(28) Water attack on **4**H^+ would require protonation of **4** to produce **4**H^+, leading to terms in the rate law which would be second order in $[H^+]$. The good fit of the experimental data to eq 1 rules out this possibility.
(29) This value of $K_N^{OH^-}$ for **2f** was estimated using values of $k_1^{H_2O} = 2 \times 10^{-3}$ s^{-1}, $K_a' = 2.5 \times 10^{-4}$ (taken from the value for β-alanine), and $K_N \leqslant 0.1$ (an upper limit based on the large extinction coefficient measured for **2f**H^+).
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Reactions in Moderately Concentrated Acids. 1.[1] A Novel Perspective in the Interpretation of Reaction Mechanisms

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Abstract: Equations to correlate rate constants with the acidity of the medium are derived from the hypothesis, already verified in protonation equilibria measurements, that linear free energy relationships exist between acidity functions. These equations require plotting against ($H_0 + \log [H^+]$) the quantity $\log k_\psi - \log ([SH^+]/[S]_{st})$, where the ratio $[SH^+]/[S]_{st}$ assumes different values depending on the basic strength of the substrate. The slope parameters obtained give information on the differences in solvation requirements on going from protonated substrates (strongly and moderately basic compounds) or from the substrate (weakly basic) in its free base form to the transition state. Information on the structure of the transition state may be inferred from the comparison of these solvation requirements with those observed in protonation equilibria studies. The hydrolysis rates of methyl *tert*-butyl ether, *tert*-butyl acetate, phenyl *tert*-butyl sulfoxide, and *N-tert*-butyl-2,4-dinitroaniline are reported as a function of the acid concentration and discussed, together with selected examples from the literature, in the light of the above treatment.

The field of equilibria and reactions in moderately concentrated aqueous solutions has attracted much attention by physical organic chemists both because of the challenging problems encountered and of the practical interest of acidic water as reaction solvent.[2-7] The interpretation of the results in this area has been largely based on the acidity function concept first proposed by Hammett and Deyrup[8] in 1932. Since then many aspects of the subject have been drastically revised mainly as a consequence of the observations made in recent years that (1) each class of bases, or at the limit of precision each base, follows its own acidity function;[9] (2) linear correlations exist between the various acidity functions.[10] Point 2 is of peculiar importance since it offers a means to reassess the entire field by choosing a single acidity function to which the acid–base behavior of any given compound can be related.

The equation[11] of choice (for reasons detailed elsewhere)[12] is that proposed by Bunnett and Olsen[10a,b] in the form suggested by Hammett:[10d]

$$H_S + \log [H^+] = (1 - \phi_e)(H_0 + \log [H^+]) \qquad (1)$$

Since $pK_{SH^+} = \log [SH^+]/[S] + H_S$, it follows from eq 1 that

$$\log ([SH^+]/[S]) + H_0 = \phi_e(H_0 + \log [H^+]) + pK_{SH^+} \quad (2)$$

from which the pK_{SH^+} value of any given base may be evaluated.

The slope parameter ϕ_e is a measure of the solvation requirements of the species involved in the protonation equilibrium,[12-14] as may be appreciated by rewriting eq 1 in term of activity coefficients:[12-14]

$$\log f_{H^+} - \log (f_{SH^+}/f_S) = (1 - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \qquad (3)$$

Indeed, since $f_{H^+} > f_{SH^+} > f_S$, positive ϕ_e values are to be expected for (f_{SH^+}/f_S) larger than (f_{BH^+}/f_B). Since $\log f$ is related to the free energy of transfer from water to the acid solution, a positive ϕ_e value implies a larger interaction of the solvent with the cation in the case of protonation of the base S than in the case of the Hammett base B. The ϕ_e values, which range from +1.0 to −1.6 and are tabulated elsewhere,[12,14] can be assembled according to the type of cation formed upon protonation. In fact, formation of oxonium ions requires[12] more positive ϕ_e values (e.g., for protonated alcohols $\phi_e = +0.85$ to $+0.75$) than formation of ammonium (0.0 to −0.4) and of carbonium (−0.7 to −1.6) ions. This finding was explained[12-15] in terms of a greater interaction of the solvent with the cation when this is small and the positive charge localized.[16]

The same approach may be applied to kinetic data of acid-catalyzed reactions to obtain information on the solvation, on the amount of charge localization, and hence on the structure of the transition state.

The rate equation for an acid-catalyzed reaction of the general type

$$S + H^+ \rightleftarrows SH^+ \rightarrow \ddagger \rightarrow \text{products} \qquad (4)$$

may be expressed as in

$$\text{rate} = k_\psi[\text{S}]_{\text{st}} = k_0[\text{SH}^+]f_{\text{SH}^+}/f_\ddagger \quad (5)$$

which may be rearranged into

$$\log k_\psi - \log([\text{SH}^+]/[\text{S}]_{\text{st}}) = \log k_0 + \log(f_{\text{SH}^+}/f_\ddagger) \quad (6)$$

Equation 6 shows that, apart from changes in degree of protonation, the variations observed in reaction rates of acid-catalyzed reactions arise only from differences in the free energy of solvation between the protonated substrate and the transition state, i.e., in the term $\log(f_{\text{SH}^+}/f_\ddagger)$. To evaluate this term one needs to define two acidity functions: H_S pertinent to the protonation equilibrium $\text{S} + \text{H}^+ \rightleftarrows \text{SH}^+$, and $H_\ddagger$ defined by the equilibrium $\text{S} + \text{H}^+ \rightleftarrows [\ddagger]$.[17] By virtue of eq 1, which correlates every acidity function to H_0, we may write eq 7 for the acidity function $H_\ddagger$. The ratio $f_{\text{SH}^+}/f_\ddagger$ may then be evaluated through eq 8, obtained by combining eq 1 and 7; this value, introduced into eq 6, gives the general eq 9:

$$H_\ddagger + \log[\text{H}^+] = (1 - \phi_\ddagger)(H_0 + \log[\text{H}^+]) \quad (7)$$

$$\begin{aligned} H_\text{S} - H_\ddagger &= \log(f_{\text{SH}^+}/f_\ddagger) \\ &= (\phi_\ddagger - \phi_\text{e})(H_0 + \log[\text{H}^+]) \quad (8) \end{aligned}$$

$$\begin{aligned} \log k_\psi - \log([\text{SH}^+]/[\text{S}]_{\text{st}}) &= \log k_0 \\ &+ (\phi_\ddagger - \phi_\text{e})(H_0 + \log[\text{H}^+]) \quad (9) \end{aligned}$$

This applies to reactions of moderately basic substrates (those undergoing protonation in the same range of acidity where they react at convenient rates and whose ionization ratio is experimentally accessible). For strongly basic substrates $[\text{SH}^+] \simeq [\text{S}]_{\text{st}}$ and eq 9 becomes

$$\log k_\psi = \log k_0 + (\phi_\ddagger - \phi_\text{e})(H_0 + \log[\text{H}^+]) \quad (10)$$

For weakly basic substrates $[\text{S}]_{\text{st}} \simeq [\text{S}]$ and hence the ratio $[\text{SH}^+]/[\text{S}]$ must be computed through eq 2. Equation 9 then becomes

$$\log k_\psi + H_0 = \log(k_0/K_{\text{SH}^+}) + \phi_\ddagger(H_0 + \log[\text{H}^+]) \quad (11)$$

The above equations hold for the simple A1 type reaction mechanism, where direct conversion of the protonated substrate to the transition state occurs. However, they may be easily extended to A2 or $\text{A}_{\text{SE}}2$ mechanism. In A2 type reactions conversion to the transition state occurs by attack of a nucleophile on the protonated species. It suffices then to substract, from the left hand of eq 9, 10, and 11, the logarithm of the activity of the nucleophile. The intervention of water as a nucleophile is just one of the possible examples for this type of reactions. In the $\text{A}_{\text{SE}}2$ type reaction mechanism the slow step is represented by the proton transfer:

$$\text{S} + \text{H}^+ \xrightarrow{\text{slow}} \ddagger \longrightarrow \text{products} \quad (12)$$

The rate equation (eq 13), since $[\text{S}]_{\text{st}} = [\text{S}]$, becomes eq 14:

$$\text{rate} = k_\psi[\text{S}]_{\text{st}} = k_0[\text{S}]f_\text{S}a_{\text{H}^+}/f_\ddagger \quad (13)$$

$$\log k_\psi = \log k_0 + \log f_\text{S}a_{\text{H}^+}/f_\ddagger \quad (14)$$

By definition of acidity function the last term in eq 14 is equal to $-H_\ddagger$ and hence it is correlated through eq 7 to $(H_0 + \log[\text{H}^+])$. By substituting the value obtained from eq 7 and rearranging we obtain

$$\log k_\psi + H_0 = \phi_\ddagger(H_0 + \log[\text{H}^+]) + \log k_0 \quad (15)$$

Equations 9, 10, 11, and 15 were first derived by Bunnett and Olsen,[10b] who actually pointed out the existence of such linear free energy relationships, and verified them in a number of instances.[10b] The present approach, however, offers the advantage that, being derived from the same basic equation used in equilibria measurements (eq 1), it allows us to attach a straightforward meaning to the slope parameters.

To elaborate on this point, we will discuss in this paper the acid-catalyzed reactions of several *tert*-butyl derivatives: *tert*-butyl acetate (**1**), methyl *tert*-butyl ether (**2**), *N*-*tert*-butyl-2,4-dinitroaniline (**3**), and phenyl *tert*-butyl sulfoxide (**4**). All four substrates, when protonated, release the *tert*-butyl cation. The reactions are expected to follow the typical scheme for an A1 type reaction (eq 4). We will also discuss two limiting examples taken from the literature concerning A1 and A2 type reactions. An example of $\text{A}_{\text{SE}}2$ type reaction is discussed in the following paper.

Results

Equations 9–11 may be used for A1 type reactions depending on the base strength of the substrates, which must therefore be evaluated.

Basicity of Compounds 1–4. The basicity of the substrates can be conveniently determined by applying the Bunnett and Olsen equation (eq 2) to the ionization ratio ($[\text{SH}^+]/[\text{S}]$) data. Direct definition of eq 2, however, is possible[18] only for compound **4**, since the fragmentation of substrates **1–3**, which becomes too fast well before the attainment of complete protonation, prevents the direct evaluation of their basicity parameters. These have been estimated as follows.

***tert*-Butyl Acetate (1).** This compound reacts at convenient rates in a range of acidity where the protonated fraction is very small. For example, at the highest sulfuric acid concentration at which rates could be measured (H_2SO_4 3.47 M, $t_{1/2} = 52.5$ s) the ratio $[\text{SH}^+]/[\text{S}]$ may be evaluated for **1** as 3.9×10^{-4} (by using $\phi_\text{e} = +0.53$, $\text{p}K_{\text{SH}^+} = -4.05$, as estimated after Lee and Sadar[19]) or as 1.0×10^{-3} (by using $\phi_\text{e} = +0.4$, and $\text{p}K_{\text{SH}^+} = -4.61$, as estimated after Yates and McClelland[10c]). From these values it is safe to assume that this ester is too weak a base to be substantially protonated in the range of acidity studied. Therefore, in order to correlate rates with acidity we have used eq 11 which provides the $\phi_\ddagger$ values. The other slope parameter $(\phi_\ddagger - \phi_\text{e})$ may then be estimated by assuming a ϕ_e value between the reasonable limits of +0.4 and +0.5.

Methyl *tert*-Butyl Ether (2). The protonation of **2** can be monitored by the same NMR technique used[13] for other dialkyl ethers up to H_2SO_4 8 M. The chemical shift of the completely protonated species can be extrapolated from the corresponding values for other dialkyl ethers. The obtained $\text{p}K_{\text{SH}^+}$ and ϕ_e values (see Table III) are slightly different from those previously reported, since we have been able to use in the present case more recent and accurate H_0 data.[20]

***N*-*tert*-Butyl-2,4-dinitroaniline (3).** To describe the protonation of **3** we have chosen as a model compound *N*-*n*-butyl-2,4-dinitroaniline (**5**). The protonation of **5** has been monitored by following the changes of its UV spectra as a function of the acid concentration. By plotting the molar extinction of **5** at 365 nm, we obtained a good sigmoid curve from which $\log[\text{SH}^+]/[\text{S}]$, $\text{p}K_{\text{SH}^+}$, and ϕ_e values were derived as usual.[9b,13,21]

Dependence of Reaction Rates on Acidity. The fragmentation of methyl *tert*-butyl ether to *tert*-butyl cation and methanol has been monitored in aqueous sulfuric acid from 2.65 to 6.6 M at 25 °C by following either the decrease in absorbance at 194 nm or the decrease in intensity of the ^1H NMR signal of the methyl group (see Experimental Section). The pertinent data are collected in Table I; see paragraph at end of paper regarding supplementary material.

The rate of *N*-*tert*-butyl-2,4-dinitroaniline (**3**) fragmentation to 2,4-dinitroaniline has been measured by monitoring changes in the UV spectra of the acid solutions (see Experimental Section for details). Data are in Table II together with the $[\text{S}]_{\text{st}}/[\text{SH}^+]$ ratios evaluated through eq 2 using the $\text{p}K_{\text{SH}^+}$ and ϕ_e values of the reference compound **5**; see paragraph at

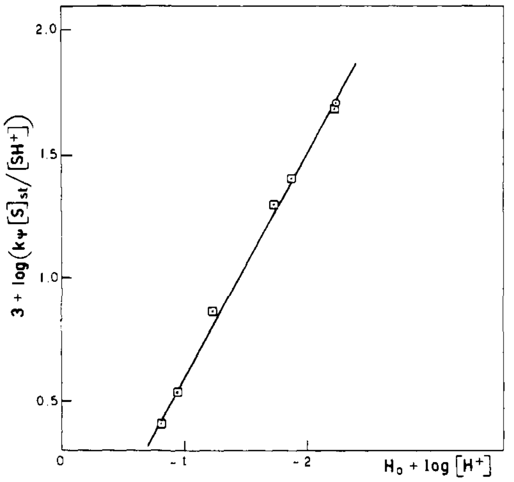


Figure 1. Effect of acid concentration upon the rate constants for the hydrolysis of methyl *tert*-butyl ether in aqueous sulfuric acid at 25 °C: □, monitored by NMR; ○, monitored by UV.

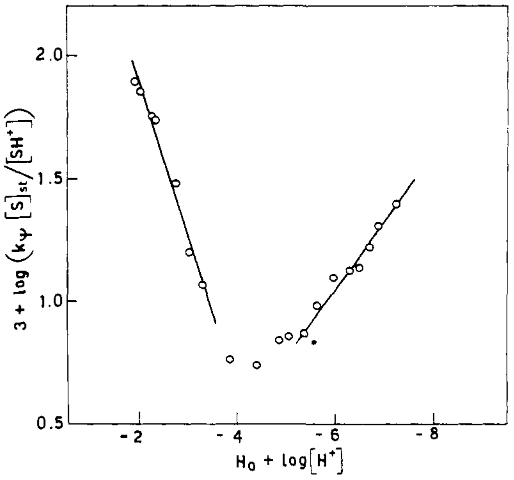
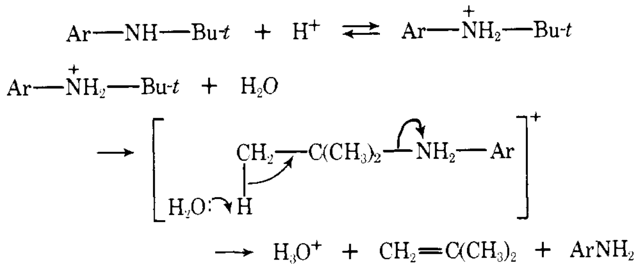


Figure 2. Effects of acid concentration upon the rate constants for the hydrolysis of *N*-*tert*-butyl-2,4-dinitroaniline in aqueous sulfuric acid at 25 °C.

end of paper regarding supplementary material.

Plots according to eq 9 are reported for compounds **2** and **3** in Figures 1 and 2, respectively.

The fragmentation of *N*-*tert*-butyl-2,4-dinitroaniline clearly follows different reaction paths depending on the acid concentration. Up to H_2SO_4 8 M the rate decreases with increasing acid concentration. It is well known that an increase in acid concentration is accompanied by a decrease in the activity of water; therefore, we take the above decrease in reaction rates as evidence of direct participation of water as nucleophile in the fragmentation of the *tert*-butylamine **3.** The reaction scheme at low acidity must be therefore modified as follows:



To describe the dependence of this reaction on acidity we have therefore to take into account the variation of the activity of water (a_{H_2O}) and the appropriate equation is

$$\log k_\psi - \log([SH^+]/[S]_{st}) - \log a_{H_2O} = (\phi_\ddagger - \phi_e)(H_0 + \log[H^+]) + \log k_0 \quad (16)$$

In acid solutions more concentrated than H_2SO_4 12 M the rates of fragmentation of compound **3** increase with the acidity, as expected for the A1 type mechanism, and therefore the data were treated according to eq 9.

The hydrolysis of *tert*-butyl acetate has been studied in several acids by Bunton, Crabtree, and Robinson.[22] We have analyzed, according to eq 11 (see above), their data for aqueous sulfuric acids where rates have been measured in the range 1.32–3.47 M.

The data concerning the fragmentation of *tert*-butyl phenyl sulfoxide in aqueous perchloric acid from 5.11 to 11.9 M have been reported elsewhere[18] and treated according to eq 9.

We have collected in Table III the information on the dependence of the reaction rates of compounds **1–4** on the acidity obtained through the treatment described by eq 9 and 11, together with the basicity parameters obtained through eq 2.

Table III. Dependence of Fragmentation Rates on Acidity for *tert*-Butyl Derivatives (RX-*t*-Bu)[a]

RX	CH_3COO[b]	CH_3O	2,4-$(NO_2)_2$-C_6H_3NH	C_6H_5SO[c]
$(\phi_\ddagger - \phi_e)$[d]	(−0.86 to −0.96)[e]	−0.90	+0.26[f] and −0.26[g]	−0.22
ϕ_e[h]	(+0.4 to +0.5)[i]	+0.60	−0.05[j]	+0.49
pK_{SH^+}[h]	(−4.6 to −4.1)[i]	−2.72	−4.55[j]	−1.79

[a] In aqueous sulfuric acid at 25 °C, unless otherwise indicated. [b] Reference 22. [c] In aqueous perchloric acid at 25 °C, ref 18. [d] This is the slope of the plots $\log k_\psi - \log([SH^+]/[S]_{st})$ vs. $H_0 + \log[H^+]$, unless otherwise indicated. [e] Estimated from the experimental $\phi_\ddagger$ value (−0.46) obtained as slope of the plot $\log k_\psi + H_0$ vs. $(H_0 + \log[H^+])$. [f] This is the slope of the plot $\log k_\psi - \log([SH^+]/[S]_{st}) - \log a_{H_2O}$ vs. $(H_0 + \log[H^+])$ for data reported in Table II up to H_2SO_4 8.95 M. [g] This is the slope of the plot $\log k_\psi - \log([SH^+]/[S]_{st})$ vs. $(H_0 + \log[H^+])$ for data reported in Table II for $H_2SO_4 > 12.0$ M. [h] pK_{SH^+} and ϕ_e values were obtained as intercept and slope from plots of $\log([SH^+]/[S]) + H_0$ vs. $(H_0 + \log[H^+])$; see eq 2. [i] Estimated from data reported in ref 19 and 10c. [j] These values refer to the model compound *N*-*n*-butyl-2,4-dinitroaniline.

We have also used eq 11 to correlate available rate data for the interconversion γ-butyrolactone ⇄ γ-hydroxybutyric acid. The lactone hydrolysis in $HClO_4$ and HCl was studied by Long et al.,[23] who also reported data for the equilibrium constant, from which the rate of the lactonization reaction was calculated. The $\phi_\ddagger$ values obtained are reported in Table IV together with the parameters obtained through the use of the Zucker–Hammett treatment[23,24] or the Bunnett relationship based on the evaluation of the *w* parameter.[25]

The last example is the comparison of thioacetamide[26] and butyramide[27] or benzamide[28] hydrolysis. All three substrates undergo protonation in the range of acidity where they react at convenient rates and hence the ratio $[SH^+]/[S]_{st}$ has been evaluated from the available pertinent pK_{SH^+} and ϕ_e values.[14,29] Moreover, the hydrolysis reaction (A2) involves the intervention of a water molecule and hence eq 16 must be used to correlate the rate data. The $(\phi_\ddagger - \phi_e)$ values obtained are collected in Table V together with the *r* values obtained by applying the Yates modification[10c,30] of Bunnett *w* treatment.[25]

Discussion

Interpretation of Rate Correlations. By applying eq 9, 11, and 16 we have obtained the slope parameters $(\phi_\ddagger - \phi_e)$ and

Table IV, Correlation with Acidity of Hydrolysis (k_h) and Lactonization (k_l) Rates for the γ-Hydroxybutyric acid ⇄ γ-Butyrolactone Reaction[a]

	k_l		k_h	
Correlation	$HClO_4$[b]	HCl[c]	$HClO_4$[b]	HCl[c]
Zucker-Hammett[a]	Follows $[H^+]$		Follows h_0	
w[d]	2.21	2.23	8.50	6.11
$\phi_\ddagger$[e]	0.23 (±0.06)	0.31 (±0.02)	0.96 (±0.06)	0.73 (±0.02)

[a] Rate data taken from ref 23, where k_h was directly measured and k_l evaluated from k_h and $K_{eq} = k_l/k_h$ data; the H_0 values used for computation are at 25 °C. [b] At 5 °C. [c] At 0 °C. [d] From plots of log $k + H_0$ vs. log a_{H_2O} as reported in ref 25. [e] As evaluated from plots of ($\log k_l + H_0$) or ($\log k_h + H_0 - \log a_{H_2O}$) vs. $H_0 + \log [H^+]$; data in parentheses are standard deviations from least-squares analysis.

$\phi_\ddagger$ correlating reaction rates with acidity. In the original Bunnett–Olsen treatment[10b] these slope parameters were empirically related to reaction mechanisms according to the role played by the water molecule in the transition state. We imply that the slope parameters cannot offer such direct mechanistic evidence. Instead, they are related to the solvent effect experienced by the protonated substrate or by the free base on going to the transition state and in this way they may offer useful inference regarding the structure of the transition state. In fact, if we rewrite eq 8 in terms of activity coefficients we obtain

$$\log f_\ddagger - \log f_{SH^+} = (\phi_\ddagger - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \quad (17)$$

which links the slope parameter to the changes in activity coefficients on going from the conjugate acid of the substrate to the activated complex. By taking into account that the term in brackets of eq 17 is always positive and that it represents the same reference scale used for protonation equilibria,[12-14] it follows that (1) a positive slope means that $\log f_\ddagger$ increases with acid concentration faster than $\log f_{SH^+}$, i.e., that the transition state is more solvated than the conjugate acid of the substrate; (2) the magnitude of the slope parameter compared with the available reported ϕ_e data offers qualitative information on structural changes in going from initial to transition state; and (3) a quantitative evaluation[31] of $\log f_\ddagger$ becomes feasible if $\log f_{SH^+}$ is available from independent measurements.

The slope parameter obtained from eq 11 ($\phi_\ddagger$) refers to the overall equilibrium from substrate to transition state, including the protonation step. By expressing eq 7 in terms of activity coefficients we obtain

$$\log f_{H^+} - \log (f_\ddagger/f_S) = (1 - \phi_\ddagger)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \quad (18)$$

which shows that positive $\phi_\ddagger$ values are related to higher values for the ($f_\ddagger/f_S$) than for the (f_{BH^+}/f_B) ratio. A reasonable guess of the ϕ_e value, for the weakly basic substrate involved in the acid-catalyzed reaction described by eq 11 and 15, may allow us to estimate the ($\phi_\ddagger - \phi_e$) parameter in these cases also. As detailed below, since we know from direct measurements[15] as well as from measurements of protonation equilibria[12-14] how the structure influences the activity coefficient behavior, the slope parameters may be used to deduce the structure of the transition state.

The A1 Type Fragmentation of *tert*-Butyl Derivatives. The fragmentation of *tert*-butyl derivatives **1–4** occurs through the transformation of an oxonium or ammonium ion into a carbonium ion. Since we know, from activity coefficients[15] and from protonation equilibria[12-14] measurements, that carbonium ions are the least solvated ions, we expected to find in all the above examples a negative value for the slope parameter ($\phi_\ddagger - \phi_e$) as found (see Table III). The magnitude of these slopes, however, must be different even for the simple A1 reactions described above, for at least two main reasons: (1) The slope parameter is related to the difference between the activity coefficients of the transition state and the protonated substrate. It is known[12-15] that the activity coefficients of the latter depend on their individual structure (compare, for example, the ϕ_e value for the ether and the amine); therefore, even if the $\log f_\ddagger$ term is the same, the ($\phi_\ddagger - \phi_e$) parameter must assume different values. (2) Though the reaction may belong to the same mechanistic group, the degree of carbonium ion character of the transition state may vary and with it its solvation requirements (i.e., $\log f_\ddagger$).

Table V, Correlation of Hydrolysis Rates with Acidity for Amides and Thioacetamide

Correlation	CH_3CSNH_2[a]	n-$C_4H_9CONH_2$[b]	$C_6H_5CONH_2$[c]
r[d]	8.2	1.9–0.7	3.0–1.7
$\phi_\ddagger - \phi_e$[e]	1.09 (±0.02)	0.01 (±0.04)	0.42 (±0.01)

[a] In aqueous perchloric acid at 25 °C;[26] $pK_{BH^+} = -2.53$,[29] $\phi_e = -0.48$.[29] [b] In aqueous sulfuric acid at 64 °C;[27] H_0 and $\log a_{H_2O}$ data were at 25 °C, pK_{BH^+} (−0.74)[14] and ϕ_e (+0.59)[14] at 33 °C. [c] In aqueous sulfuric acid at 25 °C,[28] $pK_{BH^+} = -1.50$,[14] $\phi_e = +0.42$.[14] [d] From plots of ($\log k_\psi - \log [SH^+]/[S]_{st}$) vs. $\log a_{H_2O}$. The limit slopes are reported for the curved plots obtained with amides. [e] From ($\log k_\psi - \log [SH^+]/[S]_{st} - \log a_{H_2O}$) vs. ($H_0 + \log [H^+]$); values in parentheses are standard deviations from least-squares analysis.

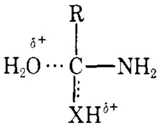
Let us now compare the fragmentation reactions of the esters, the ether, and the sulfoxide. The oxonium ions have similar solvation requirements, as judged from the ϕ_e values. The ($\phi_\ddagger - \phi_e$) parameters are, however, of quite different magnitude: ca. −0.9 for the ether and the ester, and −0.22 for the sulfoxide.[32] This indicates a different carbonium ion character in the transition states, with a higher solvation requirement for the reaction of the sulfoxide. This is not unexpected on the basis of the detailed study carried out on the fragmentation of *tert*-butyl phenyl sulfoxide,[18] which did show that this reaction occurs via an intimate ion–molecule pair. The transition state must therefore have little carbonium ion character and, certainly, must be more similar to the reactants than in the case of the hydrolysis of the *tert*-butyl ester, where a clear $A_{Al}1$ mechanism has been demonstrated.[10c,22,34]

We may now turn our attention to the amine **3**. The reaction of this compound is slightly more complex, since a new reaction path is evident at low acidities. In order to compare the behavior of compounds **1–4** we will limit our discussion to the unimolecular fragmentation which for compound **3** is predominant above H_2SO_4 12.0 M. Also in this case, we expect a negative ($\phi_\ddagger - \phi_e$) value, since the solvation requirements of the ammonium ions are greater than those of the carbonium ions. However, as judged from the ϕ_e values, the differences are smaller in the case of the ammonium than in the case of the oxonium ions. Accordingly, a smaller absolute value of the slope parameter is found in the reaction of compound **3** compared to compounds **1–4**.

The γ-Butyrolactone ⇄ γ-Hydroxybutyric Acid Interconversion. Interpretation of the reaction mechanism following the Zucker–Hammett treatment[23,24] or the Bunnett relationship based on the evaluation of the w parameter[25] classified the former and the reverse process as having different transition states, since the water molecule was implied as nucleophile only in the former reaction (see Table IV). As pointed out by

Bunnett,[25] these conclusions are unacceptable, since both forward and reverse reactions must have a common transition state. The $\phi_{\ddagger}$ parameters obtained through eq 11 (see Table IV) are positive for both hydrolysis and lactonization; this means (see eq 18) that for both reactions the term $f_{\ddagger}/f_{S}$ is greater than f_{BH^+}/f_{B} and hence that the transition state has a fairly large solvation energy. Since both forward and reverse reactions have a common transition state,[25] i.e., equal $f_{\ddagger}$s, the larger $\phi_{\ddagger}$ value for hydrolysis must be due to a smaller f_{S} term for the lactone than for the acid. This is in agreement with the fact that the γ-hydroxybutyric acid is salted out in sodium chloride or sodium perchlorate much more effectively than the γ-butyrolactone which is actually salted in by sodium perchlorate. As a final point, since the transition state is a protonated species, the $\phi_{\ddagger}$ value for hydrolysis can be compared to the ϕ_e values of protonation equilibria. It is much closer to the ϕ_e[35] for ethers and alcohols (+0.8–+0.9)[13] than to the ϕ_e for esters (+0.4–+0.6)[19]. This clearly indicates that the transition state of the hydrolysis of the lactone has an oxonium ion character which resembles a protonated alcohol as might be expected when a water molecule is involved in the nucleophilic attack on the esters.

The Hydrolysis of Amides and Thioamides. The title reactions give ($\phi_{\ddagger} - \phi_e$) values (see Table V) which increase on going from butyramide (about zero) to benzamide (+0.42) to thioacetamide (+1.09). We expect that the solvation requirement of the transition state is similar in the three cases since it can be represented as **6** and therefore it has the character of an oxonium ion. Furthermore, we know from protonation equilibria measurements that protonated amides are much more solvated than protonated thioamides;[36] in fact, the ϕ_e values are +0.59 for butyramide,[14] +0.42 for benzamide,[14] and −0.48 for thioacetamide.[29] It follows that the different ($\phi_{\ddagger} - \phi_e$) values found in the three hydrolyses are simply explained by taking into account the differences in solvation requirements of the protonated substrates with no need for claiming different modes of participation of water molecules in the transition states. The advantage of using the above treatment becomes obvious when one compares the data obtained using the Yates modification[10c,30] of the Bunnett *w* treatment[25] (see Table V). The *r* type treatment, in fact, yields unreasonably high values (thioacetamide) or curved plots.



6

Conclusions

We have reassessed a method to correlate reaction rates with medium acidity by deriving it directly from the linear free energy relationships already tested in protonation equilibria measurements. Following our treatment, the parameters obtained from eq 9–11 and 16, ($\phi_{\ddagger} - \phi_e$) and $\phi_{\ddagger}$, allow us to obtain information on the solvent effect experienced by the protonated substrate or by the free base on going to the transition state.

The results above discussed show how sensitive the slope parameter is to minor variations in the structure of either the initial or the transition state. As information on the activity coefficient behavior of free and protonated substrates is now available,[12,15] this also means that it is possible to obtain, through the above linear free energy relationships, a fine description of the solvation requirements, and hence of the structure, of the transition state. The sensitivity of the ($\phi_{\ddagger} - \phi_e$) parameter to the individual reactions rules out the possibility of finding a simple correlation between slope parameters and mechanistic categories. This is, on the other hand, expected since, independently of the kind of equation or formalism used, the correlations of rates with acidity are really only a measure of a medium effect, i.e., of the changes in initial and transition state activity coefficients.

Experimental Section

Materials. Methyl *tert*-butyl ether has been synthesized and purified as reported elsewhere.[13] ***N*-Alkyl-2,4-dinitroanilines 3** and **5** were prepared in essentially the same manner from recrystallized 2,4-dinitrochlorobenzene and reagent grade amines following a described procedure:[37] ***N-tert*-butyl (3)**, mp 153–153.5 °C, from ethanol;[37] ***N-n*-butyl (5)**, mp 90 °C, from ethanol.[38]

Basicity Measurements. The basicity parameters of methyl *tert*-butyl ether have been derived from NMR measurements of the methyl proton chemical shift as a function of the medium acidity following the procedure described elsewhere.[13] *N*-*n*-Butyl-2,4-dinitroaniline (0.082 g) was dissolved in CH_2Cl_2 (50 mL); a 2-mL aliquot of this solution was transferred to a 50-mL flask. The solvent was removed under reduced pressure and the flask was filled to the mark with concentrated H_2SO_4. One milliliter of this solution was then diluted to 50 mL with thermostated aqueous sulfuric acid of the appropriate concentration. The final solution was then titrated with standard NaOH. UV spectra were recorded with a Cary 15 spectrometer by using 50-mm cells. The concentration of **5** was in each solution 5.48 × 10^{-6} M. The optical densities measured at 365 nm are reported in Table VI as a function of the acid concentration; see paragraph at end of paper regarding supplementary material.

From the sigmoid curve obtained from data of Table VI we have evaluated the optical density corresponding to the free base, $(OD)_S$, and to its conjugate acid, $(OD)_{SH^+}$. The ionization ratios (I) are then estimated at each acidity as $I = [(OD)_S - OD/OD - (OD)_{SH^+}]$. By applying the Bunnett and Olsen equation[10a] (eq 2) the ϕ_e and pK_{SH^+} values are then easily computed. It is convenient, when the ϕ_e values are near zero, to apply the modified form of the Bunnett and Olsen equation:[10a]

$$\log([SH^+]/[S]) - \log[H^+] = (\phi_e - 1)(H_0 + \log[H^+]) + pK_{SH^+} \quad (19)$$

In this case the slope parameter is near 1 and hence the least-squares analysis can be carried out more conveniently. The correlation coefficient obtained for data of Table VI is 0.9981; the pK_{SH^+} and ϕ_e values are collected in Table III. The H_0 values were obtained by interpolation of published data.[20]

Kinetic Measurements. Solutions of methyl *tert*-butyl ether (ca. 0.05 M) in thermostated aqueous sulfuric acid of the appropriate concentration were examined at 25 °C with a Bruker HFX-10 spectrometer. The disappearance of the methyl signal was monitored either by comparison of its peak height with that of $Me_4N^+BF_4^-$, added as internal standard, or, in the case of faster reactions, by pointing the recorder pen on the signal and following continuously its disappearance.

N-*tert*-Butyl-2,4-dinitroaniline (0.5 g) was dissolved in methanol (50 mL) and 20 μL of this solution was added to the thermostated (25 °C) aqueous sulfuric acid (50 mL) of the appropriate concentration. This solution was transferred to a 10-mm cuvette and examined with a Gilford 2400 spectrometer for the increase in absorbance at 372 nm. In the case of sulfuric acid solutions more concentrated than 10 M, 3 μL of the methanolic solution was added to 2 mL of the aqueous acid directly in a 10-mm cuvette and analyzed for the decrease in absorbance at 240 nm.

The computation of the rate constants has been carried out as described elsewhere.[18,39]

Supplementary Material Available: Kinetic data for compound **2** (Table I) and **3** (Table II) fragmentation, and spectral data for protonation of **5** (Table VI) (3 pages). Ordering information is given on any current masthead page.

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(32) We should notice that the reaction of the sulfoxide has been studied[18] in perchloric acid whereas those of the other two substrates have been run in sulfuric acid. Different dependences on acidity are observed in the two media, as reported by other authors;[25,33] in the case of *tert*-butyl acetate, for instance, the $(\phi_\pm - \phi_e)$ parameter is ca. −1.3 in perchloric acid. This trend is perhaps a general one and we shall return to this point in a forthcoming paper. For the purposes of the present discussion it suffices to consider that, had the fragmentation of the sulfoxide been studied in H_2SO_4, the slope parameter would have been even more positive than −0.22.
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(36) The reason for this behavior resides in the fact that the sulfonium ion interacts less than the oxonium ion with water molecules since the positive charge is more delocalized by the large and polarizable sulfur atom. In the case of amides the positive charge is obviously more easily dispersed in the substrate bearing a phenyl substituent; hence the cation formed by protonation of benzamide is less solvated than the one derived from butyramide.
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Reactions in Moderately Concentrated Acids. 2.[1] Solvation Effects in the Acid-Catalyzed Hydration of Olefins and Acetylenes

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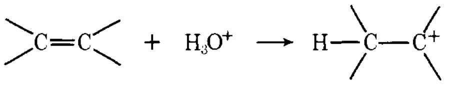
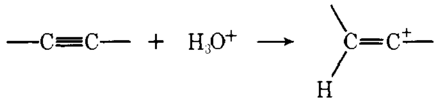
Abstract: Rate data for the hydration of substituted styrenes and phenylacetylenes and of *trans*-3-hexene and 3-hexyne in moderately concentrated aqueous sulfuric acid solutions have been analyzed in terms of the proper linear free energy relationship (for $A_{SE}2$ type mechanisms) discussed in the previous paper. The analysis indicates that the solvation requirements of the transition states of the reaction and hence of the corresponding carbonium ions and vinyl cations are rather modest and closely similar for analogous pairs of olefins and acetylenes. It also appears that the substituent effects within the series of both styrenes and phenylacetylenes increase on going toward more concentrated acid solutions.

Ethylene derivatives undergo hydration in moderately concentrated acids at similar or slower rates than the corresponding acetylene derivatives;[2] typical $k_{\text{olefin}}/k_{\text{acetylene}}$ (k_o/k_a) ratios range between 3.6 (1-hexene/1-hexyne, 48.7% H_2SO_4), 0.7 (styrene/phenylacetylene 48.7% H_2SO_4[3,4]), and 10^{-2} (ethoxyethylene/ethoxyacetylene in aqueous buffers[5]). Clear evidence has been reported,[6] particularly for styrene[7] and phenylacetylene[4] derivatives, that in both cases the hydration mechanism involves a slow proton transfer to the unsaturated reagent (eq 1 and 2) and that the transition states of the reactions closely resemble[8] the cationic intermediates, carbonium ions **1** and vinyl cations **2**.



1

$+ H_2O \longrightarrow$ products (1)



2

$+ H_2O \longrightarrow$ products (2)