atom reorganization. This interpretation is consistent with the fact that $\Delta S^{\ddagger}$ for proton transfer from carbon to hydroxide ion is a much more negative value than the corresponding value for phenoxide.[51,52] The fact that no hydroxide ion anomaly (equivalent to curvature) has been found for proton transfers between electronegative atoms[1,2] might reflect the fact that these reactions occur through solvent molecules[53,54] whereas those involving carbon do not,[55] as suggested by Kresge.[1]

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The Effect of Solvation on β Values for Nucleophilic Reactions

D. J. Hupe,* Dorothy Wu, and Paul Shepperd

Contribution from the Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109.

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Abstract: The rates of enolization of **1** catalyzed by a series of oxyanions are compared with the reactions of esters in which the oxyanions function as nucleophiles involved in rate-determining attack. The similarity in curvature of these two plots is demonstrated. The cause of the curvature for nucleophilic reactions of PNPA and PNTPA is suggested to arise from a perturbation due to solvation similar to that proposed for **1**. The value of β_{nuc} for phenoxides is enhanced because of the solvation shell accompanying the oxyanion in the transition state. A countervailing force arises because of the unfavorable position in which solvent molecules are left which results in the lower value of β for high pK_a oxyanions. This proposed explanation is consistent with two other experimental facts. The curvature due to the solvation perturbation disappears when the reaction involves rate-determining breakdown of the tetrahedral intermediate, as expected if enough time exists for relaxation of solvent molecules to occur. The reactions of the same oxyanions with the pivalate esters PNPP and PNTPP show a lower β_{nuc} value for phenoxides and smaller negative deviations for alkoxides as expected if these more hydrophobic and sterically hindered substrates were to inhibit transition state solvation.

In the previous paper, evidence was presented to show that Brønsted plots for proton transfer from carbon were sharply curved.[1] This curvature was suggested to be caused by a solvation effect rather than by a "Hammond postulate" type of change in transition state structure. An essential feature of the solvation argument was the requirement that proton transfer occurred more rapidly than solvent reorganization. This increased the rates of reaction (and β for low pK_a bases) by stabilizing the partial negative charge on oxygen in the transition state. An offsetting force arose for high pK_a bases because of the energetically unfavorable position in which solvating molecules were left, resulting in the observed curvature.

The same type of argument might be made for reactions in

Table I. Second-Order Rate Constants for the Reaction of Oxyanions with *p*-Nitrothiophenyl Pivalate at 25 °C in Aqueous Solution, $\mu = 1.0$[a]

Nucleophile	pK_a[b]	Concn, M	pH	k, M^{-1} s^{-1}
$H_2O(OH^-)$	15.75			2.16
CH_3CH_2OH	16.0	0.180-0.920	10.9	<10
CH_3OH	15.7	0.230-1.160	11.0	5
$HOCH_2CH_2OH$	15.1	0.175-0.878	11.3	3.3
$CH_3OCH_2CH_2OH$	14.8	0.173-0.866	11.6	<5
		0.021-0.106	11.1	
$HC\equiv CCH_2OH$	13.55	0.249-1.250	11.0	3.5
F_3CCH_2OH	12.37	0.084-0.420	10.9	1.21
p-$CH_3C_6H_4OH$	10.07	0.00626-0.0358	10.0	0.108
p-$CH_3OC_6H_4OH$	10.06	0.00586-0.0293	9.9	0.213
C_6H_5OH	9.86	0.00908-0.0454	9.9	0.0605
p-$AcNHC_6H_4OH$	9.49	0.00289-0.0144	10.0	0.0670
m-$AcNHC_6H_4OH$	9.38	0.00326-0.0163	9.8	0.0505
p-ClC_6H_4OH	9.20	0.00346-0.0173	9.40	0.0673
3,4-$Cl_2C_6H_3OH$	8.51	0.00286-0.0143	8.51	0.0163
3,5-$Cl_2C_6H_3OH$	7.92	0.00273-0.0136	8.0	0.0140
3,4,5-$Cl_3C_6H_2OH$	7.69	0.00256-0.0128	8.8	0.0126
		0.00225-0.0113	8.6	

[a] Between 8 and 12 runs were carried out under each set of conditions. [b] Reference 1.

Table II. Second-Order Rate Constants for the Reaction of Oxyanions with *p*-Nitrophenyl Pivalate at 25 °C in Aqueous Solution, $\mu = 1.0$[a]

Nucleophile	pK_a[b]	Concn, M	pH	k, M^{-1} s^{-1}
$H_2O(OH^-)$	15.75			2.75
CH_3CH_2OH	16.0	0.185-0.923	10.8	<10
CH_3OH	15.7	0.232-1.16	11.0	20
$HOCH_2CH_2OH$	15.1	0.176-0.878	11.3	2.8
$CH_3OCH_2CH_2OH$	14.8	0.216-1.081	10.5	<3
		0.206-1.030	11.2	
$HC\equiv CCH_2OH$	13.55	0.263-1.315	10.6	2.83
F_3CCH_2OH	12.37	0.0951-0.476	10.0	1.63
p-$CH_3C_6H_4OH$	10.07	0.00718-0.0359	10.0	0.0522
p-$CH_3OC_6H_4OH$	10.06	0.00448-0.0224	10.0	0.135
		0.00468-0.0234	9.8	
C_6H_5OH	9.86	0.00944-0.0472	10.0	0.0284
p-$AcNHC_6H_4OH$	9.49	0.00295-0.0148	9.9	0.0320
m-$AcNHC_6H_4OH$	9.38	0.00274-0.0137	9.3	0.0198
p-ClC_6H_4OH	9.20	0.00249-0.0125	9.4	0.0296
3,4-$Cl_2C_6H_4OH$	8.51	0.00270-0.0136	8.0	0.00882
3,5-$Cl_2C_6H_3OH$	7.92	0.00273-0.0136	7.9	0.00563
3,4,5-$Cl_3C_6H_2OH$	7.69	0.00225-0.0112	8.7	0.00520

[a] Between 8 and 12 runs were done under each set of conditions. [b] Reference 1.

which attack occurs on carbon rather than on hydrogen, as in nucleophilic reactions with esters.[2] One might expect that for the reaction of oxyanions with esters a larger β_{nuc} would be found than is consistent with the amount of bond formation between the nucleophile and carbon in the transition state.[3] Curvature similar to that found for enolization reactions would also be predicted resulting in "anomalously" low rates of reaction for hydroxide and alkoxides. A complication arises in the study of ester reactions because of the possibility of having the rates measured reflect either rate-determining formation or rate-determining breakdown of the tetrahedral intermediate. A change in β_{nuc} therefore might reflect a change in rate-determining step. Fortunately, this problem has recently been examined, and it is now known[2] whether a given reaction involves rate-determining attack or breakdown for acyl transfer between oxygen or sulfur nucleophiles. With this potential source of confusion removed, it is possible to make a rational comparison of the rates of attack of oxyanions on hydrogen with the corresponding rates of attack on carbon.

In addition to this comparison it seemed useful to attempt to perturb the proposed solvation shell in the transition states for these reactions by using more hydrophobic, hindered substrates. There is presented below, therefore, a comparison of the rates of reaction of *p*-nitrophenoxy-2-butanone (**1**) and a series of oxyanions with the corresponding rates of reaction with *p*-nitrophenyl acetate (PNPA), *p*-nitrothiophenyl acetate (PNTPA), *p*-nitrophenyl pivalate (PNPP), and *p*-nitrothiophenyl pivalate (PNTPP).

Experimental Section

Reagents. The synthesis of *p*-nitrothiophenyl pivalate was accomplished by slowly adding pivaloyl chloride to a cooled solution of 3.35 g (0.22 mol) of *p*-nitrothiophenol in 40 mL of pyridine. The acid chloride was added with vigorous stirring until the dark red solution became yellow. This mixture was stirred and then added to 250 mL of cold water. The product was collected by filtration and recrystallized twice from 100 mL of boiling hexane to yield 4.03 g (0.17 mol, 77%) of *p*-nitrothiophenyl pivalate: mp 76–77 °C; NMR (s, 9 H) δ 1.29, (d, 2 H) δ 7.48, J = 8 Hz, (d, 2 H) δ 8.08, J = 8 Hz; IR 1698 cm^{-1}.

Phenyl pivalate, bp 90 °C (20 mm) (lit.[4] 112 °C, 25 mm), and *p*-nitrophenyl pivalate, mp 93–84 °C (lit.[4] 95–97 °C), were prepared by reaction of the phenol with a small excess of pivaloyl chloride in pyridine. Phenols were either recrystallized or sublimed several times and alcohols were doubly distilled. Water was doubly distilled from glass and boiled vigorously just before use.

Kinetics. Solutions of *p*-nitrophenyl acetate and *p*-nitrothiophenyl pivalate were prepared by stirring finely powdered samples of each in boiled distilled water at 40 °C under nitrogen. After filtration, the solutions were cooled to 25 °C and mixed with an equal volume of dilute NaOH and the A_∞ point was measured at 400 nm for *p*-nitrophenoxide and 412 nm for *p*-nitrothiophenoxide. Each typically gave an A_∞ of 0.3–0.4. The solutions of the phenoxides and alkoxides were prepared as described previously[1,2] and the reactions were initiated by mixing the substrate and nucleophile solutions at $t = 0$. The ionic strength was maintained at 1 M with KCl. The pH measurements on each solution were taken after the run. Typically between 8 and 12 runs were done for each nucleophile. The rates were measured by observing the absorbance due to *p*-nitrophenoxide or *p*-nitrothiophenoxide at 400 or 412 nm, respectively. The calculation of rate constants was accomplished as described previously.[1,2]

Identification of the product of reaction of *p*-nitrophenyl pivalate with phenoxide ion under conditions similar to those used in the kinetic studies was done. A solution of PNPP in aqueous solution was prepared by stirring 30 mg of the ester with 500 mL of doubly distilled water. After filtration, the resulting solution was shown to be 3×10^{-5} M in PNPP by hydrolyzing an aliquot with NaOH solution and measuring the released *p*-nitrophenol spectrophotometrically. This solution was mixed with an equal volume of a 0.1 M solution of phenol adjusted to pH 9.9 and allowed to stir for 3 h. An aliquot was observed spectrophotometrically to ensure that the reaction was complete. The reaction mixture was extracted with 3 × 100 mL of ether and the extracts were combined, washed with 3 × 25 mL of 5% NaOH and 1 × 25 mL of saturated NaCl, and then dried over Na_2SO_4. After filtration the solvent was removed to yield a small amount of oil which was dissolved in 1 mL of ether. An identical set of operations was performed on a 1.5×10^{-5} M solution of phenyl pivalate. These two samples were compared by VPC on a 10 ft, 3% SE-30 column using a column temperature of 105 °C. The two samples gave peaks of comparable areas at the retention time for phenyl pivalate.

Results

The rates of reaction of PNPP and PNTPP were found to follow the rate law $v = k_b[RO^-] + k_{OH}[OH^-]$, in a manner similar to that found for PNPA and PNTPA.[2] The rate constants measured for the phenoxides and alkoxides are listed in Tables I and II along with the conditions used for the experiments. The pivalate esters showed a smaller ratio of alkoxide rate constants to the hydroxide ion rate constant than did the corresponding acetate esters. As a result, it was generally more

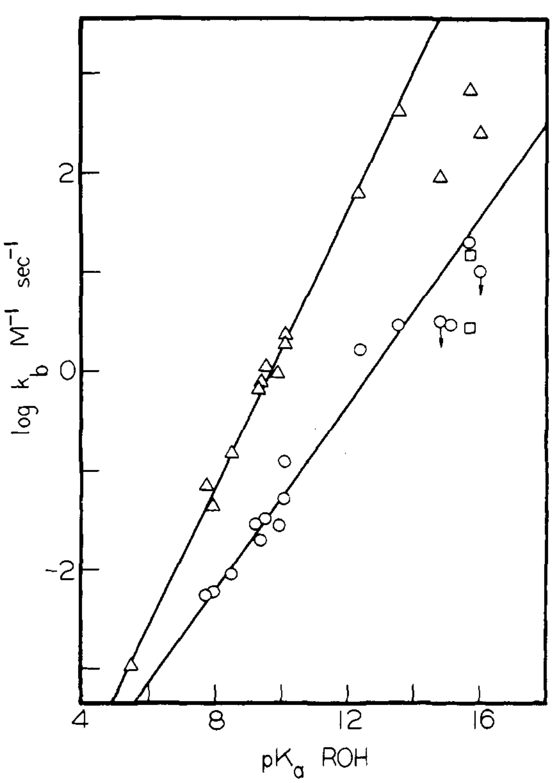

Figure 1. A plot of log k vs. pK_a for a series of oxyanions with PNPA (△)[2] and PNPP (○). The solid lines are the least-squares slopes for the phenoxide points. The slopes for PNPA and PNPP, respectively, are 0.71 (corr coeff 0.990) and 0.471 (corr coeff 0.922). The hydroxide ion points are indicated by squares.

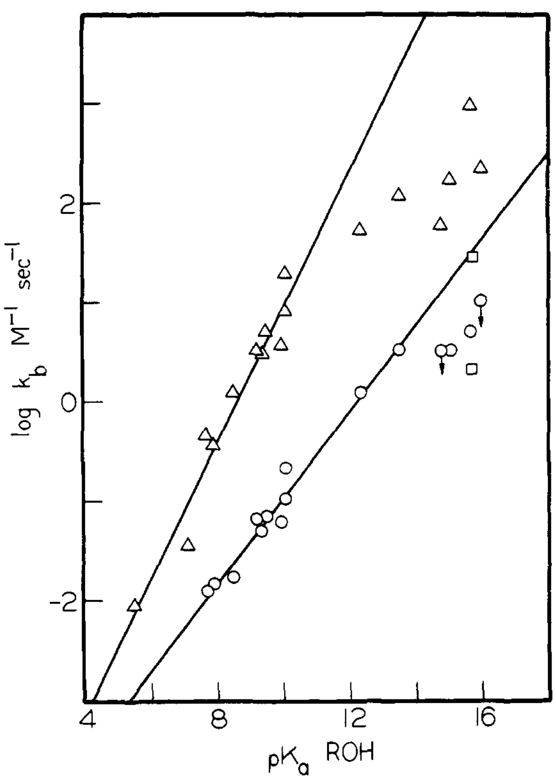

Figure 2. A plot of log k vs. pK_a for a series of oxyanions with PNTPA (△)[2] and PNTPP (○). The solid lines are the least-squares slopes for the phenoxide points. The slopes for PNTPA and PNTPP, respectively, are 0.68 (corr coeff 0.973) and 0.44 (corr coeff 0.935). The hydroxide ion points are indicated by squares.

difficult to measure the alkoxide rates than it was with the acetate esters because of the large background rate due to hydroxide ion. For some of the alkoxides listed in Tables I and II, therefore, only upper limits of the rate constants could be determined.

In order to ensure that the difference in β values for pivalate vs. acetate esters was not due to an entirely different mechanism operating (such as general base catalysis rather than a nucleophilic reaction), product analysis was done for one typical nucleophile, phenol, with PNPP. The analysis of the product of the reaction by VPC showed that the mechanism was nucleophilic and that phenyl pivalate was produced.

Discussion

The uncatalyzed transfer of an acyl group from one oxygen or sulfur nucleophile to another has been studied in detail previously,[2] and it has been shown that the reaction of phenoxides and alkoxides or hydroxide with PNPA or PNTPA involves rate-determining attack of the nucleophile followed by rapid breakdown of the intermediate. The data shown in Figures 1 and 2 for the reaction of a series of phenoxides and alkoxides with esters of p-nitrophenol (pK_a = 7.14) and p-nitrothiophenol (pK_a = 4.50) involve rate-determining attack and therefore any change in β_{nuc} observed for these substrates is not due to a change in rate-determining step.

The rate data for PNPA and PNTPA are not fit by a single line since the points for phenoxides with PNPA are fit by a least-squares line of slope 0.71 while the alkoxide ion and hydroxide ion points fall below this line. A similar slope of 0.68 is found for phenoxides with PNTPA with comparable deviations for the highly basic oxyanions. Possible causes for this behavior have been discussed previously,[2,5] and they include the differences in the types of nucleophiles used, a severe "Hammond postulate" type of change in transition state structure due to changing basicity, or a perturbation on the β value due to the solvation shell accompanying the attacking nucleophiles.

The data shown in Figures 1 and 2 for PNPA and PNTPA are comparable to β_{nuc} plots for phenoxides, alkoxides, and hydroxide ion with a variety of electrophiles, including acetylimidazolium ion,[2] 2,4-dinitrophenyl acetate,[5] acetoxy-4-methoxypyridinium perchlorate,[5] 4-methylacetylpyridinium ion,[7] m-nitrophenyl methanesulfinate,[8] and Ritchie's N^+ values, which are generalized constants for nucleophilic behavior.[9] The negative deviation of approximately three orders of magnitude from the lines for hydroxide ion reflects the notion that hydroxide ion is, in general, a poor nucleophile for its basicity.[10]

In Figure 3 are shown values of the deviations from the least-squares line through the low pK_a points for **1** with alkoxides and hydroxide. The corresponding deviations for the nucleophilic reactions with PNPA and PNTPA are plotted against them. Were the curvatures of the enolization and nucleophilic data identical, all of the points would fall on a line of slope 1.0 passing through zero. The line shown in Figure 3 has a slope of 1.1 indicating a substantial degree of similarity of the data sets.

The fact that the nucleophilic and enolization data are alike suggests that the curvature arises from a similar cause, and that β_{nuc} for phenoxides is enhanced because of solvation of the partial negative charge on oxygen in the transition state. As with the enolization reaction, the lower rates for hydroxide and alkoxide reflect the fact that stabilization of the negative charge is offset by the energy required to leave the solvation shell in an unfavorable position. A set of three-dimensional energy diagrams identical with those in the preceding paper (but with O–C bond formation rather than O–H bond formation) could be drawn for these reactions. This is consistent with the previously proposed concept of lagging solvation.[2]

This proposal is consistent with the picture of nucleophilic

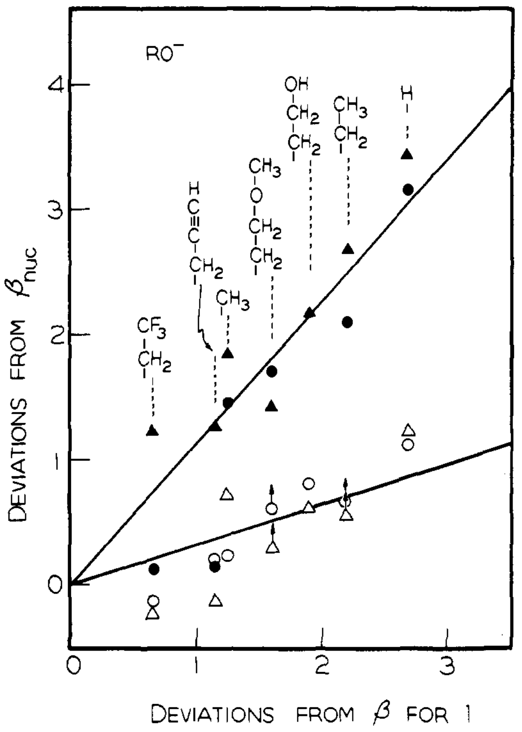

Figure 3. A plot designed to show the similarities in the curvature of Brønsted plots for enolization and nucleophilic reactions of phenoxides and alkoxides. The values on the abscissa are the deviations of alkoxide points from the least-squares line through the phenoxide points of substrate 1.[1] They are plotted vs. the corresponding values of deviations found with PNPA (●), PNTPA (▲), PNPP (○), and PNTPP (△). The arbitrary lines drawn through the origin have slopes of 1.1 and 0.33.

attack on esters constructed from isotope effect data. Kirsch has shown that, despite the low β_{nuc} value for alkoxides with esters (which would translate into little bond formation in the transition state), isotope effects indicate approximately 0.5 bond order between attacking nucleophile and the carbonyl carbon. If β_{nuc} reflected only the bond order in the transition state,[2,3,11] then this would predict a fit with a line of slope 0.5 for PNPA or PNTPA rather than the changing slopes shown in Figures 1 and 2.

It seems reasonable to propose, therefore, that a solvation perturbation dominates the structure–reactivity correlations for nucleophilic reactions in aqueous solution in a manner similar to that found for proton transfer reactions from carbon.[1] Like the proton transfer case, the effect results from the fact that the change in charge within the encounter complex occurs more rapidly than the reorganization of solvent molecules. Several mechanistic predictions are possible to test this model. A priori, it might be expected that if time were allowed for the reorganization of solvent, the perturbation would disappear and phenoxides, alkoxides, and hydroxide ion would fall on the same straight correlation line. Another prediction would be that substrates which were more hydrophobic and sterically hindered would tend to exhibit less of the perturbing influence of the solvation shell around the nucleophile. The rates should be slower because there is less stabilization of the charge on the attacking atom. The β_{nuc} value for phenoxides should be lower and the negative deviations for alkoxides and hydroxide should be smaller.

The first of these predictions is borne out by the data for the rates of reaction of phenoxides and alkoxides with acetic acid to form the corresponding esters which were calculated from the equilibrium constants for acyl transfer between alcohols and phenols and from the rates of reaction of hydroxide ion with various esters.[7] A dramatic difference exists between the β_{nuc} plots for this reaction which involves rate-determining breakdown of the tetrahedral intermediate and the typical ester reactions listed above for which attack is rate determining. The points for all oxyanions fall on the same correlation line with no negative deviations for alkoxides as is consistent with the proposed solvation perturbation since there is more than enough time for solvation relaxation to occur as the reaction passes through the tetrahedral intermediate.

Shown in Figures 1 and 2 are the data for the rates of reaction of oxyanions with PNPP and PNTPP. These substrates should be more hydrophobic and sterically hindered electrophiles than are the corresponding acetate esters. A large decrease in the β_{nuc} values for phenoxides occurs when the ester is changed from acetate to pivalate. For PNPA, β_{nuc} is 0.71 whereas for PNPP a value of 0.47 is found. A corresponding change in β_{nuc} of from 0.68 to 0.44 occurs when PNTPA is compared with PNTPP. As predicted above, there is a lower slope and slower rates because of a decrease in the solvation accompanying the oxyanion during the transition state. The negative deviations for alkoxides and hydroxide ion are considerably smaller than they are for the acetate esters as shown in Figure 3. The overall shapes of the plots for the pivalate esters are closer to that expected for reactions in which the solvation perturbation is not present.

We propose, therefore, that nucleophilic and proton transfer reactions are influenced by the effects of solvation in a similar manner and in a way that is consistent with behavior predicted on theoretical grounds.[12] The values of β or β_{nuc} for these processes cannot be accurately transformed into transition state bond orders unless this solvation effect is taken into account. Also implicit in discussion above is the fact that any completely general prediction of nucleophilic reactivity in aqueous solution must include a factor which depends on whether or not desolvation may occur in a step prior to the transition state.

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