dominate the polarizability density. The Sitter ρ_1 values from eq 13 are compared with the three-term fit without the self-interaction correction in Figure 9. The parameters of the polarizability density function are listed in Table I and the function is plotted in Figure 6. The total polarizability of 10.702 au was 0.7% below the Sitter value (10.774). The total field is plotted in Figure 7.

In an earlier calculation for the argon atom,³ the polarizability density was represented by a linearly decreasing function, as illustrated in Figure 10. The Poisson equation prediction of ρ_1 for this function is also shown in Figure 10. The large discrepancy illustrates the sensitivity of ρ_1 to the form of X(r). The linearly decreasing X(r) was also used to evaluate the pair polarizability tensor of argon,³ with reasonable results. We conclude that the pair polarizability is probably not as sensitive to the form of X(r)as the charge increment. (New calculations of the pair polarizability are now being carried out.)

Discussion

The preceding calculations illustrate the deduction of atomic polarizability density functions from quantum charge density increments using the Poisson equation form of the continuum dielectric theory. By successive approximations, reasonably close fits of ρ_b to ρ_1' were obtained. The accuracy of the results is limited by several factors. First, the quantum calculations⁹ are at the Hartree-Fock level and do not include all effects of electron

correlation. The uncertainty of the quantum results seems to be about 10%, and the deviation of our fit from the quantum results is in the 5-10% range. Second, the classical dielectric formalism does not recognize the nonlocal effects of electronic momenta,⁷ and the use of our results with nonuniform applied fields will lead to additional uncertainties.

It is interesting to note that the negative polarizability density region of neon could not be fitted by the continuum dielectric model. It also seems impossible to obtain an angular dependence other than $P_1(\cos \theta)$ from the dielectric theory if the polarizability density is taken as an isotropic function of r. Thus, the P_0 and $P_2(\cos \theta)$ contributions in the quantum results for argon were beyond the scope of the present calculations. The possible effects of anisotropic polarizability density⁷ remain to be explored in this connection.

Our results for the polarizability density functions (Figure 6) are more compressed than some of the earlier estimates, suggesting that the polarizability anisotropy of atom pairs will follow the point polarizability interaction model more closely near the potential minimum. At shorter distances typical of bonded atoms, the point polarizability interaction model will remain inadequate, however.

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Pressure Dependences of Rates of Nucleophilic Attack by Water in Aqueous Solution. Hydrolyses of Methyl p-Nitrobenzenesulfonate and Ethyl Trichloroacetate

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The pressure dependences of the rates of two formally uncatalyzed reactions of water in aqueous solution have been measured in the range 0-2 kbar at 25 °C. A plot of $\ln k$ vs. P for the hydrolysis of ethyl trichloroacetate (water-catalyzed water addition, followed by ethanol elimination) is smoothly and gently curved with ΔV^* = -33 ± 3 cm³ mol⁻¹ near P = 0. The corresponding plot for the hydrolysis of methyl p-nitrobenzenesulfonate (direct methyl transfer from $ArSO_3^-$ to H_2O) shows an abrupt change in slope near 0.1 kbar; the slope between 0 and 0.07 kbar corresponds to $\Delta V^* = -24 \pm 5$ cm³ mol⁻¹, while that between 0.14 and 2.07 kbar corresponds to $\Delta V^* = -6.3 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$. Comparison to the data of Baliga and Whalley for CH₃Br hydrolysis at higher temperatures suggests that the pressure dependences of rates of methyl transfer to water may commonly show such changes in slope and that increasing temperature shifts the slope change to higher pressure and decreases its sharpness.

Introduction

Measurement of the pressure dependence of a reaction rate allows evaluation of the volume of activation (ΔV^*) and its pressure dependence. As is evident from a recent review,¹ few precise measurements of this type exist for reactions of solvent water in dilute aqueous solutions. In fact, for reactions in water and particularly in water-organic cosolvent mixtures, the observed pressure dependences are sufficiently diverse and complex to have prompted an admonition to avoid the use of such solvents.²

However, evidence from kinetic isotope effects and transition-state acidities implies that methyl transfer to water in aqueous solution may not follow the traditional S_N2 mechanism, and suggests that a change in solvent configuration may be the principal contributor to the ac-tivation process for such reactions.³⁻⁷ Thus, since different structural configurations of solvent water are likely to have

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Nucleophilic Attack by Water in Aqueous Solution

different partial molal volumes, studies of ΔV^* and its pressure dependence for these reactions might help elucidate the nature of the activation process; perhaps some of the diverse and complex behavior alluded to above might prove to result from this suspected nontraditional mechanism.⁶

We are aware of only one precise previous study of ΔV^* for methyl transfer to water in the absence of cosolvents, that of Baliga and Whalley;⁸ they determined the pressure dependence of the rate of hydrolysis of methyl bromide at 60, 70, and 80 °C. In the hope that volume changes resulting from changes in solvent configuration would be more pronounced at lower temperatures, we chose to study the hydrolysis of methyl p-nitrobenzenesulfonate (MeONs)

$$H_{2}0 + CH_{3}0SO_{2} \longrightarrow NO_{2} \longrightarrow CH_{3}0H + H^{\dagger} + O_{2}N \longrightarrow SO_{3}^{-} (1)$$

which has a conveniently measurable rate at 25 °C. For comparison, we also determined the pressure dependence of the rate of a reaction of water which is known⁹⁻¹³ to take place by a very different mechanism, the water-catalyzed hydrolysis of ethyl trichloroacetate (EtTCA) at 25 °C (eq 2).

$$H_2O + C_2H_5OCOCCl_3 \rightarrow C_2H_5OH + H^+ + Cl_3CCO_2^-$$
(2)

Experimental Section

Materials. MeONs (Kodak) and p-nitrophenol (Fisher Reagent) were recrystallized to constant melting point from methanol and water, respectively. EtTCA was from a previously described¹² highly purified sample. Other compounds were of reagent grade and were used without further purification.

Rate Measurements. Both reactions were followed spectrophotometrically in aqueous solutions with ionic strength equal to 0.20 (NaClO₄ added). The absorbance changes were accurately first order for more than three half-times. The MeONs hydrolyses were monitored at 290 or 275 nm; the initial MeONs concentration was ca. 1.6 \times 10⁻⁴ M. The EtTCA hydrolyses were run in the presence of a dilute p-nitrophenol buffer, and the protonation of p-nitrophenolate ion by the trichloroacetic acid produced in the ester hydrolyses was monitored at 415 nm; initial concentrations were ca. 3×10^{-5} M EtTCA, 5×10^{-5} M p-nitrophenolate ion, 1.6×10^{-3} M p-nitrophenol, and 2 \times 10⁻⁵ M EDTA. The solvent in the EtTCA hydrolyses contained 0.02 M CH₃CN from the stock solution used to introduce the ester; no organic cosolvent was present in the MeONs hydrolyses.

The reactions were run in an Aminco medium-pressure optical absorption cell. Thermostating water was circulated through a 10-turn copper coil which encircled the cell and was cemented to the cell with copper-filled epoxy resin; cell and coil were encapsulated in polyurethane foam insulation. After application of pressure, the time required to reestablish a stable $(\pm 0.1 \text{ °C})$ internal cell temperature was ca. 4 min; optical absorption data were taken only after the temperature had been reestablished. The cell was mounted in the appropriately modified sample compartment of a Cary 16K spectrophotometer. Water was used

as the pumping and pressure transmission fluid; this water was separated from the reaction solution by a piston fitted with two O-rings which moved in a 3/16-in. i.d. tube. Pressures below 10 kpsi (0.69 kbar) were measured with a 0-10 kpsi Aminco Bourdon gauge; higher pressures were measured with a similar 0-50 kpsi gauge. Rate measurements were made at 0, 1, 2, 5, 10, 20, and 30 kpsi (0, 0.069, 0.138, 0.345, 0.690, 1.379, and 2.069 kbar, where 1 kbar = 0.1 GPa). Each reaction solution was prepared at 25 °C, immediately degassed by boiling under vacuum at 25 °C, and injected into the pressure cell through a syringe filter.

Results

The reproducibility of rate constants (k) in the pressure cell was within $\pm 1\%$ for the MeONs hydrolyses and was ca. $\pm 2\%$ for the EtTCA hydrolyses. Values of k measured in the pressure cell near 1 atm were checked by running identical reactions in conventional 10-mm cuvettes in the thermostated carousel of a Varian Cary 219 spectrophotometer, giving means for MeONs of 6.05×10^{-5} (pressure cell) and 5.90 \times 10⁻⁵ (Cary 219) s⁻¹, and for EtTCA of 2.31 \times 10⁻⁴ (pressure cell) and 2.29 \times 10⁻⁴ (Cary 219) s⁻¹. These values for EtTCA hydrolysis are consistent with previously reported¹² values for the water-catalyzed hydrolysis of EtTCA in aqueous NaClO₄; those previous values had been measured by an independent method. Numerical values of k for individual runs at all pressures are given in the supplementary material (see paragraph at end of text regarding supplementary material).

It is known⁹ that the EtTCA hydrolysis rate is very sensitive to base catalysis, and the *p*-nitrophenolate indicator system was selected to allow accurate measurement of the hydrolysis rate while avoidng unacceptable contributions to that rate from catalysis by hydroxide ion or indicator base. At the concentration used here, p-nitrophenolate ion does not measurably catalyze the hydrolysis but does provide an efficient sink for the hydrogen ions produced in the hydrolysis; the very large p-nitrophenol/p-nitrophenolate buffer ratio reduces the pH so that only 2% of the observed k at 1 atm arises from hydroxide catalysis. The known¹⁴ negative value of ΔV° for *p*-nitrophenol ionization and the expectation that ΔV^* will be small for the hydroxide-catalyzed rate imply that the contribution of hydroxide catalysis to the observed k will be even smaller at higher pressures. Since the total range of variation of this contribution is no greater than the 2% uncertainty in the observed value of k, no correction was applied to the observed k values.

Figure 1 compares the pressure dependences of the two hydrolysis rates. On such a plot of $\ln k$ vs. P, the slope is equal to $-\Delta V^*/RT$. The data for the EtTCA hydrolysis follow a smooth, gentle curve; the slope near zero pressure (estimated by linear least squares from the points at P =0, 0.069, and 0.138 kbar) gives $\Delta V^* = -33 \pm 3 \text{ cm}^3 \text{ mol}^{-1}$.

In contrast, the data for the MeONs hydrolysis show a change in slope near 0.1 kbar; that change is even more evident in Figure 2, which has an expanded vertical scale. Within experimental scatter, the five points at higher pressures ($P \ge 0.138$ kbar) fall on a straight line; fitting those points to a linear equation by least squares gives an intercept of -9.637 ± 0.004 and a slope of 0.254 ± 0.004 kbar⁻¹. That slope corresponds to $\Delta V^* = -6.3 \pm 0.1 \text{ cm}^3$ mol⁻¹. That intercept corresponds to a zero-pressure k of $(6.53 \pm 0.03) \times 10^{-5} \text{ s}^{-1}$, which is 8% larger than the value experimentally observed in the pressure cell near 1 atm. $6.05 \times 10^{-5} \,\mathrm{s}^{-1}$. Since the reproducibility of that observed

⁽⁸⁾ Baliga, B. T.; Whalley, E. J. Phys. Chem. 1969, 73, 654-66.

 ⁽⁹⁾ Jencks, W. P.; Carriuolo, J. J. Am. Chem. Soc. 1961, 83, 1743-50.
 (10) Kurz, J. L.; Wexler, D. N. J. Am. Chem. Soc. 1975, 97, 2255-8.

⁽¹⁴⁾ Hamann, S. D. Mod. Aspects Electrochem. 1974, 9, 47-158, Table 17.



Figure 1. Pressure dependences of k (s⁻¹) for methyl *p*-nitrobenzenesulfonate (MeONs) and ethyl trichloroacetate (EtTCA) hydrolyses at 25.0 °C. All points shown are averages of k values from between two and four runs; standard deviations are smaller than the diameters of the circles representing the MeONs points and comparable in size for the EtTCA points. The straight lines drawn through the MeONs data are intended to illustrate the slope change and do not imply any expected linearity. The curve through the EtTCA data is meant only to guide the eye; its form has no theoretical significance. Numerical values of rate constants are given in the supplementary material.

rate constant is better than $\pm 1\%$, we regard this difference as being significantly outside of likely experimental error. Since no such slope change was observed for the EtTCA hydrolysis, it is not an artifact of our apparatus. The observed points at 0 and 0.069 kbar correspond to an average value of ΔV^* within that range of -24 ± 5 cm³ mol⁻¹; the uncertainty was estimated by assuming an uncertainty of $\pm 1\%$ in the k values at both pressures.

Discussion

The plot of $\ln k$ for EtTCA hydrolysis vs. pressure (Figure 1) has the form which is most commonly reported for reactions in solution:¹ a smooth curve whose slope gradually decreases in magnitude as pressure increases. The mechanism of this reaction is well established⁹⁻¹³ to be general base catalysis by water of the addition of a water molecule to the ester carbonyl, followed by elimination of ethanol from the resulting tetrahedral intermediate. The large negative value of ΔV^* (-33 cm³ mol⁻¹ near P = 0) observed for this reaction is consistent with the transition-state structures proposed^{9,11,13} for that mechanism (containing more than one tightly bound H₂O moiety and having extensive charge separation) and with the known¹¹ large negative value of ΔS^* , -42.7 cal deg⁻¹ mol⁻¹ at 25 °C.

The abrupt change in the slope of the plot of $\ln k$ for MeONs hydrolysis vs. pressure (Figures 1 and 2) is *not* a commonly reported feature. However, many papers report values of rate constants only for pressures which are too widely spaced to reveal such a discontinuity in slope near 0.1 kbar even if one were present. For example, in the present work, if the rate constant measurements at 0.069 and 0.138 kbar had been omitted, the fit of the remaining five points to a smooth curve would have appeared acceptable; if the reproducibility of the rate constants had been no better than ± 2 or 3%, instead of $\pm 1\%$, then that fit would have appeared to be entirely satisfactory. Thus, it is not possible to be certain how rare such transitions in ΔV^* may be in this low pressure range.

We are aware of only one previous study of methyl transfer to water in aqueous solution which both has



Figure 2. Pressure dependences of *k* for methyl *p*-nitrobenzenesulfonate (MeONs) at 25 °C and for CH_3Br at 60, 70, and 80 °C. Data for CH_3Br at those three temperatures are displaced vertically by 0.5, 0.7, and 0.9 In unit, respectively, and are taken from ref 8. The straight lines are drawn to illustrate the slope changes and do not imply any expected linearity.

sufficient precision (better than 0.2% in k) and includes measurements at sufficiently closely spaced pressures to reveal such slope changes: that of Baliga and Whalley.⁸ Their data for methyl bromide hydrolysis are shown in Figure 2 along with ours for MeONs. Inspection of those plots reveals that the pattern of their data is consistent with our observations. Slope changes are evident, but, as temperature increases, those changes become less sharp and move to higher pressures. At 60 and 70 °C, the slope changes are becoming increasingly gradual and have moved from near 0.1 kbar (MeONs at 25 °C) out to the neighborhoods of 0.6 and 0.8 kbar, respectively; at 80 °C, the change appears to have moved beyond the 1.0-kbar maximum pressure for which rate constants were reported at that temperature.

The available experimental evidence suggests that the mechanism for the hydrolyses of methyl arenesulfonates (including MeONs) is the same as that for methyl halide hydrolyses (including CH₃Br) and is certainly quite different from that for the hydrolysis of EtTCA; the mechanism for MeONs and CH₃Br hydrolysis involves direct single-step transfer of the CH₃ from the leaving group (e.g., ONs⁻ or Br⁻) to a water molecule. For example, these methyl transfers to water are not general base catalyzed; the pK_a 's of the water moieties in these transition states are near 12 (e.g., at 25 °C and 1 atm when corrected to zero ionic strength,³ $pK_a(*) = 12.4$, 12.3, 11.9, and 11.7 for MeONs,¹⁵ MeOTs,⁴ CH₃Cl,³ and CH₃Br,¹⁶ respectively, while $pK_a(*) = 7.1$ for the mean of the two transition states in the EtTCA hydrolysis¹⁷), and the values of ΔS^* are

⁽¹⁵⁾ From $k_{H_{2}0} = 5.66 \times 10^{-5} \text{ s}^{-1}$; $k_{OH} = 3.89 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. (16) Harris, J. I. C. Ph.D Thesis, Washington University, St. Louis,

⁽¹⁶⁾ Harris, J. I. C. Ph.D Thesis, Washington University, St. Louis MO, 1970, p 68.

⁽¹⁷⁾ From $k_{\rm H_{20}} = 2.40 \times 10^{-4} \, {\rm s}^{-1,11} \, k_{\rm OH} = 2.57 \times 10^{\circ} \, {\rm M} \, {\rm s}^{-1,-1}$ (18) Euranto, E. K.; Moisio, A. L. Suom. Kemistil. B 1964, 37, 92–101.

much less negative than that $(-42.7 \text{ cal deg}^{-1} \text{ mol}^{-1})$ quoted above for EtTCA hydrolysis (e.g., at 25 °C and 1 atm, ΔS^* $= -7.9, -9.4, -4.7, \text{ and } -2.9 \text{ cal } \text{deg}^{-1} \text{ mol}^{-1} \text{ for MeONs},$ MeOTs, CH₃Cl, and CH₃Br, respectively¹⁹).

The identity of the rate-determining process in these methyl transfers to water remains in dispute. The transition state is most commonly described in terms of the traditional $S_N 2 \mod l^{21}$ as having a structure in which the CH_3 has fractional bonds both to H_2O and to the leaving group, and as having a decomposition coordinate which is composed of coupled changes in the lengths of those fractional bonds. However, alternative descriptions of these transition states have been proposed. Originally those proposals were based on interpretations of solvent isotope effects^{7,20} and of the values of $pK_a(\ddagger)$ cited above.^{3,4,22} More recent measurements^{5,6} of deuterium and oxygen kinetic isotope effects on methyl transfer to monomeric water and alcohols in aprotic solvents have strengthened the arguments for these nontraditional descriptions. These isotope effects and $pK_a(\ddagger)$ values imply that there is no significant covalent H_2O-CH_3 bonding in the transition state, that motion along the reaction coordinate through the transition state is a cooperative fluctuation of solvent structure rather than a coupled making and breaking of bonds to the methyl group, and that the polarization of the solvent in the transition state has shifted toward that appropriate for the internal charge distribution in product $(H_2O^+-CH_3,X^-)$ rather than remaining in equilibrium with the reactant-like (H₂O,- CH_3-X) internal charge distribution in the transition state.

The pressure dependences depicted in Figure 2 cannot yet be interpreted with certainty in terms of either of these possible mechanisms. However, the direction of the slope change (high slope to low slope) does allow two firm conclusions; this direction is opposite to that which would result either from a single mechanism whose transition state is more compressible than the initial state of reactants or from the existence of two mechanisms with different values of ΔV^* . If two competitive mechanistic paths were present, than the one with the more negative ΔV^* would be favored by higher pressures and the slope would increase instead of decreasing as pressure increases.²³

There are two possible simple explanations for the observed direction of the slope change: the existence of an intermediate, and a transition state which is less compressible than the initial state. We favor the latter alternative.

Consider first the effect of an intermediate, such as I in eq 3. If the k_{-1} and k_2 steps had different values of ΔV^* ,

$$\mathbf{R} \xleftarrow{k_1}{\underset{k_{-1}}{\longleftarrow}} \mathbf{I} \xrightarrow{k_2} \mathbf{P} \tag{3}$$

then increasing pressure would change the k_{-1}/k_2 ratio in the direction which causes the observed value of ΔV^* for $R \rightarrow P$ to become less negative. The observed sharpness of that slope change, however, would require that the difference between ΔV_{-1}^* and ΔV_2^* be so large that it would be physically unreasonable.

To illustrate this conclusion, we fitted values of the observed rate constants kobsd for MeONs at 25 °C and CH_3Br at 60 °C by generalized least squares to eq 4, where $k_{\text{obsd}} = (k_1)_0 \exp(-P\Delta V_1^*/RT)/\{1 +$

$$(k_{-1}/k_2)_0 \exp(-P\Delta\Delta V^*/RT)$$
 (4)

 $\Delta \Delta V^* = \Delta V_{-1}^* - \Delta V_2^*$, and a subscript 0 denotes a value at zero pressure. This equation can be derived for mechanism 3 by using the stationary-state approximation for the concentration of I (the validity of which is required by the observed kinetics) and assuming that the value of ΔV^* for each of the three steps is independent of pressure. Two fits to eq 4 are possible for each set of k_{obsd} values, corresponding to $\Delta\Delta V^* > 0$ (k_2 more sensitive to pressure than k_1) and $\Delta\Delta V^* < 0$ (k_2 less sensitive than k_1). The magnitude of $\Delta\Delta V^*$ is the same for both fits; this magnitude is 482 ± 185 cm³ mol⁻¹ for MeONs at 25 °C and 73 $\pm 17 \text{ cm}^3 \text{ mol}^{-1}$ for CH₃Br at 60 °C. These magnitudes are sufficiently large to make it very unlikely that the observed slope change really results from the presence of an intermediate. Further evidence that an intermediate is not responsible for the slope change is provided by the poor quality of the fit of the CH_3Br data to eq 4. The standard deviations of the observed k values from the curve of best fit are ± 0.048 and ± 0.033 s⁻¹ for MeONs at 25 °C and CH_3Br at 60 °C, respectively; both of these are ca. ± 0.5 to 1% of the average k values, which is consistent with the estimated $\pm 1\%$ precision of our MeONs data but significantly larger than the $\pm 0.2\%$ precision⁸ of the CH₃Br data. The complete results of these least-square fits, values of $(k_1)_0$, ΔV_1^* , $(k_{-1}/k_2)_0$, and $\Delta \Delta V^*$, together with standard deviations and error correlation matrices, are given in the supplementary material.

Consider now the second possible explanation for the direction of the slope change: reaction via a single mechanism, with no intermediate, in which the initial state is more compressible than the transition state. The abruptness of the change, particularly at 25 °C, invites description in terms of a cooperative collapse of solvent structure around the reactant into some more compact form. Since comparable slope changes are observed for reactants as different in structure and in ability to hydrogen bond to solvent as CH₃Br and MeONs, it might be expected that comparable slope changes would result from structural collapse of the solvent around most reactant solutes in aqueous solution. Thus, if the rarity of reports of such large and/or abrupt slope changes reflects a real absence of this phenomenon for most reactions, an explanation is needed. No slope change would be observed, of course, if such a collapse of solvent structure occurred around the activated complex as well as around the reactant, so that a transition state for methyl transfer to water in which the solvent structure is more resistant to compression than is the solvent structure surrounding most other solutes (either activated complexes or reactants) could account for the observation.

Further constraints on any proposed molecular origin of the slope change are imposed by the observed values of ΔS^* . Many structural changes which decrease the partial molal volume of a solute are expected also to decrease its partial molal entropy. For example, a breakdown of hydrophobic solvation (which has been proposed²⁰ as a significant part of the activation process for solvolysis in water) should increase both \bar{S} and \bar{V} by comparable amounts.²⁴ Similarly, any increase in solvent polarization

⁽¹⁹⁾ Calculated from parameters in ref 20, Table IIIA.
(20) Robertson, R. E. Prog. Phys. Org. Chem. 1967, 4, 213-80.
(21) E.g.: Albery, A. J.; Kreevoy, M. M. Adv. Phys. Org. Chem. 1978, Org. Chem. 197

^{16.87-157.}

 ⁽²²⁾ Kurz, J. L.; Harris, J. C. J. Am. Chem. Soc. 1970, 92, 4117.
 (23) As discussed by Baliga and Whalley,⁸ there is an increase in slope above 2 kbar for CH₃Br hydrolysis which is consistent with the incursion of a second mechanism. Our measurements for MeONs did not extend into that higher pressure region.

⁽²⁴⁾ E.g., for transfer of CH₄ from a fixed position in H₂O to a fixed position in a hydrocarbon solvent, $\Delta \hat{V}^{\circ} \approx 19 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta S^{\circ} \approx 14$ cal deg⁻¹ mol⁻¹ at 25 °C.²⁵ (25) Ben-Naim, A. "Hydrophobic Interactions"; Plenum Press: New

York, 1980; Chapter 5.

will increase solvent electrostriction (decreasing \bar{V}) and decrease the rotational freedom of solvent molecules (decreasing \bar{S}). Thus, correlations of ΔS^* with ΔV^* and of ΔS° with ΔV° are expected for reactions in solution. A simple electrostatic model²⁶ predicts ΔS (cal deg⁻¹ mol⁻¹)/ ΔV (cm³ mol⁻¹) ≈ 2.4 for processes in water at 25 °C and 1 bar; this is in qualitative agreement with the commonly observed values (near or slightly less than 2) of $\Delta S^*/\Delta V^*$ for heterolytic reactions in water²⁷ and of $\Delta S^\circ/\Delta V^\circ$ for the ionizations of phenols and carboxylic acids in water.^{28,29}

The values of ΔV^* observed for MeONs and CH₃Br hydrolyses in the low pressure region (ca. -24 and -16 cm³ mol⁻¹ for MeONs at $P \leq 0.069$ kbar and 25 °C and for CH₃Br at $P \leq 0.249$ kbar and 60 °C) are much more negative than might be anticipated from the observed values of ΔS^* at 1 atm (-7.9 and -8.0 cal deg⁻¹ mol⁻¹ for MeONs at 25 °C and CH₃Br at 60 °C);¹⁹ these values give $\Delta S^*/\Delta V^*$ ratios of 0.3 and 0.5, far outside of the expected range. Thus, whatever the mechanism for these methyl transfers may be, it is one which generates large contributions to ΔV^* and/or ΔS^* which are *non*electrostatic and which do *not* arise from breakdown of hydrophobic solvation in the initial state.

Similarly, the direction of the change in ΔS^* which accompanies an increase in pressure is not what might be anticipated from the observed increase in ΔV^* . For example, in the range 0–0.7 kbar, ΔV^* for CH₃Br hydrolysis at 60 °C increases by ca. 10 cm³ mol⁻¹ while ΔS^* decreases by ca. 2 cal deg⁻¹ mol^{-1.8} Apparently the more compact solvent structure around the initial state of the reactant at higher pressures is one which places fewer constraints

on motions of solvent molecules.

There is, of course, no abrupt large increase in the observed density of bulk liquid water in the pressure range that we are discussing, and we are not aware of any data for dilute aqueous solutions of nonreactant solutes which could confirm or deny our suggested compaction of the solvent shells around MeONs and CH₃Br. There may, however, be a relationship between the origins of the change in slope of ln k vs. P and of extrema which are observed for dynamic properties of bulk water. The viscosity of liquid water has a minimum near 1 kbar when the temperature is near 0 °C; that minimum becomes more diffuse as temperature increases and vanishes above ca. 30 °C.^{30,31} Comparable behavior also is shown by more direct measures of rotational freedom such as proton and deuteron spin-lattice relaxation times in H₂O and D₂O.^{31,32}

It is clear that significant mechanistic information is contained in the observed pressure dependence of these methyl-transfer rates. Before we can extract that information in detail, however, more data are required, both concerning the behavior of $\partial \ln k / \partial P$ for other chemical reactions in the low pressure region and concerning the pressure dependences of physical properties of dilute solutions of nonreactant solutes.

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Registry No. MeONs, 6214-20-6; EtTCA, 515-84-4.

Supplementary Material Available: Individually measured k values and the results of generalized least-square fits of those k values to eq 4 (4 pages). Ordering information is given on any current masthead page.

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⁽²⁷⁾ E.g.: Laidler, K. J.; Chen, D. Trans. Faraday Soc. 1958, 54, 1026-33.

⁽²⁸⁾ Reference 1, Table 5.

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⁽³⁰⁾ Stanley, E. M.; Batten, R. C. J. Phys. Chem. 1969, 73, 1187-91.

⁽³¹⁾ DeFries, T.; Jonas, J. J. Chem. Phys. 1977, 66, 896-901.
(32) Jonas, J.; DeFries, T.; Wilbur, D. J. J. Chem. Phys. 1976, 65, 582-5.