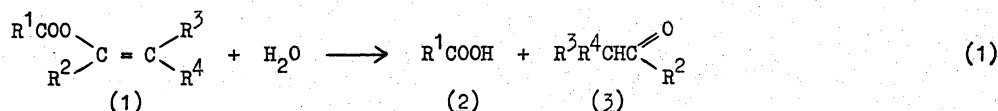# MECHANISMS AND CATALYSIS IN VINYL ESTER HYDROLYSIS

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Abstract – A critical survey of literature concerning the catalysis, mechanisms, and kinetics in vinyl ester hydrolysis is presented together with new results. The relatively fast alkaline and acid-catalysed hydrolyses usually take place with acyl-oxygen fission. General base and nucleophilic catalyses are known. Appreciable neutral ester hydrolysis by general base catalysis of water occurs generally. The unsymmetrically acid-catalysed partition of the tetrahedral intermediate formed in the neutral hydrolysis has been found to lead to acid catalysis if the ester has electronegative substituents. Vinyl esters differ from other esters by the possible electrophilic addition to the double bond. Thus mercury(II) and thallium(III) ions catalyse the reaction, and acid catalysis takes place by AS_E2 mechanism at high acidities or when the formed carbenium ion is structurally stabilized.

INTRODUCTION

$$R^1COO \underset{R^2}{\overset{}{>}} C = C \underset{R^4}{\overset{R^3}{<}} + H_2O \longrightarrow R^1COOH + R^3R^4CHC \underset{R^2}{\overset{O}{<}} \qquad (1)$$

$$\underset{(\underline{1})}{} \qquad\qquad \underset{(\underline{2})}{} \qquad \underset{(\underline{3})}{}$$

Vinyl esters ($\underline{1}$) are of importance as raw material for polymers. The following discussion is, however, limited to monomeric esters. The term vinyl ester is used for all kinds of 1-alkenyl or enol esters excluding, however, phenyl esters and similar compounds in which the double bond belongs to an aromatic system. The first hydrolysis products of vinyl esters are the carboxylic acid ($\underline{2}$) and an aldehyde, a ketone, or even an acid halide ($\underline{3}$) depending on whether R^2 is hydrogen, an alkyl or aryl group, or halogen. As far as I am aware, there is only one extensive review of the kinetics and mechanisms in vinyl ester hydrolysis. It is written in Russian by Rekasheva (1) and it deals also with vinyl ethers. The subject is considered in general reviews of ester hydrolysis (Ref. 2 & 3).
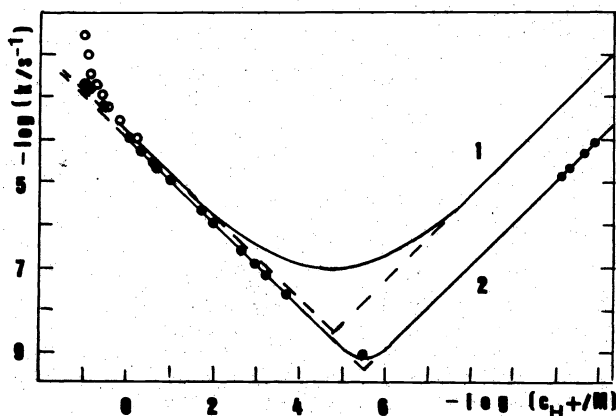

Fig. 1. The logarithm of the experimental rate coefficient in water at 25 °C for the hydrolysis of vinyl acetate (1, Ref. 4-7) and ethyl acetate (2, Ref. 2) as a function of the logarithm of hydrogen ion concentration.

Typical of the hydrolysis of ordinary esters is that the rate is proportional to the oxonium or hydroxide ion concentration over wide pH ranges in the absence of other catalysts with a minimum at the acid side as shown in Fig. 1 for ethyl acetate. Vinyl esters differ from the corresponding saturated esters as follows: (i) the acid-catalysed hydrolysis is slightly faster, (ii) the alkaline hydrolysis is considerably faster, (iii) they have a significant pH-independent or neutral hydrolysis, (iv) electrophilic addition to the double bond occurs.

The well-known Ingold's classification of ester hydrolysis mechanisms (Ref. 2 & 8) is used in this review. The only Ingold's mechanisms for which there is evidence in the case of vinyl esters are the $B_{AC}2$, $A_{AC}2$, and $A_{AC}1$ mechanisms. Vinyl esters can hydrolyse also by the AS_E2 mechanism. For the nucleophilic and general base catalyses the notations $B_{AC}N$ and $B_{AC}3$, respectively, are proposed by myself (Ref. 9) to distinguish them from the alkaline hydrolysis, $B_{AC}2$. The acid catalysis due to unsymmetrically catalysed partition of the intermediate formed in the $B_{AC}3$ reaction also needs a special notation. I propose the symbol $A-B_{AC}3$ for it.
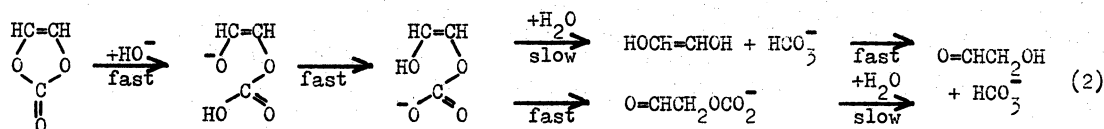
ALKALINE HYDROLYSIS ($B_{AC}2$)

Surprisingly few reliable kinetic data are available for the alkaline hydrolysis of vinyl esters. This is certainly caused by the high reaction rates and also by the tendency of vinyl esters to polymerize in alkaline solutions. Many published data are erroneous. In some cases buffer solutions were employed, when general base catalysis by buffer is possible. That probably was the case in the first kinetic study of vinyl esters performed by Skrabal and Zahorka (4) in 1927. The alkaline hydrolysis of vinyl acetate was followed in a borate buffer, and the value obtained for the rate coefficient seems to be too high by a factor of 2 or 3. This is noticed if their value, 10.3 M^{-1} s^{-1} in water at 25 ^{o}C, is compared with the more recent values 2.34 and 2.6 at 27 ^{o}C by Sharma and Sharma (10), 4.30 (?) by Rostovskii et al. (11), and 3.28 at 20 ^{o}C by DePuy and Mahoney (7). Another reason for erroneous results may be the common use of alcoholic solutions with low water content in kinetic determinations. Alcoholysis which accompanies the hydrolysis may lead to the formation of the corresponding alkyl ester, the hydrolysis of which is then followed if the liberated acid is determined. This can be the explanation, why in a study (Ref. 11) performed in 95.5 % aqueous ethanol almost identical values were obtained for the rate coefficients of vinyl and ethyl acetates. In another case (Ref. 12) the esters were employed as methanol solutions, where methanolysis could have occurred as similar values (6.22 and 6.59x 10^{-3} M^{-1} s^{-1}, respectively) were obtained for vinyl and ethyl acetate in 60 % aqueous methanol. At least in one case (Ref. 13) evidently the rate of solution rather than that of reaction was followed.

In spite of the paucity of data and of the above-mentioned shortcomings, several generalizations can be made. (i) The reaction follows second-order kinetics. (ii) The rate is 13-45 times higher for a vinyl ester than for the corresponding saturated ester under the same conditions. Experimental results include the following data: k(vinyl acetate)/k(ethyl acetate) = 44 in water at 25 ^{o}C (Ref. 7 & 2) and 38 in 70 vol.% acetone-water at 24.8 ^{o}C (Ref. 15), k(isopropenyl acetate)/k(isopropyl acetate) = 15 in water at 25 ^{o}C (Ref. 10 & 2), k(1-cyclopentenyl acetate)/k(cyclopentyl acetate) = 32 in water at 40 ^{o}C (Ref. 7), k(1-phenylvinyl acetate)/k(1-phenylethyl acetate) = 13 (Ref. 16). (iii) The corresponding values of activation parameters for vinyl esters ($\Delta H^{\ddagger}$ = 40-50 kJ/mol, $\Delta S^{\ddagger}$ = -80 - (-150) J/(mol K), Ref. 7, 15 & 17) and ethyl esters (Ref. 2) are similar. (iv) Structural effects are similar for vinyl and corresponding saturated esters. Electronegative substituents increase the rate similarly in both cases (Ref. 14, 18 & 2). Hammett's equation is followed in the case of substituted benzoates, the reaction constant ρ being similar for vinyl (ρ = 2.48 in 13 M water in ethanol at 25 ^{o}C, Ref. 14) and ethyl esters (ρ = 2.43 in 88 % ethanol-water at 25 ^{o}C, Ref. 2). (v) Vinyl acetate hydrolyses about 10 times faster than isopropenyl acetate: k(vinyl acetate)/k(isopropenyl acetate) = 11 in water at 20 ^{o}C (Ref. 7) and 6 in water at 10 ^{o}C (Ref. 10), and 12 in 70 vol.% acetone-water at 25 ^{o}C (Ref. 15). (vi) Electronegative substituents in the vinyl group increase the rate (ρ = 0.47 for substituted 1-phenylvinyl acetates in 5 vol.% ethanol-water at 29.9 ^{o}C, Ref. 16).
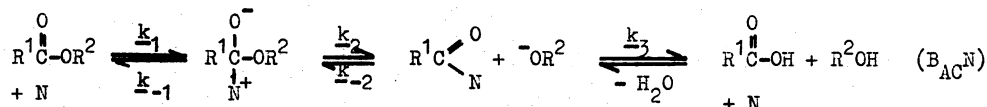
All of the above-mentioned facts are in accordance with the $B_{AC}2$ mechanism. Some inconsistent results were obtained when the site of bond fission was determined by the oxygen-18 method. Kiprianova and Rekasheva hydrolysed vinyl acetate and benzoate in alkaline aqueous solutions containing oxygen-18 (Ref. 19) and several vinyl esters having an excess of oxygen-18 in the ethereal oxygen or in both oxygen atoms (Ref. 14). The results were interpreted by assuming that both vinyl-oxygen and acyl-oxygen fissions take place (Ref.14 & 19) or that intramolecular vinyl shift occurs in the formed tetrahedral intermediate (Ref. 1). To clarify this controversy we redetermined the site of the bond fission by a slightly modified oxygen-18 method (Ref. 20). The results obtained for both vinyl and ethyl acetate were very similar: The ratio m(46)/m(44) was found to be 2.31 or 2.38 in carbon dioxide obtained from the acetate ion formed in the hydrolysis of vinyl acetate. The corresponding ratio was 2.24 or 2.28 for ethyl acetate. The calculated values were 2.35 for acyl-oxygen fission and 0.41 for alkyl-oxygen fission. These results are in accordance with the kinetic data and indicate that the alkaline hydrolysis of vinyl acetate takes place by the normal $B_{AC}2$ mechanism with acyl-oxygen fission.

The rate of hydrolysis of vinylene carbonate was found by Saadi and Lee (21) to be independent of the hydroxide ion concentration, even if the concentration range was narrow. The reaction was faster than that of ethylene carbonate with activation enthalpy considerably lower and activation entropy more negative. The results were interpreted as follows:

$$HC=CH \underset{fast}{\xrightarrow{+HO^-}} HC=CH \xrightarrow{fast} HC=CH \underset{slow}{\xrightarrow{+H_2O}} HOCH=CHOH + HCO_3^- \xrightarrow{fast} O=CHCH_2OH$$

$$\xrightarrow{fast} O=CHCH_2OCO_2^- \underset{slow}{\xrightarrow{+H_2O}} + HCO_3^- \quad (2)$$
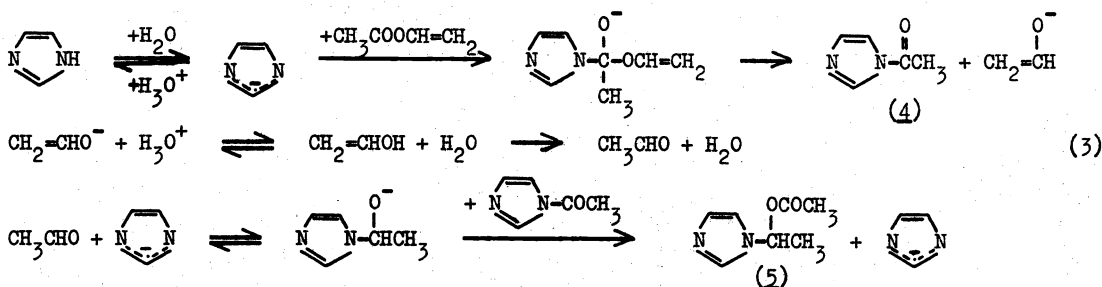
NUCLEOPHILIC CATALYSIS ($B_{AC}N$)

The mechanism of nucleophilic catalysis in ester hydrolysis may according to Bender and Turnquest (22) be written as follows:

$$R^1\overset{O}{\overset{\|}{C}}-OR^2 + N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^1\overset{O^-}{\underset{\overset{+}{N}}{\overset{|}{\underset{|}{C}}}}-OR^2 \underset{K_{-2}}{\overset{k_2}{\rightleftharpoons}} R^1C\overset{O}{\underset{N}{\diagdown}} + {}^-OR^2 \underset{-H_2O}{\overset{k_3}{\rightleftharpoons}} R^1\overset{O}{\overset{\|}{C}}-OH + R^2OH \quad (B_{AC}N)$$
$$+ N$$

The notation $B_{AC}N$ is proposed for this mechanism (Ref. 9) to distinguish it from the $B_{AC}2$ mechanism of alkaline ester hydrolysis in which $N = HO^-$ and where instead of the last step a proton transfer takes place and where in strict sense no catalysis occurs at all because HO^- is consumed in the reaction.

Nucleophilic catalysis is common in the hydrolysis of phenyl esters, but is documented only in a few cases in the hydrolysis of vinyl esters because of their poorer leaving groups. One of the cases seems to be the imidazole-catalysed hydrolysis of vinyl acetate studied by Reddy and Gehring (23). They found by proton NMR spectroscopy that first the concentration of N-acetylimidazole (4) increased to a maximum and then remained constant until most of the vinyl acetate had reacted. The final product was 1-imidazolylethyl acetate (5). No kinetic measurements were performed. The suggested mechanism (3) is actually a general base-catalysed nucleophilic catalysis with water as the base.

$$(3)$$

In the hydrolysis of diketene, 4-methylene-2-oxetanone, pyridine seems to act as a nucleophilic catalyst, as concluded by Briody and Satchell (24). Several bases were found to catalyse the reaction, but only pyridine seems to function as a nucleophile. Its catalytic constant is about sixty times higher than that of the about equally basic acetate ion and ca. 200 times higher than that of the sterically hindered 2,4-lutidine. The reaction will be considered in the next chapter, where also some indications of nucleophilic catalysis in the hydrolysis of 2,2-dichlorovinyl chloroacetate will be presented.

A very efficient intramolecular nucleophilic catalysis has been found by Kirby and Meyer (25) in the case of 2-acetoxycyclohexene- (6) and -cyclopentene-1-carboxylate ions. The hydrolyses were too fast to be measured, having half-lives of a second or less. The mechanism was concluded to be the following:

$$(4)$$
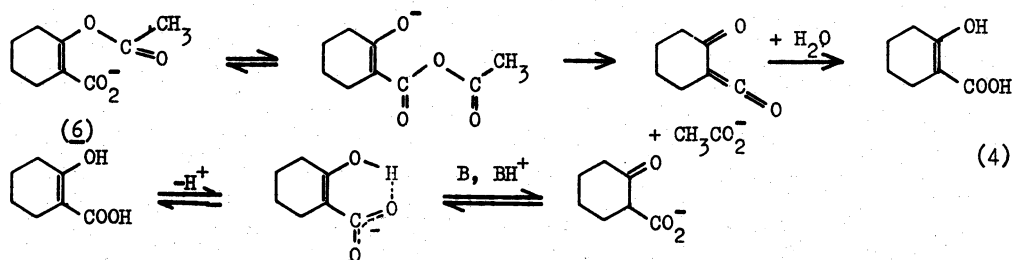
GENERAL BASE CATALYSIS ($B_{AC}3$)

The first kinetic measurements of the hydrolysis of vinyl acetate by Skrabal and Zahorka (4) already include data that show that acetate ion catalyses the reaction, although the authors supposed that the rate increase was an electrolyte effect. The only case where general base catalysis has been claimed to take place in vinyl ester hydrolysis is the above-mentioned study by Briody and Satchell (24), when chloroacetate, acetate, and acetoacetate ions were concluded to function as general bases when catalysing the hydrolysis of diketene.
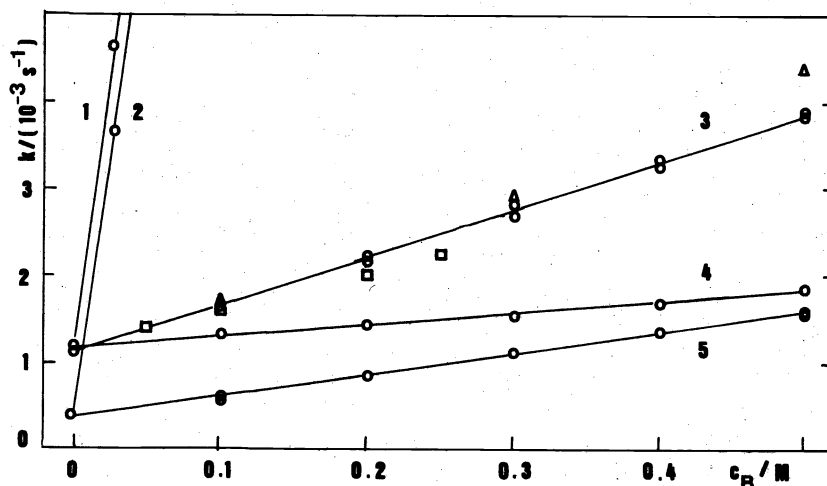

Fig. 2. Plots of the experimental rate coefficients against the base concentration for the hydrolysis of 2,2-dichlorovinyl chloroacetate in aqueous buffer solutions with ionic strength 0.5 M at 25 °C. The buffer ratio was 1:1 (circles) except of some acetate buffers where $c(AcO^-):c(AcOH)$ was 5:1 (triangles) or 1:2 (squares). Buffer bases: hydrogen phosphate ion in ordinary water (1), hydrogen phosphate ion in deuterium oxide (2), acetate ion in ordinary water (3), chloroacetate ion (4), and acetate ion in deuterium oxide (5).

We have recently performed a study of general base catalysis in the hydrolysis of 2,2-dichlorovinyl chloroacetate (Ref. 26). The spectrophotometrically determined rates were found to depend almost linearly on the base concentration (Fig. 2). A slight increase was sometimes found at the highest concentrations employed and when the acid-base ratio of the buffer was decreased. A constant buffer ratio (1:1) was used in actual determinations. An appreciable neutral hydrolysis was always observed. The results obtained for the base catalysis are collected in Table 2. The data are in general agreement with those earlier found for general base-catalysed ester hydrolysis (Ref. 9 & 27). Especially characteristic are the values for the solvent isotope effect of the neutral and acetate ion-catalysed hydrolysis, the low values of activation enthalpy, and the highly negative values of activation entropy. The solvent isotope effect for the hydrogen phosphate ion-catalysed hydrolysis is exceptional. The rate of the imidazole-catalysed reaction was found to depend on the wave length used, which may be due to the formation of some intermediate. These observations together with the high rates (see below) can be indications of nucleophilic catalysis by the two last-mentioned bases although it was not studied closer.

TABLE 1. Catalytic data of the hydrolysis of 2,2-dichlorovinyl chloroacetate in aqueous solution with the ionic strength of 0.5 M ($NaClO_4$ or $LiClO_4$) at 25 °C.

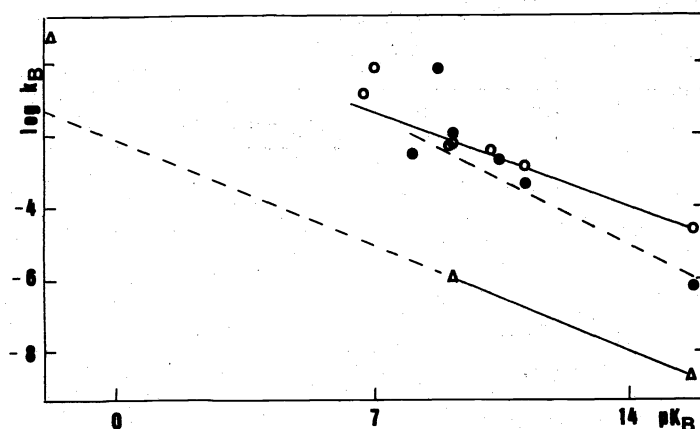| Base	pK_B	$\dfrac{k_B}{10^{-3} \text{ M}^{-1}\text{s}^{-1}}$	$\dfrac{k_B(H_2O)}{k_B(D_2O)}$	$\dfrac{\Delta H^{\ddagger}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta S^{\ddagger}}{\text{J mol}^{-1}\text{ K}^{-1}}$
H_2O	15.73	0.0213	2.97	49.7±0.9	− 135 ± 3
$CH_2ClCO_2^-$	11.15	1.30			
HCO_2^-	10.25	3.68			
$CH_3CO_2^-$	9.24	5.51	2.25	51.6±2.5	− 115 ± 8
$CH_3CH_2CO_2^-$	9.12	5.33			
HPO_4^{2-}	6.79	120	1.10		
imidazole	7.05	400-1000			

Fig. 3. Brönsted plots for 2,2-dichlorovinyl chloroacetate (o) and vinyl acetate (Δ, Ref. 4) in water and diketene (•, Ref. 24) in 40 % dioxane-water at 25 °C.

The Brönsted plots for the above data are shown in Fig. 3. No statistical corrections were made. The points for 2,2-dichlorovinyl chloroacetate satisfactorily obey the Brönsted relationship, with the exceptional point for imidazole and possibly also for the hydrogen phosphate ion. The other points give for the Brönsted coefficient the value 0.37, which is in agreement with the earlier values 0.47 for ethyl dichloroacetate (Ref. 27), 0.39 for chloromethyl chloroacetate (Ref. 9), and 0.40 for substituted 2,2-dimethyl-1,3-dioxane-4,6-diones (Ref. 28), It is to be noted that the point for water falls on the same line indicating that the mechanisms of neutral ester hydrolysis and the reaction catalysed by carboxylate anions are the same.

From Fig. 3 it is also seen that the two points calculated for water and the acetate ion from Skrabal and Zahorka's (4) data for vinyl acetate give a parallel line. The point for the alkaline hydrolysis of vinyl acetate lies clearly above the Brönsted's line as is found also in other cases (Ref. 9 & 27). A direct nucleophilic attack of the hydroxide ion evidently takes place without catalysis. Figure 3 further includes the data for the hydrolysis of diketene measured by Briody and Satchell (24). Although the points are more scattered, they seem to confirm their conclusion that the chloroacetate and acetoacetate ions and evidently also 2,4-lutidine act as general bases and pyridine as a nucleophile in this reaction. In the case of the acetate ion general base catalysis is accompanied by other reactions.

The mechanism for general base-catalysed ester hydrolysis (Ref. 29) is included in the reaction scheme presented in the chapter for the acid catalysis due to unsymmetrically catalysed decomposition of the tetrahedral intermediate in neutral ester hydrolysis. The notation $B_{AC}3$ was proposed for it to distinguish it from the mechanism of alkaline hydrolysis and to indicate that three molecules, ester, water, and the base, are in the transition state (Ref. 9). The same notation should be used for neutral ester hydrolysis.

NEUTRAL ESTER HYDROLYSIS

Only few data for the neutral hydrolysis of vinyl esters can be found in the literature; Skrabal and Zahorka (4) determined the rate coefficient for vinyl acetate and Yrjänä (30) for vinyl chloroacetate in water. Yrjänä also found that the values of activation enthalpy and entropy for the last-mentioned ester are of the same magnitudes as the values for other esters reacting by the $B_{AC}3$ mechanism (Ref. 2). Briody and Satchell (24) found that diketene has a pH-independent hydrolysis in the region of 1-8 and concluded on the basis of the low value of activation energy that acyl-oxygen fission occurs. More extensive measurements have been performed in our laboratory (Ref. 26, 31 & 32) in connexion with our studies on neutral ester hydrolysis in general. The choice of the esters and solvents was based on the possibility to obtain the most accurate results by the conductometric and spectrophotometric methods employed. This sometimes limited severely the range of conditions where investigations could be made.

Data illustrating structural effects in the neutral hydrolysis of vinyl esters are collected in Table 2. It is seen that electronegative substituents increase the rate greatly, as is usually found in neutral ester hydrolysis in accordance with the proposed mechanism (Ref. 2). More quantitative consideration of these structural effects is not possible because of the paucity of data under comparable conditions.

TABLE 2. Absolute and relative rate coefficients for the neutral hydrolysis of vinyl esters in $\underline{p}$ "%" acetonitrile-water solutions at 25 °C.

Ester	$\underline{p}$	$\underline{k}/(10^{-4}\ s^{-1})$	$\underline{k}_{rel.}$				Ref.
$CH_3COOCH=CH_2$	0	0.00113	1				4
$CH_2ClCOOCH=CH_2$	0	0.591	523				30
$CH_3COOCH=CCl_2$	0	0.0427	38	1/410			31
$CH_2ClCOOCH=CCl_2$	0	17.5	15,000	1			31
$CH_2ClCOOCH=CCl_2$	40	1.22		1			31
$CHCl_2COOCH=CCl_2$	40	142		116			31
$CHCl_2COOCH=CCl_2$	64	38.2			1		31
$CCl_3COOCH=CCl_2$	64	2440			64		26
$CHCl_2COOCCl=CCl_2$	64	661			17		32
$CCl_3COOCH=CH_2$	64	36.8	(1.7×10^6)		0.96		26
$CF_3COOCH=CH_2$	64	562	(27×10^6)		15		26

Solvent effects in the neutral hydrolysis of vinyl esters are seen from Fig. 4. The plots are of the same general type as usually found for the reaction. The slopes of the curves, sometimes called the apparent order of reaction in respect to water, vary between 5 and 7 in acetonitrile solutions rich in water and diminish to a value below two in solutions containing about 25 per cent of water.

The activation enthalpy is plotted as a function of the mole fraction of water for the neutral hydrolysis of vinyl esters in acetonitrile-water solutions in Fig. 5. It is seen that the values of activation enthalpy are low, around 40 kJ/mol. All of the curves have similar forms. There is a minimum at the mole fraction of about 0.95 followed by a maximum at $\underline{x}$(water) of ca. 0.7. The detailed form of the curves depends on the structure of the ester, probably mostly on that of its alkyl component. For methyl trifluoroacetate the curves are very shallow around the extreme values, which become clearer for chloromethyl dichloroacetate and are most pronounced for the vinyl esters.
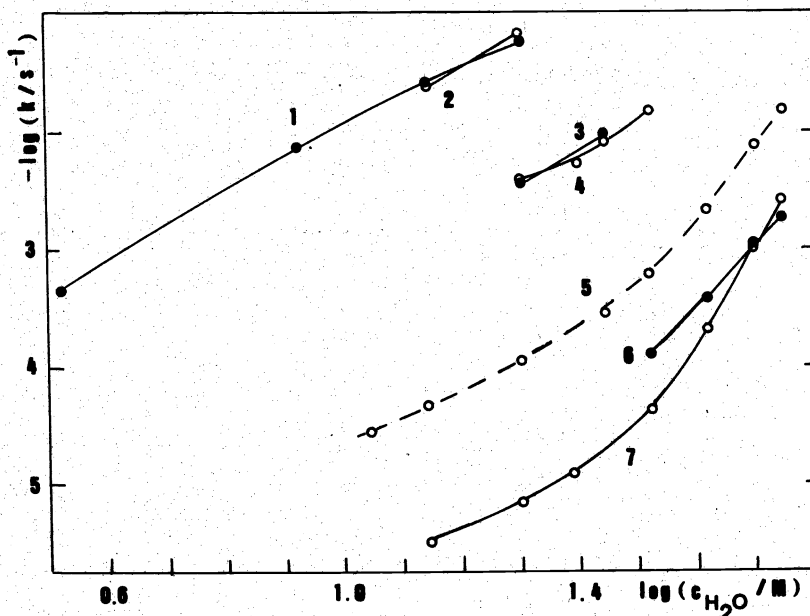
Fig. 4. Plots of the logarithm of the rate coefficient against the concentration of water in acetonitrile-water solutions at 25 °C for the neutral hydrolysis of vinyl trifluoroacetate (1), 1,2,2-trichlorovinyl dichloroacetate (2), vinyl trichloroacetate (3), 2,2-dichlorovinyl dichloroacetate (4), 2,2-dichlorovinyl chloroacetate (6), and E-1,2-dichloro-1-propenyl 2-chloropropionate (7). The broken line is for chloromethyl dichloroacetate (5, Ref. 33).
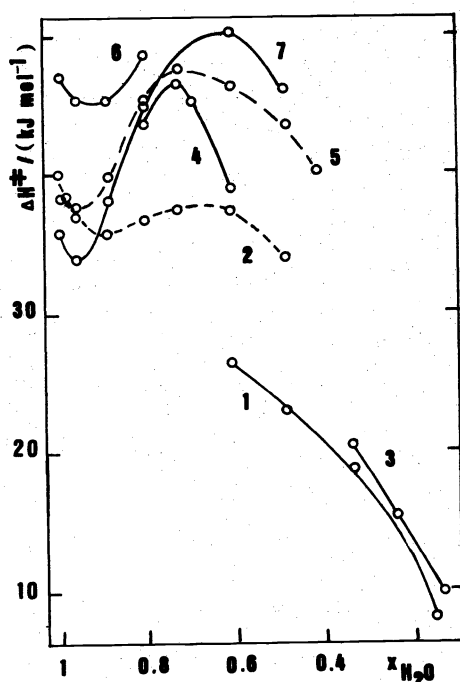
Fig. 5.

Fig. 6.

Variation of activation enthalpy (Fig. 5) and entropy (Fig. 6) as a function of the mole fraction of water in acetonitrile-water mixtures at 25 °C for the neutral hydrolysis of vinyl trifluoroacetate (1), 2,2-dichlorovinyl trichloroacetate (3), 2,2-dichlorovinyl dichloroacetate (4), 2,2-dichlorovinyl chloroacetate (6), and E-1,2-dichloro-1-propenyl 2-chloropropionate (7). Curves of comparison: Chloromethyl dichloroacetate (5, broken line, Ref. 33) and methyl trifluoroacetate (2, dotted line, Ref. 34).
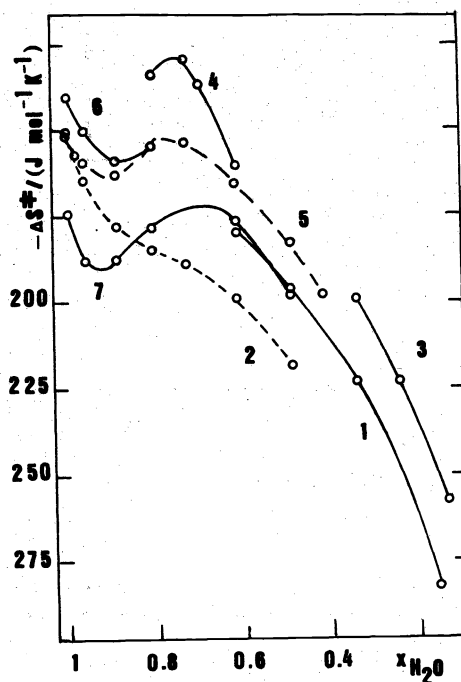
The curves for activation entropy (Fig. 6) show similar trends as those for activation enthalpy. The values are highly negative, around -200 J/(mol K). Methyl trifluoroacetate exhibits no extreme values at all, but chloromethyl dichloroacetate and the vinyl esters have maxima and minima, which are located at almost the same water contents as the extreme values for activation enthalpy. Hence the same factors, probably changes in solvent structure, influence activation enthalpy and entropy. Because they depend on temperature, their dependence on the composition of solvent is different at different temperatures.

TABLE 3. Values of the heat capacity of activation, $\Delta \underline{C}_{\underline{p}}^{\ddagger} = \partial(\Delta \underline{H}^{\ddagger})/\partial \underline{T}$, for the neutral hydrolysis of vinyl esters in $\underline{p}$ "%" acetonitrile-water (AN) and dimethylsulfoxide-water (DMSO) solutions.

Ester	$\underline{p}$	Temperature interval/°C	$\dfrac{\Delta \underline{C}_{\underline{p}}^{\ddagger}}{\text{J mol}^{-1} \text{ K}^{-1}}$	Ref.
$CF_3COOCH=CH_2$	64 AN	0-25	- 656 ± 10	26
	75 AN	-3-25	- 540 ± 8	26
	85 AN	0-65	- 297 ± 13	26
	94 AN	0-65	- 182 ± 16	26
	94 DMSO	7-55	- 477 ± 46	26
	97 DMSO	15-85	- 176 ± 38	26
	99 DMSO	18-85	- 138 ± 59	26
$CCl_3COOCH=CH_2$	50 AN	0-40	- 423 ± 4	26
	64 AN	0-45	-384 ± 4	26
$E-CH_3CHClCOOCCl=CClCH_3$	0		- 225 ± 21	32
	10 AN		- 46 ± 8	32
$CHCl_2COOCCl=CCl_2$	64 AN		- 619 ± 50	26
	75 AN		- 305 ± 71	26

We have directed much attention to the temperature dependence of the rate of neutral ester hydrolysis, especially to structural and solvent effects on the heat capacity of activation. Neutral ester hydrolysis is a suitable reaction for studying these effects because of the low activation energy. Data for vinyl esters are given in Table 3. All the values of the heat capacity of activation are negative, as generally found in reactions where transition state is more polar than initial state (Ref. 29, 33, 34 & 35). The large variation of the values depends mainly on strong solvent effects. Cleve's (33 & 34) thorough investigations have shown that the values of the heat capacity of activation for the neutral hydrolysis of methyl trifluoroacetate and chloromethyl dichloroacetate in acetonitrile-water solutions have a maximum at a mole fraction of water of about 0.85 and a minimum at ca. 0.7. It was found that the height of the maximum and the depth of the minimum are more profound for the last-mentioned ester. The data for the vinyl esters studied seem to exhibit similar behaviour but with still higher maxima and much lower minima. Negative values of the heat capacity of activation are explained to be due to the necessity of breaking the solvation shell around the reaction centre in activation. Therefore the heat capacity of activation should be an important parameter when kinetic solvent effects are studied. The structure of the ester and especially of its alkyl component seems to be of importance in this respect. The data for vinyl esters are, however, too few for any detailed discussion.

TABLE 4. Kinetic data for the neutral hydrolysis of isomeric 1,2-dichloro-1-propenyl 2-chloropropionates, $CH_3CHClCOOCCl=CClCH_3$, in 10 "%" acetonitrile-water at 25 °C (Ref. 32).
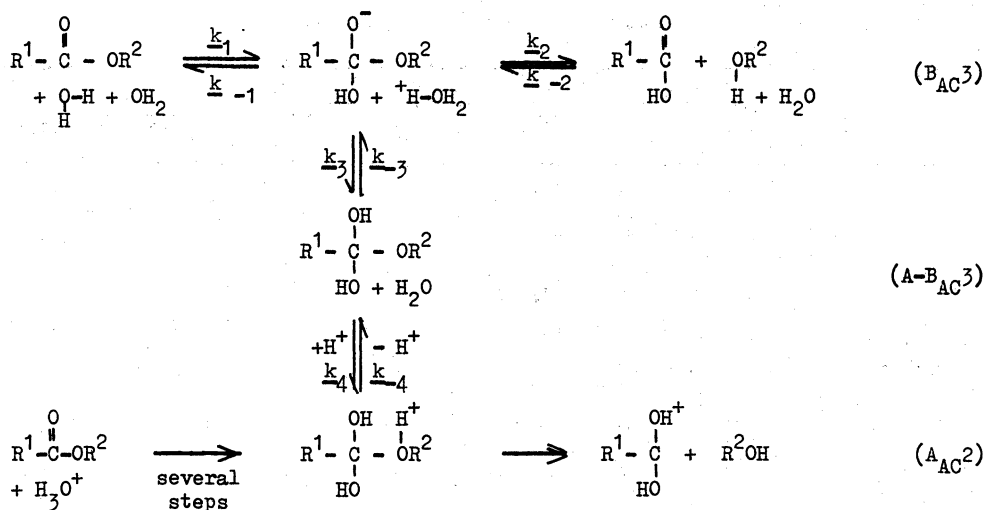
Isomer	$\dfrac{k}{10^{-3} \text{ s}^{-1}}$	$\dfrac{\Delta H^{\ddagger}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta S^{\ddagger}}{\text{J mol}^{-1} \text{ K}^{-1}}$	$\dfrac{\Delta C_p^{\ddagger}}{\text{J mol}^{-1} \text{ K}^{-1}}$
Z	1.526 ± 0.003	34.9 ± 0.1	− 182.0 ± 0.4	− 84 ± 8
E	1.073 ± 0.003	33.8 ± 0.1	− 188.3 ± 0.4	− 46 ± 8

An interesting case is presented by Rossi (32), who studied the hydrolysis of the isomeric 1,2-dichloro-1-propenyl 2-chloropropionates. The observed clear differences are shown in Table 4. Structurally the isomers differ in regard to whether the 2-chlorine or the 2-methyl of the propenyl component comes in the vicinity of the carbonyl group in the main conformer with the plain of the vinyl group about perpendicular against the carbonyl group. The water structure around these groups was proposed to be the most important factor.

ACID CATALYSIS DUE TO UNSYMMETRICALLY CATALYSED PARTITION OF THE TETRAHEDRAL INTERMEDIATE IN NEUTRAL ESTER HYDROLYSIS ($A\text{-}B_{AC}3$)

Esters which have an appreciable neutral hydrolysis exhibit an acid-catalysed hydrolysis with several exceptional features (Ref. 2) as shown by Euranto and Cleve (36). (i) Polar factors are more important than in the case of common esters. Electronegative substituents increase the rate, which then is higher than estimated. (ii) They have a lower activation enthalpy and a more negative activation entropy than ordinary esters. (iii) There is often a rate maximum at ca. 2 M acid followed by a minimum at higher acidities. The maximum is partly due to a negative salt effect in the accompanying neutral hydrolysis, but also the rate calculated as the difference between rates at equal concentrations of an acid and a corresponding salt and the rate measured at constant ionic strength behave exceptionally. The plot of the rate against the acid concentration is first concave downwards and rises steeply at higher concentrations. The rise was shown (Ref. 37) to represent the normal $A_{AC}2$ reaction. (iv) There is a strong negative salt effect as in neutral ester hydrolysis, but in contrast to the normal acid-catalysed hydrolysis. (v) Added organic solvent components decrease their rate much more than the rate of simple esters. (vi) The kinetic deuterium oxide solvent isotope effect is the opposite to that of other esters, but in accordance with neutral ester hydrolysis.

The above-mentioned several similarities of this exceptional acid catalysis with neutral ester hydrolysis suggested a special mechanism with a common intermediate which, in addition to the general acid-catalysed partition to reaction products and starting materials, could also decompose via another path requiring an additional proton. This path was supposed to lead to the same intermediates that lie on the reaction path of the $A_{AC}2$ hydrolysis. No conclusive evidence for this mechanism, which we have also called a general base - specific oxonium ion catalysis, could then be presented. A reaction scheme, represented on the next page, was suggested. Last year, Kurz and Farrar (38), in a very thorough and elegant experimental and theoretical study of the hydrolysis of ethyl trichloroacetate, presented very convincing evidence for essentially the same mechanism. The notation $A\text{-}B_{AC}3$ is now proposed for it because of the experimental acid catalysis and of the common intermediate with the $B_{AC}3$ reaction.

$$R^1 - \underset{\substack{+ \; \underset{H}{O}-H + OH_2}}{\overset{O}{\overset{\|}{C}}} - OR^2 \underset{\underline{k}_{-1}}{\overset{\underline{k}_1}{\rightleftharpoons}} R^1 - \underset{\substack{HO + \; ^+H-OH_2}}{\overset{O^-}{\overset{|}{\underset{|}{C}}}} - OR^2 \underset{\underline{k}_{-2}}{\overset{\underline{k}_2}{\rightleftharpoons}} R^1 - \underset{HO}{\overset{O}{\overset{\|}{C}}} + \underset{H + H_2O}{\overset{OR^2}{\overset{|}{\underset{|}{}}}} \qquad (B_{AC}3)$$

$$\underline{k}_3 \big\Updownarrow \underline{k}_{-3}$$

$$R^1 - \underset{HO + H_2O}{\overset{OH}{\overset{|}{\underset{|}{C}}}} - OR^2 \qquad (A\text{-}B_{AC}3)$$

$$+H^+ \big\Updownarrow -H^+ \atop \underline{k}_4 \;\; \underline{k}_{-4}$$

$$R^1 - \underset{+\; H_3O^+}{\overset{O}{\overset{\|}{C}}} - OR^2 \xrightarrow[\text{steps}]{\text{several}} R^1 - \underset{HO}{\overset{OH \;\; H^+}{\overset{|}{\underset{|}{C}}}} - OR^2 \longrightarrow R^1 - \underset{HO}{\overset{OH^+}{\overset{|}{\underset{|}{C}}}} + R^2OH \qquad (A_{AC}2)$$

It may be expected that also vinyl esters exhibit the above-mentioned acid catalysis. Because the factors which determine the relative contributions of the different reaction paths are very poorly known, we have performed experiments with 2,2-dichlorovinyl chloroacetate. The results are shown in Fig. 7. Somewhat unexpectedly the added acid acts as an inhibitor of the reaction. However, sodium perchlorate lowers the rate more strongly. The difference

$$\underline{k}_H = \underline{k} \, (HClO_4) - \underline{k} \, (NaClO_4) \qquad (5)$$

is positive and can be considered to represent acid catalysis. As a function of acid concentration, the values of $\underline{k}_H$ give a slightly downward concave curve with initial slope of $3.3 \times 10^{-4} \; M^{-1} \; s^{-1}$. A similar value, $3.0 \times 10^{-4} \; M^{-1} \; s^{-1}$, was obtained from runs performed at a constant ionic strength of 1 M. The low accuracy achievable in these measurements prevents a detailed analysis of the results. The general form of the rate curves and the observed increase of the rate in the range of 4 to 11 M perchloric acid suggests that the acid-catalysed hydrolysis at low acidities follows the A-$B_{AC}3$ mechanism. The values of the rate coefficients are higher than those for the $A_{AC}2$ hydrolysis of ethyl acetate, ethyl chloroacetate, and vinyl acetate with the $\underline{k}_H/(10^{-4} \; M^{-1} \; s^{-1})$ values of 1.12, 0.81 (Ref. 2), and 1.45 (Ref. 5), respectively.
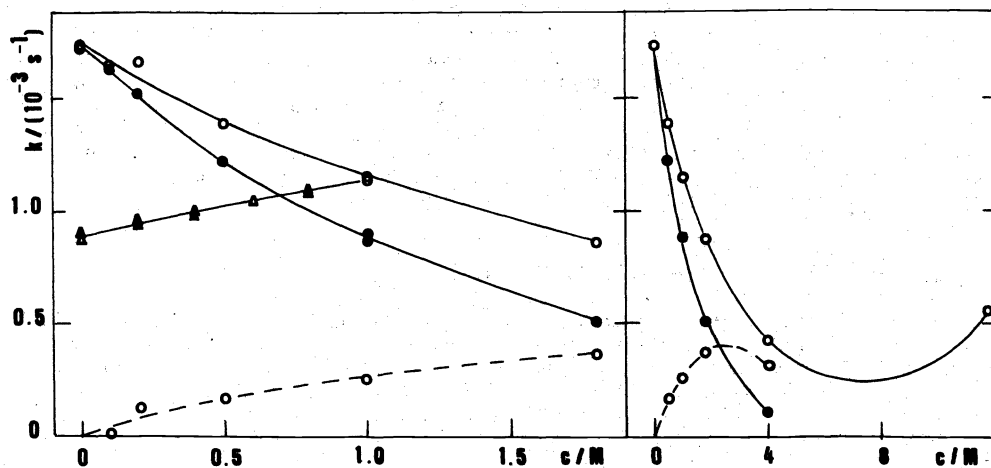
Fig. 7. The first-order rate coefficients for the hydrolysis of 2,2-dichlorovinyl chloroacetate in aqueous perchloric acid solutions with variable (o) or constant $(NaClO_4)$ ionic strength of 1 M (Δ) and in sodium perchlorate ($\bullet$) solutions at 25°C. The dotted curve is calculated from equation (5).

BIMOLECULAR ACID-CATALYSED HYDROLYSIS ($A_{AC}2$)

Skrabal and Zahorka (4) were the first to study the acid-catalysed hydrolysis of vinyl acetate. On the basis of the reaction rate Skrabal (39) concluded that the reaction takes place by the same mechanism as the hydrolysis of "ether-like" esters. Palomaa et al. (40)

TABLE 5. Kinetic data for the acid-catalysed hydrolysis of esters $R^1COOCR^2=CH_2$.

R^1	R^2	Solvent (Note a)	$\frac{t}{°C}$	$\frac{k_H}{10^{-4}M^{-1}s^{-1}}$	k_{rel}^{sat} (Note b)	$\frac{k_H(H_2O)}{k_H(D_2O)}$	$\frac{\Delta H^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S^{\ddagger}}{J\ mol^{-1}K^{-1}}$	Ref.
CH_3	H	W	25	1.45	1.36	0.75	61.7	− 112	5
		50% DW	65	20.0			64.3	− 108	5, 43
		11M DW	80			0.74	72	− 88	44
H	H	W	25	46.7	1.52				45
		50% AW	25	17.8			61.2	− 92	45
CH_3CH_2	H	50% DW	65	15.4			55.5	− 136	43, 5
$CH_3CH_2CH_2$	H	50% DW	65	9.12			61.5	− 123	43, 5
		11M DW	80			0.70	68	− 105	44
$C(CH_3)_3$	H	50% DW	65	1.21			84	− 72	43, 5
CH_2Cl	H	11M DW	60				59	− 133	41
$C_6H_5CH_2$	H	11M DW	60				77	− 73	41
CH_3	CH_3	W	25	0.847	1.37		74.4	− 73	5
		50% DW	25	0.495					5
		5.6M DW	80			0.78	86	− 53	42

Note a. W = water, 50% AW = 50 wt.% acetone-water, 50% DW = 50 wt.% dioxane-water, 11M DW = dioxane-water with $\underline{c}(H_2O)$ 11 M, 5.6M DW = dioxane-water with $\underline{c}(H_2O)$ 5.6 M.

Note b. $\underline{k}_{rel}^{sat}$ = $\underline{k}_H$ $(R^1COOCR^2=CH_2)$ / $\underline{k}_H$ $(R^1COOCHR^2CH_3)$

observed, however, the approximate equality of the temperature coefficients for vinyl and primary and secondary acetates. Kiprianova, Rekasheva, Kulish, and co-workers (Ref. 19, 41 & 42) performed oxygen-18 experiments with several vinyl and isopropenyl esters and found only little incorporation of oxygen-18 from water to the produced acids. They concluded therefore that the hydrolysis occurred by alkyl-oxygen fission with a mechanism similar to that of vinyl ethers (Ref. 1). On the basis of these oxygen-18 results and his own kinetic investigations, Landgrebe (43) proposed several mechanisms with alkyl-oxygen fission, which differed from the above mechanism. Yrjänä (5) showed that the values of activation entropy were erroneously calculated in Landgrebe's paper and ca. 26 cal/(mol K) too high. He performed a thorough kinetic investigation of several vinyl esters. The most essential kinetic information about the acid-catalysed hydrolysis of vinyl esters known in 1968 is shown in Table 5. All these kinetic data are in full agreement with the opinion that vinyl esters without strong electronegative or -positive substituents obey the $A_{AC}2$ mechanism in aqueous solutions with low acidity. Because the above-mentioned oxygen-18 experiments were inconsistent with the kinetic data we redetermined the site of bond fission (Ref. 46). Oxygen exchange between acetic acid and water was determined separately under the experimental conditions and taken into account when the expected oxygen-18 excesses were calculated. The experimental results were in accordance with those calculated for acyl-oxygen but not for alkyl-oxygen fission in the case of both vinyl and ethyl acetate. On the other hand, the results for tert-butyl acetate showed alkyl-oxygen fission.

UNIMOLECULAR ACID-CATALYSED HYDROLYSIS ($A_{AC}1$)

The only case where a unimolecular acid-catalysed hydrolysis with acyl-oxygen fission probably takes place in the hydrolysis of vinyl esters is that of diketene studied by Briody and Satchell (24). They concluded from the linear dependence of log $\underline{k}$ against $\underline{H}_0$ with a slope of 0.91 that this unimolecular mechanism prevails analogically with other β-lactones. The observed rate was 20-30 times higher than that of β-propiolactone.

ACID CATALYSIS INVOLVING RATE-LIMITING PROTON ATTACK ON CARBON (AS_E2 MECHANISM)

Vinyl esters differ from other esters in that the carbon-carbon double bond is a second potential functional group. Thus the AS_E2 mechanism, known to be involved in vinyl ether hydrolysis, is possible. Its occurrence in vinyl ester hydrolysis was first proposed by Kiprianova and Rekasheva (19). Even though their interpretation was considered to be wrong in the above-mentioned cases, their data include cases where this mechanism very probably is functioning. They found that the rates of vinyl benzoate and anisate (Ref. 44) and isopropenyl benzoate (Ref. 42) followed $\underline{H}_0$ rather than $\underline{c}_H+$ in aqueous dioxane solutions where the water concentration was low (0.44 M). They also found that the rate was higher by a factor of 1.5-2 in ordinary water than in deuterium oxide under similar conditions. A change in

mechanism is also indicated by the about 60 times higher rate of isopropenyl than of vinyl benzoate (Ref. 42). Also the values of Hammett's reaction constant ρ, -1.3 for vinyl benzoates (Ref. 44) and -1.1 for isopropenyl benzoates (Ref. 42), are in accordance with this mechanism. Landgrebe (47) investigated by proton NMR spectroscopy the behaviour of isopropenyl acetate in strong sulfuric and deuteriosulfuric acids and showed that protonation of the carbon-carbon double bond takes place and is followed by vinyl-oxygen fission.

$$R^1COOCR^2=CH_2 + H^+ \xrightarrow{slow} R^1COO\overset{+}{C}R^2CH_3 \xrightarrow{+H_2O} R^1COOCR^2CH_3$$
$$\overset{+}{\underset{OH_2}{|}}$$

$$\longrightarrow R^1\underset{+}{COO}\overset{H}{\underset{|}{-}}\overset{OH}{\underset{|}{C}}R^2CH_3 \longrightarrow R^1COOH + CH_3\overset{O}{\overset{\|}{C}}R^2 + H^+ \qquad (AS_E2)$$

Noyce and co-workers thoroughly studied substituent effects, the dependence of rate on acid concentration, and solvent isotope effects in the hydrolysis of several vinyl esters and showed convincingly that the $A_{AC}2$ mechanism really is accompanied by the AS_E2 mechanism (Ref. 6, 48 & 49). The last-mentioned mechanism is favoured by high acidities and the stability of the carbenium ion formed. The plots of log k against Hammett's acidity function H_0 are for esters with electron-donating substituents, like p-methoxy-α-acetoxystyrene, almost linear with slopes between -1.0 and -1.1. For other vinyl esters the plots are more or less complex and they could be quantitatively analysed in terms of the two mechanisms. By this method it could be estimated (Ref. 6) that at $H_0 = 0$ the AS_E2 mechanism accounts less than 0.5 % of the rate for vinyl acetate but about 20 % of the rate for isopropenyl acetate. When the $A_{AC}2$ mechanism prevails, an inverse isotope effect (k (H_2O) / k (D_2O) $\approx$ 0.75) was obtained, whereas normal isotope effects in the range of 2.5-3.2 were found when the mechanism was AS_E2.

METAL ION CATALYSIS

Kiprianova, Rekasheva, and Samchenko investigated the site of bond fission (Ref. 19) and the kinetics of the hydrolysis of vinyl esters catalysed by mercury(II) acetate or perchlorate in acid solutions (Ref. 50 & 51). Halpern et al. (Ref. 52 & 53) studied by NMR and IR spectroscopy the kinetics of the mercury(II) and thallium(III) ion-catalysed hydrolysis of isopropenyl acetate. Both groups proposed essentially similar mechanisms with somewhat different views of the structures of the intermediates and of the rate-limiting stage. The mechanism presented by Abley, Byrd, and Halpern (53) seems to be based on a more detailed experimental study. It is essential that the catalyst adds to the double bond and thus helps the addition of water. The rate-limiting step is the alkyl-oxygen fission of the addition compound. It differs in this respect from the otherwise similar AS_E2 mechanism. Actual catalysts are organomercury(II) and bis(organo)thallium(III) ions, which also can be formed from the ester and inorganic ions.

REFERENCES

1. A.F. Rekasheva, Usp. Khim. 37, 2272-2299 (1968).
2. E.K. Euranto in S. Patai (Ed.), The Chemistry of Carboxylic Acids and Esters, Ch. 11, pp. 505-588, Interscience, London (1969).
3. A.J. Kirby in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 10, Ch. 2, pp. 57-207, Elsevier, Amsterdam (1972).
4. A. Skrabal and A. Zahorka, Monats. Chem. 48, 459-473 (1927).
5. T. Yrjänä, Suom. Kemistil. B 39, 81-86 (1966).
6. D.S. Noyce and R.M. Pollack, J. Am. Chem. Soc. 91, 7158-7163 (1969).
7. C.H. DePuy and L.R. Mahoney, J. Am. Chem. Soc. 86, 2653-2657 (1964).
8. C.K. Ingold, Structure and Mechanism in Organic Chemistry, Ch. XV, pp. 1128-1163, 2nd Ed., Cornell University Press, Ithaca, N.Y. (1969).
9. E.K. Euranto, Ann. Acad. Sci. Fenn. Ser. A 2, No. 152 (1970).
10. R.C. Sharma and M.M. Sharma, Bull. Chem. Soc. Jpn. 43, 642-645 (1970).
11. E.N. Rostovskii, S.N. Ushakov, and A.N. Barinova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 59-63 (1958).
12. S. Lee and I. Sakurada, Z. Phys. Chem. Abt. A 184, 268-272 (1939).
13. M. Hauser, J. Org. Chem. 27, 43-46 (1962).
14. L.A.Kiprianova and A.F. Rekasheva, Dokl. Akad. Nauk SSSR 153, 642-645 (1963).
15. C.G. Evans and J.D.R. Thomas, J. Chem. Soc. B, 1502-1504 (1971).
16. M. Novak and G.M. Loudon, J. Am. Chem. Soc. 98, 3591-3597 (1976).
17. G.G. Skvortsova, Yu.A.Mansurov, and N.M. Deriglazov, Khim. Geterotsikl. Soedin., 33-36 (1974).
18. A.M. Shur and M.M. Filimonova, Zh. Obshch. Khim. 37, 2603-2608 (1967).
19. L.A. Kiprianova and A.F. Rekasheva, Dokl. Akad. Nauk SSSR 144, 386-389 (1962).
20. E.K. Euranto and A. Alhoniemi, Acta Chem. Scand. 26, 855-856 (1972).
21. A.H. Saadi and W.H. Lee, J. Chem. Soc. B, 5-6 (1966).
22. M.L. Bender and B.W. Turnquest, J. Am. Chem. Soc. 79, 1656-1662 (1957).

23. G.S. Reddy and D.G. Gehring, J. Org. Chem. 32, 2291-2293 (1967).
24. J.M. Briody and D.P.N. Satchell, J. Chem. Soc., 3778-3785 (1965).
25. A.J. Kirby and G. Meyer, J. Chem. Soc. Perkin Trans. 2, 1446-1451 (1972).
26. E.K. Euranto, H. Suontausta, and K. Lappalainen, unpublished results.
27. W.P. Jencks and J. Carriuolo, J. Am. Chem. Soc. 83, 1743-1750 (1961).
28. K. Pihlaja and M. Seilo, Acta Chem. Scand. 23, 3003-3010 (1969).
29. E.K. Euranto and N.J. Cleve, Acta Chem. Scand. 17, 1584-1594 (1963).
30. T. Yrjänä, Suom. Kemistil. A 39, 109-110 (1966).
31. H. Suontausta, Master's Thesis, Univ. Turku (1974).
32. K. Rossi, Licentiate's Thesis, Univ. Turku (1976).
33. N.J. Cleve, Suom. Kemistil. B 45, 235-243 (1972).
34. N.J. Cleve, Ann. Acad. Sci. Fenn. Ser. A 2, No. 167 (1972).
35. R.E. Robertson, Prog. Phys. Org. Chem. 4, 213-280 (1967).
36. E.K. Euranto and N.J. Cleve, Reaktsionnaya Sposobnost Organ. Soedin, Tartusk Gos. Univ.
    2 (1), 183-185 (1965); E.K. Euranto, Tidsskr. Kjemi Bergves. Metall. 25, 214 (1965).
37. E.K. Euranto and N.J. Cleve, Suom. Kemistil. B 43, 213-219 (1970).
38. J.L. Kurz and J.M. Farrar, J. Am. Chem. Soc. 97, 2250-2254 (1975).
39. A. Skrabal, Z. Elektrochem. 33, 322-348 (1927).
40. M.H. Palomaa, E.J. Salmi, J.I. Jansson, and T. Salo, Ber. Dtsch. Chem. Ges. 68, 303-307
    (1935).
41. L.F. Kulish and O.I. Korol', Ukr. Khim. Zh. 34, 495-497 (1968).
42. L.F. Kulish, L.A. Kiprianova, Yu.K. Fershal, and A.F. Rekasheva, Zh. Org. Khim. 4, 1385-
    1391 (1968).
43. J.A. Landgrebe, J. Org. Chem. 30, 2997-3000 (1965).
44. L.F. Kulish, L.A. Kiprianova, and A.F. Rekasheva, Ukr. Khim. Zh. 33, 934-941 (1967).
45. E. Euranto, Ann. Univ. Turku. Ser. A 1, No. 42 (1960).
46. E.K. Euranto and L. Hautoniemi, Acta Chem. Scand. 23, 1288-1294 (1969).
47. J.A. Landgrebe, J. Org. Chem. 30, 2105-2107 (1965).
48. D.S. Noyce and R.M. Pollack, J. Am. Chem. Soc. 91, 119-124 (1969).
49. D.S. Noyce and A.M. Myers, J. Org. Chem. 35, 2460-2461 (1970).
50. L.A. Kiprianova and A.F. Rekasheva, Dokl. Akad. Nauk SSSR 154, 423-426 (1964).
51. I.P. Samchenko and A.F. Rekasheva, Ukr. Khim. Zh. 34, 450-456 (1968).
52. J.E. Byrd and J. Halpern, Chem. Commun., 1332-1333 (1970).
53. P. Abley, J.E. Byrd, and J. Halpern, J. Am. Chem. Soc. 94, 1985-1989 (1972).