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Nonlinear Brønsted Correlations: The Roles of Resonance, Solvation, and Changing Transition-State Structure[1]

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Abstract: Brønsted-type correlations for nucleophilic attack of the anions of weakly basic fluorinated alcohols and carbonyl hydrates on the esters 1-acetoxy-4-methoxypyridinium ion, 2,4-dinitrophenyl acetate, and *p*-nitrophenyl acetate exhibit slopes of $\beta_{\text{nuc}} = 0.5–0.8$. Similar slopes are observed for catalysis of proton removal from carbon acids by these bases, which is less subject to steric hindrance. The results do not support a specific role of resonance delocalization as a cause for the relatively large Brønsted slopes for phenolate anions in these reactions. There is suggestive evidence for a modest change in transition-state structure with changing basicity of the anion, but this is insufficient sufficient to account for the observed curvature of Brønsted plots for catalysis by oxygen anions. The curvature may be accounted for, in part, by a requirement for partial desolvation of basic aliphatic oxygen anions that decreases the observed Brønsted slope for these compounds.

Structure–reactivity correlations provide one of the most powerful tools for probing the structure of transition states. Changes in these correlations, which represent second derivatives of log *k* with respect to one or more structural parameters, have been of special interest to physical–organic chemists because they may provide insight into the nature of the energy surface that is responsible for changes in the structure of transition states. Bell, Marcus, Hammond, Polanyi, Thornton, and Leffler, among many others, have proposed ways of describing such relationships.[2] Changes in structure–reactivity correlations and transition-state structure frequently appear as a curvature in the correlation. However, such curvature may represent a change in rate-determining step or the manifestation of an additional variable that affects the rate, rather than a change in transition-state structure.[3] It is important, therefore, to examine critically the reasons for nonlinear structure–reactivity correlations.

It has been suggested that the nonlinear Brønsted-type correlations for nucleophilic attack of oxygen anions on esters result, in part, from a requirement for partial desolvation of basic oxygen anions that is less important for weakly basic anions.[4,5] Desolvation of an oxygen anion becomes more difficult with increasing basicity and can cause a decrease in the observed Brønsted slope, β_{nuc}, for basic nucleophiles. Hupe and Wu observed virtually identical curvature in the Brønsted plot for proton removal from a carbon acid by oxygen anions and ascribed this curvature to a solvation effect, rather than to a change in transition-state structure, because the curvature for a series of different carbon acids is a function only of the base strength of the anion, not of $\Delta G°$ for the reaction.[6]

However, most of the weaker bases in these reaction series are phenolate ions and Kovach et al. have recently suggested that delocalization of negative charge into the aromatic ring specifically decreases the observed rate for phenolate ions, so as to cause a downward curvature for these bases.[7] This suggestion is of special interest because two classes of "α-effect" compounds, substituted oximate[8] and hydroperoxide anions,[9] exhibit low values of β_{nuc} that are similar to those observed for basic oxygen anions. This raises the possibility that the high observed reactivity of some α-effect compounds actually represents an abnormally low reactivity of the resonance-stabilized, weakly basic phenolate ions to which they are compared, rather than an abnormally high reactivity of the α-effect compounds.

We describe here an examination of the nucleophilic reactivity toward esters and carbon acids of weakly basic oxygen anions in which the charge is not delocalized by resonance in an attempt to evaluate the role of such resonance in nonlinear structure–reactivity correlations.

Experimental Section

Materials. 1-Acetoxy-4-methoxypyridinium perchlorate (AMPP)[10] (mp 130–132 °C) was prepared by the method of Traynelis and Pacini.[11] Stock solutions were prepared shortly before use in acetonitrile, which had been dried over molecular sieves and redistilled. *p*-Nitrophenyl acetate (PNPA) and 2,4-dinitrophenyl acetate (DNPA) were recrystallized. *N*-Ethylmorpholine, 1,1,1,3,3,3-hexafluoro-2-propanol, 1,1,3,3-tetrafluoroacetone, 2,2,2-trifluoroethanol, phenyl acetate, and water were redistilled. Inorganic salts, Tris (Ultrapure, Schwartz/Mann), hexafluoroacetone sesquihydrate, pentafluoropropionaldehyde hydrate, 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol, and perfluoro-2-methyl-2-propanol were used as received. 2,2,2-Trifluoroacetaldehyde hydrate and 1,1,1-trifluoroacetone contained 1–3% of an acid impurity that was removed by adjusting the hydrate solution to pH 6.5–7 with potassium hydroxide[12] or mixing the solution with 0.05 mol of potassium carbonate and water, followed by distillation. These fluorinated compounds were obtained from P.C.R. Research Chemicals or Aldrich Chemical Co. except for 1,1,3,3-tetrafluoroacetone, which was obtained from Pfaltz and Bauer. The concentration of the acidic hydrates was determined by titration with alkali.

Solutions of methylene glycol were diluted from a concentrated aqueous solution (Fisher Scientific Co.), allowed to stand for at least 15 h, and adjusted to pH 6–7. They were found to contain <0.1% formic acid. Concentrations of the stock solutions were determined by titration with sodium sulfite.[13]

Methods. Pseudo-first-order rate constants were measured spectrophotometrically at 25 °C as described previously[14] at ionic strength 1.0 M, maintained with potassium chloride in water. The nucleophilic reagent was present in large excess except for hexafluoro-2-methyl-2-

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(10) Abbreviations: AMPP, 1-acetoxy-4-methoxypyridinium cation; DNPA, 2,4-dinitrophenyl acetate; PNPA, *p*-nitrophenyl acetate.

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Table I. Rate Constants for Nucleophilic Reactions of Oxygen Anions with *p*-Nitrophenyl Acetate, 2,4-Dinitrophenyl Acetate and 1-Acetoxy-4-methoxypyridinium Ion at 25 °C, Ionic Strength 1.0 M (KCl)[a]

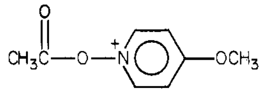
nucleophile anion of	pK_a	pH	concn range, M	no. of runs	k_2, M^{-1} s^{-1}
		p-Nitrophenyl Acetate			
$(CF_3)_2C(OH)_2$	6.45[b]	7.0	0.23–0.75	4	3.3×10^{-5}
$(CHF_2)_2C(OH)_2$	8.90[b]	9.4	0.08–0.32	4	1.3×10^{-3}
$(CF_3)_2CHOH$	9.22[b]	9.0	0.004–0.18	4	2.1
$CH_3(CF_3)C(OH)_2$	10.45[b]	9.9	0.04–0.08	4	4.2×10^{-3}[c]
		2,4-Dinitrophenyl Acetate			
$(CF_3)_2C(OH)_2$		6.1	0.06–0.25	4	7.1×10^{-4}
		6.6	0.13–0.50	2	8.9×10^{-4}
					8.0×10^{-4}[d]
$(CHF_2)_2C(OH)_2$		8.9	0.05–0.20	4	0.019[e]
		9.5	0.16–0.48	4	0.024
$(CF_3)_2CHOH$		7.14[f]	$(1.9–5.6) \times 10^{-4}$	4	28
		7.44[f]	$(3.8–11) \times 10^{-4}$	4	27
$CH_3(CF_3)C(OH)_2$		9.81	0.013–0.050	4	0.051[c]
CF_3CH_2OH	12.37[g]	9.47[h]	$(8.4–25) \times 10^{-6}$	4	330
		9.80[h]	$(8.9–27) \times 10^{-6}$	4	353
					342[d]
		1-Acetoxy-4-methoxypyridinium Ion			
$(CF_3)_3COH$	5.10[j]	6.13	0.02–0.10	5	0.082[c]
$(CF_3)_2C(OH)_2$		5.95–6.96	0.05–0.14	10	0.75
in D_2O		7.1	0.10–0.20	3	0.76[i]
$(CHF_2)_2C(OH)_2$		8.06	0.003–0.013	9	10.7
$(CF_3)_2CHOH$		5.48[k]	0–0.10	9	8200
$CH_3(CF_3)_2COH$	9.55[j]	7.98[l]	$(0–3) \times 10^{-4}$	8	280
$CF_3CH(OH)_2$	10.04[j]	7.08[k]	0–0.01	7	9400
$CH_3(CF_3)C(OH)_2$		8.64[l]	0–0.001	10	60
$H_2C(OH)_2$	13.2[m]	7.04[k]	$(0–6) \times 10^{-7}$	12	4.4
		8.2[n]	$(0–25) \times 10^{-7}$	5	4.4
		8.5[n]	$(0–25) \times 10^{-7}$	6	4.5

[a] The hydrates and alcohols were used as buffers, unless indicated otherwise. [b] Reference 12. [c] Estimated error ±25%. Only 10–50% rate increase was observed. [d] Average value. [e] Ionic strength 0.7–0.9 M (KCl). [f] 0.05 M phosphate buffer. [g] Reference 14. [h] 0.05 M carbonate buffer. [i] In D_2O. [j] Determined by titration at 25 °C, ionic strength 1.0 M (KCl). [k] 0.02 M phosphate buffer. [l] 0.01 or 0.02 M Tris buffer. [m] Estimated for ionic strength 1.0 M from a reported value (Bell, R. P.; Onwood, D. P. *Trans. Faraday Soc.* 1959, *58*, 1557–1561) of 13.27. [n] 0.012 M *N*-ethylmorpholine buffer.

propanol, which was present in ≥9-fold excess. End points for the slow reactions of hexafluoroacetone hydrate with *p*-nitrophenyl acetate were determined in dummy reaction mixtures to which hydrolyzed *p*-nitrophenyl acetate was added. Satisfactory first-order kinetics were generally followed over more than 3 half-times. In experiments in which there was a significant change in pH with buffer concentration, the observed first-order rate constants were corrected for changes in the rate constant for alkaline hydrolysis. Second-order rate constants were obtained from the slopes of observed or corrected first-order rate constants against the concentration of the anion of the nucleophilic reagent. The intercepts at zero buffer concentration were found to agree satisfactorily with the rate constants expected for alkaline hydrolysis and reaction with added buffers. The pH of reaction mixtures was measured before and after reaction. Titrations were carried out at 25 °C at ionic strength 1.0 M (KCl).

Results

Pseudo-first-order rate constants for the reaction of methylene glycol anion with AMPP, **1**, in phosphate and *N*-ethylmorpholine buffers are shown in Figure 1. In this and other reactions using buffers other than the nucleophilic reagent, no catalysis by buffers of the reaction with the nucleophile was observed.



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Rate constants for reactions of the anions of a series of alcohols and carbonyl hydrates with AMPP, DNPA, and PNPA were measured similarly. Second-order rate constants for these reactions are shown in Table I. These rate constants are estimated to be accurate to within ±10% unless noted otherwise in the table.

Discussion

Resonance. The rate constants for the reactions of alkoxide, phenolate, and acetate anions with AMPP,[10] measured in these and previous[14] experiments, follow a nonlinear Brønsted-type correlation (Figure 2, upper line). The curvature of this correlation is virtually identical with that for rate-determining attack of oxygen anions on PNPA, DNPA, *p*-nitrophenyl thiolacetate, and *N*-

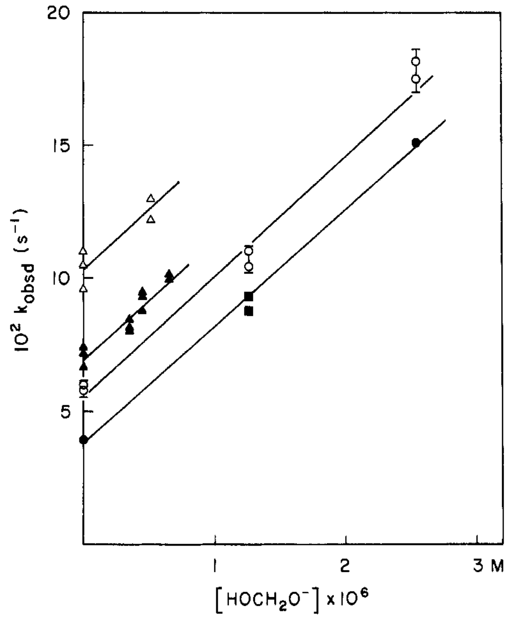

Figure 1. Dependence of the pseudo-first-order rate constants for the disappearance of AMPP on the concentration of the anion of methylene glycol at 25 °C, ionic strength 1.0 M (KCl). Buffers: △, 0.028 M phosphate, pH 7.25; ▲, 0.020 M phosphate, pH 7.04; ○, 0.002 M *N*-ethylmorpholine, pH 8.50; ●, 0.012 M *N*-ethylmorpholine, pH 8.19; ■, 0.024 M *N*-ethylmorpholine, pH 8.19, but corrected for the additional reaction of the buffer.

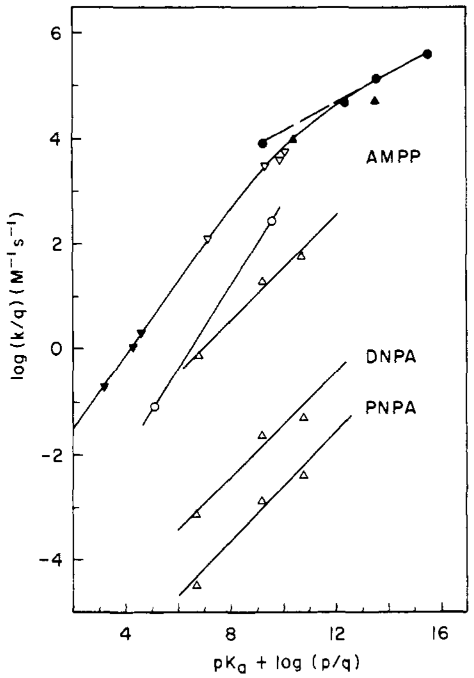

Figure 2. Brønsted plots for the reactions of different classes of anionic oxygen nucleophiles with AMPP and for the reactions of ketone hydrates with DNPA and PNPA at 25 °C, ionic strength 1.0 M (KCl). Simple alkoxide ions, ●; substituted phenolates, ▽; substituted acetates, ▼;[14] hexafluoro-*tert*-butyl and perfluoro-*tert*-butyl alcohol anions, ○; aldehyde hydrate anions, ▲; ketone hydrate anions, △. The rate and equilibrium constants are statistically corrected.

acetyl-4-methylpyridinium ion.[4,5,14-16] Attack of the nucleophile on AMPP is expected to be rate determining in these reactions because the nucleophiles ($pK_a = 3-15$) are more basic than the leaving group ($pK_a = 2$), so that a tetrahedral intermediate would be expected to expel the leaving group to give products more rapidly than it expels the nucleophile to regenerate the reactants. The absence of a solvent deuterium isotope effect for the reaction of the anion of hexafluoroacetone hydrate (Table I) provides evidence for a nucleophilic reaction of the anion, rather than general base catalysis of the attack of water. Very similar Brønsted curves for oxygen anions in aqueous solution have been observed for rate-determining proton abstraction from carbon in elimination reactions,[6] and a similar decrease in β_{nuc} with increasing pK, from ~0.75 to ~0, has been observed for the attack of substituted phenolate and alkoxide ions on *m*-nitrophenyl methanesulfinate.[17]

The rate constants for reactions of the anions of fluorinated alcohols and carbonyl hydrates provide no evidence for a specific contribution of resonance delocalization in phenolate anions to the β_{nuc} values or to the curvature of the Brønsted plot. Rate constants for the anions of two fluorinated *tert*-butyl alcohols give a slope ($\beta_{nuc} = 0.8$, open circles, Figure 2) that is as large as that for phenolate and acetate anions ($\beta_{nuc} = 0.7$, inverted triangles, Figure 2). More basic oxygen anions of fluorinated alcohols (two of the closed circles in Figure 2) and two aldehyde hydrates (closed triangles in Figure 2) have rate constants and values of β_{nuc} = 0.2–0.3 that are essentially the same as those for other basic alkoxide anions, whereas the less basic anions of fluorinated acetone hydrates show a larger slope, with $\beta_{nuc} = 0.5$ (open triangles in Figure 2). The relatively slow rates for the anions of acetone hydrates and *tert*-butyl alcohols may be attributed in large part to steric hindrance. Slopes of $\beta_{nuc} = 0.5$ are also observed for the reactions of fluoroacetone hydrates with DNPA and PNPA (Figure 2); these values are larger than the values of $\beta = 0.2-0.3$ for reactions of more basic alkoxide anions with these esters.[5,14]

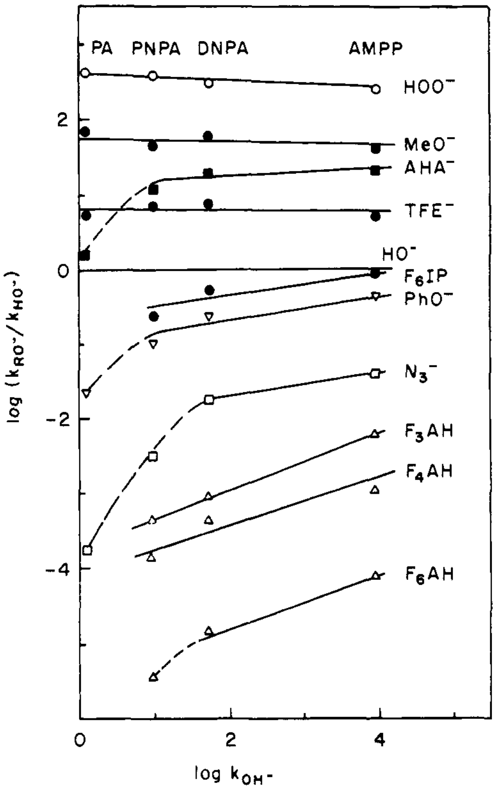

Figure 3. Ratios of the rate constants for the reactions of anionic nucleophiles and hydroxide ion with AMPP, PNPA, DNPA, and PA (phenyl acetate) as a function of ester reactivity, at 25 °C, ionic strength 1.0 M (KCl). Fluorinated acetone hydrates are indicated by F_nAH, hexafluoroisopropyl alcohol by F_6IP, trifluoroethanol by TFE, and acetohydroxamic acid by AHA. Data from Table I and ref 14.

The ratios of rate constants for the reactions of anionic nucleophiles and hydroxide ion with phenyl acetate, PNPA, DNPA, and AMPP are shown in Figure 3 as a function of k_{OH^-}, which is taken as a measure of ester reactivity with rate-determining attack of the nucleophile. There are sharp downward breaks that correspond to a change in the nature of the rate-determining step, shown by dashed lines, when the pK of the leaving group becomes equal to or larger than that of the less basic nucleophiles. These breaks are observed in the reactions of phenolate and acetohydroxamate ions with phenyl acetate and azide ion with PNPA and phenyl acetate. The other nucleophiles show small changes in slope but no evidence for a change in rate-determining step, with the possible exception of the reaction of the anion of hexafluoroacetone hydrate with PNPA. A significant role of leaving group departure is expected in the rate-determining step of this reaction because of the pK_a of the nucleophile, 6.5, is similar to that of the leaving group, 7.1. We conclude that, with this exception, attack of the nucleophile is rate determining for the acetone hydrates and the steric demands of these compounds do not cause a change in rate-determining step. Very similar behavior is observed for the fluorinated nucleophiles over a range of 10^7 in reaction rate and 10^4 in k_{RO^-}/k_{HO^-} and with anions of acetone hydrates that are up to 10^8 more basic than the leaving group of AMPP.

There is also no evidence for a special effect of resonance in the reactions of substituted phenolate and alkoxide ions with carbon acids. The curved Brønsted correlations for some of these reactions are identical with those for reactions of the same anions with esters.[6,18] The upper line in Figure 4 describes the rate constants for proton removal by alkoxide, phenolate, cacodylate, and acetate anions and tertiary amine bases in the E1cB (irreversible) elimination reaction of a (2-(*p*-nitrophenyl)ethyl)am-

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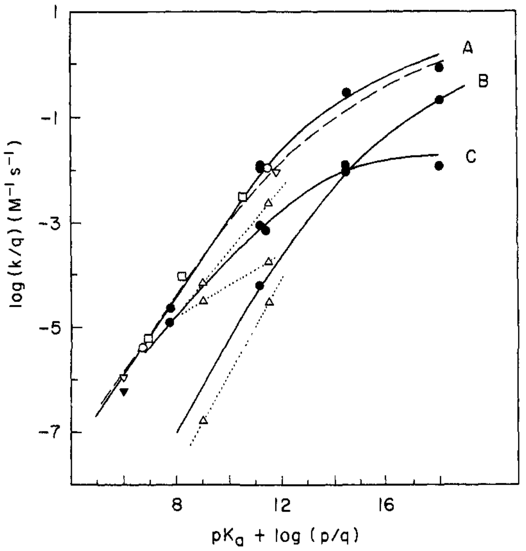


Figure 4. Brønsted plots for catalysis by oxygen anions and substituted quinuclidines of β-elimination reactions of substituted 2-phenylethyl derivatives in 60% Me$_2$SO in water (v/v) at 40 °C and ionic strength 0.3 (KCl). Curve A: (2-(*p*-nitrophenyl)ethylquinuclidinium ion; B: (2-(*p*-cyanophenyl)ethyl)-1,4-diazabicyclo[2.2.2]octanium ion; C: 2-(*p*-nitrophenyl)ethyl bromide.[18] Quinuclidines, □; other symbols as in Figure 2. The dashed line corresponds to the upper solid line in Figure 2. The dotted lines are drawn through the rate constants for catalysis by anions of ketone hydrates; they refer to the same substrate as the solid line immediately above.

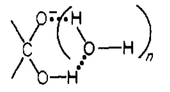
monium ion. These reactions are in 60% Me$_2$SO in water and the pK_a values refer to the same solvent. The dashed line shows the Brønsted curve for the reactions of oxygen anions with AMPP in water (Figure 2). All of the bases of moderate basicity show the same behavior and follow a Brønsted slope with $\beta = 0.7$. Rate constants for the anions of the two fluorinated *tert*-butyl alcohols (open circles) fall on the same Brønsted line as the other catalysts for this proton abstraction from carbon; i.e., the Brønsted slope is the same for these bases as for phenolate anions.

Similar curvature is observed in the Brønsted correlations for general base catalysis of other elimination reactions that have larger (curve B, Figure 4) and smaller (curve C) normalized values of β. In all three reactions the anions of fluoroacetone hydrates (triangles and dotted lines) show small negative deviations from the lines, but have larger Brønsted slopes than more basic oxygen anions.

These results confirm the observation by Hupe and Wu that phenolate anions are at least as reactive as weakly basic alkoxide anions for general base catalysis of proton abstraction from carbon. The anion of hexafluoroacetone hydrate fits the same curved Brønsted correlation as a number of other alkoxide and phenolate anions for the E1cB (irreversible) elimination reaction of 4-(*p*-nitrophenoxy)-2-butanone.[6]

The fit of the rate constants for the anions of fluorinated *tert*-butyl alcohols on the Brønsted line of Figure 4 shows that steric hindrance is not significant for these proton abstractions. The same bases show a negative deviation of ~30-fold in the nucleophilic reaction with the ester AMPP (Figure 2). A still larger negative deviation of ~500-fold is observed in the reaction with PNPA of *tert*-butylamine, compared with primary amines.[19] This is consistent with a modest steric effect for rate-determining nucleophilic attack of the alkoxide anions and a more stringent steric requirement when breakdown of a tetrahedral addition intermediate is rate determining and the bond to the nucleophile is fully formed, in the transition state for ester aminolysis.[20] Steric hindrance causes a decrease in $\beta_{\rm nuc}$ for the reactions of oxygen anions with pivalate esters[15] and may possibly contribute to the slightly decreased values of $\beta_{\rm nuc}$ for fluoroacetone hydrates. However, there is no indication of larger steric effects for the reactions with DNPA compared with other esters (Figure 3) and the anion of hexafluoro-2-propanol has a normal reactivity (Figure 2).

It is possible that the additional negative deviations of the rate constants for the anions of fluoroacetone hydrates in Figures 2 and 4 reflect a requirement for removal of a solvating water molecule(s) from a cyclic, internally hydrogen-bonded complex, **2**. Stabilization of the anion in such a complex has been suggested previously as a contributing factor to the low pK_a of hexafluoroacetone hydrate[20] and might be more important for ketone than for aldehyde hydrates because of the greater accessibility of the oxygen anion of aldehyde hydrates to solvation by the bulk solvent. Such solvation could also account for the small decrease in $\beta_{\rm nuc}$ for these anions if it is more important for the more basic anions, as described below.



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We conclude that there is no significant difference between the effects of electron withdrawal by field, inductive, or resonance effects in these and related systems. The curved Brønsted plots in Figures 2 and 4 and elsewhere[4–6,15–18] reflect some nonlinear relationship between changes in basicity and reactivity that is independent of the mechanism by which substituents decrease the electron density on oxygen. This conclusion is also consistent with the absence of a negative deviation of phenolate ion from the Brønsted correlation for attack of alkoxide ions on thiol esters[5] and the normal rate constants for transfer of a proton to *p*-nitrophenolate ion from anilinium and imidazolium ions, even when the Δp*K* between the proton donor and acceptor is small.[21] On the other hand, there is evidence for a larger value of $\beta_{\rm nuc}$ for reactions of anilines than of aliphatic amines in reactions with methyl perchlorate[22] and *p*-nitrophenyl (triphenylmethane)-sulfenate,[23] which could reflect a specific resonance delocalization of anilines in these reactions.

The reason for the unusual behavior of the α-effect compounds is still not established. The low values of $\beta_{\rm nuc}$ for some of these compounds[8,9] mean that the magnitude of the rate increase from the α-effect is larger for less basic nucleophiles and provide one reason why the α-effect is larger for reactions with a large $\beta_{\rm nuc}$ for the reference reaction.[23] There is no indication of an unusually large amount of bond formation in the transition state with these compounds; the small values of $\beta_{\rm nuc}$ might suggest the opposite and the data shown in Figure 3 show that the value of $\beta_{\rm lg}$ for rate-determining attack of acetohydroxamate anion is approximately the same as that for other nucleophiles of similar basicity. The reaction of acetohydroxamate anion undergoes a change in rate-determining step with phenyl acetate (pK_a = 10 for phenol) at approximately the point expected from its pK_a of 9.4 (Figure 3), so that the enhanced stability of the transition state for its reaction is similar when the bond to carbon is partly or fully formed. Thus, the α-effect for this compound may be described as an enhanced carbon basicity relative to proton basicity in both transition states and addition intermediates.[24,25]

Few, if any, generalizations hold for all α-effect compounds. Other nucleophiles in this class, including hydrazines[25,26] and hydroxamic acids,[27] exhibit larger values of $\beta_{\rm nuc}$ that are similar to those for normal nitrogen and oxygen compounds of comparable

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p*K*. The low value of β_{nuc} for oxime anions might be accounted for by an electrophilic interaction of the nucleophile with the developing charge on the carbonyl oxygen atom of the ester that is facilitated by electron-withdrawing substituents on the oxime.[8,19,24]

Solvation. We briefly review here the hypothesis that solvation effects make a significant contribution to the observed decrease in β values for basic alkoxide ions. It is important to emphasize that hypotheses based on solvation effects (or on "water structure") should be viewed with skepticism, because they can be used to "explain" almost anything.

The fact is that in the great majority of reactions the Brønsted β values are small, usually 0.2–0.3, for alkoxide ions of $pK_a > 12$ that have comparable steric requirements. When β values are larger for less basic anions, this means that polar substituents "see" a larger fractional decrease in negative charge on going from the initial solvated ion to the transition state than with the more basic anions. The solvation energies of these basic anions from the gas phase are enormous and it is probable that at least one of the three solvating water or alcohol molecules[28,29] is removed before reaching the transition state of most reactions of such molecules in aqueous solution. It would be surprising if such desolvation did not contribute in some way to the observed structure–reactivity behavior of these anions.

In order to give rise to curvature in the Brønsted plot, it is not sufficient that such partial desolvation should be more unfavorable for basic anions. The desolvation must itself follow a nonlinear Brønsted relationship because a constant β value for desolvation would give a constant (though altered) observed β value. There are several reasons to expect such a nonlinear Brønsted relationship because the unfavorable Gibbs free energy change for the removal of one of three hydrogen-bonded solvating water molecules in aqueous solution decreases and eventually disappears as the anion becomes less basic.

(1) The number of water molecules that are hydrogen bonded to an oxygen anion decreases with decreasing basicity of the oxygen atom. In the limit of liquid water itself both lone pairs of oxygen are not hydrogen bonded in every molecule. Removal of the first of three solvating water molecules is expected to be easier than removal of the remaining molecules and will have a negligible free energy change at some intermediate p*K*; the free energy change becomes negligible when the solvation energy for this water molecule becomes equal to that for solvent self-association.[30]

(2) Two ortho *tert*-butyl groups increase the basicity of phenolate anions by up to two p*K* units (three p*K* units in 50% ethanol) because of interference with solvation, but this effect decreases with decreasing basicity and disappears with phenolate anions of $pK \leq 7$. There is little or no difference between the effects of substituents that withdraw electrons by resonance or field/inductive effects, except for a somewhat larger decrease with the *p*-nitro group.[31] The slope of $\beta = 0.59$ for a plot of ΔpK against p*K* provides a measure of the dependence on basicity of the solvation free energy that is lost in the presence of the two *tert*-butyl groups.[5,31] A larger effect would be expected for partial desolvation of basic alkoxide ions than of phenolate ions. The desolvation brought about by the two *tert*-butyl groups, although large, is less than 10% of the desolvation in going to the gas phase, which gives a 6.6–6.8-fold increase in the sensitivity of the p*K* to substituents.[30,32]

(3) There is a progressive decrease with decreasing p*K* of the solvent deuterium isotope effect for the ionization of oxygen acids, which can be accounted for by a decrease and eventual disappearance of an interaction of the anionic base with solvent molecules that decreases the O–H stretching frequency of these molecules. The solvent isotope effect decreases from approximately $\Delta pK = 0.86$ for water, 0.7 for aliphatic alcohols of p*K* 12–14, 0.6 for phenols, to 0.4–0.5 for carboxylic acids.[33,34] Roughly half of the effect for water has been attributed to hydrogen bonding of hydroxide ion to three water molecules, similar to that for methoxide ion with three methanol molecules.[28,35] A contribution to isotope effect of $\log l^{-3} = 0.48$ may be attributed to the fractionation factor of the three protons of L_3O^+; this contributes to the observed isotope effect for all acids.[28,35] Thus, the contribution from solvation of the anion is negligible for carboxylate and small for phenolate anions.

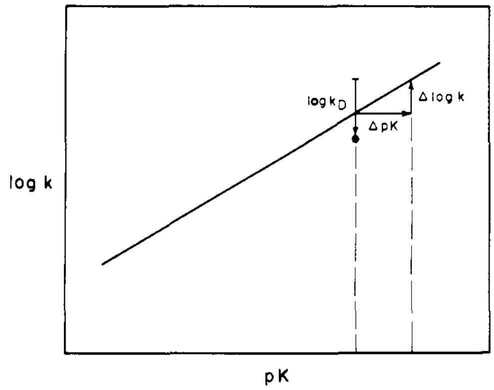

Figure 5. Schematic Brønsted plot to show how a requirement for partial desolvation can cause a negative deviation from a Brønsted plot by its effects on the observed p*K*, reactivity, and concentration of solvated and desolvated ions.

(4) The solvation energies of basic alkoxide ions are much larger than those of phenolates and weaker bases. The increase in basicity of alkoxide ions in the series trifluoroethoxide to ethoxide over that of phenolate ion, in the gas phase compared with water, corresponds to a free energy difference of 9–17 kcal mol^{-1} that reflects primarily the stronger solvation of the aliphatic oxygen anions in water.[36]

It is essential to take account of two points in order to evaluate the effect of desolvation, or any other perturbing effect, on a structure–reactivity correlation such as a Brønsted plot. First, it is necessary to evaluate the effect of desolvation on the reference ionization reaction, as well as on the observed reaction.[37] Second, there must be an *imbalance* in the expression of the perturbing effect in the transition state in order for it to influence the correlation. In the case of desolvation this is likely for early transition states, because desolvation must occur before nucleophilic attack. The solvation effect will become less important for late transition states in which the reacting ion resembles the uncharged alcohol of the reference ionization reaction.[5]

There is not enough information available at this time to permit a quantitative treatment of the data, but it is useful to consider the kind of behavior that can be expected from desolvation. The reaction may be described by eq 1, in which RO^-_s is the starting,

$$RO^-_s \overset{K_d}{\rightleftharpoons} RO^-_d \rightarrow \ddagger \qquad (1)$$

fully solvated anion and RO^-_d is an anion from which one of three solvating water molecules has been removed. The effect of desolvation is illustrated schematically by the Brønsted plot of Figure 5, in which the left-hand part of the line is based upon reactions of weakly basic anions for which this desolvation is not significant

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(37) This description assumes that solvation is more important for a basic oxygen anion in the ground state than in the transition state and that the transition state is at quasi-equilibrium with respect to the rearrangement of solvent molecules, which may occur before the transition state is reached.

($K_d > 1$). Consider a more basic anion, for which desolvation is energetically unfavorable ($K_d \ll 1$), with an observed pK corresponding to the left-hand dashed line. The pK of the desolvated ion, $RO^-{}_d$, will be higher than the observed pK by the amount $-\log K_d$ and its reactivity will be larger than that predicted by the observed pK by the amount $-\beta \log K_d$. However, the observed value of log k will be decreased by log K_d, because only a small fraction of RO^- is the reactive species, $RO^-{}_d$. The result is that the observed log k is reduced below that expected for a base of the observed pK by the amount $(1 - \beta) \log K_d$. This reduction will become larger for more basic anions as the desolvation term becomes larger and will give a decrease in the observed value of β. It is apparent that the effect will become smaller when β is larger and the transition state resembles uncharged ROH more closely. This is observed for the reactions of phenolate and alkoxide ions with acetates when expulsion of RO^- and HO^- is rate determining, for example. The rate constants for both classes of nucleophile are correlated by a single line with $\beta_{nuc} = 1.5$ in these reactions.[16]

Inverse solvent deuterium isotope effects of $k_D/k_H = 1.33$ and 1.35 for the alkaline hydrolysis of ethyl and phenyl acetates and $k_D/k_H = 1.5$–2.1 for the attack of methoxide ion on phenyl acetates and methyl phenyl carbonates provide evidence for a significant loss of solvation of the nucleophile in the transition states of these reactions.[38] In contrast, there is no solvent isotope effect for the reaction of the weakly basic anion hexafluoroacetone hydrate with AMPP, although the weakly basic anions have a larger value of β_{nuc} (Table I). The smaller observed value of β_{nuc} for reactions of oxygen anions with *p*-nitrophenyl pivalate compared with PNPA[15] is consistent with a larger amount of desolvation in the more crowded transition states of the pivalate reactions. No decrease in β_{nuc} is observed for the reactions of *p*-nitrophenyl pivalate with thiol anions, which are generally believed to be less strongly solvated than oxygen anions.[39] Finally, it has been suggested that the high density of negative charge in phosphate and phosphonate dianions is responsible for a relatively large energy requirement for desolvation of these nucleophiles in their reactions with *p*-nitrophenyl acetate and other esters; these reactions are relatively slow and exhibit a value of $\beta_{nuc} = 0.3$.[40]

Thus, the available data are consistent with a desolvation requirement for reactions of basic oxygen anions that is responsible for a decreased slope and downward curvature for these anions in Brønsted-type correlations. This behavior is observed for a number of quite different reactions. It is of interest that virtually identical behavior is observed in water and in 60% dimethyl sulfoxide, v/v (which is 0.72 mol fraction of water). Anions of p$K < 10$ are generally well behaved and exhibit little or no deviation from linearity. The attack of oxygen anions on a 5-nitrosultone follows a linear Brønsted plot with $\beta_{nuc} = 0.83$ for anions of pK = 3–10, for example.[41] The large β values for anions of pK up to 10 suggest that the desolvation is important only for the more basic aliphatic oxygen anions; i.e., desolvation in the transition state of these reactions is less than in phenolate anions with two ortho *tert*-butyl groups, as might be expected.

A decrease in β_{nuc} because of desolvation in the forward direction corresponds to a more negative value of β_{lg} because of relatively weak solvation of the developing anion when alkoxide ions are expelled in the reverse direction. Such an imbalance in solvation has been proposed as a contributing factor toward the large negative values of β_{lg} for a number of reactions, including values of $\beta_{lg} = -1.05, -1.1$, and -1.2 for the elimination of alkoxide ions from carbinolamine ethers,[42] formaldehyde hemiacetals,[43] and benzimidates,[44] respectively. Again, a polar substituent on the leaving alcohol "sees" more negative charge than would be expected from the amount of C–O bond cleavage in the transition state, as estimated from small or positive values of ρ for substituents on the remaining group or from secondary α-deuterium isotope effects. The values of β_{lg} are -1.4 and -1.0 for the expulsion of alkoxide and phenolate ions, respectively, in the intramolecular reactions of a carboxylate group with the ester groups of diisopropylmaleate[45] and glutarate[46] monoesters, for which leaving group expulsion is rate determining. These values reflect the same behavior that is observed for rate-determining attack of oxygen anions in the other direction and correspond to values of $\beta_{nuc} = 0.3$ and 0.7, respectively, based on a value of $\beta_{eq} = 1.7$ for the equilibrium formation of alkyl and aryl acetates from the oxygen anions.[47]

Changes in Transition-State Structure. Curvature in structure–reactivity correlations, such as that shown in Figures 2 and 4, is commonly explained in terms of changes in transition-state structure with changing reactant structure according to the Bell–Marcus–Hammond–Polanyi–Thornton–Leffler hypothesis.[2] Hupe and Wu's conclusion that most of the curvature in Brønsted plots for reactions of oxygen anions depends on the basicity of the oxygen bases, rather than the *difference* in energies of the reactants and products that is predicted by various forms of this hypothesis, was based on the observation that the curvature is a function of the absolute pK of the oxygen base, not the difference in pK between the oxygen base and the carbon acid for carbon acids of pK 6–20.[6] Essentially the same curvature is observed for correlations of several reactions of oxygen anions with esters and other proton abstractions from carbon in ionization and elimination reactions,[5,15,18,39] including the reactions described here (Figure 2 and Figure 4, curve A).

This conclusion is supported by comparison of the curvature in Figure 2, which represents a decrease in β with increasing pK of the attacking bases, and the change in slope of the correlations in Figure 3 with different bases, which may indicate a change in transition-state structure with changing pK of the leaving group and base. It is convenient to describe these changes by the coefficients $p_x = \delta\beta/-\delta(pK_{BH})$, a direct interaction term, and $p_{xy} = \delta\beta/\delta(pK_{lg}) = \delta\beta_{lg}/\delta(pK_{BH})$, a term that describes the cross interaction between the nucleophile and the leaving group, respectively.[48,49] It is notoriously difficult to interpret direct interaction terms that give curvature in Brønsted plots, such as p_x, because the curvature may represent differences in transition-state structure, structures of the different classes of base over a wide range of pK, solvation, resonance, and other effects. Cross interaction terms, such as p_{xy}, are easier to interpret because they represent changes in the relative slopes of a series of Brønsted plots as the pK of the leaving groups is varied, for example, so that ground-state solvation effects of the oxygen base are the same for each line and will cancel. Even the cross interaction coefficients can be ambiguous if different chemical classes, such as mono- and diketones, are included in the correlations.[49]

The ratios k_{RO^-}/k_{HO^-} for trifluoroethoxide, methoxide, and hydroperoxide anions show no significant change as the pK of the leaving group of acetate esters is changed from 2 to 10 (Figure 3). This means that over a range of $>10^6$ in overall rate and 10^4 for a given nucleophile there is no significant change in β_{lg} with changing pK of the nucleophile or β_{nuc} with changing pK of the leaving group; i.e., the coefficient p_{xy} is ~ 0. With nucleophiles of p$K \leq 10$ this ratio increases with increasing reactivity and decreasing pK of the leaving group to give a slope of 0.2–0.3 against log k_{OH^-}. This change corresponds to a small positive coefficient $p_{xy} = \delta\beta_{lg}/\delta(pK_{BH}) = \delta\beta_{nuc}/\delta(pK_{lg})$. This result

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suggests that the leaving group "sees" a larger negative charge development from the attack of the anion in the transition state for weakly basic compared with strongly basic nucleophiles. The change depends on the basicity rather than the reactivity of the nucleophile, as shown by the change in slope for acetohydroxamate anion, and may be influenced by the class of nucleophile, because all of the compounds of p$K \leq 10$ are secondary or tertiary alcohols except for the acetohydroxamate anion. The change in slope corresponds to a change in the value of β_{lg} from –0.3 to –0.4 for the weakly basic nucleophiles.

This change probably represents a small change in transition-state structure, with a larger amount of bond formation for the less basic nucleophiles. There is evidence consistent with a similar change for the attack of thiol anions on acetaldehyde.[50] However, the change in β_{lg} from –0.3 to –0.4 for attack of oxygen anions on esters is much smaller than the change in β_{nuc} from 0.7 to 0.2–0.3 with increasing pK of the nucleophile (Figure 2).[51] This disparity in the changes of β_{nuc} and β_{lg} provides additional evidence that factors other than changes in transition-state structure are required to account for the curvature of the Brønsted plot in Figure 2.

This conclusion is consistent with the observation that there is little or no change in the secondary α or β deuterium isotope effects for rate-determining nucleophilic attack of oxygen anions on formate or acetate esters with changing basicity of the nucleophile or leaving group.[7,52] In particular, the secondary α-deuterium isotope effect of $k_D/k_H = 1.22$ for the attack of a series of phenolate and alkoxide ions on p-nitrophenyl formate is large and constant, suggesting that there is a considerable amount of bond formation and little change in the structure of the transition states for these nucleophiles.[53] Similarly, the p_{xy} coefficient for deprotonation of a series of (2-(p-nitrophenyl)ethyl)quinuclidinium ions is indistinguishable from zero, although the large curvature of the Brønsted plot corresponds to a value of $p_x = 0.07$.[18]

This work provides additional support for the conclusions (1) that observed β values for basic oxygen anions do not provide a reliable measure of the amount of bond formation or cleavage in the transition state[44] and (2) that curved structure–reactivity plots for reactions involving these anions do not necessarily represent changes in transition-state structure.[5,6,49]

Registry No. D_2O, 7789-20-0; $(CF_3)_2(OH)_2$, 677-71-4; $(CHF_2)_2C(OH)_2$, 918-45-6; $(CF_3)_2CHOH$, 920-66-1; $CH_3(CF_3)C(OH)_2$, 421-76-1; $(CF_3)_3COH$, 2378-02-1; p-nitrophenyl acetate, 830-03-5; 2,4-dinitrophenyl acetate, 4232-27-3; 1-acetoxy-4-methoxypyridinium ion, 46123-02-8; 1-acetoxy-4-methoxypyridinium perchlorate, 19921-03-0.

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Conversion of Allyl Alcohols to 1,3-Dienes by Sequential Sulfenate–Sulfoxide [2,3] Sigmatropic Rearrangement and Syn Elimination[1]

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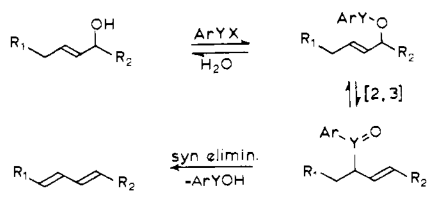
Abstract: A method for the 1,4 dehydration of allyl alcohols to give 1,3-dienes has been developed. The technique involves treatment of the allyl alcohol with 2,4-dinitrobenzenesulfenyl chloride and triethylamine. The sulfenate ester so formed undergoes [2,3] sigmatropic rearrangement to the isomeric allylic sulfoxide, followed by thermal syn elimination to give a diene. A number of different systems were studied to establish the conditions needed for successful reaction, tolerance to various substitution patterns, regiospecificity, the stereochemistry of the double bonds formed, and the side reactions that occur. Successful reactions were carried out with allyl alcohols having alkyl, phenyl, furyl, sulfide, dithiane, sulfone, halide, and acetoxy substituents. The 1,4 dehydration was shown to occur with overall cis stereochemistry in a cyclic system, consistent with the postulated mechanism. The dehydration can also be performed with selenenyl halides, but conditions are more severe, and the reaction is less general than with 2,4-dinitrobenzenesulfenyl chloride.

The dehydration of allyl alcohols to dienes has been a reaction of limited general utility because yields are often modest and both 1,2 and 1,4 eliminations are observed under typical dehydration conditions.[3] In addition to treatment with catalytic amounts of sulfonic acids, Burgess reagent,[3a] pyrolysis over alumina,[3b] acetate pyrolysis,[3c,d] and other standard olefin dehydration procedures, allyl alcohols have been dehydrated by treatment of the derived acetates with Pd(II) salts[3e] and by a multistep sequence involving epoxidation, base-catalyzed elimination, and reductive elimination.[4]

Scheme I



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