

## Concurrent Carbon and Oxygen Protonation in the Hydrolytic Decomposition of $\beta$ -Acetyl Substituted Vinyl Ethers

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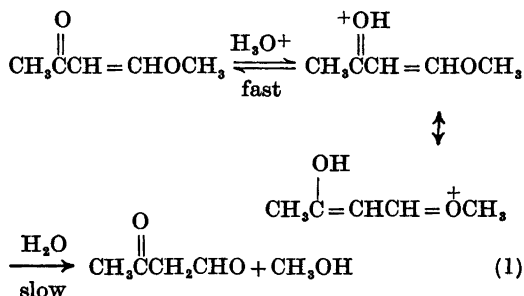
The acid-catalyzed decomposition of  $\beta$ -acetyl substituted vinyl ethers was studied kinetically in light water-heavy water and in dimethyl sulfoxide-water mixtures. Some measurements were also performed in various buffer solutions in order to study the nature of the acid catalysis. The kinetic data reveal that the hydrolytic decomposition of 4-ethoxy-3-penten-2-one proceeds through two different routes. In the first route the carbonyl oxygen is protonated in a pre-equilibrium process followed by the rate-limiting attack of water ( $A$ -2 mechanism). In the second route the proton attack at the  $\beta$ -position of the carbon-carbon double bond occurs in the rate-limiting step of the reaction ( $A$ -S<sub>E</sub>2 mechanism). The contributions of these reactions were estimated on the basis of the deuterium solvent isotope effect. The third possible route, the pre-equilibrium protonation of the  $\beta$ -carbon atom followed by attack of water at the protonated substrate, could be excluded in the present case.

It is well known that the rate-limiting step in the acid-catalyzed hydrolysis of vinyl ethers is the transfer of the proton at the  $\beta$ -position of the carbon-carbon double bond.<sup>1,2</sup> Although in some cases alternative mechanisms have been suggested for vinyl ether hydrolysis,<sup>3-6</sup> the experimental evidence for these conclusions seems to be inconclusive. Stamhuis *et al.*<sup>3</sup> proposed that in the hydrolytic decomposition of some furans, which are closely related to vinyl ethers, the rate-limiting proton transfer takes place at the  $\alpha$ -position of the carbon-carbon double bond. In contradiction to this proposal it has been found<sup>4-7</sup> that furan and 2-methylfuran exchange  $\alpha$ -hydrogens in aqueous solution at rates which are markedly higher than the rates of the subsequent reactions. Thus no arguments can be found for the assumption of

Unverferth *et al.*<sup>4</sup> that the rate-limiting proton transfer at the  $\beta$ -position could be excluded in the hydrolysis of furans on the basis of the kinetic results obtained for the hydrogen exchange reactions. Recently<sup>8</sup> it was shown that all these kinetic results could, at least in the case of 2-methylfuran, best be explained in terms of a rate-limiting protonation of the  $\beta$ -carbon. Vitullo *et al.*<sup>5</sup> assumed on the basis of buffer experiments that in the hydrolysis of a cyclic vinyl ether the rate-limiting step changes with the change in the buffer concentration. It seems, however, evident that this apparent anomaly is only due to the changes in the hydronium ion concentration of the used buffer mixtures in which the pH has been kept constant; experimental evidence for this kind of changes in different buffer systems is available.<sup>9</sup> The proposed mechanistic change can also be criticized on the basis of previous kinetic data for the hydrolysis of related cyclic vinyl ethers.<sup>10</sup> Recently Loudon *et al.*<sup>6a</sup> assumed on the basis of structural effects that the hydrolytic decomposition of 1-methoxy-1-(*p*-methoxyphenyl)ethene does not proceed through the  $A$ -S<sub>E</sub>2 mechanism. Later Loudon *et al.*<sup>6b</sup> have, however, neglected this concept of the exceptional reaction mechanism of vinyl ether hydrolysis.

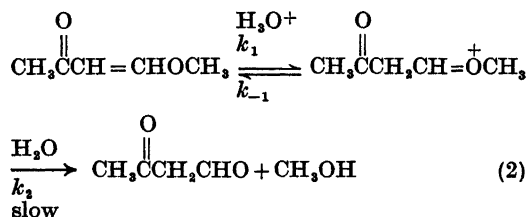
There is, however, a particular case of vinyl ether hydrolysis, namely the hydrolysis of alkyl  $\beta$ -alkoxyvinyl ketones, in which the catalysis by Brønsted acids, typical of the  $A$ -S<sub>E</sub>2 mechanism has not been observed.<sup>11</sup> The kinetic data for these derivatives have been interpreted in terms of a mechanism in which the protonation of the carbonyl oxygen is a pre-equilibrium process followed by the rate-limiting attack of

water at carbon 4 (eqn. 1). Thus the reaction



had no characteristics typical of vinyl ether hydrolysis in spite of the structural similarity, since the acid-catalyzed decomposition proceeded through the alternative oxygen protonation.

Although it is likely that the reaction proposed by Fedor *et al.*<sup>11</sup> is operating in the hydrolysis of 4-methoxy-3-buten-2-one, another mechanism, a pre-equilibrium protonation of the  $\beta$ -position of vinyl ether and the subsequent attack of water in the rate-limiting stage of the reaction (eqn. 2) might also be in accordance with the kinetic data. In the hydroly-



ysis of 4-methoxy-3-buten-2-one structural factors favor the proton abstraction from the oxocarbenium ion. If this structural effect is sufficient then  $k_{-1} \gg k_2$ , as is the case in reaction (2). Therefore the hydrolysis of 4-methoxy-3-buten-2-one (I) was subjected to a thorough kinetic study. In addition the kinetics of the hydrolysis of 4-ethoxy-3-penten-2-one (II) was studied since this compound can be assumed to be more favorable for carbon protonation than is compound I due to the electropositive methyl group attached to the carbenium ion formed during the hydrolytic decomposition.

## EXPERIMENTAL

**Materials.** 4-Methoxy-3-buten-2-one was a product of EGA-Chemie and was purified by

distillation. The purity of the compound was checked by NMR spectroscopy (10% solution in carbon tetrachloride with tetramethyl silane as internal standard):  $\delta$  2.13 (3 H, s), 3.72, (3 H, s), 5.52 (1 H, d), and 7.56 (1 H, d). The coupling constant  $J_{\text{H}_\beta, \text{H}_\alpha}$  13.2 Hz reveals that the product has the *trans* configuration (see Ref. 12). No peaks from the *cis* isomer could be detected.

A fraction of 4-ethoxy-3-penten-2-one used in the kinetic measurements was a gift by E. Taskinen.<sup>13</sup> The *trans* configuration of this sample was verified by the following NMR data:  $\delta$  1.34 (3 H, t), 2.05 (3 H, s), 2.20 (3H, s), 3.84 (2H, q), and 5.38 (1 H, s).<sup>13</sup>

**Kinetic measurements.** Most of the kinetic measurements were performed on a Unicam SP 800 spectrophotometer. The progress of the reaction was followed by checking the disappearance of the absorption at 260 nm. In some cases the reactions were followed on a Perkin-Elmer 46 BCD spectrophotometer. The concentration of the substrate varied in the kinetic measurements from  $3 \times 10^{-5}$  to  $3 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . The cell-housing block of the spectrophotometer was adjusted to the desired temperature with water circulation from a Lauda thermostat.

Perchloric acid was used as catalyst in the lyonium ion-catalyzed reactions. When the effect of the acid concentration was studied in 0.002–0.1 mol  $\text{dm}^{-3}$  perchloric acid solutions the second-order rate coefficients were found to be independent of the acid concentration. Deuterium oxide, used in the measurements in heavy water and in light water-heavy water mixtures, was a product of New England Nuclear. The catalysis by Brønsted acids was studied in formic acid-sodium formate and in monochloroacetic acid-sodium monochloroacetate buffers. In both cases the ratio of the concentration of the acid to the base was 1 to 1. The concentration of the undissociated acid varied between 0.1 and 0.0167 mol  $\text{dm}^{-3}$ . The ionic strength was kept constant at 0.1 mol  $\text{dm}^{-3}$  with sodium chloride. The rate coefficients  $k_{\text{HA}}$  for the reactions catalyzed by formic acid and monochloroacetic acid were calculated from the slopes of the plots of  $k_{\text{obs}}$  versus [HA] by the method of least squares.

Some measurements were also performed in dimethyl sulfoxide (DMSO)-water mixtures. The applied DMSO was purified by distillation under reduced pressure from calcium hydride and the pressure was adjusted so that the temperature did not exceed 363 K. In the experiments in solvent mixtures the perchloric acid concentration was 0.1 mol  $\text{dm}^{-3}$ . In the case of the hydrolysis of 4-ethoxy-3-penten-2-one the measurements in water-DMSO mixtures were performed by spectrophotometry. When the hydrolytic decomposition of 4-methoxy-3-buten-2-one was studied the spectrophotometric method could be applied only in solutions in which the mol fraction of DMSO was lower than 0.3. For higher

Table 1. Kinetic data for the hydronium ion-catalyzed hydrolysis of 4-methoxy-3-buten-2-one (I) and 4-ethoxy-3-penten-2-one (II) in water at different temperatures. The thermodynamic functions of activation are given at 298.15 K.

Com- pound	Temp./K	$k/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$k_{298}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
I	298.6	0.198 ± 0.001	75.15 ± 0.03	-79 ± 2	51.6 ± 0.7	0.424 ± 0.004
		0.215 ± 0.001				
	298.2	0.421 ± 0.002				
		0.435 ± 0.001				
	298.4	0.437 ± 0.004				
		0.440 ± 0.006				
	308.3	0.427 ± 0.002				
		0.857 ± 0.008				
		0.798 ± 0.002				
	317.8	0.872 ± 0.007				
1.653 ± 0.008						
1.653 ± 0.006						
II	297.8	1.66 ± 0.01	77.76 ± 0.05	-57 ± 4	60.8 ± 1.1	0.143 ± 0.003
		0.1469 ± 0.0008				
	298.1	0.1517 ± 0.0004				
		0.138 ± 0.002				
	298.2	0.134 ± 0.001				
		0.139 ± 0.002				
		0.149 ± 0.001				
	308.1	0.1577 ± 0.0007				
		0.1452 ± 0.0009				
		0.359 ± 0.003				
		0.358 ± 0.006				
	317.6	0.337 ± 0.003				
		0.726 ± 0.005				
	327.9	0.717 ± 0.004				
1.371 ± 0.008						
		1.51 ± 0.01				

mol fractions of DMSO the progress of the reaction was followed by NMR from the disappearance of the peaks at  $\delta$  5.52 and 7.56. The practical performance of the kinetic runs took place as follows: 10 cm<sup>3</sup> of perchloric acid solution (0.02 mol dm<sup>-3</sup>) was thermostated to the desired temperature. The mixture contained about 5 vol. % of chloroform as internal standard. After 2 cm<sup>3</sup> of the substrate had been added, the reaction mixture was shaken vigorously. At suitable intervals 1 cm<sup>3</sup> samples were withdrawn from the reaction mixture and transferred to an equivalent amount of sodium hydroxide to stop the reaction. The samples were analyzed on a 60 MHz Perkin-Elmer Model R 10 NMR spectrometer. When the first-order rate coefficients were calculated, the ratio of the peak heights of the doublets at  $\delta$  5.52 and 7.56 to the peak height of the internal standard, chloroform, was used as a quantitative measure of the progress of the reaction.

## RESULTS AND DISCUSSION

The kinetic data for the hydronium ion-catalyzed hydrolysis of 4-methoxy-3-buten-2-one (I) and 4-ethoxy-3-penten-2-one (II) are collected in Table 1. If both of the studied compounds were hydrolyzed through the  $A-S_E2$  mechanism, the ratio of the rate coefficients of (II) and (I) should be of the magnitude 10<sup>3</sup> due to the electropositive methyl group in (II) attached to the center of the intermediate carbenium ion.<sup>3</sup> This is, however, in contradiction to the kinetic data, since the rate coefficients for the hydronium ion-catalyzed hydrolysis of I and II are seen to be almost equal and the small difference which can be observed is even in favor of compound (I) which should be hydrolyzed slower by the  $A-S_E2$  mechanism. In reaction (1) the total structural effect may remain relatively low: the electropositive methyl group favors the pre-equilibrium protonation,

Table 2. The acid-catalyzed hydrolysis of 4-methoxy-3-buten-2-one (I) and 4-ethoxy-3-penten-2-one (II) in buffer solutions. The molar ratio of the acid HA to the base A<sup>-</sup> is 1 to 1. The ionic strength has been adjusted at 0.1 mol dm<sup>-3</sup> with sodium chloride.

HA/ mol dm <sup>-3</sup>	k/ mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>	k <sub>HA</sub> / mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>
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I; 298.3 K; HA = ClCH<sub>2</sub>COOH

0.100	1.12 ± 0.02 1.124 ± 0.009 1.017 ± 0.004	
0.0833	1.09 ± 0.01 1.146 ± 0.006	
0.0667	1.134 ± 0.005 1.087 ± 0.005 1.100 ± 0.004	
0.0500	1.028 ± 0.005 1.069 ± 0.008	
0.0333	0.974 ± 0.005 1.068 ± 0.006 1.095 ± 0.006	(1.3 ± 0.4) × 10 <sup>-3</sup>
0.0167	1.02 ± 0.01 0.973 ± 0.004 0.979 ± 0.016	corr.coeff. 0.655

II; 298.2 K; HA = ClCH<sub>2</sub>COOH

0.100	0.394 ± 0.003 0.400 ± 0.004	
0.0833	0.393 ± 0.003 0.363 ± 0.003	
0.0667	0.369 ± 0.003 0.371 ± 0.002	
0.0500	0.334 ± 0.003 0.327 ± 0.002	
0.0333	0.326 ± 0.001 0.327 ± 0.004 0.321 ± 0.001	(1.4 ± 0.1) × 10 <sup>-3</sup>
0.0167	0.284 ± 0.003 0.281 ± 0.002 0.273 ± 0.001	corr.coeff. 0.962

II; 327.5 K; HA = ClCH<sub>2</sub>COOH

0.100	4.18 ± 0.05 4.28 ± 0.04	
0.0833	3.94 ± 0.02 4.06 ± 0.03	
0.0667	3.69 ± 0.03 3.97 ± 0.03	
0.0500	3.55 ± 0.02 3.67 ± 0.03	
0.0333	3.25 ± 0.02 3.39 ± 0.03	(1.6 ± 0.1) × 10 <sup>-2</sup>
0.0167	2.88 ± 0.02 2.86 ± 0.02	corr.coeff. 0.971

II; 346.7; HA = HCOOH

0.100	3.08 ± 0.02 3.35 ± 0.01	
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	3.30 ± 0.03	
0.0800	2.82 ± 0.02 2.72 ± 0.01	
0.0600	2.52 ± 0.02 2.57 ± 0.02	
0.0400	2.12 ± 0.02 2.23 ± 0.02	(1.6 ± 0.1) × 10 <sup>-2</sup>
0.0200	1.90 ± 0.01 2.05 ± 0.02	corr.coeff. 0.978

but this substitution similarly reduces the nucleophilic attack of water at the carbenium ion center. Thus the only conclusion which can be drawn on the basis of structural effects is that at least one of the studied compounds hydrolyzes through the A-S<sub>E</sub>2 mechanism. Additional kinetic data are required to get information of the possible reaction routes.

The activation entropies for the studied reactions, -79 and -57 J K<sup>-1</sup> mol<sup>-1</sup> for the hydrolysis of I and II, respectively, are slightly smaller than generally observed for the A-S<sub>E</sub>2 hydrolysis of vinyl ethers.<sup>1,2</sup> The magnitude of the activation entropy, however, can be considered as a poor criterion of the reaction mechanism since in the hydrolysis of vinyl ethers the value of ΔS<sup>‡</sup> has been observed to vary remarkably with the structure of the substrate.<sup>14</sup> In this context it is more important to note that in the hydrolytic decomposition of 4-ethoxy-3-penten-2-one (II) ΔS<sup>‡</sup> is about 20 J K<sup>-1</sup> mol<sup>-1</sup> higher than in the hydrolysis of compound (I). As compounds I and II are closely related, the observed difference may reflect a definite change in the reaction mechanism. Although the A-S<sub>E</sub>2 mechanism cannot be excluded on the basis of the magnitude of the activation entropy, it must be remembered, that the calculated ΔS<sup>‡</sup> values are in accordance with a mechanism in which pre-equilibrium protonation of the oxygen atom is followed by the rate-limiting attack of water at the carbenium ion center (A-2 mechanism).<sup>15</sup>

*General acid catalysis.* As shown above the choice between the A-S<sub>E</sub>2 mechanism and the A-2 mechanism cannot be made on the basis of structural effects and the temperature dependence of the rate coefficients, but additional kinetic data are required. In this context buffer experiments might be informative, since in the reaction proceeding through the A-S<sub>E</sub>2 mechanism general acid catalysis should be detected in contrast to the alternative reaction (A-2

**Table 3.** The hydronium ion-catalyzed hydrolysis of 4-methoxy-3-buten-2-one (I) and 4-ethoxy-3-penten-2-one (II) in dimethyl sulfoxide-water mixtures at 298 K.

Compound	$x_{\text{DMSO}}$	$k/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
I	0.000	0.428 <sup>a</sup>
	0.119	0.480 ± 0.003
		0.476 ± 0.001
		0.465 ± 0.002
	0.214	0.501 ± 0.003
	0.299	0.473 ± 0.002
		0.419 ± 0.003
		0.425 ± 0.001
	0.733	0.442 ± 0.001
		0.439 ± 0.002
0.192 ± 0.002		
0.769	0.191 ± 0.003	
	0.166 ± 0.005	
	0.171 ± 0.004	
0.846	0.129 ± 0.008	
	0.125 ± 0.007	
	0.144 <sup>a</sup>	
II	0.000	0.144 <sup>a</sup>
	0.214	0.0701 ± 0.0005
		0.0695 ± 0.0007
		0.0307 ± 0.0003
	0.414	0.0298 ± 0.0002
		0.0180 ± 0.0002
		0.0180 ± 0.0002
	0.615	0.0180 ± 0.0002
		0.0128 ± 0.0001
		0.0124 ± 0.0002
0.791	0.0108 ± 0.0002	
	0.00539 ± 0.00003	
	0.00574 ± 0.00004	
0.926		

<sup>a</sup> The average from Table 1.

mechanism), which is catalyzed only by the hydronium ion. Kinetic measurements were therefore performed both in monochloroacetic acid-sodium monochloroacetate and in formic acid-sodium formate buffers. The obtained rate coefficients are collected in Table 2. When the first-order rate coefficients for the hydrolytic decomposition of 4-ethoxy-3-penten-2-one (II) were plotted against the concentration of the undissociated acid, a linear correlation (eqn. 3) was obtained the correlation coefficients being

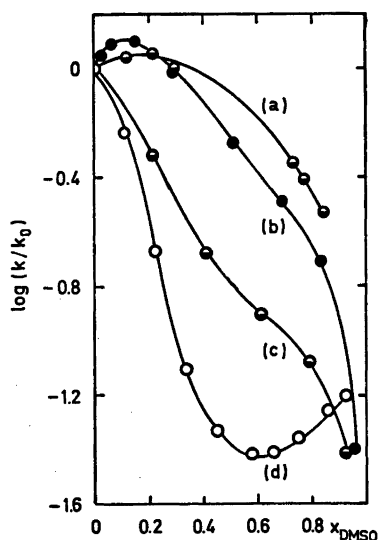
$$k_{\text{obs}} = k_{\text{HA}}[\text{HA}] + \text{constant} \quad (3)$$

0.962 and 0.978 in the case of monochloroacetic acid and formic acid, respectively. The catalytic coefficients  $k_{\text{HA}}$  were calculated from the experimental data by the method of least squares (Table 2).

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In the hydrolysis of 4-methoxy-3-buten-2-one (I) the general acid catalysis is less probable due to the fact that the observed first-order rate coefficients are almost independent of the concentration of the undissociated acid. When the first-order rate coefficients determined in monochloroacetic acid-sodium monochloroacetate buffer are plotted against the concentration of the undissociated acid (eqn. 3) the correlation coefficient of the plot is found to be only 0.65. Thus the contribution of the  $A\text{-S}_{\text{E}}2$  reaction must be relatively small in the hydrolytic decomposition of 4-methoxy-3-buten-2-one. Fedor *et al.*<sup>11</sup> have previously studied the hydrolysis of 4-methoxy-3-buten-2-one in formic acid-sodium formate buffer and a general acid catalysis could not be observed.

**Solvent effects.** Since the kinetic measurements in solvent mixtures have been found to be an excellent method to distinguish between the  $A\text{-S}_{\text{E}}2$  and  $A\text{-2}$  mechanisms,<sup>16-17</sup> the hydrolysis of 4-methoxy-3-buten-2-one and 4-ethoxy-3-penten-2-one was subjected to kinetic studies in water-dimethyl sulfoxide mixtures. The measured first-order rate coefficients are collected in Table 3. To illustrate the solvent effects in the



**Fig. 1.** The dependence of the rate coefficients on the solvent composition: (a) the hydrolysis of 4-methoxy-3-buten-2-one, (b) the  $A\text{-2}$  hydrolysis of ethyl acetate,<sup>18</sup> (c) the hydrolysis of 4-ethoxy-3-penten-2-one, and (d) the  $A\text{-S}_{\text{E}}2$  hydrolysis of 2-methyl-4-methylene-1,3-dioxolane.<sup>17</sup>

Table 4. The lyonium ion-catalyzed hydrolysis of 4-methoxy-2-buten-3-one (I) and 4-ethoxy-3-penten-2-one (II) in the mixture of light and heavy water. Temperature 298.2 K.

Deuterium atom fraction	$k_{\text{L}_2\text{O}^+}/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	$k_n/k_H$
<b>I</b>		
0.000	0.428 <sup>a</sup>	1.000
0.199	0.485 ± 0.001	1.140
	0.491 ± 0.001	
0.399	0.564 ± 0.001	1.276
	0.528 ± 0.002	
0.599	0.633 ± 0.001	1.484
	0.637 ± 0.003	
0.799	0.736 ± 0.003	1.715
	0.731 ± 0.003	
0.998	0.903 ± 0.007	2.078
	0.875 ± 0.003	
0.998 <sup>b</sup>	0.871 ± 0.004	
	0.847 ± 0.003	
<b>II</b>		
0.000	0.144 <sup>a</sup>	
0.199	0.1478 ± 0.0009	1.047
	0.1527 ± 0.0006	
0.399	0.169 ± 0.001	1.160
	0.165 ± 0.001	
0.599	0.1771 ± 0.0004	1.237
	0.1780 ± 0.0008	
0.799	0.191 ± 0.001	1.365
	0.201 ± 0.001	
0.998	0.2181 ± 0.0007	1.499
	0.212 ± 0.001	
	0.205 ± 0.002	
	0.204 ± 0.003	
	0.221 ± 0.002	
0.998 <sup>c</sup>	2.11 ± 0.02	
	2.02 ± 0.02	
	2.09 ± 0.04	

<sup>a</sup> The average from Table 1. <sup>b</sup> Temperature 298.4 K. <sup>c</sup> Temperature 327.3 K.

studied reactions the logarithms of the relative rate coefficients were plotted against the mol fraction of dimethyl sulfoxide (Fig. 1). The observed effect for the hydrolysis of 4-methoxy-3-buten-2-one (plot a) is seen to be typical of the A-2 mechanism since the rate dependence is almost equal to that observed in the A-2 hydrolysis of ethyl acetate (plot b).<sup>18</sup>

The measured solvent effect in the hydrolysis of 4-ethoxy-3-penten-2-one is shown in plot c in Fig. 1. For comparison the logarithms of the rate coefficients of a model A-S<sub>E</sub>2 reaction, the hydrolysis of 2-methyl-4-methylene-1,3-dioxolane,<sup>17</sup> are plotted in Fig. 1 as well (plot d). The form of plot c as compared with plots b and d

reflects the existence of concurrent A-S<sub>E</sub>2 and A-2 reactions in the hydrolysis of 4-ethoxy-3-penten-2-one. In solutions in which the mol fraction of dimethyl sulfoxide is lower than 0.4 a remarkable rate decrease can be observed with increasing DMSO content of the solvent. As shown in plot d this trend is typical of the A-S<sub>E</sub>2 mechanism. The effect of the possible A-2 route remains negligible under these conditions, since the rate of the A-2 reaction is almost independent of the solvent composition in solutions in which  $x_{\text{DMSO}}$  is less than 0.4 (plot b).

If the hydrolysis of 4-ethoxy-3-penten-2-one proceeds, at least partially, through the A-2 route, its contribution should be increased with increasing DMSO content of the solvent while the rate of the A-S<sub>E</sub>2 reaction is decreased. In Fig. 1 it can be seen that this is really the case. In solutions in which the mol fraction of DMSO is higher than 0.6, plot c for the hydrolysis of 4-ethoxy-3-penten-2-one is similar to that for the A-2 hydrolysis of ethyl acetate (plot b). Thus in solutions in which the mol fraction of DMSO is higher than 0.6 the contribution of the A-S<sub>E</sub>2 reaction in the hydrolysis of 4-ethoxy-3-penten-2-one must be negligible, since otherwise, especially at the lowest water concentrations, the effect of the A-S<sub>E</sub>2 reaction should also be observed.

Although the kinetic data determined in dimethyl sulfoxide-water mixtures reveal that the hydrolysis of 4-ethoxy-3-penten-2-one proceeds through concurrent A-S<sub>E</sub>2 and A-2 reactions the contributions of the different routes remain still undetermined. This analysis can be performed from kinetic data determined in mixtures of light and heavy water.

*Deuterium solvent isotope effects.* The kinetic data for the hydrolysis of 4-methoxy-3-buten-2-one (I) and 4-ethoxy-3-penten-2-one (II) in mixtures of light and heavy water are collected in Table 4. In the hydrolysis of the former compound the observed deuterium solvent isotope effect,  $k_{\text{D}_2\text{O}^+}/k_{\text{H}_2\text{O}^+} = 2.08$ , is in contradiction to the A-S<sub>E</sub>2 hydrolysis of vinyl ethers, since a reverse isotope effect,  $k_{\text{D}_2\text{O}^+}/k_{\text{H}_2\text{O}^+} = 0.3-0.5$ , was to be expected.<sup>1,2</sup> The measured isotope effect is also in excellent agreement with the value obtained by Fedor *et al.*<sup>11</sup> Thus the A-S<sub>E</sub>2 mechanism can be excluded in the hydrolysis of 4-methoxy-3-buten-2-one, especially in

view of the fact that catalysis by general acids could not be detected (see above). The measured deuterium solvent isotope effect is, however, in accordance with the *A-2* mechanism, since in this case  $k_{D_2O^+}/k_{H_2O^+}$  values higher than unity are to be expected.<sup>10</sup> Thus the mechanism proposed by Fedor *et al.*<sup>11</sup> (eqn. 1) seems to be the most probable one when considering the present kinetic data. However, the mechanism given in eqn. 2 cannot be excluded on the basis of the kinetic data discussed above. Therefore additional measurements were performed in heavy water in order to study the possible deuteration of the  $\alpha$ -hydrogen of the vinyl ether which would be the case in the hydrolytic decomposition through reaction (2). When the disappearance of the  $\alpha$ - and  $\beta$ -hydrogens was followed, it was found that these rates were equal within the limits of the experimental error. In addition it was found that the coupling of the  $\alpha$ -hydrogens remained unaltered during the protolytic reaction. These results can be understood only if the deuteration does not take

place during the progress of the hydrolytic decomposition. Thus reaction (2) can be excluded in the hydrolysis of 4-methoxy-3-buten-2-one.

In the hydrolytic decomposition of 4-ethoxy-3-penten-2-one the deuterium solvent isotope effect is found to be 1.50 (Table 4) which is slightly lower than that for the hydrolysis of 4-methoxy-3-buten-2-one but markedly higher than the deuterium solvent isotope effect in the *A-S<sub>E</sub>2* hydrolysis of vinyl ethers. This situation could be explained if the hydrolysis of 4-ethoxy-3-penten-2-one took place through concurrent *A-S<sub>E</sub>2* and *A-2* reactions. This conclusion was also drawn on the basis of the solvent effects (see above).

Let us denote by  $k'$  the rate coefficient for the reaction proceeding through the *A-2* mechanism (oxygen protonation) and by  $k''$  the rate coefficient for the *A-S<sub>E</sub>2* reaction (carbon protonation). In the mixture of light and heavy water, in which the deuterium mol fraction is  $n$ , the total rate coefficient can be expressed by eqn. (4). In the particular cases when  $n=0$  and  $n=1$  the observed rate coefficient can be

$$k_n = k_n' + k_n'' \quad (4)$$

expressed by eqn. (5). As discussed above 4-methoxy-3-buten-2-one (I) hydrolyzes mainly through the *A-2* mechanism. As I is closely

$$\begin{aligned} k_{0,0} &= k_{0,0}' + k_{0,0}'' \\ k_{1,0} &= k_{1,0}' + k_{1,0}'' \end{aligned} \quad (5)$$

related to II it can be assumed that in the *A-2* hydrolysis of compounds I and II the  $k_{D_2O^+}/k_{H_2O^+}$  values are almost equal. Thus the value  $k_{1,0}'/k_{0,0}' = 2.078$ , obtained for the hydrolysis of 4-methoxy-3-buten-2-one, can also be applied to the hydrolysis of 4-ethoxy-3-penten-2-one proceeding through the *A-2* route. The deuterium solvent isotope effect in the *A-S<sub>E</sub>2* hydrolysis of 4-ethoxy-3-penten-2-one can be estimated on the basis of the kinetic data for vinyl ether hydrolysis. If  $\beta$ -chloroethyl vinyl ether is chosen as the model compound, since its hydrolysis has been studied thoroughly in  $H_2O$ - $D_2O$  mixtures,<sup>2</sup> then  $k_{1,0}''/k_{0,0}'' = 0.397$ . When the deuterium solvent isotope effects given above and the observed rate coefficients for the hydrolysis of 4-ethoxy-3-penten-2-one (Table 4) are substituted into eqn. 5, the following partial rate

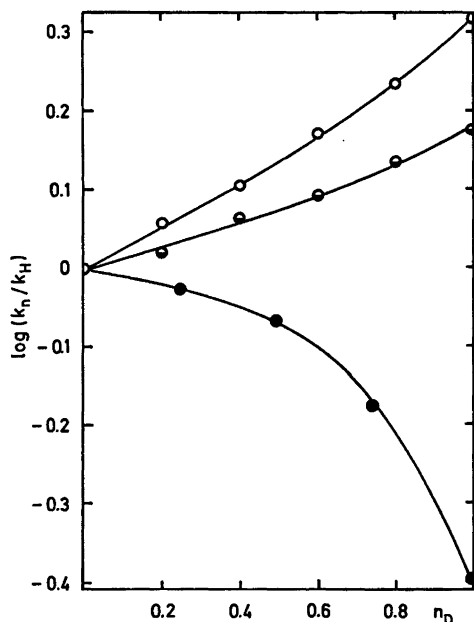


Fig. 2. The logarithms of the rate coefficients in the hydrolysis of vinyl ethers as a function of the deuterium mol fraction of the solvent. Notation: 4-methoxy-3-buten-2-one (open circles), 4-ethoxy-3-penten-2-one (half-filled circles), and 2-chloroethyl vinyl ether (filled circles).<sup>2</sup>

coefficients are obtained in light water;  $k_{0,0}'' = 0.051 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (carbon protonation) and  $k_{0,0}' = 0.092 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (oxygen protonation). Thus the contribution of the carbon protonation is about 35 % in light water, but in heavy water it decreases to 10 % as can be estimated on the basis of the kinetic data.

The existence of concurrent  $A-2$  and  $A-S_E2$  reactions in the hydrolysis of 4-ethoxy-3-penten-2-one (II) is apparent also on the basis of the kinetic data in the mixtures of light and heavy water. From Fig. 2 it can be seen that in all solvent mixtures the deuterium solvent isotope effect in the hydrolysis of compound II is an intermediate between those of  $A-2$  and  $A-S_E2$  reactions. When the rate coefficients of the hydrolysis of 4-ethoxy-3-penten-2-one are calculated from the partial rate coefficients  $k_{0,0}'$  and  $k_{0,0}''$  given above and from the ratios  $k_n'/k_{0,0}'$  and  $k_n''/k_{0,0}''$  obtained from plots b and c in Fig. 2, it is found that the calculated values are in excellent agreement with the experimental data, since the difference between the measured and calculated values is in all cases lower than 3 %.

From the kinetic data obtained in the present study it can thus be concluded that the protonation of the  $\beta$ -carbon atom is not a pre-equilibrium process in the hydrolysis of  $\beta$ -acetyl substituted vinyl ethers. The hydrolysis of 4-methoxy-3-buten-2-one proceeds mainly through oxygen protonation. Although in the hydrolysis of 4-ethoxy-3-penten-2-one some evidence for carbon protonation could be observed the general acid catalysis reveals that proton transfer takes place in the rate-limiting step of this reaction.

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