Rate–Equilibrium Relationships based on the CH-Acidity Constants of Oxocarbenium Ions, for Proton Transfer from Hydronium Ion to α-Methoxystyrenes: Evidence for Perfect Synchronization between Bond Cleavage, Bond Formation, and Positive-charge Delocalization[1]

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The CH-acidity constants in water for the oxocarbenium ions derived from ring-substituted α-methoxystyrenes have been calculated from the following literature data. (*i*) Equilibrium constants for oxocarbenium-ion formation from the corresponding acetals; (*ii*) equilibrium constants for the acetal-to-enol ether process in methanol; (*iii*) Gibbs free energies of transfer of acetals and enol ethers from methanol to water. The plot of the logarithms of hydronium-ion-catalytic rate constants against the pK_a values of the intermediate ions exhibits a slightly curved relationship, with a mean slope β_S = 0.58, which can be accounted for by the Marcus equation with an intrinsic barrier of *ca.* 15 kJ mol^{-1} and work terms W_r = 44 kJ mol^{-1} and W_p = 52 kJ mol^{-1}. The agreement of all these parameters with those derived when the catalyst is changed indicates that C–H bond formation and O–H bond cleavage are synchronous concerted primitive changes. Separation of substituted-ring polar effects and direct resonance interactions from the overall substituent effects on rates and equilibria also shows that there is perfect synchronization between proton transfer and positive-charge delocalization.

When the Marcus theory[2] is used to account for rate-equilibrium relationships in the cases of proton-,[3,4] atom-, or group-[5] transfer reactions, it is implicitly assumed that the variations in transition-state energy and structure only depend on those of the initial and final states (Hammond effect). This usually implies that bond cleavage and bond formation are synchronous concerted primitive changes,[6] *i.e.* that the sum of bond orders is always equal to unity at the transition state, and that electron rearrangements within the substrate are synchronized with bond-formation and -cleavage.[7,8] If there is some lag between the events, it is expected that the Marcus relationship observed for a series of substrates will not agree with that for a series of proton or group donors. In the case of proton-transfer reactions of a series of acids, HA_i, with a series of substrates, S_j, and since the α and β Brönsted exponents correspond to local values of $\pm\partial(\log k)/\partial(pK_a)$, it is expected that the mean β_S Brönsted exponent observed when the substrate is changed will not correspond to α_{HA}, where α_{HA} is the Brönsted exponent for a series of acids reacting with one substrate. Such a phenomenon, called 'transition-state imbalance'[9] or 'imperfect synchronization',[10] has been observed in many cases and has been discussed at length for deprotonation of neutral CH-acids when the proton is removed from a carbon atom adjacent to nitro, carbonyl, cyano, phenyl, *etc.* groups which are able to delocalize the formed negative charge.[11] Usually a lag between charge delocalization and C–H bond cleavage is assumed.

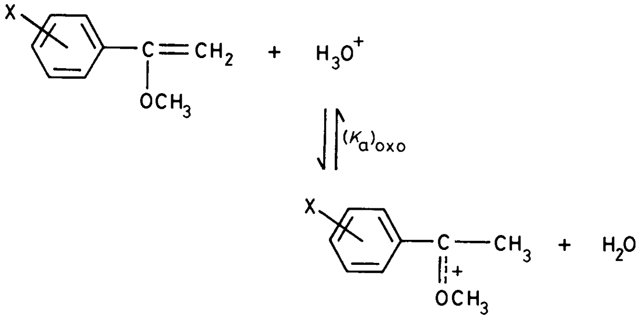
Because of the lack of data on basicity constants for most neutral organic substrates, there are only few examples of reactions of such compounds with acids, for which Brönsted and Marcus plots observed when the substrate is changed can be compared with those drawn classically for a series of acidic reagents, and for which strict balance has been demonstrated. Kresge *et al.*[12,13] reported that the β_S values obtained by plotting H_3O^+-catalytic constants against carbenium ion pK_a values are close to α_{HA} for protonation of hydroxy- and alkoxy-benzenes, as well as for protonation of azulenes. Similar behaviour has been observed by Terrier *et al.*[14] in the case of pyrrole-derivative *C*-protonation, but the agreement is limited to $H_2PO_4^-$-catalytic constants; the β_S value obtained from the Brönsted plot of log $k_{H_3O^+}$ against pK_a is very much lower than α_{HA}.

One of the reactions most often used as a reaction model for proton-transfer mechanism studies is acid-catalysed enol ether hydrolysis. As is clearly shown,[4,15] the rate-limiting step of this process corresponds to proton addition to the double bond. The most significant advantages for mechanistic studies, in light of the most recent theories, lie in the fact that enol ethers hydrolyse with convenient rates for kinetic studies, and that buffer catalysis and solvent isotope effects are large. The Brönsted α exponents observed when the acid catalyst is varied range typically from 0.5—0.7 and depend on the substrate as expected from the Marcus theory and the Hammond–Leffler postulate;[4b] the more reactive the enol ether, the lower the Brönsted exponent. Also as expected, H_2O–D_2O isotope effects are close to the theoretical maximum when α_{HA} is close to 0.5.[4b] To examine whether or not there is some imbalance between O–H bond cleavage, C–H bond formation, and positive-charge delocalization in the case of enol ether protonation, we have calculated from literature data the CH acidity constants of the oxocarbenium ions derived by protonation from α-methoxystyrenes (Scheme 1).

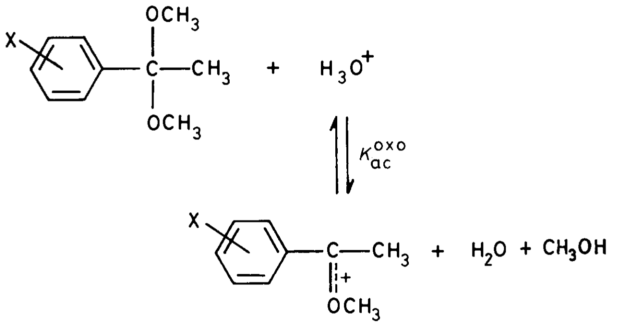
As suggested in a previous report[1] the acidity constant, $(K_a)_{oxo}$, of the oxocarbenium ions derived from α-methoxystyrenes can be obtained by combining the data of Young and Jencks,[16] who calculated equilibrium constants between acetals and oxocarbenium ions (Scheme 2), with data on acetal-to-enol ether equilibrium constants [Scheme 3 and equation (1)].

$$(K_a)_{oxo} = K_{ac}^{eth}/K_{ac}^{oxo} \qquad (1)$$

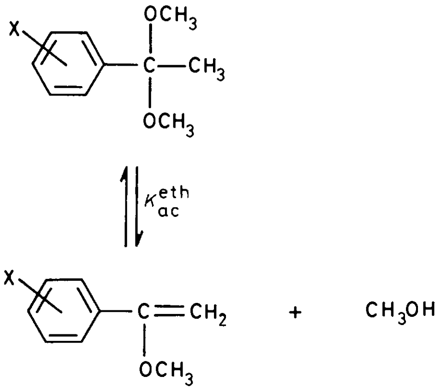
However, this preliminary approach suffered from the fact that the acetal-to-enol ether equilibrium constants were known only in methanol (as the ratios of the rate constants for the forward



Scheme 1.



Scheme 2.



Scheme 3.

and reverse reactions). Our more recent data[17] on Gibbs energies of transfer of α-methoxystyrenes and of acetophenone dimethyl acetals from methanol to water now make it possible to calculate the CH-acidity constants of the oxocarbenium-ion intermediates in water and to examine the relationships between rate and equilibrium constants.

Results and Discussion

Table 1 lists the CH-acidity constants for the oxocarbenium ions derived from ring-substituted α-methoxystyrenes (Scheme 1). These have been calculated from equation (1) by taking into account Young and Jencks's data for the acetal-to-oxocarbenium ion equilibrium (Scheme 2), which were obtained from kinetic- and product-composition results for acetophenone dimethyl acetal hydrolysis in the presence of oxocarbenium-ion-trapping sulphite ions. In this work, equilibrium-constant determination was based on two assumptions: (*i*) the nucleophilic attack on the oxocarbenium ions by SO_3^{2-} is diffusion-controlled and the rate constant for this process can be estimated as 5×10^9 dm^3 mol^{-1} s^{-1}; and (*ii*) methanol and water react with the ions with the same rate constants. The first of these two assumptions was shown to be valid in view of the low value observed for the reactivity ratio of SO_3^{2-} and water, and in view of the large substituent effects on this ratio. The second assumption was based on the observation by Cordes and Wenthe[18] that different oxocarbenium ions derived from acetals and orthoesters react with D_2O and CD_3OD with closely similar rate constants. Although none of these assumptions is questionable, it follows that the absolute K_{ac}^{oxo} values are known to within a factor of 2 or 3, and which value depends on the value chosen for the diffusion-controlled rate constant and on the true reactivity ratio between water and methanol. However, since this factor should be substituent-independent, it can be taken for granted that the relative K_{ac}^{oxo} values, from one substituent to another, are known with a large degree of confidence.

Table 2 lists the rate constants for hydronium ion-catalysed α-methoxystyrene hydrolysis in water at 25 °C reported in literature[4b] or calculated from literature data,[15c,19] and Figure 1 shows the Brönsted plot of log $k_{H_3O^+}$ *versus* $(pK_a)_{oxo}$. The slope of the approximately linear relationship [equation (2)] is in agreement with α_{HA} values observed for the hydrolysis of enol ethers of comparable reactivities.[4b]

$$\log k_{H_3O^+} = -(0.584 \pm 0.038)(pK_a)_{oxo} + (2.713 \pm 0.098)$$
$$(r = 0.992;\ \text{standard deviation} = 0.129) \qquad (2)$$

The observed α_{HA} values in the 0.5—0.7 range for the hydrolysis of most enol ethers have been interpreted by assuming that the proton is usually little more than half-transferred in the transition state. It was a general finding that α_{HA} depends significantly on enol reactivity, and Kresge *et al.*[4b] reported a roughly linear relationship between α_{HA} and log $k_{H_3O^+}$. These results were supported by solvent isotope effects: the large ratio between H_3O^+ and D_3O^+ catalytic constants, close to the maximum expected for such a process when the proton in the transition state is not far from half-transferred, depends on reactivity roughly as expected by the Marcus theory.[4b]

The Marcus theory of proton-transfer reactions suggests that linear Brönsted relationships are first approximations to curved relationships and that $\Delta G^{\ddagger}$ depends on the difference between Gibbs free energies of the initial and final states by a quadratic equation [equation (3)], where W_r is a 'work term' for the

$$\Delta G^{\ddagger} = W_r + \Delta G_0^{\ddagger} + \Delta G_R^{\circ}/2 + (\Delta G_R^{\circ})^2/16\Delta G_0^{\ddagger} \qquad (3)$$

formation of an encounter complex between the reactants, ΔG_R° is the difference between G° values for encounter complexes before and after the actual proton transfer [equation (4), where

$$\Delta G_R^{\circ} = \Delta G^{\circ} - W_r + W_p \qquad (4)$$

W_p is the work term for the dissociation of the products], and $\Delta G_0^{\ddagger}$ is the intrinsic barrier, *i.e.* the formal barrier when $\Delta G_R^{\circ} = 0$. Different pieces of data made it possible to determine $\Delta G_0^{\ddagger}$ and W_r for enol ether hydrolysis: (*i*) hydrolyses of ethyl isopropenyl ether and of ethyl cyclopentenyl ether, catalysed by a series of carboxylic acids and monohydrogen phosphonate anions, exhibit curved plots accounted for by equation (3) with $\Delta G_0^{\ddagger} = 4$ kcal mol^{-1} (16.7 kJ mol^{-1}) and $W_r = 9$ kcal mol^{-1} (37 kJ mol^{-1}), and with $\Delta G_0^{\ddagger} = 2$ kcal mol^{-1} (8.2 kJ mol^{-1}) and $W_r = 14$ kcal mol^{-1} (58.5 kJ mol^{-1}), respectively;[4b,15d] (*ii*) the variations of α_{HA} for a series of enol ethers agree with $\Delta G_0^{\ddagger} =$ 4.9 kcal mol^{-1} (20.5 kJ mol^{-1}) and $W_r = 10.6$ kcal mol^{-1} (44.3 kJ mol^{-1});[4b] (*iii*) the solvent isotope effects roughly fit a theoretical

Table 1. Calculated CH-acidity constants for oxocarbenium ions derived from α-methoxystyrenes (25 °C)

X[a]	$10^4(K_{ac}^{eth})_m$ [b]	$(\Delta G^\circ_{m\rightarrow w})_{ac}$ [c]	$(\Delta G^\circ_{m\rightarrow w})_{eth}$ [d]	$10^2(K_{ac}^{eth})_w$ [e]	$10^4K_{ac}^{oxo}$ [f]	$(pK_a)_{oxo}$ [g]
4-OCH_3	9.58	13.48	11.67	7.7	720	−0.03
4-CH_3	9.16	18.54	17.28	6.1	41	−1.17
H	8.32	16.44	14.97	6.0	9.3	−1.81
4-F	8.10	18.94	17.32	6.2	6.3	−1.99
4-Cl	7.35	21.14	19.32	6.1	1.8	−2.53
3-Cl	5.75	23.64	20.88	7.0	0.29	−3.39
3-NO_2	5.38	19.25	17.71	4.0	0.023	−4.23

[a] X in $XC_6H_4C(OMe)=CH_2$, $XC_6H_4C(OMe)_2CH_3$, and $XC_6H_4C(CH_3)OMe^+$. [b] Equilibrium constants between acetophenone dimethyl acetals and α-methoxystyrenes in pure methanol (=[enol ether]$_{eq}$/[acetal]$_{eq}$); data from ref. (17). [c] Gibbs free energies of transfer of acetophenone dimethyl acetals from methanol to water; data from ref. (17); in kJ mol^{-1}. [d] Gibbs free energies of transfer of α-methoxystyrenes from methanol to water; data from ref. (17); in kJ mol^{-1}. [e] Equilibrium constants between acetophenone dimethyl acetal and α-methoxystyrenes in water (=[MeOH]$_{eq}$[enol ether]$_{eq}$/[acetal]$_{eq}$), calculated from equilibrium constants in methanol and Gibbs free energies of transfer by the equation: $RT \ln (K_{ac}^{eth})_w = RT \ln (K_{ac}^{eth})_m + (\Delta G^\circ_{m\rightarrow w})_{ac} - (\Delta G^\circ_{m\rightarrow w})_{eth}$, where $(\Delta G^\circ_{m\rightarrow w})_m$ is the Gibbs energy of transfer of methanol to water (0.79 kJ mol^{-1}) [see ref. (17)]; in mol dm^{-3}. [f] From ref. (16); missing values are calculated using equation (6) with $\rho^n = -3.6$ and $\rho^r = -2.2$. [g] Calculated from equation (1).

Table 2. Application of the Marcus equation to the hydronium-ion catalytic rate constants for hydrolysis of substituted α-methoxystyrenes

X[a]	$k_{H_3O^+}$ [b]	$\Delta G^{\ddagger}$ [c]	ΔG° [c,d]	ΔG°_R [c,e]	$\Delta G^{\ddagger}_{calc}$ [c,f]	β[g]
4-OCH_3	385 (645)	58.32	−9.79	−2.80	58.16	0.48
4-CH_3	124 (277)	61.13	−3.26	3.73	61.47	0.53
H	53.3 (118)	63.18	0.38	7.37	63.43	0.56
4-Cl	16.4 (38.1)	66.15	4.19	11.49	65.86	0.59
3-Cl	7.51 (17.5)	66.08	10.08	16.38	69.04	0.64
3-NO_2	1.22 (3.64)	72.60	14.22	21.22	72.02	0.68

[a] X in $XC_6H_4C(OMe)=CH_2$. [b] Second-order rate constants at 25 °C for hydronium-ion catalysed hydrolysis of α-methoxystyrenes in water [calculated from ref. (15*c*); see ref. (19)]. For comparison, catalytic constants for α-ethoxystyrenes from ref. (15*d*) [see also ref. (19)] are given in parentheses. In dm^3 mol^{-1} s^{-1}. [c] In kJ mol^{-1}. [d] Calculated from $(pK_a)_{oxo}$ values in Table 1. [e] Calculated from equation (4) with W_r = 44.5 kJ mol^{-1} and W_p = 52.0 kJ mol^{-1}. [f] Calculated from equation (3) with $\Delta G^{\ddagger}_0$ = 15.0 kJ mol^{-1}. [g] Calculated from equation (5).

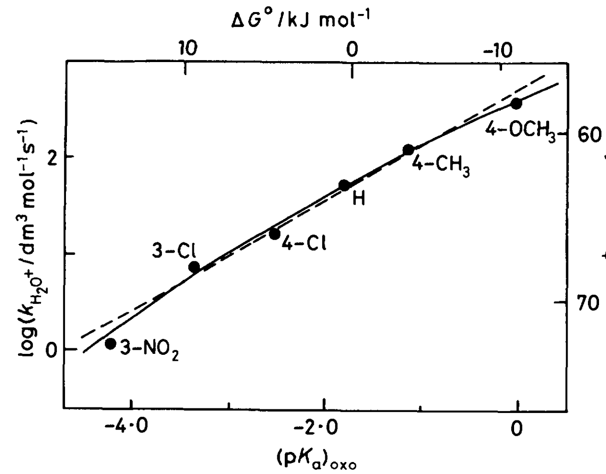


Figure 1. Brönsted plot of the second-order rate constants for hydronium-ion catalysed hydrolysis *vs.* pK_a CH-acidity constants of the parent oxocarbenium ion intermediates. The solid line is that calculated from the Marcus equation [equation (3)]

equation, derived from the Marcus theory, when $\Delta G^{\ddagger}_0$ and W_r are taken as 4.3 kcal mol^{-1} (18 kJ mol^{-1}) and 9.7 kcal mol^{-1} (40.5 kJ mol^{-1}), respectively.[4b] From these latter data, Kresge *et al.*[4b] also concluded that the transition state for catalysis by H_3O^+ should be symmetrical ($\alpha_{HA} = 0.5$) for $\Delta G^{\ddagger} \approx 14$ kcal mol^{-1} (58.5 kJ mol^{-1}), *i.e.* for $k_{H_3O^+} \approx 200$ dm^3 mol^{-1} s^{-1}.

Note that the work terms W_r, although consistent with results for other proton transfers to carbon, are far larger than those generally observed or assumed for proton- or group-transfer reactions.[2,3] This anomaly has been explained[4b] by considering that encounter-complex formation results in extensive desolvation of the reacting acids prior to the actual proton transfer to the alkene. However, it is also noteworthy that this interpretation is not in agreement with views of desolvation[20] as considered more as a decrease in hydrogen-bond strengths, due to changes in covalent bonds, than in the number of solvating molecules. It follows that the separation of the energy terms in equation (3) might be questioned and that the unexpectedly large work terms might reflect some inadequacy of the Marcus equation in its usual form, based on the inverted-parabola model of the reaction barrier[2e] or on other barrier models with the same 'scaled symmetry.'[2h] Notwithstanding, whatever the real meaning of the energy terms in the Marcus equation, it is of interest, for testing synchronization of the primitive changes, to compare the Marcus-equation parameters obtained by substrate variation with those calculated from data for different catalysts.

Figure 1 shows that the log $k_{H_3O^+} - pK_a$ curve calculated from equation (3), with $\Delta G^{\ddagger}_0$ = 15.0 kJ mol^{-1}, W_r = 44.5 kJ mol^{-1}, and W_p = 52.0 kJ mol^{-1}, fits the experimental data slightly better (standard deviation = 0.098) than the straight line does. Since $\Delta G^{\ddagger}_0$ and W_R values are close to those listed above and although it is not fully established that the plot is really curved (slight curvature and uncertainties on rate and equilibrium constants), it is clear that the variations of the hydronium-ion catalytic constant with $(pK_a)_{oxo}$ agree with those expected when taking into account the Marcus equation parameters based on α values observed when the catalyst was varied. Moreover, W_r and W_p parameters imply that $\Delta G^{\circ}_R = 0$ for $\Delta G^{\ddagger} \approx 60$ kJ mol^{-1}, *i.e.* for a value close to that derived by Kresge.

Marcus theory also makes it possible to define Brönsted β_S and α_{HA} exponents as $\partial(\Delta G)/\partial(\Delta G^{\circ}_R)$ for each substrate and each proton donor and to calculate these coefficients using equation (5). Table 2 also lists the β_S values obtained for proton transfer from hydronium ion to different substituted α-methoxystyrenes by taking into account the calculated $\Delta G_0^\ddagger$, W_r, and W_p parameters. The average of the calculated β_S values corresponds to the slope of the straight line in Figure 1.

$$\beta_S \text{ or } \alpha_{HA} = 0.5 + \Delta G_R^\circ/8\Delta G_0^\ddagger \qquad (5)$$

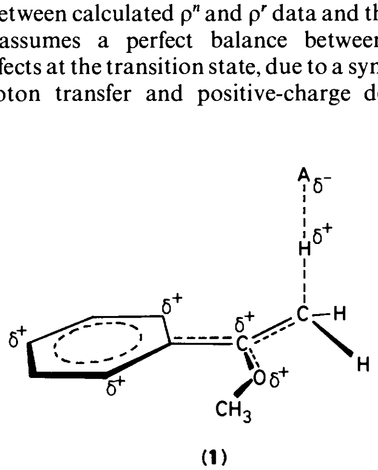
It has previously been shown[19] that the log $k_{H_3O^+}$ variations with substituent are accounted for by a Young–Jencks equation [equation (6)][16,19,21,22] with $\rho^n = -2.33$ and $\rho^r = -0.97$.

$$\log k \text{ or } \log K = \rho^n\sigma_x^n + \rho^r(\sigma_x^+ - \sigma_x^n) + \text{i} \qquad (6)$$

Using this equation, polar effects, due to the substituted ring, can be separated from resonance effects arising from conjugation between the carbenium centre and the substituted ring. A similar treatment for full protonation equilibrium constants yields equation (7). The ratio of the ρ^n values ($-2.33/-3.41 = 0.68$), which expresses the ratio of the substituted-ring polar effects on transition-state and oxocarbenium energies, is significantly larger than the average β_S (0.58); the difference stems from the fact that ρ^n depends mainly on the points associated with electron-withdrawing substituents for which β_S is larger than the average. On the other hand, the ratio of ρ^r values ($-0.97/-2.28 = 0.43$), which indicates the relative through-resonance effects at the transition state, is slightly lower than the average β_S. This is due to the fact that the point associated with X = 4-OCH_3 has a large weight in ρ^r calculations. Moreover, because of the shift of the transition state towards the starting materials (decrease in β_S values), which makes the polar contribution lower on going from X = 3-NO_2 to X = 4-OCH_3, the resonance contribution is slightly underestimated by the Young–Jencks equation. A better estimate of this latter contribution can be obtained from equation (8), where β_S values are those calculated by the Marcus equation (Table 2). The ratio (0.46) between the thus-calculated ρ^r (-1.04) and that observed for full equilibrium (-2.28) is in fairly good agreement with β_S values observed for X = 4-OCH_3 and 4-CH_3. It can therefore be concluded that there is perfect agreement between calculated ρ^n and ρ^r data and those expected when one assumes a perfect balance between polar and resonance effects at the transition state, due to a synchronization between proton transfer and positive-charge delocalization.

$$(pK_a)_{oxo} = -(3.41 \pm 0.16)\sigma_X^n - (2.28 \pm 0.21)(\sigma_X^+ - \sigma_X^n) - 1.594 \qquad (7)$$
$$(r = 0.998;\ \text{standard deviation} = 0.104)$$

$$\log k_{H_3O^+} + 3.41\beta_S\sigma_X^n = -(1.04 \pm 0.09)(\sigma_X^+ - \sigma_X^n) + 1.687$$
$$(r = 0.986;\ \text{standard deviation} = 0.05) \qquad (8)$$



(1)

The positive charge gained by the substrate in the transition state (**1**) is delocalized by the methoxy and aryl groups to the same relative extents as the unit positive charge is delocalized in the oxocarbenium ion. The perfect agreement between Brönsted β_S and α_{HA} exponents, and between the parameters used in the Marcus equation to account for the curvature of the Brönsted plots, both for catalyst variations and changes in the substrate, also requires that the amount of C–H bond formation (say, the bond order n_{C-H}) is equal to the amount of A–H bond cleavage ($1 - n_{A-H}$).

Imperfect synchronization between proton transfer and charge delocalization has recently been dealt with by contour diagrams where the two progress variables correspond to proton transfer and charge delocalization.[8,9,23] In the case of α-nitrotoluene ionization, for example, Jencks and Jencks[23] suggested that the two primitive changes,[6] proton transfer and electron rearrangement, show a large disparity at the transition state, and that the disparity can be represented by a triangle diagram in which one of the corners corresponds to the hypothetical $Ar\text{–}\overset{-}{C}H\text{–}NO_2$ species (with a negative charge located on the central carbon atom). Recently, Grunwald[8] suggested a more quantitative treatment of the lack of synchronization between the two primitive changes on the basis of a square contour diagram with the top-left and bottom-right corners associated with $Ar\text{–}CH{=}N(O)OH$ and $Ar\text{–}\overset{-}{C}H\text{–}NO_2$, respectively, and disparity depending on the difference in energy of these real or hypothetical species and on the depth of the well along the path perpendicular to the reaction co-ordinate.

In the case of α-methoxystyrene protonation, the situation is, at first sight, different from that of carbon-acid ionization because the charge is not formed on the sp^3 carbon from which proton leaves, with orbital overlap depending on the conformation of the starting material, but on the adjacent sp^2 carbon with π orbitals interacting with the n and π orbitals of the methoxy and phenyl groups in the initial planar system; however, it is analogous when one considers that oxocarbenium-ion deprotonation requires C–H bond cleavage and 'neutralization' of the negative charge formed by the adjacent carbenium centre. It follows that in the approach based on square contour diagrams it is necessary to consider hypothetical states or species corresponding to $Ar\overset{+}{C}(OMe)CH_2^-$, with the positive charge delocalized on Ar and OMe to similar extents as in oxocarbenium ions, and to $Ar\overset{+}{C}(OMe)CH_3$, with charge localized on carbon only.

The first of these species corresponds to charge separation from π orbitals, resulting from a 90° twist as for triplet-state biradical formation, or to deprotonation of the ion with the sp^3 methylene group; it is formally similar to that considered for carbon-acid ionization. However, since the energy of the π bond is probably *ca.* 200 kJ mol^{-1},[24] it can be expected that zwitterionic species will have an energy level far higher than the initial and final states and far higher than the transition state. It can therefore be suggested that synchronization between C–H bond formation or cleavage and electron reorganization stems from the very large energy differences between these states. On the other hand, the significant lags in the negative-charge delocalization observed for carbon-acid ionization[11] are probably due to far smaller energy differences between transition states and the hypothetical species in which the charge is not delocalized.

Whereas it is easy to consider zwitterionic species to deal with the lag between proton transfer and electron reorganization in the course of oxocarbenium-ion formation, it is more difficult to conceive of a state of the system of atoms with the positive charge formed located only on the carbon atom adjacent to the methoxy and phenyl groups; this would require the n orbitals of the methoxy group and the π orbitals of the phenyl group not to

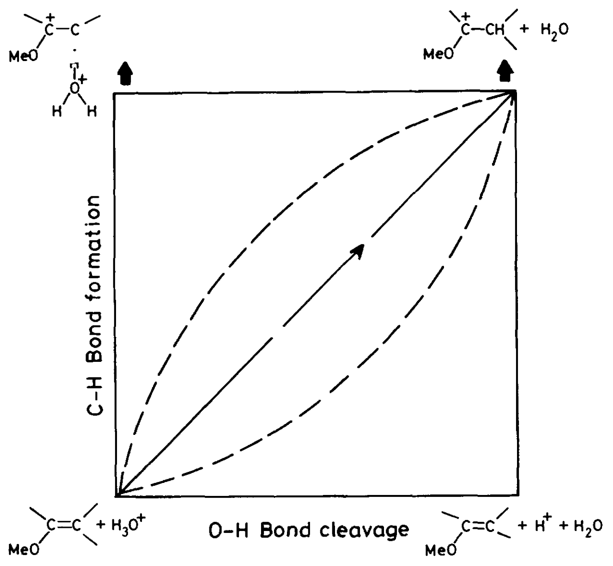


Figure 2. Schematic contour map for synchronous (——) and asynchronous (- - -) C–H bond formation and O–H bond cleavage in the course of proton transfer from H_3O^+ to enol ethers. Changes in oxocarbenium-ion stability result in the transition state moving along the first diagonal line because of the high energy levels of the top left- and bottom right-hand corners. The arrows indicate the effects on corner energies and on transition-state location due to withdrawing subsitutuent effects

overlap with the vacant *p* orbital of the carbenium-ion centre. Since the geometry is favourable to orbital interactions, and since the *ca.* 120° angle between the *n* orbitals of the methoxy group make the *n* and *p* orbitals overlap whatever the torsional angle around the C–O bond, it seems unlikely that positive-charge delocalization can lag behind C–H bond formation.

Perfect synchronization between O–H bond cleavage and C–H bond formation could be dealt with by considering the contour diagram of Figure 2, where the top left-hand corner corresponds to the hypothetical $Ph\overset{+}{C}(OMe)CH_2\text{-}\overset{-}{H}\text{-}\overset{+}{O}H_2$ species (C–H bond formation without any O–H bond cleavage), and the bottom right-hand corner to [Ph-C(OMe)=CH_2 + H^+ + H_2O] with an unsolvated 'flying' proton. Since to these real or hypothetical species or states would correspond very high energies (the H^+-desolvation energy for the bottom right-hand corner) and since, according to the contour-diagram approach, the 'disparity character' depends on the depth of the energy well on going from the bottom right-hand corner to the top left-hand one, through the transition state, as well as on the difference in the energies associated with these corners,[7,8] the transition state should be located close to the diagonal of the diagram. It is also probably significant that imbalance phenomena are observed only in the case of processes with large intrinsic barriers and that the intrinsic barrier calculated for proton addition to enol ethers is fairly low because of the large W_r term. However, the contour-diagram approach suggests that synchronization between O–H bond cleavage and C–H bond formation should not be general for proton transfer from H_3O^+ to carbon bases; when the intrinsic barrier is large and the potential-energy surface asymmetrical, the two primitive changes can be asynchronous. A significant difference between the α_{HA} and β_S (H_3O^+) values has been observed by Terrier *et al.*[14] in the case of proton transfer to pyrrole derivatives and interpreted, on the basis of the large and negative entropy of activation observed, in terms of a lag of hydronium-ion desolvation. Since desolvation and O–H bond cleavage are certainly closely related events (since in modern views 'desolvation' should usually be considered more as a decrease in hydrogen-bond strength than in the number of the solvating molecules[20]) the difference in α_{HA} and β_S values might reflect a lag between O–H bond cleavage behind C–H bond formation.

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