for K_1 and K_2 were evaluated from a least-squares fit to the data to be 5.5 (7) $\times$ 10^5 M^{-1} and 1.4 (5) $\times$ 10^{-2} M, respectively. Both values are in reasonable agreement with those obtained from the kinetic measurements of the equilibration reaction of **1** ($K_1 = 3.2 \times 10^5$ M^{-1} and $k_2/k_{-2} = K_2 = 0.025$ M).

Summary and Conclusions

Two related series of complexes containing the (μ-oxo)bis(μ-XO_4)Fe^{III}_2 core with $XO_4 = O_3P(OC_6H_5)^{2-}$, HPO_4^{2-}, $HAsO_4^{2-}$, and CrO_4^{2-} (type A) or, alternatively, the tris(μ-XO_4)Fe_2 unit with $XO_4 = O_3P(OC_6H_5)^{2-}$, HPO_4^{2-}, and $HAsO_4^{2-}$ (type B) have been synthesized. Their electronic spectra and magnetic properties have been studied. The following conclusions are derived:

(1) Complexes of type A display rich electronic spectra in the near-UV, visible and near-IR. In contrast, type B complexes are featureless in the visible and near-IR, exhibiting only one charge-transfer absorption in the near-UV.

(2) In complexes of type A, strong intramolecular antiferromagnetic coupling of the high-spin ferric ions is observed via a superexchange mechanism mediated by the single atom bridge (J, -80 to -120 cm^{-1}). In type B complexes, very weak antiferromagnetic coupling is observed (J, -7.5 to -2,0 cm^{-1}).

(3) The (μ-oxo)bis(μ-phosphato)diiron complexes **2** and **3** model the known structural and to some degree the physical properties of the oxidized uteroferrin phosphate complex. The Fe$\cdots$Fe and Fe$\cdots$P distances in both the model compounds and the biomolecules are very similar, which suggests the presence of an Fe–O–Fe unit and bidentate bridging phosphate in the biomolecule.

(4) The very strong exchange coupling observed for the purple, oxidized phosphate containing enzyme from bovine spleen with a lower limit of $-2J \geq 300$ cm^{-1} is proposed to be indicative of very short Fe–O_{oxo} bonds ($\approx$1.78 Å).[50] In the μ-phosphato model complexes, this bond is longer (1.82 Å), and consequently, the exchange coupling is weaker.

Finally, the first kinetic and equilibrium study of a complex containing the (μ-oxo)bis(μ-carboxylato)diiron core has been carried out. This unit has been identified in the oxidized form of hemerythrin, and possibly ribonucleotide reductase[3] (**1**) hydrolyses in alkaline aqueous solutions with dissociation of one acetato group. The resulting (μ-oxo)(μ-acetato)diiron(III) species is reactive toward nucleophiles such as $O_3P(OC_6H_5)^{2-}$, HPO_4^{2-}, and $HAsO_4^{2-}$. The formation of **2** from **1** was found to be independent of the $O_3P(OC_6H_5)^{2-}$ concentration; the formation of the (μ-oxo)(μ-acetato)diiron species is rate determining.

These observations raise the possibility that binding of phosphate to the enzyme uteroferrin occurs with concomitant displacement of μ-carboxylato bridges.

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Supplementary Material Available: Tables S1–S12 and Tables II–VII listing bond distances, bond angles, anisotropic displacement parameters, and calculated positional parameters for hydrogen atoms of complexes **2**, **5**, and **8**, Table S13 listing proposed hydrogen positions of hydrogen bonds in **8**, and Table S14 listing kinetic data (18 pages). Ordering information is given on any current masthead page.

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[50] The general problem of the distance dependence of the exchange coupling constant J for Fe^{III}–O–Fe^{III} complexes has been discussed: Gorun, S. M.; Lippard, S. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 416.

Nonequilibrium Transition-State Solvation and Marcus Work Terms. Comparison of Their Contributions to Solvent Effects on Intrinsic Rate Constants for Proton Transfers

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Abstract: Within the context of his principle of nonperfect synchronization, Bernasconi explained H_2O/Me_2SO solvent effects on intrinsic rate constants (k_0s) for proton transfer ($AH + B^- \rightarrow A^- + HB$) as the result of nonequilibrium transition-state (TS) solvation that arises from asynchrony between transfer of charge and reorganization of the solvation of that charge during the transfer step ($AH,B^- \rightarrow A^-,HB$); such nonequilibrium solvation would contribute a solvent-dependent addition to the intrinsic barrier ($\Delta G_0^{\ddagger}$). When AH is uncharged and B^- is an anion (or an uncharged solute with a tightly solvated basic electron pair), an alternative origin exists: as defined by Bernasconi, k_0 is a function of the Marcus work term (w^r) as well as of $\Delta G_0^{\ddagger}$, so that an observed solvent effect on k_0 could result from the partial desolvation of B^- that must accompany formation of the precursor complex ($AH + B^- \rightleftharpoons AH,B^-$); this desolvation would contribute a solvent-dependent addition to w^r. Analogous ambiguities concerning the origins of observable differences between k_0s also exist for other charge-transfer reactions, including electron transfers. The separate contributions to solvent effects on k_0 that arise from the solvent dependencies of w^r and $\Delta G_0^{\ddagger}$ are here estimated by modeling the charged solutes (B^-, precursor complex, and TS) as charges inside spherical or ellipsoidal cavities in dielectric continua. Free energies of TS models containing nonequilibrium polarization of those continua are calculated by Marcus' method. Calculations based on these models predict values of the H_2O/Me_2SO solvent effect on k_0s for proton transfers from uncharged AHs to RCO_2^- that are consistent with observed values and are composed of approximately equal contributions from those two sources. They also predict that, if significant charge/solvation disequilibrium really is present in the TS, then k_0 for a proton transfer of this charge type in Me_2SO should be larger than k_0 for the same transfer in MeCN; observation of this direction of this solvent effect could not be explained if all solutes were assumed to have equilibrated solvation, but would be consistent with the proposed nonequilibrium TS solvation.

Asynchrony between transfer of charge in a chemical reaction and reorganization of the solvation of that charge can result in nonequilibrium solvation in the transition state (TS). Since the free energy required for complete desolvation of an ion in a polar solvent is very large (ca. 50–100 kcal mol^{-1} for singly charged ions), the disequilibrium that could result from even a relatively small charge transfer/solvation asynchrony might be expected to make a significant addition to the barrier height ($\Delta G^{\ddagger}$) for the reaction.

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Contributions to $\Delta G^\ddagger$ from this source recently have been proposed for several organic reactions.[1] For example, evidence has been presented that barriers for methyl transfers to water result almost entirely from a fluctuation in the polarization of the solvent surrounding the unbonded H_2O,CH_3X pair,[3,4] and Jencks[5,6] and Hupe[6,7] have shown how observed large decreases in the reactivity of strongly basic anions could result from desolvation of those anions having proceeded further than bond formation in the TS.

Bernasconi[8] included such charge transfer/solvation asynchronies as one aspect of his general principle of nonperfect synchronization (PNS) and has proposed that *intrinsic* barriers ($\Delta G_0^\ddagger$s) for charge-transfer reactions commonly contain large contributions from "late" solvation of developing charges (or, equivalently from the viewpoint of the reverse reaction, "early" desolvation of vanishing charges). He measured[9,10] the corresponding *intrinsic* rate constants (k_0s) for proton transfers from several carbon acids, using H_2O/Me_2SO mixtures as solvents, and has argued[10] that the change in a k_0 as the Me_2SO content of the solvent increases arises from two sources: these late solvation/early desolvation asynchronies and a dynamic solvent effect.

By seeking to interpret solvent effects on a k_0 for proton transfer from a single carbon acid to a series of related bases (instead of on the observed rate constant for proton transfer from that acid to one given base), Bernasconi simplified the problem. According to Marcus' rate–equilibrium relationship,[11,12] much of the solvent effect on a rate constant for a single reaction merely reflects the solvent effect on the equilibrium constant for that reaction; the solvent effect on k_0 for a reaction series should be free from that contribution. Thus, Bernasconi's solvent effects on k_0 values can be compared directly to theoretical estimates of the effects to be expected from late solvation/early desolvation asynchronies. One problem with such a comparison, however, is that an observed solvent effect on a k_0 for a series of bimolecular proton transfers ($AH + B^- \rightarrow A^- + HB$) could result from a change in the equilibrium constant for formation of the AH,B^- precursor complex as well as from a change in the rate constant for the transfer step ($AH,B^- \rightarrow A^-,HB$). Bernasconi assumed that his observed solvent effects on k_0s arise from solvent effects on rates of the transfer steps. Although desolvation contributions to the equilibrium constant for formation of AH,B^- are one form of early desolvation and thus are formally consistent with Bernasconi's PNS, they are conceptually distinct from early desolvation in the transfer step and, as is shown below, should be experimentally distinguishable from charge-transfer/solvation asynchronies in the transfer step.

The purpose of this paper is threefold: (1) to estimate the solvent effect on k_0 that could result from late solvation/early desolvation asynchrony in the transfer step, and to see if it is likely to have the magnitude required by Bernasconi's interpretation of his observed solvent effects, (2) to estimate the solvent effect on k_0 that could result from a change in the equilibrium constant for formation of the precursor complex and to see if this is a possible alternative origin for the changes in k_0 which Bernasconi ascribed to changes in the rate of the transfer step, and (3) to provide a basis for the design of experiments that could distinguish between these alternative origins.

General Theoretical Considerations

Within the context provided by Marcus' rate–equilibrium relationship and its application to proton-transfer rates,[11,12] the mechanism of a bimolecular proton transfer from a carbon acid, HA, to an oxygen or nitrogen base, B^-, is written in three steps (eq 1); formation of the AH,B^- precursor complex, the transfer step, and dissociation of the A^-,BH successor complex, Bernasconi's interpretation of his observations implicitly assumed that the transfer step is rate-determining, as would be expected for these slow proton transfers from carbon acids. Thus, AH,B^- and A^-,HB are in equilibrium with $AH + B^-$ and A^- and HB, respectively. In eq 1, the "work terms" (w^r and w^p) are the conventional designations for the standard free energy changes for formation of AH,B^- and A^-,HB respectively from those separated components, and $\Delta G_{Tr}^\ddagger$ denotes the standard free energy of activation for the transfer step in the forward direction.

$$AH + B^- \overset{w^r}{\rightleftharpoons} AH,B^- \xrightarrow{\Delta G_{Tr}^\ddagger} A^-,HB \overset{-w^p}{\rightleftharpoons} A^- + HB \qquad (1)$$

If the identity of HB is varied, then both $\Delta G_{Tr}^\ddagger$ and the corresponding standard free energy change for the transfer step (ΔG_{Tr}°) will vary, and the value assumed by $\Delta G_{Tr}^\ddagger$ when $\Delta G_{Tr}^\circ = 0$ is defined as the intrinsic barrier ($\Delta G_0^\ddagger$) for this series of proton transfers from AH. Bernasconi defined the intrinsic rate constant (k_0) for these proton transfers as the value assumed by the *observed* rate constant for the complete reaction ($AH + B^- \rightarrow A^- + HB$) when the *observed* value of the standard free energy change for this complete reaction (ΔG°_{obsd}) equals zero. An approximate value ($\Delta G_0{}^\ddagger{}_{obsd}$) for $\Delta G_0^\ddagger$ can be estimated from an observed k_0 via eq 2 by assuming that $w^r \approx 0$ and that the transmission coefficient equals unity.

$$\Delta G_0^\ddagger \approx \Delta G_0{}^\ddagger{}_{obsd} = RT \ln (k_BT/k_0h) \qquad (2)$$

Bernasconi's original interpretation of the solvent effect on k_0 equates the solvent effect on $\Delta G_0^\ddagger$ to the solvent effect on $\Delta G_0{}^\ddagger{}_{obsd}$ (eq 3).[13] Later, Bernasconi and Terrier[10] attempted to dissect from their observations the extent to which dynamic solvent effects[14,15] cause the transmission coefficient ratio to differ from unity and thus contribute to $\Delta G_0{}^\ddagger{}_{obsd}$.

$${}^{I}\delta^{II}\Delta G_0^\ddagger \approx {}^{I}\delta^{II}\Delta G_0{}^\ddagger{}_{obsd} = RT \ln (k_0{}^{I}/k_0{}^{II}) \qquad (3)$$

Two approximations (besides the uncertainty in the transmission coefficient ratio) are present in eq 3. One, that $w^{rI} = w^{pI}$ and $w^{rII} = w^{pII}$, is evident from the relationship (eq 4) between the values of ΔG° for the complete reaction (observed) and for the transfer step.

$$\Delta G^\circ_{obsd} = w^r + \Delta G_{Tr}^\circ - w^p \qquad (4)$$

If $w^r \neq w^p$ in either solvent, then $\Delta G_{Tr}^\circ \neq 0$ when $\Delta G^\circ_{obsd} = 0$ in that solvent. However this approximation is likely to be nearly exact when A^- and B^- have equal charges and comparable steric hindrance of solvation of those charges (as is true for those

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[1] Such contributions to $\Delta G^\ddagger$ have long been accepted for outer-sphere electron transfers.[2] Attention here is on similar contributions to $\Delta G^\ddagger$s for reactions that make and break bonds.

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(13) Solvents are denoted by Roman numerals; ${}^{I}\delta^{II}X = X^{II} - X^{I}$ = (value of X in solvent II) – (value of X in solvent I).

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of Bernasconi's reaction series in which $B^- = RCO_2^-$), and the following analysis will assume that no significant error arises from this approximation.

The second approximation in eq 3, that $w^{r^{II}} = w^{r^{I}}$, is evident from the relationship (eq 5) between the values of $\Delta G^{\ddagger}$ for the complete reaction (observed) and for the transfer step. Errors

$$\Delta G^{\ddagger}_{\mathrm{obsd}} = w^{r} + \Delta G_{\mathrm{Tr}}^{\ddagger} \qquad (5)$$

arising from this approximation could be significant, particularly when either HA or B^- is charged, and this expectation is reinforced by observations that appear to imply[12d,16] that $w^r > \Delta G_0^{\ddagger}$ for many proton transfer from carbon acids in aqueous solution. The following analysis will compare values predicted for $^{1}\delta^{11}w^{r}$ and for $^{1}\delta^{11}\Delta G_0^{\ddagger}$ when $B^- = RCO_2^-$ and AH is uncharged.

Before separate values for $^{1}\delta^{11}w^{r}$ and $^{1}\delta^{11}\Delta G_0^{\ddagger}$ can be predicted or discussed, the identity of the precursor complex (PC) (i.e., of the boundary between the w^r process and the transfer step) must be understood. The PC for a proton transfer is *not* simply the encounter complex.[11c,12b,17] The transfer step starts from the PC and includes bond making and breaking, transfer of charge between A and B, and the associated changes in solvation. These three components of the transfer step are not necessarily synchronous, but they behave similarly in that the contribution of each to the value of $\Delta G_{\mathrm{Tr}}^{\ddagger}$ must decrease smoothly in response to an increase in the basicity of B^-, reflecting the decrease in $\Delta G_{\mathrm{Tr}}^{\circ}$ and the increasing similarity of the TS to the PC. The w^r process, which creates the PC, thus includes the diffusion together, rotational orientation, and partial desolvation that are required in order for AH and B^- to become nearest neighbors with the correct orientations to allow the transfer step to commence. Contributions to w^r from these processes are unlike the contributions to $\Delta G_{\mathrm{Tr}}^{\ddagger}$ in that they may be insensitive to changes in $\Delta G_{\mathrm{Tr}}^{\circ}$ (e.g., Coulombic work when both AH and B^- are charged and rotational entropy loss) or may even increase as $\Delta G_{\mathrm{Tr}}^{\circ}$ decreases; e.g., as B^- becomes more basic, $\Delta G_{\mathrm{Tr}}^{\circ}$ and $\Delta G_{\mathrm{Tr}}^{\ddagger}$ decrease, but the desolvation work required to replace a polar solvent molecule adjacent to B^- with AH will increase.[18]

A second, and critical, difference between the behaviors of w^r and $\Delta G_{\mathrm{Tr}}^{\ddagger}$ is found in their responses to changes in solvent polarity. In this comparison, one simplification is possible; since we require an understanding only of the responses of w^r and of the intrinsic barrier, $\Delta G_0^{\ddagger}$ (for which $\Delta G_{\mathrm{Tr}}^{\circ} = 0$), we can ignore those effects on $\Delta G_{\mathrm{Tr}}^{\ddagger}$ that reflect changes in $\Delta G_{\mathrm{Tr}}^{\circ}$. In the w^r process, both initial and final states have equilibrated solvation; the positive contribution to w^r that results from partial desolvation of B^- when it forms AH,B^- merely reflects the difference between the free energies of solvation of large and small stable anions. In contrast, the TS in the transfer step may contain nonequilibrium solvation as a consequence of asynchronous changes in solvation and internal structure, and the direction of the response to changes in solvent polarity of a $\Delta G_0^{\ddagger}$ for formation of such a nonequilibrium state can be different for components of the solvation that have different relaxation times.

This difference between the effects of rapidly relaxing and slowly relaxing solvation components is well-known for outer-sphere electron transfers,[2] in which only the rapidly relaxing electronic component of the solvent polarization is always in equilibrium with the internal charge distribution. In a proton transfer, it usually is assumed that transfer of charge is synchronous with transfer of the proton, which occurs on a time scale that is vibrational (if transfer is by crossing over the barrier) or faster (if transfer is by tunneling through the barrier).[19] Thus, only the electronic (and possibly some of the vibrational) components of solvent polarization are necessarily equilibrated with the internal charge distribution in a proton-transfer TS; it is primarily the slowly relaxing orientational component of the solvent polarization (i.e., that part of the solvation of the charge resulting from rotational orientation of the permanent dipoles in the solvent molecules) that is out of equilibrium when charge transfer/solvation asynchrony is present in the transfer step.

Table I. Qualitative Electrostatic Contributions to Solvent Effects on $\Delta G_0^{\ddagger}{}_{\mathrm{obsd}}$

charge type[a]	solvent change	additive contribns from: w^r	$\Delta G_0^{\ddagger}{}_{\mathrm{eq}}$[b]	$\Delta G_0^{\ddagger}{}_{\mathrm{noneq}}$[c]
$(0) + (-) \rightarrow (\delta-,\delta-)$	$D_s\uparrow$	↑[d]	↑	↑
	$D_{op}\uparrow$			↓
$(0) + (0) \rightarrow (\delta-,\delta+)$	$D_s\uparrow$	(↑)[e]	↓	↑
	$D_{op}\uparrow$			↓
$(+) + (-) \rightarrow (\delta+,\delta-)$	$D_s\uparrow$	↑[f]	↑	↑
	$D_{op}\uparrow$			↓
$(-) + (-) \rightarrow (-2)$	$D_s\uparrow$	↓[f]	↓	↑
	$D_{op}\uparrow$			↓

[a] For AH + B → TS. [b] Intrinsic barrier when the TS has equilibrated solvation. [c] Correction to be added to $\Delta G_0^{\ddagger}{}_{\mathrm{eq}}$ because of nonequilibrium solvation in the TS. [d] From desolvation of the anion. [e] From desolvation of the basic lone pair on B. [f] From Coulombic interaction.

The effect of such a disequilibrium in the TS always will be to increase the chemical potential of the TS and thus to increase $\Delta G_0^{\ddagger}$. However, the interaction of the TS charge distribution with the rapidly relaxing (electronic and possibly vibrational) components of solvent polarization always is stabilizing and thus tends to decrease $\Delta G_0^{\ddagger}$. In consequence, a change in solvent polarity will have two effects on the contribution of nonequilibrium TS solvation to $\Delta G_0^{\ddagger}$; an increase in the slowly relaxing components of solvent polarizability will tend to *increase* that contribution, while an increase in the rapidly relaxing components of solvent polarization will tend to *decrease* it. The directions of these effects are independent of the charge type of the activation process. Since the directions of solvent effects on w^r and, in the absence of charge transfer/solvation asynchrony, on $\Delta G_0^{\ddagger}$ do depend on reactant charges, the net effect of nonequilibrium TS solvation can be either to reinforce or to oppose the solvent effect on k_0 that would be present in its absence.

To a first approximation, the ability of a solvent to stabilize a static charge by using all components of its polarizability is measured by its static dielectric constant (D_s), and its corresponding ability when only its electronic polarizability is available is measured by its optical frequency dielectric constant (D_{op}, equal to the square of the visible light refractive index). Thus, the above discussion of the directions of the changes in the equilibrium and nonequilibrium contributions to $\Delta G_0^{\ddagger}$ that should result from increases in the different components of solvent polarization can be recast in terms of D_s and D_{op}. If all components of solvent polarization were out of equilibrium, any rise in D_s would increase the nonequilibrium addition to $\Delta G_0^{\ddagger}$; however, the rapidly relaxing components are not out of equilibrium, so that any rise in D_{op} that accompanies the rise in D_s will oppose the increase in $\Delta G_0^{\ddagger}$. Table I qualitatively compares these nonequilibrium effects (column 5) to the more familiar effects of equilibrium solvation on w^r and $\Delta G_0^{\ddagger}$ (columns 3 and 4). It is possible to select solvent pairs whose differences in D_s and in D_{op} have either the same sign or opposite signs. Thus, Table I shows that, for some choices of the charges on HA and B^-, it is possible to select solvent pairs that have the qualitative potential to produce a solvent effect on k_0 in a direction that could *not* result from equilibrated TS solvation. An observation of such a solvent effect would provide strong evidence for the existence of charge transfer/solvation asynchrony in the transfer step. The calculations described in the remainder of this paper illustrate a method for estimating the relative magnitudes

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(19) It has been proposed[20] that charge transfer always occurs on an electronic time scale and thus is not synchronous with a formally accompanying transfer of a proton or heavier group. If this proposal is correct, its effect is to accentuate the dichotomy between the rapidly and slowly relaxing components of solvation.

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to be expected for the opposing contributions of equilibrium and nonequilibrium solvation to those solvent effects.

Electrostatic Models

Free energy changes that result from changes in charge–solvent interactions are here estimated by using a dielectric continuum model for the solvent. The solute species (AH, B^-, the PC, and the TS) are modeled as spherical or ellipsoidal cavities in that continuum. The parameters for which values must be chosen are the cavity sizes and shapes, the dielectric constants that characterize the rapidly and slowly relaxing components of the solvent polarization, and the dielectric constant of the cavity interiors. The following sections first assign values to these parameters that are consistent with quasi-experimental values for the free energies of solvation of the ionic reactants. Second, the expected value of the H_2O/Me_2SO solvent effect on w^r is estimated, assuming equilibrated solvation of B^- and the PC. Third, the expected solvent effect on $\Delta G_0^{\ddagger}$ is estimated as a function of the extent of charge/solvation disequilibrium in the TS. Fourth, these predicted solvent effects are compared to Bernasconi's observed solvent effects on k_0. Fifth, calculations of $Me_2SO/MeCN$ solvent effects are shown to imply that this solvent pair should allow an experimental demonstration of the presence of nonequilibrium TS solvation if such is present to a significant extent. Finally, approximate equations are derived, which allow rough but facile "back-of-an-envelope" estimations of solvent effects on w^r and $\Delta G_0^{\ddagger}$.

Evaluation of Parameters. Consider a reaction series in which the reactant bases, B^-, are carboxylate anions, RCO_2^-, and the carbon acid, HA, is uncharged. If B^- is modeled as a charge at the center of a spherical cavity in a dielectric continuum with equilibrated polarization, then the electrostatic contribution to the partial molal Gibbs free energy of the ion is given by eq 6,[21,22]

$$G_{\mathrm{el}} = G_{\mathrm{self}} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{z^2}{2b}\right)\left(\frac{1}{D_{\mathrm{s}}} - \frac{1}{D_{\mathrm{i}}}\right) \tag{6}$$

where z is the number of protonic charges ($z = -1$ for RCO_2^-), e is the protonic charge, b is the radius of the cavity, D_{s} is the static dielectric constant of the continuum, D_{i} is the dielectric constant of the interior of the cavity, and G_{self} is the self-energy[23] of the charge. If it is assumed that the value of b is independent of solvent, then the change in G_{el} that results from transfer of the ion from solvent I into solvent II (i.e., the electrostatic contribution to the "free energy of transfer") is given by eq 7.

$${}^{\mathrm{I}}\delta^{\mathrm{II}}G_{\mathrm{el}} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{z^2}{2b}\right)\left(\frac{1}{D_{\mathrm{s}}^{\mathrm{II}}} - \frac{1}{D_{\mathrm{s}}^{\mathrm{I}}}\right) \tag{7}$$

If solvent I is vacuum ($D_{\mathrm{s}} = 1$), then eq 7 becomes the Born equation[24] for the "free energy of solvation" of the ion. It is well-known that the Born equation gives reasonable values of free energies of solvation of anions in water ($D_{\mathrm{s}} = 78.5$ at 25 °C) if b is assigned a value that is a few tenths of an angstrom larger than the anion's crystal radius; tabulations of estimated values for free energies of solvation of anions[25] suggest a value near −75 kcal mol^{-1} for $CH_3CO_2^-$, which corresponds via the Born equation to $b = 2.19$ Å; this value is here adopted for the entire series ($B^- = RCO_2^-$), since changes in the size of R should not greatly affect the solvation of the carboxylate oxygens.

Table II. Solvent Properties (at 25 °C) Used in Calculations

solvent	D_{eff}	D_{op}[a]
H_2O	78.5[b]	1.777
Me_2SO	5.8[c]	2.184
MeCN	4.9[c]	1.806

[a] Square of refractive index at wavelength of sodium D lines. [b] Equal to D_{s}; see text. [c] Effective dielectric constant for solvation of anions; calculated from eq 7, with $b = 2.19$ Å and ${}^{\mathrm{I}}\delta^{\mathrm{II}}G_{\mathrm{el}} = +12.0$ and $+14.6$ kcal mol^{-1} for I = H_2O and II = Me_2SO and MeCN, respectively.[26]

Values[26] of free energies of transfer from H_2O into a dipolar aprotic solvent, such as Me_2SO, are much larger for small anions than for cations with similar sizes. This less effective solvation of anions relative to cations presumably results from the primary charge separation responsible for the dipole moment being at one end of the solvent molecule (e.g., from S to the lone pairs on O in Me_2SO). This results in the distance of closest approach of an ion to the positive end of a solvent dipole being much longer than that to the negative end (e.g., X^-,Me_2SO vs. $X^+,OSMe_2$); the analogous distance difference in water is much less. Thus, use of the observed bulk value of D_{s} for II in eq 7 would predict too small a value of ${}^{\mathrm{I}}\delta^{\mathrm{II}}G_{\mathrm{el}}$ for an anion when II is a dipolar aprotic solvent and I is H_2O. To account for this hindered solvation of anions, an effective value of D_{s} (D_{eff}) is here calculated for each dipolar aprotic solvent from eq 7 and the quasi-observed value[26] of the free energy of transfer of $CH_3CO_2^-$ from H_2O into that aprotic solvent; in these calculations, b equals the value derived above for H_2O (2.19 Å). The resulting values of D_{eff} are included in Table II.

Although this difference between anion solvation in hydroxylic solvents and in dipolar aprotic solvents often is discussed in terms of hydrogen bonding of the hydroxylic solvent to the anion, such hydrogen bonding is well approximated as a short-range classical ion–dipole interaction and thus is here assumed to be analogous to the weaker, longer range anion–dipole interactions responsible for anion solvation in dipolar aprotic solvents. The validity of this assumption is supported by the above-cited success of the Born equation in accounting for free energies of solvation in water,[34] so that the principal assumption remaining in the following applications of a dielectric continuum model for solvent is that the empirically evaluated D_{eff}s are sufficiently independent of cavity shape. Any solvent dependence of b is implicitly included in these D_{eff} values.

The correct value to use for the dielectric constant that characterizes the contributions to solvent polarity from rapidly relaxing components of solvent polarization is somewhat uncertain. For most polar solvents, the value of D_∞ for the principal (and slowest) component of dielectric relaxation (4.2, 5.7, and ~2 for H_2O,[27] Me_2SO,[28] and MeCN,[29] respectively) is appreciably larger than the optical frequency value, D_{op} (Table II). If charge transfer occurs on an electronic time scale, then D_{op} is the correct choice. If charge transfer is synchronous with classical proton transfer and is not retarded by coupling to solvation changes, then the equilibrated components are approximately those with relaxation times $\lesssim h/2k_{\mathrm{B}}T = 0.08$ ps near 25 °C. Although this is long compared to the period of the sodium D line (0.002 ps) for which D_{op} is commonly measured, it is short compared to the longitudinal relaxation times for the principal relaxation ($\tau_{\mathrm{L}} = 0.5$, 2,4, and ~0.2 ps for H_2O,[27] Me_2SO,[28] and MeCN[29]). Since the effective relaxation time for orientational solvent polarization in the neighborhood of a reaction event appears to fall between τ_{L} and the even longer Debye relaxation times ($\tau_{\mathrm{D}} = 8$, 20, and 3 ps for

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(21) (a) Kirkwood, J. G.; Westherimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506–512. (b) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351–361.

(22) For convenience in calculations: when distances are in angstroms and free energies are in kcal mol^{-1}, $e^2/4\pi\epsilon_0 = 332.1$ kcal Å mol^{-1}.

(23) The self-energy of a charge distribution inside a cavity is independent of properties of the medium outside the cavity. Thus, self-energies do not contribute to predicted values of solvent effects. To avoid the infinite self-energies of point charges, each point charge can be replaced by a uniformly charged sphere, which surrounds the site of the point charge and has an arbitrarily small radius, r_0. The self-energy of such a charge is then $z^2e^2/8\pi\epsilon_0 D_{\mathrm{i}} r_0$. So long as z and r_0 are unchanged in a transfer of charge from one cavity to another, the values of G_{self} will cancel in ΔG_{el} for the transfer.

(24) For a review, see: Criss, C. M.; Salomon, M. In *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum: London, 1973; pp 253–329.

(25) Reference 24, Appendix 2.11.2.

(26) Marcus, Y. *Pure Appl. Chem.* **1983**, *55*, 977–1021.

(27) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973; p 47.

(28) Behret, H.; Schmithals, F.; Barthel, J. *Z. Phys. Chem. Neue Folge* **1975**, *96*, 73–88.

(29) Eloranta, J. K.; Kadaba, P. K. *Trans. Faraday Soc.* **1970**, *66*, 817–823.

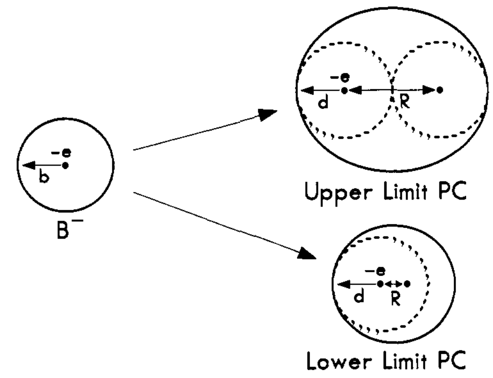

Figure 1. Models for the w^r process. In both PCs, $d = b$. For the upper limit, $R = 2d$; for the lower limit, PC volume = 2(B^- volume). Dashed spheres inside the PC ellipsoids depict the B^- sphere for size comparison.

H_2O,[27] Me_2SO,[28] and $MeCN$[29]),[30] it is likely that the correct value to use for the dielectric constant that corresponds to rapidly relaxing polarization is near or only slightly larger than D_{op}. Effective values of D_{op} for the aprotic solvents analogous to those obtained above for D_s from free energies of solvation are not available. However, D_{op} arises from electronic polarization, so that contributions to D_{op} from different parts of a solvent molecule differ by much less than do the contributions from bond and lone-pair dipoles to the orientational part of D_s that were considered earlier. Thus, no large error is expected to result from using values of D_{op} calculated from refractive indexes of the bulk solvents.

The calculations below use those bulk values of D_{op} together with the D_{eff} values previously discussed, No changes in qualitative conclusions would result either from small decreases in the values used for D_{op} (reflecting possible nonuniform electronic polarizabilities in solvent molecules) or from use of the larger D_∞ values. In fact, use of D_∞ in place of D_{op} would increase (by a factor near 5) the anomalous Me_2SO/$MeCN$ solvent effect on $\Delta G_0^‡$ that is predicted (vide infra) to result from charge/polarization disequilibrium in the transition state. Similarly, use of D_s in place of D_{eff} would increase that predicted anomalous effect on $\Delta G_0^‡$ by ca. 50%.

A Model for the w^r Process. When AH and B^- form the PC, the charge on B^- is partially desolvated as a result of one AH having replaced solvent in the inner solvent shell of B^-. The work against electrostatic forces (w^r_{el}) that accompanies this replacement makes a positive contribution to w^r. This process can be modeled as the transfer of charge from the center of the B^- spherical cavity (whose radius was evaluated above) to one focus of an ellipsoidal cavity which models the PC. This model process is shown in Figure 1.

Table III. Values of w^r_{el}[a]

solvent	lower lim on w^r_{el}[b]	upper lim on w^r_{el}[c]
H_2O	6.17	10.47
Me_2SO	4.28	7.55
$MeCN$	3.88	6.90

[a] In kcal mol^{-1}; calculated from eq 11, with D_{eff} from Table II, $d = b = 2.19$ Å, $D_i = 2$. [b] $R_{PC} = 1.23$ Å. [c] $R_{PC} = 4.38$ Å.

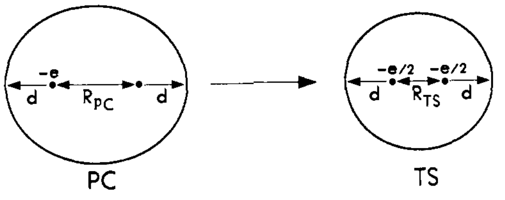

Figure 2. Model for the $\Delta G_0^‡$ process. Proportions of the ellipsoids correspond to best guess values of R_{PC} (4.0 Å), R_{TS} (2.4 Å), and d (2.19 Å).

For the special case of one charge, ze, located at one focus of a prolate ellipsoidal cavity in a dielectric continuum with equilibrated polarization, the equations derived by Westheimer and Kirkwood[31,32] can be written as eq 8–10, where R is the distance

$$G_{el} = G_{self} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{z^2}{R}\right)\left(\frac{1}{D_{eff}} - \frac{1}{D_i}\right)\sum_{n=0}^{\infty}(2n + 1)C_n(\lambda_0,D_{eff}) \tag{8}$$

$$C_n(\lambda_0,D_{eff}) = \frac{Q_n(\lambda_0)}{P_n(\lambda_0)}\left\{1 - \frac{D_i}{D_{eff}}\,\frac{\lambda_0 - [P_{n-1}(\lambda_0)/P_n(\lambda_0)]}{\lambda_0 - [Q_{n-1}(\lambda_0)/Q_n(\lambda_0)]}\right\} \tag{9}$$

$$\lambda_0 = (r_1 + r_2)/R \tag{10}$$

between the foci, r_1 and r_2 are the distances from the foci to any point on the surface of the cavity,[33] P_n and Q_n are Legendre functions of the first and second kinds, respectively, and the other symbols have their previously defined meanings,

If A^- and B^- have similar sizes and charge distributions (as do $CH_2{=}NO_2^-$ and $CH_3CO_2^-$, for which solvent effects on k_0 have been measured[9d,10]), then the spherical cavities that model them both have $b = 2.19$ Å, and the corresponding ellipsoidal AH,B^- cavity should have its foci at a depth, d, also equal to 2.19 Å from the ends of the cavity, as shown in Figure 1. This d, measured from focus to surface along the major axis, is necessarily the minimum focus-to-surface distance and is equal to $R(\lambda_0 - 1)/2$. Thus, specification of both d and R fully defines the ellipsoid and the value of λ_0. Upper and lower limits on the physically reasonable range of R_{PC} for the precursor complex are, respectively, the sum of the radii of the A^- and B^- spheres and the value of R for which the volume of the ellipsoid equals the sum of the volumes of the A^- and B^- spheres. When $d = b(A^-) = b(B^-) = 2.19$ Å, this range of R_{PC} becomes[34] $1.23 \leq R_{PC} \leq 4.38$ Å; the corresponding ranges of λ_0 and volume are $4.562 \geq \lambda_0 \geq 2$ and $88 \leq V \leq 264$ Å^3.

Upper and lower limits on w^r_{el} can be estimated from the difference between values of G_{el} for the AH,B^- ellipsoids with R_{PC} equal to its upper and lower limits (eq 8–10) and the value of G_{el} for the B^- sphere (eq 6); the values of G_{self} cancel,[23] giving eq 11.

$$w^r_{el} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{D_{eff}} - \frac{1}{D_i}\right)\left\{\frac{1}{R_{PC}}\left[\sum_{n=0}^{\infty}(2n + 1)C_n(\lambda_0)\right] - \frac{1}{2b}\right\} \tag{11}$$

The one parameter in eq 11 to which a value has not yet been assigned is D_i; here the usual assumption is made that $D_i = 2$. The qualitative conclusions that follow are not sensitive to changes in the value of D_i within the physically reasonable range, $1.8 < D_i < 2.3$. Values of these upper and lower limits are given in Table III.

The values of w^r_{el} in Table III suggest that solvent effects on w^r are likely to make significant contributions to observed solvent effects on k_0 values for many reaction series of this charge type. The predicted range within which values of ${}^{I}\delta^{II}w^r_{el}$ for proton transfer to RCO_2^- should fall when I = H_2O and II = Me_2SO is from 1.9 to 2.9 kcal mol^{-1}, which corresponds to contributions to the observed solvent effects on k_0 in the range, $25 < k_0^{II}/k_0^{I} < 134$, at 25 °C.

The range of R_{PC} values used to estimate this range of w^r_{el} includes the R values chosen below as most appropriate for the cavities that model the TS and PC in the $\Delta G_0^‡$ process. Thus, even if these estimates of ${}^{I}\delta^{II}w^r_{el}$ contain errors arising from the crudeness of the model, it is likely that the difference between

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(30) (a) Barbara, P. F.; Jarzeba, W. *Acc. Chem. Res.* **1988**, *21*, 195–199. (b) Spears, K. G.; Gray, T. H.; Huang, D. *J. Phys. Chem.* **1986**, *90*, 779–790. (c) Robinson, G. W.; Thistlethwait, P. J. *J. Phys. Chem.* **1986**, *90*, 4224–4233.

(31) Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513–517.

(32) Huron, M. J.; Claverie, P. *J. Phys. Chem.* **1974**, *78*, 1853–1861, particularly footnote 3a.

(33) I.e., the equation of the cavity surface in prolate ellipsoidal coordinates is $\lambda = \lambda_0$.

(34) The volume of a prolate ellipsoid equals $\pi R^3\lambda_0(\lambda_0^2 - 1)/6$.

the values of ${}^1\delta^{11}w^r{}_{el}$ and ${}^1\delta^{11}\Delta G_0{}^{\ddagger}{}_{el}$ estimated for a particular reaction series has a smaller error, and it is this qualitative comparison of ${}^1\delta^{11}w^r$ and ${}^1\delta^{11}\Delta G_0{}^{\ddagger}$ that is of most interest.

A Model for the $\Delta G_0{}^{\ddagger}$ Process. When $\Delta G_{Tr}{}^{\circ} = 0$, charge transfer and proton transfer are expected to be approximately half complete in the TS, so that the activation process corresponding to the intrinsic barrier, $\Delta G_0{}^{\ddagger}$, in a series of proton transfers from an uncharged AH to a set of RCO_2^-s can be written as in eq 12.

$$\mathrm{AH,B^-} \rightarrow [\mathrm{A}^{-1/2}\cdots\mathrm{H}\cdots\mathrm{B}^{-1/2}]^{\ddagger} \qquad (12)$$

Electrostatic contributions ($\Delta G_0{}^{\ddagger}{}_{el}$) to $\Delta G_0{}^{\ddagger}$ thus can be estimated by modeling AH,B⁻ as an ellipsoidal cavity with a charge, $-e$, at one focus and modeling the TS as an ellipsoidal cavity with charges, $z_{TS} = -{}^1/_2e$ at each of the two foci (Figure 2).

The value of G_{el} for the PC, AH,B⁻, can be estimated by using eq 8, since the PC has equilibrated solvation. However, estimation of G_{el} for the TS requires a method that takes into account the nonequilibrium solvation resulting from the proposed charge transfer/solvation asynchrony. If it is assumed that the extent of charge/solvation disequilibrium is the same for both charges in the TS, then the real solvent polarization outside the ellipsoidal TS cavity can be characterized by a parameter, m, where m denotes the *slowly* relaxing polarization that would be in equilibrium with a cavity that had a charge equal to me at each focus. The *rapidly* relaxing part of the polarization always is in equilibrium with the real charges. The extent of charge/solvation disequilibrium thus is measured by $|m - z_{TS}|$, where, for a reaction of this charge type, $z_{TS} = -{}^1/_2$. If the real TS in eq 12 has $m = -{}^1/_2$, it has equilibrated solvation, and both early desolvation of the charge on B and late solvation of the charge on A correspond to $0 \le -m < {}^1/_2$.

Marcus has shown[35] that the G_{el} of a nonequilibrium system of this kind is equal to the sum of the G_{el}s of three related hypothetical equilibrated systems, as in eq 13. System 1, corresponding to the first term on the right-hand side of eq 13, contains the same charge, $z_{TS}e$, at each focus as does the real (nonequilibrium) TS, but those charges have equilibrated solvation. System 1–0, corresponding to the second term, contains a charge equal to $(z_{TS} - m)e$ at each focus, and those charges have equilibrated solvation. The third term, $(G_{1-0}{}^{op})_{el}$, corresponds to a system containing the same charges as the 1–0 system, but the equilibrated solvation of those charges is provided by a hypothetical solvent for which D_s is equal to the value of D_{op} for the real solvent. Thus, for example, for this reaction of uncharged AH with RCO_2^-, system 1 has $-0.5e$ at each focus, and if late solvation/early desolvation asynchrony caused the solvation of these charges to be inadequate to the extent that they were solvated as if they were only $-0.4e$ each, then both 1–0 systems would have a charge equal to $-0.1e$ at each focus.

$$G_{el} = (G_1)_{el} - (G_{1-0})_{el} + (G_{1-0}{}^{op})_{el} \qquad (13)$$

Each G_{el} in eq 13 can be evaluated from the equations of Westheimer and Kirkwood,[31,32] which for these cases of equal charges, ze, at both foci can be written as in eq 14 and 15, where

$$G_{el} = 2G_{self} + G_{zz} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{2z^2}{R_{TS}}\right)\left(\frac{1}{D} - \frac{1}{D_i}\right)\sum_{n=0}^{\infty}(2n + 1)[1 + (-1)^n]C_n(\lambda_0,D) \qquad (14)$$

$$G_{zz} = \frac{e^2}{4\pi\epsilon_0}\frac{z^2}{R_{TS}D_i} \qquad (15)$$

G_{self} is the self-energy of each separate charge, G_{zz} arises from the interaction between the two charges, R_{TS} is the distance between the foci in the TS, D is either D_{op} or D_{eff} (depending on whether G_{el} does or does not have an op superscript), D_i always has the same value (2) since it results from electronic polarization, and the other symbols have been defined previously.

Table IV. Values of Solvent-Dependent Contributions to $\Delta G_0{}^{\ddagger}{}_{el}$[a]

		H₂O		Me₂SO		MeCN	
R_{PC}[b]	R_{TS}[b]	$\Delta G_0{}^{\ddagger}{}_{eq}$	F_s	$\Delta G_0{}^{\ddagger}{}_{eq}$	F_s	$\Delta G_0{}^{\ddagger}{}_{eq}$	F_s
4.0	2.4	1.58	226.2	0.61	117.4	0.48	143.6
2.4	2.4	3.21	226.2	1.88	117.4	1.66	143.6
4.38	2.4	1.34	226.2	0.41	117.4	0.30	143.6
1.23	1.23	1.41	264.8	1.21	137.4	0.72	168.2
2.4	1.23	−0.99	264.8	−0.96	137.4	−0.91	168.2

[a] For eq 16; calculated from eq 17 and 18, with $d = 2.19$ Å, $D_i = 2$, and D_{eff}, D_{op} from Table II. Units of $\Delta G_0{}^{\ddagger}{}_{eq}$ and F_s are kcal mol⁻¹. The top row gives "best guess" values; see text for other rows. [b] In Å.

The electrostatic contribution to $\Delta G_0{}^{\ddagger}$ is a function of m and is equal to the difference between the values of G_{el} for the TS and for the PC; from eq 13–15 and 8–10, it can be written as in eq 16–18. In eq 16, $\Delta G_0{}^{\ddagger}{}_{int}$ is the contribution to $\Delta G_0{}^{\ddagger}{}_{el}$ from the solvent-independent "internal" terms (including both G_{zz} from eq 14 and 15, and the difference between the self-energies[23] of the two $-{}^1/_2e$ charges in the TS and the one $-e$ charge in the PC); $\Delta G_0{}^{\ddagger}{}_{eq}$ is the contribution that charge–solvent interactions would make if the TS had equilibrated solvation ($m = -{}^1/_2$), and ${}^1/_2F_s(m - z_{TS})^2$ is the added contribution from charge/solvation disequilibrium in the TS.

$$\Delta G_0{}^{\ddagger}{}_{el} = \Delta G_0{}^{\ddagger}{}_{int} + \Delta G_0{}^{\ddagger}{}_{eq} + {}^1/_2F_s(m - z_{TS})^2 \qquad (16)$$

$$\Delta G_0{}^{\ddagger}{}_{eq} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{D_{eff}} - \frac{1}{D_i}\right)\left\{\frac{1}{2R_{TS}}\sum_{n=0}^{\infty}(2n + 1)[1 + (-1)^n]C_n(\lambda_0,D_{eff}) - \frac{1}{R_{PC}}\sum_{n=0}^{\infty}(2n + 1)C_n(\lambda_0,D_{eff})\right\} \qquad (17)$$

$$F_s = \frac{e^2}{4\pi\epsilon_0}\left(\frac{4}{R_{TS}}\right)\left\{\frac{1}{D_{op}}\sum_{n=0}^{\infty}(2n + 1)[1 + (-1)^n]C_n(\lambda_0,D_{op}) - \frac{1}{D_{eff}}\sum_{n=0}^{\infty}(2n + 1)[1 + (-1)^n]C_n(\lambda_0,D_{eff})\right\} \qquad (18)$$

This disequilibrium term is written as the product of a Hooke's law force constant, F_s, and the square of the displacement from charge/solvation equilibrium[4,14c] in order to emphasize the analogy between the electrostatic force that couples a change in charge to the change in its solvation and the valence forces that couple spatial displacements of the nuclei in the internal structure. The dependence of this charge/solvation disequilibrium term on the *square* of the displacement from equilibrium arises from the dependence of $(G_{1-0}{}^{op})_{el}$ and $(G_{1-0})_{el}$ in eq 13 on the squares of the charges in the corresponding hypothetical equilibrated systems (eq 14). Also note that, since only $G_{1-0}{}^{op}$ and G_{1-0} contribute to the third term in eq 16, the value of F_s is independent of the charges on the reactants and eq 18 is applicable to reactants of any charge.

The value assigned to R_{TS} in eq 14–18 should be smaller than that assigned to R_{PC}, since the increase in the A–H distance when the A–H bond is half broken is much smaller than the decrease in the H–B distance when the H–B bond is half formed. The length of a fractional XY bond is related to its order, n_{XY}, by Pauling's rule (eq 19).[36] The single-bond lengths to the transferring proton in these reactions have about the same value, $r_{CH}(1) \approx r_{OH}(1) \approx 1.0$ Å, as do the bond orders in the TS, $n_{CH} \approx n_{HO} \approx {}^1/_2$, and the corresponding nonbonded contact distances can be approximated by the equilibrium internuclear distance in the Ne,He pair (3.0 Å).[37] Thus, physically realistic values of the

$$r_{XY}(n_{XY}) = r_{XY}(1) - 0.30 \ln n_{XY} \qquad (19)$$

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(35) (a) Marcus, R. A. *J. Chem. Phys.* **1963**, *38*, 1858–1862. (b) Marcus, R. A. *J. Chem. Phys.* **1963**, *39*, 1734–1740. (c) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979–989.

(36) (a) Sims, L. B.; Lewis, D. E. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, The Netherlands, 1984; Vol. 6, pp 178–184. (b) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542–553.

(37) Johnston, H. S. *Gas Phase Reaction Rate Theory*; Ronald: New York, 1966; p 74.

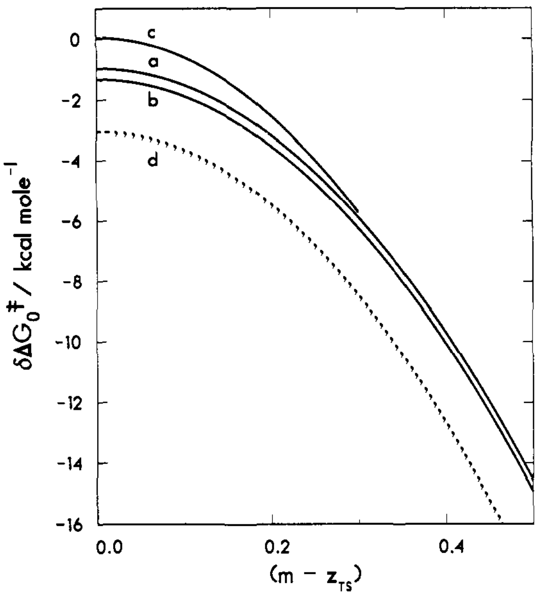

Figure 3. Solvent effects on the intrinsic barrier for transfer from I = H_2O into II = Me_2SO. Curves a–c are from eq 20, using eq 17 and 18 (from the ellipsoidal cavity models) for $\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$ and F_s; curve a corresponds to the best guess values of R_{PC} (4.0 Å) and R_{TS} (2.4 Å); curve b corresponds to a very compact, tightly coupled PC ($R_{\mathrm{PC}} = R_{\mathrm{TS}} = 2.4$ Å); curve c corresponds to both PC and TS being very compact and tightly coupled ($R_{\mathrm{PC}} = 2.4$ Å, $R_{\mathrm{TS}} = 1.23$ Å). Curve d (dashed) is from eq 20, using eq 24 and 25 (from the approximate two-sphere model) for $\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$ and F_s.

interfocus distances are expected to be near $R_{\mathrm{TS}} \approx 2{,}4$ Å and $R_{\mathrm{PC}} \approx 4{,}0$ Å.

Values of $\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$ and F_s calculated from eq 17 and 18 for various assumed values of R_{PC} and R_{TS} are given in Table IV. The first line gives the values that result from using the "best guess" choices of R_{PC} (4.0 Å) and R_{TS} (2.4 Å). The second and third lines illustrate the effect of varying R_{PC} from the upper limit (4.38 Å) used to estimate the upper limit on $w^{\mathrm{r}}{}_{\mathrm{el}}$ down to the lowest possible value ($R_{\mathrm{PC}} = R_{\mathrm{TS}}$, corresponding to the limit for reactions in which significant covalent interaction is included in the w^{r} step, as has been proposed to be possible[12b,17a] and also maximizing the charge/solvation coupling present in the precursor complex). The final two lines illustrate the effect of increasing that coupling in the TS (as might result for AH = RCH_2NO_2 from transfer of charge onto the NO_2 oxygens), The last entry also illustrates how such enhanced charge/solvation interaction in the TS could eliminate, or even slightly reverse, the solvent effect that would result from equilibrated solvation in the TS, The tabulated values of F_s show that the effect of charge/solvation disequilibrium could be very large. From eq 16, the maximum contribution to $\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$ from this disequilibrium occurs when $m = 0$ and equals $F_s/8$. For aqueous solutions, the estimates of F_s in Table IV imply $F_s/8 >$ 28 kcal mol^{-1}, which would be sufficient to contribute a factor of $>10^{-21}$ to k_0 near 25 °C.

Since $\Delta G_0{}^{\ddagger}{}_{\mathrm{int}}$ is independent of D_{eff} and D_{op}, only the last two terms in eq 16 contribute to solvent effects on $\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$. If m is assumed to be the same in both solvents, that difference is given by eq 20, Figure 3 shows this ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$ as a function of m for

$${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{el}} = {}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}} + \tfrac{1}{2}(F_s{}^{11} - F_s{}^{1})(m - z_{\mathrm{TS}})^2 \quad (20)$$

I = H_2O and II = Me_2SO; the three curves are based on parameters from lines 1, 3, and 5 of Table IV and thus illustrate the range of behavior predicted by these models when choices of R_{TS} and R_{PC} are physically reasonable for proton transfer to RCO_2^-; for any given m, this range is small.

Comparison to Observed Solvent Effects

The range of solvents spanned by Bernasconi's k_0 values[8-10] for proton transfers from uncharged carbon acids to RCO_2^- is from I = H_2O (or 10% Me_2SO in H_2O) to II = 90% Me_2SO. His values of ${}^{1}\delta^{11}\log k_0$ for this range vary from 1.89 for AH = 1,3-indandione (I = 10% Me_2SO) to 3.94 for AH = $PhCH_2NO_2$ (I = H_2O), and his estimates of approximately independent contributions to ${}^{1}\delta^{11}k_0$[10] imply a value near 4.6 for AH = CH_3NO_2 (I = H_2O).[38] For comparison to the theoretical estimates of ${}^{1}\delta^{11}w^{\mathrm{r}}{}_{\mathrm{el}}$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$, a rough extrapolation using these values together with those for I = 50% Me_2SO, II = 90% Me_2SO suggests that, for I = H_2O and II = 100% Me_2SO, $2.5 < {}^{1}\delta^{11}\log k_0 < 5.2$, which corresponds to $-3{,}4 > {}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{obsd}} > -7.0$ kcal mol^{-1} at 20 °C.

The range within which the contribution from ${}^{1}\delta^{11}w^{\mathrm{r}}{}_{\mathrm{el}}$ to this ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{obsd}}$ is expected to fall was predicted above (Table III) to be ca. −1.9 to −2.9 kcal mol^{-1}. Thus the contribution from ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$ needs to be in the range −0.5 to −4.1 kcal mol^{-1}. From Figure 3 and Table IV, this is ca. 3–27% of the predicted maximum value [$F_s(Me_2SO)/8 - F_s(H_2O)/8 + {}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}} \approx -15$ kcal mol^{-1}] and corresponds to charge/solvation disequilibrium in the TS in the range $0 < (m - z_{\mathrm{TS}}) < 0.26$. Note that this range of ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{el}}$ includes values that could result entirely from ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$; a solvent effect on the intrinsic barrier equal to ∼−1 kcal mol^{-1} is expected when the TS has completely equilibrated solvation. However, those values of ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{obsd}}$ that are significantly smaller than −4 kcal mol^{-1} (${}^{1}\delta^{11}w^{\mathrm{r}}{}_{\mathrm{el}} \approx -3$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}} \approx -1$) strongly suggest that the TS has nonequilibrium solvation. The carbon acids for which ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{obsd}}$ is this large are CH_3NO_2 and $PhCH_2NO_2$. Proton transfers from the other carbon acids may also pass through TSs with nonequilibrium solvation, but the evidence is less compelling.

Implicit in this conclusion, that Bernasconi's observed solvent effects on k_0 probably contain significant contributions from both ${}^{1}\delta^{11}w^{\mathrm{r}}$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}$ (including possibly some from ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$), is an alternative explanation of the origin of his δ_{SR} term. Bernasconi and Terrier[10] presented an analysis of observed ${}^{1}\delta^{11}\log k_0$ values which suggests that, in addition to charge transfer/solvation asynchronies, "... there must be another factor which either enhances k_0 in the presence of Me_2SO or retards the rate in the more hydroxylic solvents". They symbolized this additive term by δ_{SR} and deduced its approximate values for several reaction series. The ranges of those δ_{SR} values when I = H_2O (or 10% Me_2SO) and II = 90% Me_2SO are $0.8 < \delta_{\mathrm{SR}} < 2.8$ for AH + amine and $1.0 < \delta_{\mathrm{SR}} < 3.0$ for AH + RCO_2^-; rough extrapolation to II = 100% Me_2SO suggests $1.2 < \delta_{\mathrm{SR}} < 3.3$ for AH + RCO_2^-. They suggested a dynamic solvent effect as the most probable origin of δ_{SR}, but nothing in their analysis is inconsistent with $\delta_{\mathrm{SR}} \approx (-1/RT \ln 10)({}^{1}\delta^{11}w^{\mathrm{r}} + {}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}})$, and this range of δ_{SR} (∼ 1.2–3.3) is commensurate with the sum of the theoretical ranges of ${}^{1}\delta^{11}w^{\mathrm{r}}{}_{\mathrm{el}}$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}}$ derived above, $1.4 < ({}^{1}\delta^{11}w^{\mathrm{r}}{}_{\mathrm{el}} + {}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{\mathrm{eq}})/(-RT \ln 10) < 3.1$.

When comparing the observed solvent effects and Bernasconi's interpretations to the above theoretical predictions, it should be recognized that Bernasconi's empirical measures of the extent of charge/solvation disequilibrium in the TS, $(\alpha_{\mathrm{des}}{}^{\mathrm{B}^-} - \beta)$, $(\alpha_{\mathrm{sol}}{}^{\mathrm{NH}^+} - \beta)$ and $(\alpha_{\mathrm{sol}}{}^{\mathrm{C}^-} - \beta)$, are not directly comparable to the measure given by electrostatic theory, $(m - z_{\mathrm{TS}})$. There are several differences between these measures. (1) The empirical measures are formulated as linear free energy slopes with $\log {}^{1}\gamma^{11}$ as the independent variable. They are fractions of an *energy* range; if $(\alpha_{\mathrm{des}}{}^{\mathrm{B}^-} - \beta) = 0.1$, this implies that disequilibrium between the $\mathrm{B}^{-1/2}$ moiety and its solvation in the TS makes an addition to $\Delta G_0{}^{\ddagger}$ equal to 0.1 times ΔG^0 for transfer of β^- from I into II. In contrast, $(m - z_{\mathrm{TS}})$ measures the difference between the real charge on B (or on A, both = $-{}^{1}/{}_{2}e$) and the *charge*, *me*, that would be in equilibrium with the solvation that really is present in the TS; if $(m - z_{\mathrm{TS}}) = 0.1$, this implies that the real solvation is that which would be appropriate if the real charge were −0.4 instead of −0.5. (2) Since $(m - z_{\mathrm{TS}})$ is a measure of disparity between real and hypothetical charges and the free energy of solvation of a charge always is proportional to its square, the free energy costs of a charge/solvation disequilibrium is proportional to the *square* of $(m - z_{\mathrm{TS}})$. In contrast, that cost is proportional to the *first* power of $(\alpha_{\mathrm{des}}{}^{\mathrm{B}^-} - \beta)$. (3) The implicitly assumed maximum possible additions to $\Delta G_0{}^{\ddagger}$ from charge/solvation disequilibrium are dif-

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(38) From ref 10, $\delta_{\mathrm{B}^-} + \delta_{\mathrm{C}^-} + \delta_{\mathrm{SR}} = 0.59 + 1.01 + (2.81 + 0.22) = 4.63$.

ferent in the empirical formulation from those derived from electrostatic theory. There are three sources of this difference. (a) The maximum values of the proportionality constants corresponding to a charge of $-{}^{1}/{}_{2}e$ occur when there is no solvation, giving $(\sigma_{des}{}^{B^-} - \beta) = 0.5$ and $(m - z_{TS})^2 = 0.25$ in the two formulations. (b) The empirical formulation does not distinguish between rapidly relaxing and slowly relaxing solvation; it equates the solvent effect on $\Delta G_0{}^{\ddagger}$ to a fraction of the full value of $\Delta G°$ for transfer of B^- from I into II. The theoretical model counts only that part of $\Delta G°$ for this transfer that is contributed by slowly relaxing solvation. For a dielectric continuum model, the fraction of the full value of this $\Delta G°$ that results from slowly relaxing polarization is $(D_{op}{}^{-1} - D_{eff}{}^{-1})/(1 - D_{eff}{}^{-1})$.[4] From Table II, this fraction is 0.56 and 0.34 for H_2O and Me_2SO, respectively. Using quasi-experimental free energies of solvation (vide supra) for $CH_3CO_2{}^-$ in H_2O and Me_2SO equal to −75 and −63 kcal mol^{-1} gives the maximum possible cost of desolvating $B^{-1/2}$ as $(0.5)(-63 + 75) = 6$ kcal mol^{-1} from the empirical formulation and as $(0.25)[(-63)(0.34) - (-75)(0.56)] = 5$ kcal mol^{-1} from electrostatic theory; the near quality of these values is a consequence of the accidental cancellation of the effects of the difference between the proportionality constants and the difference between the fractions of the total solvations by these particular solvents that is contributed by the slowly relaxing components of their polarizations. (c) In this theoretical model, the charges on the B moiety in the TS and in the PC are at the foci of ellipsoids where they are more shielded from interaction with solvent than is the charge at the center of the spherical model for unassociated B^-. The empirical formulation assumes the free energy of interaction of a charge in the TS with its equilibrated solvation to be the same as it would be if that charge were on unassociated B^-. For a $-{}^{1}/{}_{2}e$ charge in H_2O, the dielectric continuum model predicts $G_{el} - G_{self} = -9.24$ and -7.09 kcai mol^{-1}, respectively, for the charge at the center of a sphere with $\beta = 2.19$ Å (eq 6) and the charge at one focus of an ellipsoid with $d = 2.19$ Å and $R = 2.4$ Å (eq 8).

Application to Design of Experiments

This section provides an example of how the equations derived above can be used to guide the selection of a solvent pair. Suppose that an experimentalist wishes to select a solvent pair that maximizes the chance of observing a $\ln(k_0{}^{1}/k_0{}^{11})$, the sign of which implies the presence of a significant contribution from charge/solvation disequilibrium in the TS. A qualitative guide to the signs of the three possible contributions has been given in Table I for reactions of several charge types. For a reaction of the charge type to which electrostatic models have been applied above, the solvent pair, $I/II = H_2O/Me_2SO$, cannot provide this kind of evidence since all three contributions (${}^{1}\delta^{11}w^{r}{}_{el}$ from eq 11, ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{eq}$ from eq 17, and ${}^{1}/{}_{2}(F_s{}^{11} - F_s{}^{1})(m - z_{TS})^2$ from eq 16 and 18) have the same sign. However, solvent pairs for which $D_{op}{}^{1} > D_{op}{}^{11}$ and $D_{eff}{}^{1}$ is only slightly greater than $D_{eff}{}^{11}$ can given small negative values of ${}^{1}\delta^{11}w^{r}{}_{el}$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{eq}$, and a larger positive value of the nonequilibrium term, ${}^{1}/{}_{2}(F_s{}^{11}-F_s{}^{1})(m - z_{TS})^2$, in eq 20.

The problem is to decide which solvent pair is most likely to maximize that positive contribution to ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{obsd}$ from nonequilibrium TS solvation and minimize the negative values of the two contributions that would be present if all species had equilibrated solvation. Equations 11, 17, and 18 allow estimation of the relative magnitudes of those three contributions for any solvent pair for which the values of D_{op} (from the optical refractive indexes) and D_{eff} (from observed free energies of transfer of the charged reactants from I to II) are available. One possible pair is $Me_2SO/MeCN$; the required values of D_{op} and D_{eff} are given in Table II. From Table III, the resulting expected possible range of ${}^{1}\delta^{11}w^{r}{}_{el}$ is ca. −0.4 to −0.6 kcal mol^{-1}, and the best guess (line 1 of Table IV) estimate of ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{el}$ is shown by curve a in Figure 4. Inspection of curves a–c in Figure 4 reveals that when $(m - z_{TS}) > 0.25$, ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{el} > |{}^{1}\delta^{11}w^{r}{}_{el}|$ and thus that the observed sign of $\ln(k_0{}^{1}/k_0{}^{11})$ for $I/II = Me_2SO/MeCN$ should implicate nonequilibrium TS solvation. This extent of charge/solvation disequilibrium is comparable to that estimated above from Bernasconi's observations for $I/II = H_2O/Me_2SO$. Use of a solvent pair with a comparable difference between $1/D_{op}{}^{1}$ and $1/D_{op}{}^{11}$ but a smaller difference between $I/D_{eff}{}^{1}$ and $1/D_{eff}{}^{11}$ should give the desired sign of $\ln(k_0{}^{1}/k_0{}^{11})$ for even smaller extents of disequilibrium.

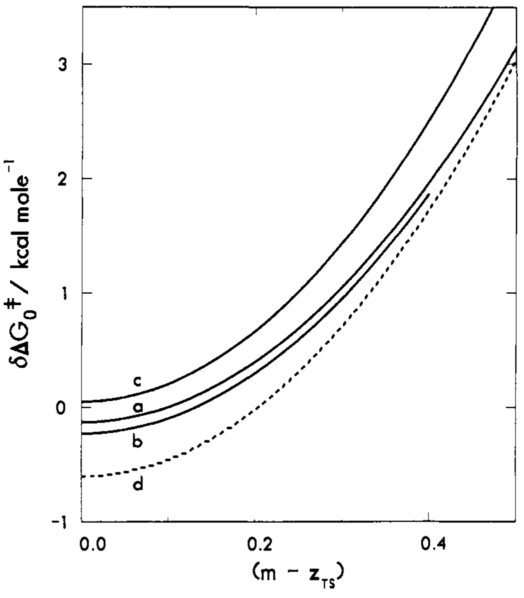

Figure 4. Solvent effects on the intrinsic barrier for transfer from I = Me_2SO into II = MeCN. Curves a–d correspond to the same cavity models as the identically labeled curves in Figure 3.

Back-of-an-Envelope Models

In the preceding section, ellipsoidal cavity models for the PC and TS in a proton transfer from an uncharged AH to $RCO_2{}^-$ were used to show that choosing I = Me_2SO and II = MeCN might allow the observation of a $\ln(k_0{}^{1}/k_0{}^{11})$, the sign of which could not result from a mechanism in which all species had equilibrated solvation. From the viewpoint of an experimentalist who wants to select an optimal solvent pair for use in the study of another charge-transfer reaction (not necessarily a proton transfer), it would be useful to have models for which the calculations did not require summations of sometimes slowly converging series of functions of Legendre functions.

Such models can be found; they replace the ellipsoidal PC and TS cavities with more approximate analogues. In this section, equations are derived for such approximate models that predict values of ${}^{1}\delta^{11}w^{r}{}_{el}$ and ${}^{1}\delta^{11}\Delta G_0{}^{\ddagger}{}_{el}$ for any choice of charges, z_{HA} and z_B, on the acid and base, and these equations are tested by comparing their predictions for the case of $z_{HA} = 0$ and $z_B = -1$ to the predictions obtained above from the physically more realistic ellipsoidal cavity models for the PC and TS.

A useful and simple approximation to the desolvation contribution to w^r for formation of a PC from an ionic reactant and an uncharged reactant is the upper limit obtained by modeling the surface of the PC cavity as an infinite planar boundary between continua characterized by D_i and D_{eff} and placing the charge, ze, at a depth, d into the D_i region. Such a model corresponds to a PC in which AH was an acidic site on a macromolecular solute, such as an enzyme. The value of $w^{r}{}_{el}$ for this PC model would be the limit as $r \to \infty$ of $w^{r}{}_{el}$ for transferring ze from the center of the β sphere to a depth, d, within a *spherical* cavity with radius, r. For this special case, Kirkwood's general expression[21b] for the G_{el} of a set of point charges within a spherical cavity reduces to eq 21, and the desired limit of eq 21 is eq 22.

$$G_{el} = G_{self} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{z^2}{2r}\right)\left(\frac{D_i - D_{eff}}{D_i}\right)\sum_{n=0}^{\infty}\frac{(n+1)[(r-d)/r]^{2n}}{(n+1)D_{eff} + nD_i} \tag{21}$$

$$\lim_{r\to\infty}(G_{el} - G_{self}) = \frac{e^2}{4\pi\sigma_0}\left(\frac{z^2}{4d}\right)\left[\frac{D_i - D_{eff}}{D_i(D_i + D_{eff})}\right] \tag{22}$$

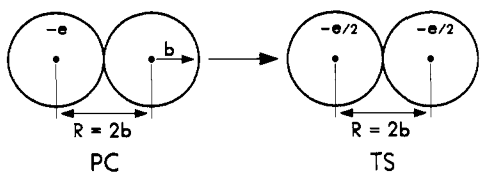

Figure 5. The two-sphere approximate model for the $\Delta G_0^\ddagger$ process. All four spheres have the same radius ($b = d$), and in contrast to Figures 1 and 2, the charges ($-e$ and $-e/2$) are uniformly distributed over the surfaces of their respective spheres rather than located at the centers.

For $z = -1$, $d = b = 2.19$ Å ($CH_3CO_2^-$), $D_i = 2$ and $D_{eff} = 78.5$ (H_2O), eq 22 gives $G_{el} - G_{self} \rightarrow -18.02$ kcal mol^{-1} for the infinitely large AH,B sphere and eq 6 gives $G_{el} - G_{self} = -36.95$ kcal mol^{-1} for the B sphere. Again the values of G_{self} are identical,[23] so that this estimate of the upper limit on w^r_{el} for reactions of $CH_3CO_2^-$ in aqueous solution is 18.9 kcal mol^{-1}. The analogous calculation for reactions in Me_2SO ($D_{eff} = 5.8$) gives $w^r_{el} = 15.6$ kcal mol^{-1}, so that ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el} = -3.3$ kcal mol^{-1} for I = H_2O and II = Me_2SO. Even though both values of w^r_{el} obtained with eq 22 are much larger than those from eq 11 (Table III), their difference provides an estimate of ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el}$ only slightly larger in magnitude than the difference (−2.9 kcal mol^{-1}) between the upper limits on w^r_{el} for a "small" AH estimated from eq 11. Differences between upper limits on ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el}$ estimated from eq 22 and eq 11 become larger, however, as D_{eff} for the less polar solvent becomes smaller (e,g., for I = H_2O and II = MeCN, eq 22 and 11 gives −4.5 and −3.6 kcal mol^{-1}, respectively).

A simple and useful approximation to $\Delta G_0^\ddagger{}_{el}$ can be obtained by modeling the PC and the TS as pairs of uniformly charged spheres (Figure 5). This is the model used by Marcus[2] in his estimation of the contribution from charge/solvent interaction to $\Delta G_0^\ddagger$ for electron transfers. To simplify the resulting equations further, the two spheres are here assumed to have equal radii, $b_{HA} = b_B = b$; modification for $b_{HA} \neq b_B$ is straightforward.

For the PC, G_{el} is then equal to the sum of three terms: two of the form, $\Delta G_{el} = (e^2/4\pi\epsilon_0)(z_i^2/2bD)$, for charging the two spheres plus $\Delta G_{el} \approx (e^2/4\pi\epsilon_0)(z_1 z_2/2RD)$ for bringing the spheres into contact (with $2b = R$),[39] where $z_1 = z_{HA}$, $z_2 = z_B$ and $D = D_{eff}$. For the TS, G_{el} is given by eq 13, where G_1, $G_{1\text{-}0}{}^{op}$, and $G_{1\text{-}0}$ are each given by a sum of three ΔG_{el}s analogous to those in G_{el} for the PC. In G_1, $D = D_{eff}$, $z_1 = z_{HA} - {}^1/_2$, and $z_2 = z_B + {}^1/_2$; in $G_{1\text{-}0}{}^{op}$ and $G_{1\text{-}0}$, $D = D_{op}$ and D_{eff}, respectively, $z_1 = (z_{HA} - {}^1/_2) - m_{HA}$, and $z_2 = (z_B + {}^1/_2) - m_B$. If it is assumed that the extents of charge/solvation disequilibrium are the same for both charges in the real TS, then, for $G_{1\text{-}0}{}^{op}$ and $G_{1\text{-}0}$, $z_1^2 = z_2^2 = (m - z_{TS})^2$ and $\Delta G_0^\ddagger{}_{el}$ is given by eq 23–25. As in eq 18, the charge/solvation coupling constant, F_s, is independent of the charges on the reactants.

$$\Delta G_0^\ddagger{}_{el} = \Delta G_0^\ddagger{}_{eq} + F_s(m - z_{TS})^2 \qquad (23)$$

$$\Delta G_0^\ddagger{}_{eq} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2RD_{eff}}\right)(z_B - z_{HA} + {}^1\!/_2) \qquad (24)$$

$$F_s = \frac{e^2}{4\pi\epsilon_0}\left(\frac{6}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_{eff}}\right) \qquad (25)$$

Since this two-sphere model assumes that both spheres are entirely surrounded by the dielectric medium, it overestimates the charge/solvent interaction both in the PC and in the TS. For example, if $R = 2.4$ Å in eq 18 and in eq 25, values of F_s for reactions of RCO_2^- ($d = b = 2.19$ Å) from eq 25 (two-sphere model) are about twice those from eq 18 (ellipsoidal cavity model). However, the convention that $R = 2b$ in the two-sphere model reduces this overestimation; for $R = 2b = 4.38$ Å, eq 25 gives F_s only 11% higher than F_s from the ellipsoidal cavity model with $d = 2.19$ Å and $R = 2.4$ Å. Also, the negative values of $\Delta G_0^\ddagger{}_{eq}$ given by eq 24 (two-sphere model) are significantly larger in magnitude than those from eq 17 (ellipsoidal cavity model). The consequence of this behavior is illustrated by the dashed curve, d, in Figure 3. This curve depicts the result of using eq 24 and 25 to estimate values of ${}^{\mathrm{I}}\delta^{\mathrm{II}}\Delta G_0^\ddagger{}_{eq}$, F_s^{II}, and F_s^{I} in eq 20 when I = H_2O, II = Me_2SO, and $R = 4.38$ Å. Comparison to curve a (from the best guess ellipsoidal cavity model, using eq 17 and 18 instead of 24 and 25) shows the large overestimation of $-\Delta G_0^\ddagger{}_{eq}$ and the slight overestimation of F_s by the two-sphere model.

If both reactants are charged, the dominant contribution to w^r_{el} is the work done against the Coulombic force between them, and eq 22 and 11 are not applicable. An estimate of the value of this Coulombic w^r_{el}, following Marcus,[2] can be obtained from the same point charge approximation to the two-sphere model than was used in the derivation of eq 24 and 25; this gives

$$w^r_{el} = (e^2/4\pi\epsilon_0)(z_{AH} z_B/2RD_{eff}) \qquad (26)$$

Application of eq 22, 6, and 23–25 to transfer of the RCO_2^- + uncharged AH reaction (using $R = 2b = 2d = 4.38$ Å) from I = Me_2SO to II = MeCN gives ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el} = -1.1$ kcal mol^{-1} and ${}^{\mathrm{I}}\delta^{\mathrm{II}}\Delta G_0^\ddagger{}_{el}$ as shown by curve d in Figure 4. From the preceding discussion, if these estimates had been obtained in a preliminary survey of solvent pairs, both this estimate of ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el}$ and the intercept at $(m - z_{TS}) = 0$ of this estimate of the ${}^{\mathrm{I}}\delta^{\mathrm{II}}\Delta G_0^\ddagger{}_{e6}$ curve would have been assumed to be significantly more negative than more accurate estimates, giving a net qualitative conclusion that the desired evidence for charge/solvation disequilibrium in the TS [i.e., that ${}^{\mathrm{I}}\delta^{\mathrm{II}}\Delta G_0^\ddagger{}_{el} > |{}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el}|$, so that $\ln (k_0^{\mathrm{I}}/k_0^{\mathrm{II}}) > 0$] should be observable for modest values of $(m - z_{TS})$. Comparison to the range of ${}^{\mathrm{I}}\delta^{\mathrm{II}} w^r_{el}$ and the best guess curve for ${}^{\mathrm{I}}\delta^{\mathrm{II}}\Delta G_0^\ddagger{}_{el}$ in Figure 4 confirms that conclusion.

Conclusions

Equations based on charge-containing ellipsoidal and spherical cavities in dielectric continua imply that observed H_2O/Me_2SO solvent effects on intrinsic rate constants (k_0s) for proton transfer to RCO_2^- from uncharged carbon acids (AHs) are the result of comparable contributions from two major sources; solvent effects on the Marcus "work terms" (w^r_s) (arising from desolvation of RCO_2^- during formation of the AH,RCO_2^- precursor complexes), and solvent effects on the intrinsic barriers ($\Delta G_0^\ddagger{}_s$) (arising from charge/solvation disequilibrium in the TS of the transfer step), The "additional factor"[10] (i.e., the contribution identified as being in addition to that from charge transfer/solvation asynchrony) that was previously tentatively ascribed to a dynamic solvent effect may be composed primarily of the solvent effect on w^r.

A different choice of solvent pair should, for a reaction of this charge type, allow observation of a solvent effect on a k_0, the direction of which could not arise either from a solvent effect on w^r or from a solvent effect on $\Delta G_0^\ddagger$ if the TS had equilibrated solvation, but could arise from a solvent effect on $\Delta G_0^\ddagger$ if the TS contained nonequilibrium solvation. The equations derived here should be useful in the selection of an optimal solvent pair for use in such experiments.

More approximate models lead to more easily applied expressions (rational functions containing no series) for the solvent effects on w^r and $\Delta G_0^\ddagger$. Comparison of numerical predictions from these more approximate models to those from the more physically realistic models suggests that the more easily applied expressions are adequate at least for the preliminary stages in the selection of a solvent pair and reactants during the design of such experiments.

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Registry No, H_2O, 7732-18-5; Me_2SO, 67-68-5; MeCN, 75-05-8.

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[39] This point charge approximation to ΔG_{el} for bringing two uniformly charged spheres up to a distance, R, between their centers becomes exact as $R/2b \rightarrow \infty$, and its error has been estimated by Marcus[40] to make a negligible contribution to $\Delta G_0^\ddagger{}_{el}$ even when $R/2b = 1$ if $D_{op}{}^{-1} \gg D_{eff}{}^{-1}$.

[40] Reference 2a, footnote 29.