# Kinetics and Mechanism of Acid-catalysed Addition of Methanol to α-Methoxystyrenes [1]

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A kinetic study of the complex behaviour of ring-substituted α-methoxystyrenes in acidic (HBr) methanol is reported. The reaction yields the corresponding acetals as the only kinetic products; these are subsequently partly hydrolysed into acetophenones with rates only a little lower than those of their formation. The rate-limiting step for methanol addition corresponds to proton attachment to the double bond, yielding an oxocarbenium ion which is trapped by methanol with a rate constant 10^4 higher than that of ion deprotonation. The rate constants for proton transfer from $CH_3OH_2^+$ are in the same range of magnitude as those for proton transfer from H_3O^+ in water. The lyonium ion catalytic constants fit a good Young–Jencks equation with ρ^n −2.86 and ρ^r −1.28.

In contrast to enol ether hydrolysis which has served as a reaction model for proton-transfer reactions,[2] the reaction of enol ethers with alcohols has not received much attention. Gold and Grist examined catalysis by HCl for the reaction of methanol with cyanoketene dimethyl acetal and reported solvent isotope effects.[3] These are in agreement with a mechanism consisting of a rate-limiting proton transfer to the double bond, followed by a trapping of the oxocarbenium ion intermediate by methanol and/or residual water. In preliminary communications we reported data on the kinetics of the reaction of methanol with isopropenyl methyl ether and with α-methoxystyrenes,[1,4,5] and showed that the lyonium ion catalytic constants can be combined with rate constants for enol ether formation from acetals in order to obtain equilibrium constants for the acetal–enol ether process. We report here an extended study of the HBr-catalysed reaction of α-methoxystyrenes (1a—i) with methanol.

$$X\text{—}C6H4\text{—}\underset{\underset{OCH_3}{|}}{C}{=}CH_2$$

(1)
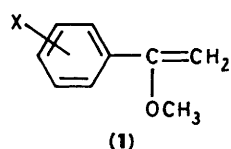
a; X = 4-OCH₃   f; X = 3-Cl
b; X = 4-CH₃   g; X = 3-CF₃
c; X = H   h; X = 3-NO₂
d; X = 4-F   i; X = 4-NO₂
e; X = 4-Cl

The reaction of enol ethers with methanol differs from that in water by the fact that the final product should be the appropriate acetal in strictly anhydrous methanol, instead of the carbonyl compound. However, since methanol always contains small amounts of residual water, and since acetophenone acetals are rather unstable in methanol,[6] a mixture of acetal and ketone should finally be obtained. This paper also deals with the timing of the successive processes, enol ether protonation, acetal formation from the intermediate oxonium ion, and acetal hydrolysis.

Results

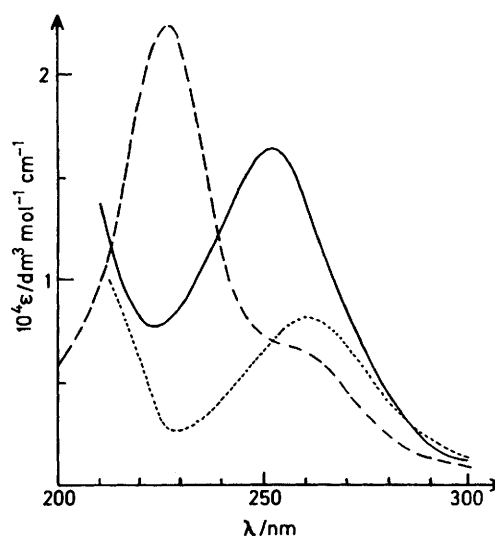*Kinetics of the Reaction of* (1h) *with Methanol.*—Figure 1 shows the u.v. spectra of (1h), 3-nitroacetophenone, and 3-

Figure 1. Absorption spectra of (1h) (——), 3-nitroacetophenone (– – –), and 3-nitroacetophenone dimethyl acetal (-----)

nitroacetophenone dimethyl acetal in methanol. The acetal and the ketone exhibit the same molar absorption coefficients at 252 nm. It follows that the rates of enol ether consumption can be measured from the rates of change of absorbance (A_t) whatever the actual product, acetal or ketone. It was observed that A_t depended on time according to equation (1), and that the

$$A_t - A_\infty = (A_0 - A_\infty)e^{-k_\psi t} \qquad (1)$$

measured A_∞ values corresponded to those expected for the complete enol ether ⟶ (ketone + acetal) reaction. Since A_t is linearly related to enol ether and (acetal + ketone) concentrations, it can be easily established that k_ψ corresponds to a first-order enol ether uptake.

Table 1 lists the values of k_ψ for different concentrations of water in methanol when the stoicheiometric acid concentration was maintained at [HBr] 2.06×10^{-2} mol dm⁻³. The dependence of k_ψ on [H₂O] can, as shown for similar reactions,[3,7,8] be related to a shift of the $CH_3OH_2^+$–H_3O^+ equilibrium [equation (2)] when water concentration is increased. Table 1

$$CH_3OH_2^+ + H_2O \underset{}{\overset{K}{\rightleftharpoons}} CH_3OH + H_3O^+ \qquad (2)$$

Table 1. Water concentration dependence of the first-order rate constant for methanol addition to (**1h**) ([HBr] 2.06 × 10⁻² mol dm⁻³; 25 °C)

$[H_2O]$/mol dm⁻³ ^{a}	$10^2 k_\psi$/s⁻¹ ^{b}	$(k_\psi/[CH_3OH_2^+])$/dm³ mol⁻¹ s⁻¹
0.0062	1.96	0.982
0.050	1.67	0.998
0.075	1.52	0.987
0.121	1.28	0.970
0.189	1.05	0.967
0.339	0.776	0.980
0.460	0.633	0.980
0.669	0.490	1.01

^{a} Overall water concentration, including water engaged in H_3O^+.
^{b} Mean values for 3 runs. Maximum deviations ±2%.

also shows that the ratio $k_\psi/[CH_3OH_2^+]$ is constant when $[CH_3OH_2^+]$ is calculated by equation (3), where $[H^+]_{st}$ is the

$$[CH_3OH_2^+] = [H^+]_{st} a_m/(a_m + K_r[H_2O]) \quad (3)$$

stoicheiometric acid concentration and a_m the activity of methanol (a_m 1 in pure solvent, but corrected for water concentration when methanol contains significant amounts of water, K_r 4.94 dm³ mol⁻¹ at 25 °C).[9] This means that the rate depends linearly on $[CH_3OH_2^+]$, but is independent of $[H_3O^+]$.

Table 2 lists the lyonium ion catalytic constants obtained when different acid concentrations were used; they are not rigorously constant, but increase slightly with acid concentration. Positive electrolyte effects have been reported for the reaction of cyanoketene dimethyl acetal with methanol;[3] the rate constant for $CH_3OH_2^+$ catalysis was shown to be dependent on HCl concentration when the ionic strength was not maintained constant, but independent of [HCl] when the solution contained a swamping concentration of sodium perchlorate. It follows that the variations of $k_\psi/[CH_3OH_2^+]$ with [HBr] can be ascribed to similar electrolyte effects. By plotting log $(k_\psi/[CH_3OH_2^+])$ against [HBr]$^{\frac{1}{2}}$ we observed that the variations of the catalytic constant are accounted for by equation (4) (r 0.9997, standard deviation 0.0014). Although the

$$\log (k_\psi/[CH_3OH_2^+]) = 0.58 \sqrt{[HBr]} + \\ \log (k_\psi/[CH_3OH_2^+])° \quad (4)$$

linear variations of the catalytic constant with the square root of the ionic strength are not in agreement with expectations for a reaction between an ion and a dipolar molecule (for this kind of reaction log k is expected to depend linearly on ionic strength),[10] this equation allows for extrapolation at infinite dilution.*

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* Catalytic rate constants for methanol addition to cyanoketene dimethyl acetal (ref. 3) fit an equation similar to (4), but with a coefficient of *ca.* 1.4 which is significantly larger than that observed here. Moreover, the three points for [HCl] < 0.25 mol dm⁻³ show large negative deviations. It is therefore possible that equation (4) does not hold for very low acid concentrations and does not allow for extrapolation to zero, as assumed in this work for all substituents. However, it can be stressed that the corrections for ionic strength are in most cases of minor importance. Furthermore, since rate measurements for methanol addition to (**1e**) were used for indirect acid determination (see Experimental section), assuming the validity of equation (4), deviations from this equation would be compensated by errors in acid determination. It follows that errors in the absolute values at zero ionic strength could result from the procedure, but that relative errors would be the same for all substituents unless the coefficient in equation (4) is significantly substituent-dependent.

Table 2. Acid concentration dependence of the lyonium ion-catalytic constant for methanol addition to (**1h**) (25 °C)

$10^2[HBr]$/mol dm⁻³	$10^2[H_2O]$/mol dm⁻³ ^{a}	$(k_\psi/[CH_3OH_2^+])$/dm³ mol⁻¹ s⁻¹
0.194	0.351	0.860
0.565	0.449	0.895
1.105	0.623	0.937
2.06	0.620	0.982
5.34	1.27	1.105
10.0	2.09	1.24

^{a} Overall water concentration, including water engaged in H_3O^+.
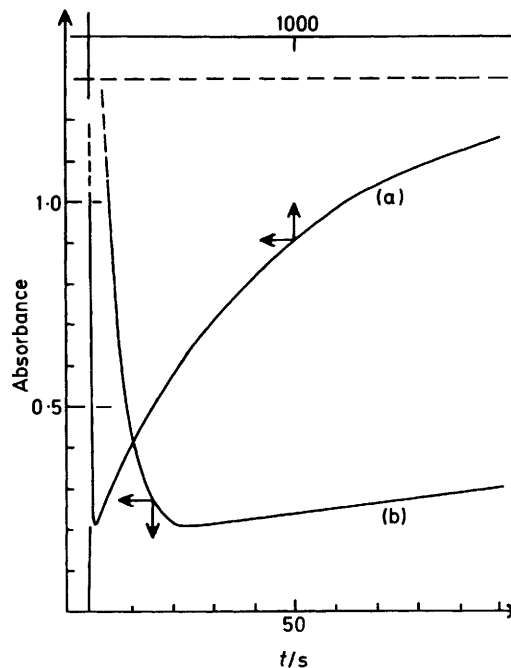
Figure 2. Typical kinetic run at 257 nm for the reaction of (**1a**) with acidic methanol ([HBr] 1.78 × 10⁻⁴ mol dm⁻³, [H₂O] 4.50 × 10⁻³ mol dm⁻³, and [eth]₀ 1.78 × 10⁻⁴ mol dm⁻³). Curve (b) corresponds to the initial part of curve (a). The dashed line represents final absorbance

In contrast to (**1h**) it was usually not possible to find any wavelengths for the other substituted enol ethers at which the absorption coefficients of acetals and ketones were the same and at which enol ether absorptivities were sufficiently different to allow kinetic measurements. For compounds (**1a—g** and **i**) the kinetics of the reaction with methanol were followed at wavelengths corresponding to maximum absorptivities of the enol ethers. It was observed that absorbances decreased at first, but that after reaching minima they increased more slowly, to final values corresponding to those expected for equilibrium mixtures of ketones and acetals. Since at the fixed wavelengths chosen the molar absorption coefficients of acetals are usually very small and those of ketones fairly large, these absorbance–time curves can be accounted for by assuming that the reaction first yields the acetal and that the acetal is subsequently partly hydrolysed more slowly by the small amounts of water. Such behaviour is shown in Figure 2 in the case of (**1a**).

When it is assumed that acetal formation and hydrolysis are two consecutive reactions [equation (5)] equations (6)—(8)

$$\text{Enol ether} \xrightarrow{k_\psi} \text{Acetal} \underset{k_F}{\overset{k_H}{\rightleftharpoons}} \text{Ketone} \tag{5}$$

$$[\text{eth}]_t = [\text{eth}]_o e^{-k_\psi t} \tag{6}$$

$$[\text{ket}]_t = \frac{k_H[\text{eth}]_o}{k_H + k_F} - \frac{[\text{eth}]_o}{k_H + k_F - k_\psi}\left[k_H e^{-k_\psi t} - \frac{k_H}{k_H + k_F} k_\psi e^{-(k_H + k_F)t} \right] \tag{7}$$

$$[\text{ac}]_t = \frac{k_F[\text{eth}]_o}{k_H + k_F} + \frac{[\text{eth}]_o}{k_H + k_F - k_\psi}\left[(k_\psi - k_F)e^{-k_\psi t} - \frac{k_H}{k_H + k_F} k_\psi e^{-(k_H + k_F)t} \right] \tag{8}$$

express the variations of enol ether, ketone, and acetal concentrations with time.[11] In these equations, k_H and k_F are the pseudo-first-order rate constants for acetal hydrolysis and formation, respectively, at given water and acid concentrations. It follows, since the absorbance at time t can be written as the sum of partial absorbances of the three chemical species, that equation (9) expresses the theoretical variations of A_t against time (ε_{eth}, ε_{ac}, and ε_{ke} are molar absorption coefficients of enol ether, acetal, and ketone, respectively).

We recently reported k_H and k_F data for the acetophenone series[7] and showed that, at least for low concentrations of water, k_H and k_F are proportional to and independent of water concentration, respectively. These data made it possible to calculate k_H and k_F under our conditions.

Pseudo-first-order rate constants k_ψ were calculated by assuming the validity of equation (9). We used a method which consisted in determining k_ψ such that the sum of the quadratic differences between calculated and experimental A_t values was a minimum. Standard deviations were usually in the 0.002—0.005 range. Table 3 lists k_ψ and $k_\psi/[\text{CH}_3\text{OH}_2^+]$ data obtained for (1a—i), as well as the extrapolated values at zero ionic strength, $(k_\psi/[\text{CH}_3\text{OH}_2^+])°$. These latter data were obtained by assuming that equation (4) is valid for all substituents with the same coefficient.
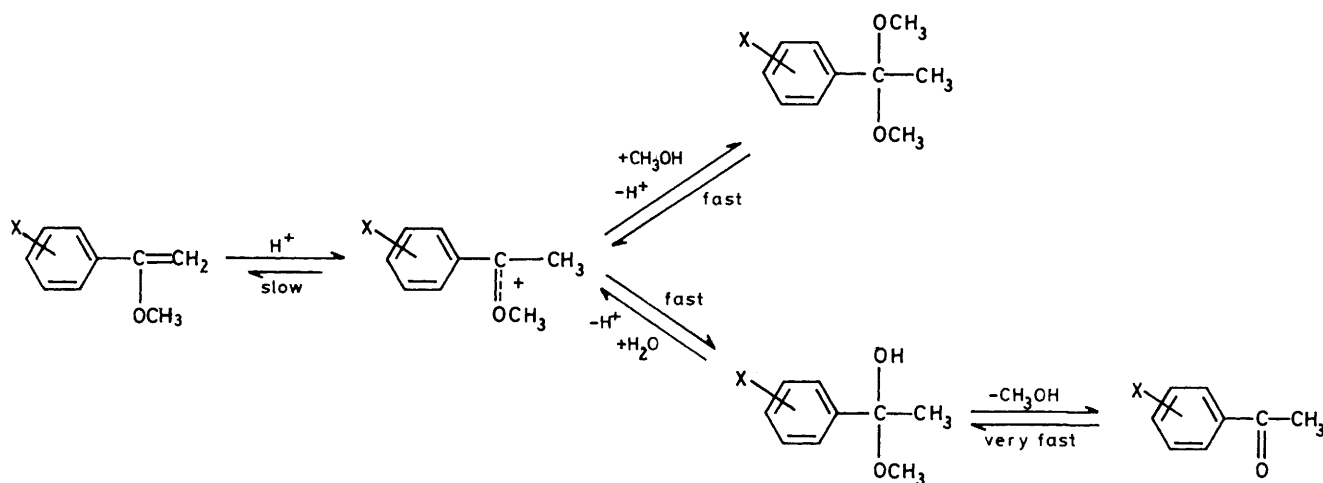
Discussion

Mechanism.—The excellent fit of the experimental data to equation (9) shows that acetal is the only kinetic product; ketone is formed subsequently. This behaviour, which can be

understood in terms of the Scheme if one assumes that the oxocarbenium ion intermediate is trapped only by bulk methanol, is in agreement with what is known about the relative reactivities of methanol and water with oxocarbenium ions. Cordes and Wenthe showed that deuterium-labelled methyl exchange for different dimethyl acetals in an acidic equimolar CD_3OD-D_2O mixture occurs at about the same rate as acetal hydrolysis.[12] This is due to roughly equal rates for methanol and water reactions with the oxocarbenium ions. The water concentration is too low under our experimental conditions for direct formation of acetophenones from α-methoxystyrenes to occur.

Data on enol ether formation from acetals[13] and on acetal hydrolysis in methanol containing small amounts of water[7] have made it possible to calculate *ca.* 3×10^4 for the ratio between rate constants for water attachment to the oxo-carbenium ions derived from acetophenone dimethyl acetals and for proton abstraction, and to show that this ratio is roughly substituent-independent.[13] It follows, since the rate constants for methanol and water attachments to the ions can be assumed to be roughly equal, that carbenium ions are trapped by methanol *ca.* 10^4 times faster than they are deprotonated. The rate of methanol addition to enol ethers is controlled by the rate of proton transfer to the double bond.

The kinetic curves are also in agreement with the assumption that acetal formation from enol ethers is an irreversible process. This is in keeping with the equilibrium constants, $K_{ac}^{eth} = [\text{enol ether}] a_m/[\text{acetal}]$ (a_m 1), which can be calculated as the ratios of the rate constants for the forward and reverse reactions, and which are in the 5.4 $\times$ 10^{-4} (1h) to 9.6 $\times$ 10^{-4} (1a) range.[5,13]

$$\frac{A_t}{[\text{eth}]_o} = (\varepsilon_{ke} - \varepsilon_{ac})\frac{k_H}{k_H + k_F} + \varepsilon_{ac} + (\varepsilon_{eth} - \varepsilon_{ac})e^{-k_\psi t} - \frac{\varepsilon_{ke} - \varepsilon_{ac}}{k_H + k_F - k_\psi}\left[k_H e^{-k_\psi t} - \frac{k_H}{k_H + k_F} k_\psi e^{-(k_H + k_F)t} \right] \tag{9}$$

Scheme.

Table 3. Kinetic parameters for the acid-catalysed addition of methanol to α-methoxystyrenes (1) (25 °C)

X^a	10^3[HBr]/mol dm^{-3}	10^2[H$_2$O]/mol dm$^{-3 b}$	$10^2 k_\psi$/s$^{-1 c}$	$(k_\psi/[CH_3OH_2^+])$/dm^3 mol^{-1} s^{-1}	$(k_\psi/[CH_3OH_2^+])^\circ$/dm^3 mol$^{-1 d}$ s^{-1}
4-OCH$_3$	0.0817	0.385	9.3	1 160	1 146
	0.178	0.450	21.6	1 240	1 218
		1.17	20.4	1 213	1 190
		1.57	18.5	1 120	1 100
		2.40	19.3	1 200	1 180
4-CH$_3$	0.178	0.450	4.82	276	271
	0.536	0.339	15.0	283	275
H	0.540	0.272	4.42	82.8	80.3
	0.966	0.294	8.15	85.4	81.9
4-F	0.966	0.294	4.62	48.5	46.5
	1.94	0.385	8.91	46.7	44.0
4-Cl	1.00	0.451	1.84	18.8	18.0
	2.19	0.281	4.21	19.5	18.3
3-Cl	1.94	0.323	1.42	7.44	7.00
	5.56	0.360	4.19	7.65	6.90
3-CF$_3$	5.62	0.352	1.65	2.98	2.69
	10.7	0.438	3.35	3.19	2.77
3-NO$_2$	see Tables 1 and 2				0.81
4-NO$_2$	20.8	0.674	1.00	0.493	0.405

^{a} X in (1). ^{b} Overall water concentration, including water engaged in H$_3$O$^+$ ^{c} Mean values from usually three runs. Maximum deviations 4%. ^{d} Corrected for electrolyte effects.

When the large differences in energies (*ca.* 20 kJ mol^{-1}) between the transition states for methanol or water attachment to the ions and for protonation–deprotonation are considered, it is at first sight surprising that the rate of acetal hydrolysis is significantly lower than that of methanol addition to enol ethers. This stems (i) from the small concentrations of water in methanol, which reduce the rate of hydrolysis, and (ii) from the large differences in initial state energies (17—19 kJ mol^{-1}) due to the fact that acetals are more stable than enol ethers.

Rate-limiting proton transfer to the double bond implies that the reaction is general acid-catalysed. Hence, k_ψ should be written as in equation (10). Data in Table 1 show that

$$k_\psi = k_{CH_3OH_2^+}[CH_3OH_2^+] + k_{H_3O^+}[H_3O^+] \quad (10)$$

$k_\psi/[CH_3OH_2^+]$ is independent of water at constant overall acid concentration; the $k_{H_3O^+}[H_3O^+]$ term is negligible even for the highest relative water concentrations. This conclusion, which is similar to Gold and Grist's for the reaction of methanol with cyanoketene dimethyl acetal,[3] is a little surprising if one considers the predicted $k_{CH_3OH_2^+}/k_{H_3O^+}$ ratio (*ca.* 15) which can be calculated if one assumes the validity of the Brönsted relation for the two ions and an α exponent of 0.6 (ref. 5) $\{k_{H_3O^+}/k_{CH_3OH_2^+} = 3[2(K_a)_{H_3O^+}/3(K_a)_{CH_3OH_2^+}]^\alpha/2$; $(K_a)_{H_3O^+}/(K_a)_{CH_3OH_2^+} = 1/K_t[CH_3OH]\}$. A contribution as large of 20% for H$_3$O$^+$ catalysis would instead be expected in the case of the reaction of (1h) with methanol.

Ring Substituent Effects.—Data in Table 3 show that, as expected, electron-donating substituents increase $k_\psi/$ [CH$_3$OH$_2^+$]. This is due to a stabilisation of the transition state, which to some extent resembles the oxocarbenium ion. When log $(k_\psi/[CH_3OH_2^+])^\circ$ (mean values) is plotted against the σ^n (ref. 14) or σ$^+$ (ref. 15) substituent parameters, no good straight line is observed. Instead, the substituent effects can be accounted for by the Yukawa–Tsuno–Sawada equation,[16] or, which is equivalent, by that more recently suggested by Young and Jencks (YJ).[17] According to YJ, log *k* variations with substituents can be written as in equation (11), where the ρ^{n}σ^n

$$\log k = \rho^n\sigma^n + \rho^+(\sigma^+ - \sigma^n) + i \quad (11)$$

Table 4. Comparison between second-order rate constants for the proton transfer to enol ethers from CH$_3$OH$_2^+$ in methanol and from H$_3$O$^+$ in water (25 °C)

Compound	$k_{CH_3OH_2^+}$/dm^3 mol^{-1} s$^{-1 a}$	$k_{H_3O^+}$/dm^3 mol^{-1} s$^{-1 b}$
CH$_2$=C(OMe)CH$_3$	290^c	278
(1a)	1 180	385
(1b)	273	124
(1c)	81.1	53.3
(1d)	45.2	37.1
(1e)	18.1	16.4
(1f)	6.95	7.51
(1g)	2.73	3.63
(1h)	0.81	1.22
(1i)	0.405	0.723

^{a} From Table 3 (except for isopropenyl methyl ether), corrected for electrolyte effect. ^{b} From data collected and calculated in ref. 20. See also ref. 21 ^{c} From ref. 4; uncorrected for electrolyte effect.

term represents the polar effect of the substituted ring, and ρ^r(ρ$^+$ − σ^n) the effect resulting from direct conjugation between the reaction centre and the substituted ring. The ρ^n and ρ^r values for methanol addition (ρ^n −2.86 ± 0.08; ρ^r −1.28 ± 0.11; *r* 0.9990; standard deviation 0.06) are close to those reported for acetal hydrolysis in methanol containing small amounts of water (ρ^n −3.26; ρ^r −1.11)[7] and for enol ether formation from acetal in methanol (ρ^n −3.12; ρ^r −1.39),[13] both catalysed by the lyonium ion. The latter reaction is the reverse of the methanol addition process and, according to the principle of microreversibility, involves the same transition state; the former involves the same oxocarbenium ions, with a transition state similar to that of acetal formation as far as charge distribution is concerned.

Comparison between Protonation Rates in Methanol and Protonation Rates in Water.—Table 4 collects catalytic constants in methanol, $k_\psi/[CH_3OH_2^+]$, for proton addition to α-methoxystyrenes and isopropenyl methyl ether (methanol addition) and these are compared with catalytic constants, $k_\psi/[H_3O^+]$, for proton addition in water (hydrolysis).[18–20] It is noteworthy that the two sets of results are very close to one

another; this confirms that the two reactions have similar rate-limiting steps with similar transition states. The small differences in reactivity probably result from two opposing factors: (i) the lyonium ion in methanol is more acidic than H_3O^+ in water, and (ii) the rate-limiting formation of positive-charged species is less favoured in methanol than it is in water because of the difference in dielectric properties. It could be significant that the first of these two factors predominates [e.g. for (1a)] when the charge of the intermediate is strongly delocalised by resonance effects.

When applied to hydrolysis of α-methoxystyrene in water, equation (11) also accounts for substituent effects (ρ^n -2.33; ρ^r -0.97).[20] These ρ values can be compared with those for full protonation equilibrium (CH acidity constants) (ρ^n -3.4; ρ^r -2.1) derived from literature equilibrium constant data for the oxocarbenium formation from acetals (ρ^n -3.6; ρ^r -2.2)[17] and for the acetal $\longrightarrow$ enol ether transformation in water (ρ^n -0.18; ρ^r -0.06).[13] The two ratios, $-2.3/-3.4$ and $-0.97/-2.1$, between the two sets of ρ values for rates and equilibria, are roughly in agreement with the well accepted structure of the transition state: the proton is a little more than half-transferred, as suggested by the α-Brönsted exponents observed for the general acid catalysis of enol ether hydrolysis,[2] and positive charge delocalisation and proton transfer are synchronous events.[21] In methanol, the larger ρ^n and ρ^r values do not necessarily mean that the proton is significantly more transferred in the transition state than in water, but should instead be related to the fact that the differences in the dielectric properties of water and methanol make substituent effects on the stability of the ionic intermediate significantly larger in methanol. The large kinetic isotope effects,[8] close to the

Cary 118 spectrophotometer, whereas kinetic measurements were performed on a Cary 16 spectrophotometer. Molar extinction coefficients of (1a—i) at maximum absorptivity, as well as those of the corresponding acetophenones and dimethyl acetals, are given in Table 5. Except for (1h) (see Results section), the time-dependent variations in absorbance were monitored at the maximum absorption wavelength of the enol ether. The content of the thermostatted 1-cm cell was stirred by means of a small Teflon magnet. Temperature (25 ± 0.05 °C) was checked in the cell by a Yellow Springs Instrument 45 CU cuvette thermometer (thermistor detector YSI 4502). The cuvette was always filled in a dry-box and closed by a soft stopper (silicon elastomer; Rhodorsil CAF 4, Prolabo). The reaction was initiated by introducing small amounts of methanolic solution rapidly through the stopper, by means of a weighed microsyringe. The absorbance trace was recorded immediately, and the time lag between enol ether introduction and recording of the first absorbance value (2—5 s) was measured carefully. Calculations were performed from the constant time-separated absorbance values, collected from the initial part of the absorbance–time curve (usually up to the absorbance minimum) by means of equation (9). The computer program (VAX 11; Digital Equipment Corporation) calculated k_ψ (k_H and k_F given) by a method based on a minimisation of the sum of the quadratic differences, Φ, between calculated A_i values ($\hat{A}_i$) and experimental data (A_i). Starting with a first estimate of k_ψ [$(k_\psi)_1$], obtained by a Guggenheim plot, we expressed Φ by equation (12) (the absorbance deviations being written as the sum of the two first terms of a Taylor series), and calculated $(\partial A_i/\partial k_\psi)_1$, the values of $\partial A_i/\partial k_\psi$ for $k_\psi = (k_\psi)_1$, by equation (13). Since $\partial \Phi/\partial k_\psi = 0$ when Φ is minimum, equation (14) was

$$\Phi = \sum_i \{A_i - \hat{A}_i + [k_\psi - (k_\psi)_1](\partial A_i/\partial k_\psi)_1\}^2 \tag{12}$$

$$\frac{\partial A_t}{\partial k_\psi} = [\text{eth}]_0 \left\{ (\varepsilon_{ke} - \varepsilon_{ac}) \frac{k_H}{(k_H + k_F - k_\psi)^2} \left[e^{-(k_H + k_F)t} - e^{-k_\psi t} \right] - t \left[(\varepsilon_{eth} - \varepsilon_{ac}) - (\varepsilon_{ke} - \varepsilon_{ac}) \frac{k_H}{(k_H + k_F - k_\psi)} \right] e^{-(k_H + k_F)t} \right\} \tag{13}$$

$$k_\psi - (k_\psi)_1 = -\sum_i (A_i - \hat{A}_i)(\partial A_i/\partial k_\psi)_1 / \sum_i (\partial A_i/\partial k_\psi)_1^2 \tag{14}$$

theoretical maximum, for enol ether formation from [$^3H_6$]acetone acetal are in agreement with the hypothesis that the change in solvent does not modify the position of the transition state along the reaction co-ordinate significantly.

Experimental

Rate Measurements.—U.v. spectra of (1a—i), acetophenones, and acetophenone dimethyl acetals were recorded on a Varian

derived, making it possible to calculate k_ψ by an iterative process with $(k_\psi)_1$ successively replaced by $(k_\psi)_2$, $(k_\psi)_3$, etc. Since there was some uncertainty in the determination of the initial time, successive calculations were performed with this initial time varied by 0.1 s steps. The rate constants finally selected were those such that the smallest quadratic differences were a minimum. The calculated zero time did not usually differ from that noted by more than 0.3 s. For (1f, g, and i) the

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Table 5. Extinction molar coefficients of α-methoxystyrenes (1), acetophenones, and acetophenone dimethyl acetals at the wavelengths chosen for the kinetic measurements

X^a	λ/nm^b	$\varepsilon_{eth}/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1\,c}$	$\varepsilon_{ke}/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1\,c}$	$\varepsilon_{ac}/\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1\,a}$
4-OCH$_3$	257	13 880 ± 50	10 330 ± 30	1 060 ± 17
4-CH$_3$	252	10 920 ± 40	14 620 ± 60	190 ± 5
H	251	8 570 ± 30	7 640 ± 40	200 ± 5
4-F	243	7 980 ± 80	11 650 ± 80	100 ± 5
4-Cl	250	10 300 ± 100	16 200 ± 100	0
3-Cl	255	7 620 ± 50	2 545 ± 15	0
3-CF$_3$	256	7 350 ± 35	495 ± 5	0
3-NO$_2$	252	16 410 ± 40	7 065 ± 50	7 040 ± 60
4-NO$_2$	224	9 390 ± 60	3 340 ± 10	2 760 ± 10

^{a} X in (1), $XC_6H_4COCH_3$, and $XC_6H_4C(OCH_3)_2CH_3$. ^{b} Except for (1h), λ corresponds to $\lambda_{max.}$ of (1) in the 210—300 nm range. ^{c} Figures after the sign ± are standard deviations.

absorbance increase after the minimum was sufficiently slow to allow determination of k_ψ by a Guggenheim plot. For (1e), the two methods were used and gave similar results.

Materials.—Methanol (Baker Analyzed Reagent) was distilled with magnesium under nitrogen. Methanolic solutions of hydrobromic acid were prepared by bubbling gaseous HBr (99.8%, Baker Chemicals) under nitrogen and subsequent dilution in a dry-box. Bulk solutions were stored at $-18\,^\circ$C. Volumetric titrations were performed by using aqueous sodium hydroxide solutions (indicator Methyl Red). For the lowest acid concentrations ([HBr] $< 2 \times 10^{-3}$ mol dm^{-3}) we determined the acid concentration indirectly by measuring the rate of addition of methanol to (1e). We assumed that equation (4) was valid and corrected the rate for electrolyte effects. The water content of methanolic HBr solutions was found, as previously described,[6,7,22] by u.v. spectral measurement of the relative concentrations of 4-methylacetophenone and its dimethyl acetal at equilibrium. The water concentration did not include water associated with the proton in H_3O^+. For (1a and b), water concentrations were calculated from the final absorbance at equilibrium, taking into account ketone–acetal equilibrium constants.[6] Compounds (1a—i) were synthesised as previously described [23] by cracking acetophenone dimethyl acetals, and distilled under reduced pressure. Compounds (1a—h) were purified by v.p.c. (Varian Aerograph Series 700, $\frac{3}{8}$ in $\times$ 10 ft column packed with 30% Carbowax on Chromosorb W). Compound (1i) was recrystallised from hexane, m.p. 84—86 °C. The low content of ketone was checked by i.r. spectroscopy.

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