

Determination of the Bond Ruptured in the Acid-Catalysed Hydrolysis of Vinyl Acetate

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The site of bond fission in the acid-catalysed hydrolysis of vinyl acetate in water has been investigated by determining mass spectrometrically the oxygen-18 content of the acetic acid produced when the ester is hydrolysed in ^{18}O -enriched water. Taking into account the oxygen exchange reactions of acetic acid, measured separately, and vinyl acetate with water, it has been shown that the results are in accordance with acyl-oxygen, but not with alkyl-oxygen fission. For comparison, the sites of bond fission of the corresponding reactions of ethyl and *tert*-butyl acetates have been determined similarly and found to be in accordance with the prevailing opinions about the reaction mechanisms ($A_{\text{AC}2}$ and $A_{\text{AL}1}$, respectively).

Skrabal¹ concluded from the rate of the acid-catalysed hydrolysis of vinyl acetate that the reaction takes place by the same mechanism as the hydrolysis of "ether-like" esters ($A_{\text{AL}1}$). Kiprianova and Rekasheva² gave evidence for alkyl-oxygen fission by determining the oxygen-18 content of the acetic acid produced in the hydrolysis of vinyl acetate in ^{18}O -enriched water. They² and later Landgrebe³ proposed therefore that the mechanism of the reaction resembles that of the acid-catalysed hydrolysis of vinyl ethers. Kulish, Kiprianova, and Rekasheva⁴ have recently published kinetic data for the acid-catalysed hydrolyses of several vinyl esters in dioxane-water mixtures which they consider to support mechanisms involving a rate-limiting hydration of the carbon-carbon double bond. Palomaa and coworkers⁵ observed already in 1935, however, the approximate equality in the temperature coefficients of the hydrolyses of vinyl acetate and acetates of primary and secondary alcohols. Yrjänä⁶ showed recently that structural effects, solvent and structural kinetic isotope effects, solvent effects, rates in moderately concentrated acids, and thermodynamic activation data are similar in the acid-catalysed hydrolyses of vinyl acetate and other simple esters like ethyl acetate and proposed that the normal $A_{\text{AC}2}$ mechanism prevails also in the case of vinyl acetate. An attempt has now been made to solve the disagreement between the above-mentioned conclusions by determining the site of bond fission using the oxygen-18 technique.

EXPERIMENTAL

Materials. The oxygen-18 enriched water was obtained from Yeda Research and Development Co., Ltd., at the Weizmann Institute of Science, Rehovoth, Israel, and contained 2.095 atom % ^{18}O and 0.139 atom % ^{17}O .

Acetic acid (Guaranteed Reagent, unaffected by chromic acid, E. Merck AG) and perchloric acid (Guaranteed Reagent, abt. 70 %, E. Merck AG) were used without further purification. Vinyl acetate (stabilized, practical, Eastman Organic Chemicals), ethyl acetate (Guaranteed Reagent, E. Merck AG), and *tert*-butyl acetate (prepared earlier in this laboratory) were allowed to stand over anhydrous potassium carbonate to remove free acid and distilled in a vacuum immediately before use.

The reaction medium was prepared by diluting 2.8723 g of the perchloric acid solution to 100 ml with ^{18}O -enriched water. The concentration of the resulting acid solution was found by titration to be 0.192 M.

Performance of the experiments. The rate of oxygen exchange between acetic acid and water was determined by the following method. About 0.1 ml of acetic acid was added to 3.0 ml of the thermostated reaction medium and shaken immediately. After an appropriate reaction time, the reaction mixture was rapidly chilled in ice-water and neutralised with a 1 M sodium hydroxide solution. The volume of the solution was reduced to about 1 ml by evaporating at reduced pressure, about 3 ml of cold concentrated silver nitrate solution was added, and the precipitate of silver acetate was collected by filtration, washed with cold water, anhydrous ethyl alcohol, and diethyl ether and dried over phosphorus pentoxide in a vacuum desiccator.

The following procedure was employed in the determination of the site of bond fission in ester hydrolysis. The perchloric acid solution was thermostated and an amount of the ester that gave a homogeneous mixture was added rapidly and shaken immediately. After a chosen reaction time (calculated by the aid of the known rate coefficients⁶⁻⁸), the reaction mixture was rapidly chilled with ice-water and immediately neutralised with a 1 M sodium hydroxide solution to about pH 6. Unreacted ester and formed acetaldehyde or alcohol were extracted with methylene chloride. The volume of the reaction mixture was reduced and the acetate ion precipitated as silver acetate as described above.

Oxygen-18 analysis. The silver acetate was pyrolysed in a vacuum to carbon dioxide which was separated from other pyrolysis products by distilling several times in a high-vacuum line. The mass ratio $m(46)/m(44+45)$ of the carbon dioxide was determined with an Atlas M.A.T. CH 4 mass spectrometer. The proportionality factor α in the obtained reading $R_{\text{exp}} = \alpha m(46)/m(44+45)$ of the mass spectrometer was eliminated by taking the ratio of R_{exp} values for the unknown sample (R_u) and a standard (R_s). At the same time the error caused by the mass 45 is eliminated because the ratio $m(45)/m(44)$ may be assumed to be constant ($=^{13}\text{C}/^{12}\text{C}$) when the ^{17}O content is low. A sample of carbon dioxide equilibrated with distilled water (about 0.26 mmole of CO_2 and 0.11 mole of H_2O) was used as a standard. Its ^{18}O content was calculated⁹ to be 0.00424 by assuming distilled water to have a normal ^{18}O content, 0.00204.

The atom fraction x of ^{18}O per oxygen atom of CO_2 is then obtained from the calculated values of $R = m(46)/m(44) = 2x/(1-x)$. The excess of ^{18}O over its normal value is given by $r = x - 0.00204$.

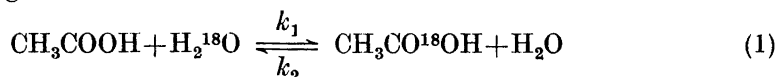
RESULTS AND DISCUSSION

Oxygen exchange between acetic acid and water. It is known that the rate of the acid-catalysed oxygen exchange between acetic acid and water is high¹⁰ compared to the rate of acid-catalysed ester hydrolysis. The rate of the former reaction was not accurately known in the conditions chosen for this investigation (aqueous perchloric acid solution at 45°C) and was therefore determined experimentally (Table 1). The mean value, $3.3_3 \times 10^{-4} \text{ s}^{-1}$, of the experimental first-order rate coefficient k_{exp} will be used in the following.

Table 1. Exchange of oxygen between acetic acid and water in a 0.192 M aqueous perchloric acid solution at $45.22 \pm 0.05^\circ\text{C}$. $[\text{CH}_3\text{COOH}] \approx 0.6$ M. For notation, see text.

t min	R_u/R_s	R	$100r$	$10^4 k_{\text{exp}}$ s^{-1}
0			0	
24.8	4.692	0.01965	0.769	3.24
81.0	8.908	0.03731	1.627	3.42
210	10.658	0.04464	1.979	(3.34)
∞			2.009	

The exchange reaction



leads to an equilibrium defined by the equilibrium constant

$$K = \frac{k_1}{k_2} = \frac{[\text{CH}_3\text{CO}^{18}\text{OH}][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{H}_2^{18}\text{O}]} \quad (2)$$

The experimental first-order rate coefficient k_{exp} is related to k_1 (calculated for total water concentration at constant pH) and K as follows

$$k_1 = k_{\text{exp}} \times \frac{K([\text{H}_2^{16}\text{O}] + [\text{H}_2^{18}\text{O}])}{[\text{H}_2^{16}\text{O}] + K[\text{H}_2^{18}\text{O}]} \quad (3)$$

If the distribution of oxygen atoms between the acid and water is statistical, the value of K is 2 and $k_1 = 2k_2$.¹¹ The data in the last row of Table 1 give the value 2.18 for K . This isotope effect, however, is ignored in the following because of the uncertainty of this value of K . From eqn. (3) the value $6.5 \times 10^{-4} \text{ s}^{-1}$ is then obtained for k_1 in 0.192 M aqueous perchloric acid solution at 45.22°C . If the rate is assumed to be proportional to the hydrogen ion concentration,^{10,11} the value $6.2 \times 10^{-5} \text{ s}^{-1}\text{M}^{-2}$ is obtained for the third-order rate coefficient of the oxygen exchange reaction between acetic acid and water at 45.22°C . It can be compared with the value, $7.10 \times 10^{-5} \text{ s}^{-1}\text{M}^{-2}$, derived from the data of Llewellyn and O'Connor¹⁰ measured at 55 and 78°C without added salts present at pH values from 2.80 to 1.42. The difference may be due to the negative electrolyte effect observed by Llewellyn and O'Connor¹⁰ as the perchloric acid concentration in our solution was 5 to 100 times as great as in their solutions. It is not, however, quite clear whether the values of their rate coefficients are those of k_{exp} or k_1 and whether the second term in the denominator of eqn. (3) was taken into account.

Determination of the site of bond fission in ester hydrolysis. When the oxygen-18 method has been applied to the acid-catalysed hydrolysis of esters, the ^{18}O content of the produced alcohol has usually been determined¹² because of the rapid oxygen exchange reactions of carboxylic acids. In the case of vinyl esters, however, acetaldehyde rather than an alcohol is formed and it is known to exchange oxygen rapidly with water because it forms an aldehyde hydrate.

It was therefore necessary to isolate the carboxylic acid after incomplete hydrolysis and to take into account the oxygen exchange between the acid and water. The carbonyl oxygen atom of the ester can also exchange with water, the rate of the exchange being, however, smaller than that of hydrolysis.¹³ On the other hand, it is highly probable that no significant oxygen exchange takes place during the experimental procedure after the solution has been neutralised because oxygen exchange between acetate anion and water is very slow.¹⁰

Table 2. The ¹⁸O content of acetic acid liberated in the acid-catalysed hydrolysis of esters. The time of hydrolysis (*t*) was either the half-life (*t*_{1/2}) or quarter-life (*t*_{1/4}) of the hydrolysis. For other notation, see text.

Ester	<i>t</i> s	<i>R_u</i> / <i>R_s</i>	100 <i>r</i> (excess atom % of ¹⁸ O per O)			
			Experi- mental	Calculated for		
				<i>A_{AC2}</i>		<i>A_{AL1}</i>
				<i>k_{ex}</i> =0	<i>k_{ex}</i> / <i>k_h</i> =1/5	
CH ₃ COOCH=CH ₂	2040 (<i>t</i> _{1/4})	6.794	1.20	1.19	1.21	0.52
	4860 (<i>t</i> _{1/2})	8.074	1.46	1.43	1.46	1.00
	4860 (<i>t</i> _{1/2})	8.207	1.49	1.43	1.46	1.00
CH ₃ COOCH ₂ CH ₃	5580 (<i>t</i> _{1/2})	8.598	1.56	1.46	1.49	1.08
	1488 (<i>t</i> _{1/2})	2.871	0.39	1.14	1.19	0.43

The experimental results are given in Table 2 together with calculated values for acyl-oxygen (*A_{AC2}*) and alkyl-oxygen fission (*A_{AL1}*). The assumptions made in the derivation of the required formulae are given in the Appendix together with the final expressions. It is clear from Table 2 that the data for vinyl and ethyl acetates are in accordance with those calculated for acyl-oxygen fission, whereas those for *tert*-butyl acetate point to alkyl-oxygen fission. Indeed, it is known that about 96 % of the hydrolysis of the last-mentioned ester in water at 50°C takes place by alkyl-oxygen fission.¹⁴ The accuracy of the data does not permit a decision as to whether an exchange between the carbonyl-oxygen of the ester and water accompanies the hydrolysis although the values for vinyl and ethyl acetates calculated by assuming the ratio *k_{ex}*/*k_h* of the rate coefficients for exchange and hydrolysis to be 1/5 are somewhat closer to the experimental data than those calculated assuming *k_{ex}*=0. This is in accordance with the results obtained by direct determination of *k_{ex}*/*k_h* for ethyl benzoate by Bender.¹³

The present results obtained by the oxygen-18 method fully confirm the conclusion drawn by Yrjänä⁶ from kinetic experiments that the hydrolysis of vinyl acetate in acid aqueous solutions takes place by acyl-oxygen fission or the normal *A_{AC2}* mechanism. It is not clear why Kiprianova and Rekasheva² obtained the opposite result by essentially the same oxygen-18 method. It may be noted, however, that they performed their only experiment in acid

solution with an alcohol-water mixture of high ester concentration and that they interrupted the reaction already after about 1 % hydrolysis. The oxygen exchange reactions certainly had only a minor influence but the presence of a relatively small amount of acetic acid in the studied ester would have introduced appreciable errors. Their purification procedure was also more complicated than ours. The kinetic results reported by Kulish, Kiprianova, and Rekasheva ⁴ for the hydrolysis of vinyl acetate and butyrate in solutions of high water content are not at variance with the A_{AC}2 mechanism.*

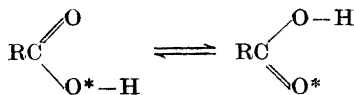
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APPENDIX. DERIVATION OF EQUATIONS

The following notation is used:

- E = ester of normal isotopic composition
 E* = ester with excess of ¹⁸O in the carbonyl group (* means always in the following an excess of ¹⁸O in any group over its normal abundance)
 A, A*, and A** = carboxylic (acetic) acid with no, one, and two ¹⁸O atoms (excess)
 [E]₀ = initial concentration of the ester
 k_h = k_{AC} + k_{AL} = first-order rate coefficient for the total hydrolysis of an ester for total water concentration at constant actual hydrogen ion concentration
 k_{AC} = first-order rate coefficient for hydrolysis by acyl-oxygen fission
 k_{AL} = first-order rate coefficient for hydrolysis by alkyl-oxygen fission
 k_{ex} = first-order rate coefficient for the oxygen exchange reaction between the carbonyl group of the ester and water
 k₁ = 2k₂ = first-order rate coefficient for the oxygen exchange reaction between the carboxylic acid and water (eqn. 1)
 α = mole fraction (excess) of H₂O* in the water

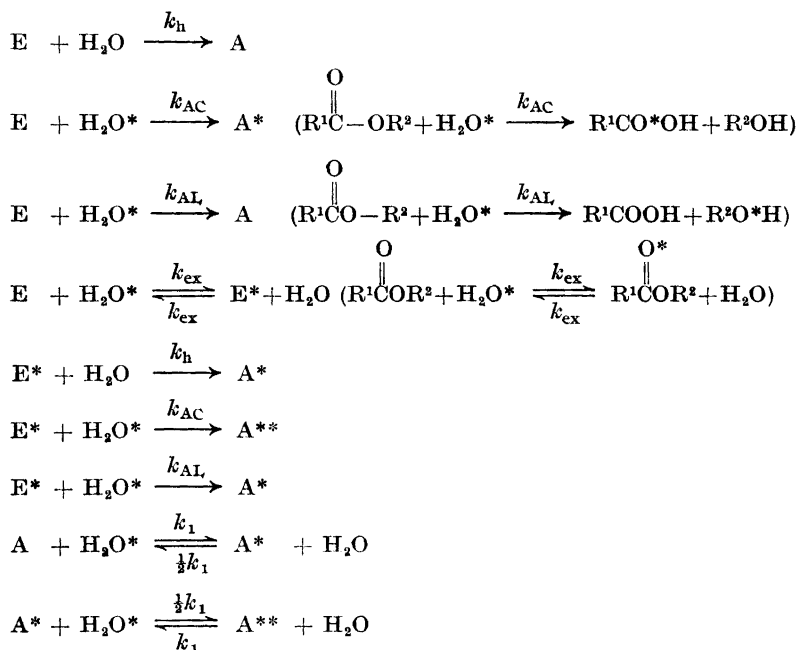
The following assumptions are made: (1) Esterification is ignored because the experiments were performed in dilute aqueous solution which did not initially contain carboxylic acid and alcohol; (2) kinetic ¹⁸O-isotopic effects are ignored; (3) water is assumed to be present in so a great excess that even [H₂O*] may be considered to remain constant; (4) the proton transfer reaction of carboxylic acids



is assumed to be fast compared to the oxygen exchange reaction, both of the two oxygen atoms of a carboxylic acid being therefore equivalent.

The following reactions are considered (only the species necessary in the following are indicated):

* Note added in proof. Rekasheva has recently (*Usp. Khim.* **37** (1968) 2272) published a review with further references. Noyce and Pollack (*J. Am. Chem. Soc.* **91** (1969) 119) have shown by studying the hydrolysis of α-acetoxystyrenes in aqueous sulfuric acid solutions that increased acidity of the solution and increased stability of the carbonium ion formed if the carbon-carbon double bond is protonated cause a change from the normal A_{AC}2 mechanism to one involving an initial, rate-limiting olefin protonation (A_{SE}2 mechanism), which is essentially the mechanism proposed by Rekasheva *et al.* Their results provide further evidence that the hydrolysis of vinyl acetate takes place by the A_{AC}2 mechanism.



These rate equations lead to the following group of differential equations which can be solved analytically.

$$\begin{aligned}
 d[E]/dt &= -(k_h + \alpha k_{ex}) [E] + (1 - \alpha) k_{ex} [E^*] \\
 d[E^*]/dt &= \alpha k_{ex} [E] - (k_h + (1 - \alpha) k_{ex}) [E^*] \\
 d[A]/dt &= (k_h - \alpha k_{AC}) [E] - \alpha k_1 [A] + \frac{1}{2} (1 - \alpha) k_1 [A^*] \\
 d[A^*]/dt &= \alpha k_{AC} [E] + (k_h - \alpha k_{AC}) [E^*] + \alpha k_1 [A] - \frac{1}{2} k_1 [A^*] + (1 - \alpha) k_1 [A^{**}] \\
 d[A^{**}]/dt &= \alpha k_{AC} [E^*] + \frac{1}{2} \alpha k_1 [A^*] - (1 - \alpha) k_1 [A^{**}]
 \end{aligned}$$

Because the excess atom % of ^{18}O per oxygen atom of carboxylic acid liberated in the hydrolysis (Table 2) is given by $r = \frac{1}{2} [A^*] / \Sigma[A]$, only the expressions for $[A^*]$ and $\Sigma[A] = [A] + [A^*] + [A^{**}]$ are given below.

$$\begin{aligned}
 [A^*] &= \alpha [E]_0 \left\{ 2(1 - \alpha) - \exp(-k_h t) \left[1 + (1 - 2\alpha) \frac{\frac{1}{2}k_1 - k_{AC}}{\frac{1}{2}k_1 - k_h} + \right. \right. \\
 &\quad + \left. \left(\frac{k_h}{\frac{1}{2}k_1 - k_h - k_{ex}} \left(1 - \frac{\alpha k_1}{k_1 - k_h - k_{ex}} \right) - \frac{2\alpha k_{AC}}{k_1 - k_h - k_{ex}} \right) \exp(-k_{ex} t) \right] + \\
 &\quad + (1 - 2\alpha) \left[\frac{k_{AL}}{\frac{1}{2}k_1 - k_h} + \frac{k_h}{\frac{1}{2}k_1 - k_h - k_{ex}} \right] \exp(-\frac{1}{2}k_1 t) + \\
 &\quad \left. + 2\alpha \frac{k_{AL}}{k_1 - k_h - k_{ex}} \exp(-k_1 t) \right\} \\
 \Sigma[A] &= [1 - \exp(-k_h t)] [E]_0
 \end{aligned}$$

The numerical values of the rate coefficients for the 0.192 M aqueous perchloric acid solution at 45.22°C used in the calculation of the values in Table 2 are the following: $k_1 = 6.5 \times 10^{-4} \text{ s}^{-1}$, $k_h = 1.43 \times 10^{-4}$, 1.25×10^{-4} , and $4.76 \times 10^{-4} \text{ s}^{-1}$ for vinyl, ethyl, and *tert*-butyl acetate, respectively. The employed value for the excess mole fraction α of $H_2^{18}O$ in the reaction medium is 0.0187.

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