n*-hexanoate in 50% aqueous acetone. Resin size: 32-48 mesh

diffusion is not a significant factor in determining the rate of reaction.

In Fig. 4 the specific rate constant of hydrolysis of *n*-propyl acetate at 30°C, carried out in water solution, 50 and 70% aqueous acetone, is diagrammed against the percent of H⁺ substituted by the quaternary ammonium ions. If $\text{PhCH}_2\text{N}^+\text{Me}_2(\text{CH}_2)_{15}\text{CH}_3$ is the replacing ion, the specific reaction rate constant increases with the fraction of H⁺ replaced, when it achieves a maximum value followed by lowering. If the hydrogen ions are replaced by $\text{PhCH}_2\text{N}^+\text{Me}_3$, the specific rate constant appears to decrease with the increase of H⁺ replacement. A similar behavior is shown by the specific rate constant of hydrolysis of ethyl *n*-hexanoate in 50% aqueous acetone at 30°C in the same range of fraction of H⁺ substituted (Fig. 5).

From the Helfferich's model (3), the specific reaction rate constant can be written as:

$$k = \bar{k} \text{ (distribution coefficient), } \quad (1)$$

where \bar{k} is the specific rate constant in the pore liquid. The last includes the loss of some internal degree of freedom suffered by the sorbed reactant molecule in its fixation on the skeleton of the resin in the formation of the transition state. Therefore, \bar{k} gives the true effect of the replacing ion referred to the alteration of the environment of the transition state.

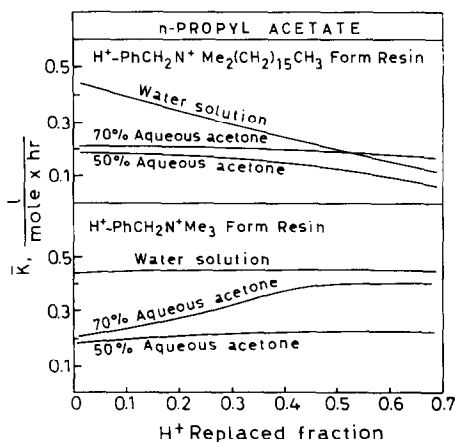


FIG. 6. Influence of partial neutralization of resin by quaternary ammonium ions upon specific rate constant in pore liquid of hydrolysis of *n*-propyl acetate in water solution and aqueous acetone.

The specific reaction rate constants in pore liquid have been calculated, through Eq. (1), by the experimental values of k and λ and reported in Figs. 6 and 7 for *n*-propyl acetate and ethyl *n*-hexanoate respectively. If $\text{PhCH}_2\text{N}^+\text{Me}_2(\text{CH}_2)_{15}\text{CH}_3$ is the replacing ion, \bar{k} decreases with the neutralization of the resin; on the contrary it increases when the active hydrogen ions are partially substituted by $\text{PhCH}_2\text{N}^+\text{Me}_3$. Hence, the presence of quaternary ammonium ion may differently influence the loss

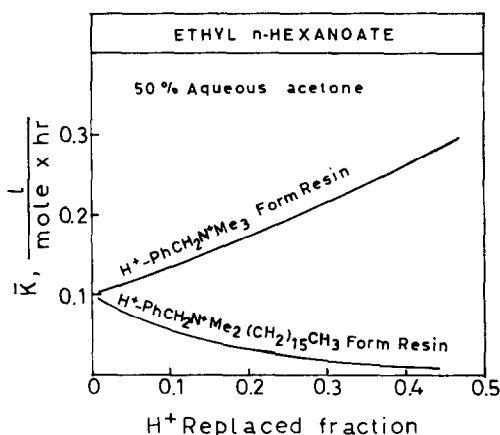


FIG. 7. Influence of partial neutralization of resin by quaternary ammonium ions upon specific rate constant in pore liquid of hydrolysis of ethyl *n*-hexanoate in 50% aqueous acetone.

of internal degrees of freedom, which is increased or reduced according to whether the replacing ion is $\text{PhCH}_2\text{N}^+\text{Me}_2(\text{CH}_3)_{15}\text{CH}_3$ or $\text{PhCH}_2\text{N}^+\text{Me}_3$.

Generally, the interactions, which control the sorption equilibrium, involve groups of the reactant molecule which are sufficiently remote from the reactive group or the reactive group itself. The reactivity of the molecule will be not changed very much by sorption in the former case, it will be reduced in the latter (7). Figures 6 and 7 show that the reactivity of sorbed *n*-propyl acetate and ethyl *n*-hexanoate, expressed by the specific reaction rate constant in pore liquid, decrease as the distribution coefficient increases in the presence of $\text{PhCH}_2\text{N}^+\text{Me}_2(\text{CH}_2)_{15}\text{CH}_3$; on the contrary, when sorption is hindered by $\text{PhCH}_2\text{N}^+\text{Me}_3$, a higher reactivity results. The observed behavior may be interpreted if the matrix of resin is assumed to interact with the sorbed ester by involving its reactive group. Hence, the stronger these interactions are, the higher the distribution coefficient and the more reduced the reactivity.

The interactions between resin and ester may be varied with the nature of solvent, and from the distribution coefficient behavior in Fig. 2 a reduction of the forces which control sorption equilibrium owing to addition of acetone to water may be expected. On the other hand, the forces be-

tween the reactants are affected by the solvent through its dielectric constant and polar properties, the lower polarity of acetone lowering the hydrolysis rate (8). From the opposite effects on reactivity of the change in solvent polarity, the dependence of \bar{k} on the acetone concentration, shown in Fig. 6, may be interpreted. As concerns the water-acetone mixtures, there is a nonuniform distribution of the solvent components and water accumulates in the resin (8).

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