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A Comparative Study of the Cosolvent Effect in *tert*-Butyl Alcohol–Water Solutions: The Solvolyses of Adamantyl Bromide and Cyclohexyl Bromide

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Abstract: The remarkable range of activation parameters for the solvolysis of 1-adamantyl bromide and cyclohexyl bromide can be accounted for in terms of the relative apparent molal properties of the *tert*-butyl alcohol and, in the case of cyclohexyl bromide, also the partial molal properties of water. The activation parameters can be corrected to constant quantities (by introducing heats and entropy effects defined by ϕL_2 and ϕS_2^e). These corrections are in agreement with the "competitive solvation theory" of Nagy.

Nagy[1b] and co-workers have recently proposed a model for the role of the solvent in solvating and/or complexing with the substrate in solution. This "competitive solvation theory" is demonstrated to account for observed kinetic anomalies in the reaction of tetrachloro-*N*-*n*-butylphthalimide with *n*-butylamine in aprotic media.

We wish to report studies in this laboratory of the comparative kinetics of solvolysis of 1-adamantyl bromide and cyclohexyl bromide in the protic cosolvent system, water–*tert*-butyl alcohol.

These studies reveal competitive preferential solvation of the substrate (bromide) by the *t*-BuOH. For reaction with water the substrate must be partially freed (desolvated) from some alcohol to permit access of water in the formation of the carbonium ion pair in the transition state. The thermodynamic functions of the alcohol which correct these kinetic parameters are just those which characterize the multiple equilibria among the *t*-BuOH polymeric species, namely, the apparent relative molal enthalpy and entropy of the *t*-BuOH. Further, the different entropy corrections needed at 26 °C and 50 °C support the salt-like carbonium ion pair as the transition state. At 50 °C the entropy correction implies local microphase separation; at 26 °C no such correction is needed. We have found support for this conjecture in studying the effect of addition of NaBr to *t*-BuOH–H_2O mixtures: phase separation at 50 °C with homogeneous solution following cooling to 25 °C.

The system *tert*-butyl alcohol–water has been the subject of considerable structural studies invoking spectroscopic, light-scattering, and ultrasonic absorption. These studies are relevant to the kinetic studies reported here.

Covington and Jones[12] have discussed at length spectroscopic and ultrasonic relaxation studies of *tert*-butyl alcohol (TBA) and water solutions. Symons[7] and Blandamer[12] found two regions: region I ($0 < X_2 < 0.04$) and region II ($0.04 < X_2 < 0.1$), where X_2 is the mole fraction of alcohol. They suggest that the alcohol dissolves in only one state in region I but in region II equilibrium between two or more states sets in. The simplest equilibrium involves a dimer of the alcohol,[12] whose structure is almost certainly not that of the normally hydrogen-bonded dimer but rather one involving "hydrophobic bonds" with the alcoholic OH group still bonded to the water cage.[12]

Recently Lucas and Marciacq-Rousselot[8] have reported extensive NMR studies of the chemical shifts of the water proton in aqueous alcoholic solutions at various temperatures and their relation to some thermodynamic properties of the solutions. At low temperatures the downfield shift of the water proton is consistent with an increase in water structure promotion by the solutes (alcohols). At high temperatures, the upfield shift is consistent with a weakening of the water structure. These results are also qualitatively consistent with what may be expected of the influence of hard-sphere molecular solutes on water structure. They disagree with others that high heat capacities of solutes are evidence for water structure promotion. Rather, they conclude, high heat capacities show that the solute structural influence changes much with temperature. Then, an increasing $\bar{C}_{p2}$ is related to a change of the solution structure with temperature more important than the pure water structural changes, since the solute is assumed to be a structure former at low temperature and a structure breaker at high temperature, at moderate concentrations.

Pierotti[14] in a study of aqueous solutions of nonpolar gases concludes that it is the entropy of cavity formation that gives rise to the large negative entropies associated with aqueous solutions. In aqueous solutions in the vicinity of room temperature or below, the free energy of cavity formation is almost entirely manifest in the entropy term, whereas in the common organic solvents it is manifest almost entirely in the enthalpy term. This implies that the cavity formation process for water is dominated by a structural change in the solvent accompanied by only small changes in the internal energy of the solvent, while for organic solvents very minor changes take place and the process is dominated by changes in the internal energy of the solvents.

Hertz[12] in a study of nuclear magnetic relaxation time measurements found that the TBA molecule exerts much faster rotational Brownian motion in the water cage than it does in pure liquid TBA. His work supports that of Frank[12] who states that the energetic effect connected with the solution of particles with both polar groups and non-polar parts is much more due to the non-polar part than to the polar group.

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Table I. Rate Constants for Solvolysis of 1-Adamantyl Bromide in *tert*-Butyl Alcohol–Water Mixtures and Corrected Enthalpies of Activation at 38 °C

$X_{t\text{-BuOH}}$	$k_{26\,°C}$,[a] s^{-1}	$k_{50\,°C}$,[a] s^{-1}	$\Delta H^{\ddagger}_{obsd}$, kcal/mol	ϕL_2, cal/mol	ΔH^{*}_{corr}, kcal/mol
0.08	$(3.45 \pm 0.03) \times 10^{-5}$	$(5.97 \pm 0.04) \times 10^{-4}$	22.11 ± 0.20[b]	−1405.0	27.73 ± 0.20[b]
0.10	$(1.45 \pm 0.01) \times 10^{-5}$	$(2.904 \pm 0.010) \times 10^{-4}$	23.30 ± 0.12	−1113.0	27.76 ± 0.12
0.15	$(3.54 \pm 0.04) \times 10^{-6}$	$(9.015 \pm 0.040) \times 10^{-5}$	25.19 ± 0.22	−685.0	27.93 ± 0.22
0.20	$(1.35 \pm 0.02) \times 10^{-6}$	$(3.974 \pm 0.007) \times 10^{-5}$	26.35 ± 0.22	−442.0	28.11 ± 0.22
				mean	27.88 ± 0.14[c]

[a] Recorded uncertainties are maximum estimated errors. *k*'s are averages of at least three separate runs. [b] Maximum estimated errors. [c] Average deviation from the arithmetic mean.

Huggins[15] and DeVoe[16] have recently dissected the free energy of mixing and found relatively large contributions of the entropy terms involving orientation, rotation and vibration.

Light scattering studies by Iwasaki and Fujiyama[17] and ultrasonic absorption studies by Tamura, Maekawa and Yasunaga[18] support clathrate hydrate formation in which the alcohol is polymeric.

Experimental Section

Materials. *tert*-Butyl alcohol (Baker Analyzed Reagent Grade) was mixed with calcium hydride to remove water and then freshly distilled as needed from the butoxide through an Oldershaw column. The water was deionized. 1-Adamantyl bromide (Aldrich Analyzed) was recrystallized from pentane at −80 °C. The purified compound had a melting point range of 119–120 °C and was stored in a tightly capped bottle in a desiccator. Aldrich Analyzed 95% cyclohexyl bromide was distilled under vacuum. The compound was first shaken with an equal volume of concentrated hydrochloric acid and then separated from the acid, and the process repeated with water, 5% sodium bicarbonate solution, and water, successively. After separation from water, the compound was dried over anhydrous calcium chloride overnight. It was collected at 110 °C under vacuum distillation. The purified material had a refractive index at 25 °C of 1.49124 and boiling points of 72 °C at 32 torr and 165 °C at atmospheric pressure.

1-Adamantyl bromide, as argued by Schleyer,[2] is a good model for S_N1 limiting solvolysis. Cyclohexyl bromide, on the other hand, has been considered an example of a compound which undergoes S_N2 reactions. The solvent composition ranged from a mole fraction (of alcohol) 0.05 to 0.20, where the solutions deviate distinctly from ideality. The thermodynamics-of-mixing functions reported by Kenttamaa, Tommila, and Martti[3] were used to evaluate both the partial molal quantities of water and the relative apparent molal quantities of *tert*-butyl alcohol at 26 °C and 50 °C, the temperatures at which the kinetics were followed. It will prove of interest that *tert*-butyl alcohol is the last of the simple aliphatic alcohols which is completely miscible with water.

Apparatus. The conductance measurements were made, as previously described,[1a] with a General Radio Model 1615-A capacitance bridge. The 1000 Hz supply was a Hewlett-Packard audio oscillator, Model 1581-A. Null detection was provided by a General Radio Model 1232-A null detector, sensitive to 1 μV. The bridge was connected to the cells via a standard three-terminal connector.

Temperature regulation for the conductance cells was provided by an oil bath previously described. The regulation achieved was ±0.002 °C at 26 °C and ±0.005 °C at 50 °C. The thermometers in the bath were calibrated against a standard calorimetric thermometer (Parr Instrument Company, Serial No. 248480). Some preliminary runs were made in a water bath containing a Sargent 7A9093 (Bureau of Standards) thermometer. A variety of conductance cells was used depending on the concentration of the substrate. The cells were aged with 0.001 M HBr solutions for runs with adamantyl bromide and with 0.02 M HBr for runs with cyclohexyl bromide. Concentrations of substrates ranged from 0.002 to 0.02 M in cyclohexyl bromide. Binary solvent systems were made up by weight. Rate constants were calculated by least-squares analysis. In the case of cyclohexyl bromide, the reaction was so slow that the Guggenheim method was employed, the time interval between pairs of readings being approximately 1 half-life. The data were also analyzed by Shank's "constant-time interval" method,[4] giving good agreement with the Guggenheim method. In the case of cyclohexyl bromide there was no evidence of cyclohexene formation at 25 °C or 50 °C.[19e]

Table II. Calculated Entropy of Activation by Method A[a]

$X_{t\text{-BuOH}}$	$\Delta S^{\ddagger}_{26\,°C}$, eu/mol	$\Delta S^{\ddagger}_{50\,°C}$, eu/mol
0.08	−5.04 ± 0.69	−4.95 ± 0.56
0.10	−2.79 ± 0.42	−2.79 ± 0.41
0.15	+0.71 ± 0.76	+0.71 ± 0.73
0.20	+2.67 ± 0.79	+2.67 ± 0.75

[a] Reported uncertainties are maximum estimated errors based on *k* and $\Delta H^{\ddagger}$.

Results and Discussion

Adamantyl Bromide. The pseudo-first-order rate constants at 26 °C and 50 °C for the solvolysis of 1-adamantyl bromide, and the activation parameters calculated therefrom and corrected for the cosolvent effect, are listed in Tables I–VI. The enthalpies of activation were calculated from the *k*'s and the Eyring equation, giving the mean enthalpy of activation at 38 °C. Over the short range of composition ($X_{t\text{-BuOH}} = 0.08$–0.20), they vary by over 4 kcal. These enthalpies were corrected to a constant value by the equation:

$$\Delta H^{*}_{corr} = \Delta H^{\ddagger}_{obsd} - 4\phi L_2$$

where ϕL_2 is the apparent relative molal enthalpy of *t*-BuOH in the binary solvent. As demonstrated in a previous paper,[1a] ϕL_2 represents an enthalpy arising from the unmixing of all polymeric species, which may have solvated the substrate, during the activation process. A reaction mechanism to explain the above energy relations is as follows:

$$\mathrm{RBr(C_1)} \rightleftharpoons \mathrm{RBr(C_2)} + n(t\text{-BuOH})_x \qquad K_{eq} \tag{1}$$

$$\mathrm{C_2} \xrightarrow{k_1} (\mathrm{C_2})^{\ddagger} \xrightarrow{+\mathrm{H_2O}} \mathrm{ROH + HBr} \tag{2}$$

C_1 and C_2 represent the solvated substrate species and differ in degree of solvation; $(t\text{-BuOH})_x$ represents the undefined polymeric species of the alcohol; rate $= k_{obsd}(\mathrm{RBr}) = k_1(\mathrm{C_2})$; $K_{eq} = [\mathrm{C_2}][t\text{-BuOH}]^n\gamma_\phi{}^n/[\mathrm{C_1}]$; and $k_{obsd} = k_1K'\gamma_\phi{}^{-n}$, where $X_{TBA}{}^n$ is included in K' for $K' << 1$ (ref 5).

$$\Delta H^{\ddagger}_{obsd} = (\bar{H}^{\ddagger} - \bar{H}_g) + n\phi L_2 + \Delta H°(\text{constant } X_{TBA}) \tag{3}$$

$$\Delta S^{\ddagger}_{obsd} = (\bar{S}^{\ddagger} - \bar{S}_g) + n\phi S_2{}^e \tag{4}$$

γ_ϕ is defined[1a] by

$$\phi G_2{}^e = RT \ln \gamma_\phi = \phi L_2 - T\phi S_2{}^e \tag{5}$$

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(19) (a) Engbersen and Engberts[10] in a study of neutral solvolysis of *p*-nitrophenyl)dichloroacetate in highly aqueous *tert*-butyl alcohol have surmized "changes in microheterogeneity" in the highly aqueous regions may be responsible for the behavior of the enthalpy and the entropy of activation. (b) Dewar and Griffin[11] in a recent study of the nematic–isotropic transition in liquid crystals have found that intermolecular forces due to dipole–dipole attractions, etc. are not the most important factors in determining mesophase stability. Rather, entropy is the dominant factor. (c) The data of Hill[12] suggest that a linear correlation exists between $S_2{}^e$ and C_{p2} for alcohol–water mixtures. See also Guggenheim's[13] discussion of mixtures "not athermal". (d) The apparent molal enthalpies of *t*-BuOH in water show no changes in the mole fraction range 0.099–0.20 in *t*-BuOH on the addition of up to 5×10^{-4} M $\mathrm{Bu_4NBr}$. (We are indebted to Dr. Gary Bertrand of the University of Missouri, Rolla, MO, for these measurements.) The low concentrations of adamantyl bromide in the kinetic experiments, we can safely assume, did not alter the ϕL's of the *t*-BuOH. (e) Heating a 0.01 M solution of cyclohexyl bromide in neat *t*-BuOH for 26 h at 52 °C produced no ether (alcoholic $\mathrm{AgNO_3}$ titration and refractive index measurements). J. Kaspi and Z. Rappoport[20] found in pure EtOH adamantyl bromide at 35 °C had a rate constant of only 9×10^{-9} s^{-1}.

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Table III. Enthalpies and Entropies at 26 °C and 50 °C (Method B)[a]

$X_{t\text{-BuOH}}$	enthalpy of activation, $\Delta H^{\ddagger}$, kcal/mol		entropy of activation, $\Delta S^{\ddagger}$, eu	
	26 °C	50 °C	26 °C	50 °C
0.08	20.23 ± 0.20	23.62 ± 0.20	−11.31 ± 0.66	−0.34 ± 0.61
0.10	21.94 ± 0.12	24.52 ± 0.12	−7.31 ± 0.40	+1.01 ± 0.36
0.15	24.44 ± 0.22	25.92 ± 0.22	−1.78 ± 0.73	+3.02 ± 0.68
0.20	25.86 ± 0.22	26.83 ± 0.22	−1.07 ± 0.76	+4.22 ± 0.71

[a] Reported uncertainties are maximum estimated errors.

Table IV. Corrected Entropies of Activation at 26 °C and 50 °C by Method B for 1-Adamantyl Bromide in t-BuOH-H_2O (eu/mol)

A. 26 °C

$X_{t\text{-BuOH}}$	$\Delta S^{\ddagger}_{\text{obsd}}$	ϕS_2^{e}	ΔS^*_{corr}
0.08	−11.31	−10.76	+10.21 ± 0.66[a]
0.10	−7.31	−9.06	10.81 ± 0.40
0.15	−1.78	−6.60	11.42 ± 0.73
0.20	−1.07	−5.23	9.39 ± 0.76
		mean	10.46 ± 0.66[b]

B. 50 °C

$X_{t\text{-BuOH}}$	$\Delta S^{\ddagger}_{\text{obsd}}$	ϕS_2^{e}	$R \ln X_2$	ΔS^*_{corr}
0.08	−0.34	−8.15	−5.02	+5.92 ± 0.61[a]
0.10	+1.01	−7.02	−4.58	5.87 ± 0.36
0.15	3.02	−5.36	−3.77	6.20 ± 0.68
0.20	4.22	−4.46	−3.20	6.74 ± 0.71
			mean	6.18 ± 0.29[b]

[a] Maximum estimated errors from $\Delta S^{\ddagger}_{\text{obsd}}$. [b] Average deviation from the arithmetic mean. With use of $\Delta C_p^* \ln (T_2/T_1) = \Delta S^*_{T_2} - \Delta S^*_{T_1}$, we obtain $\Delta C_p^* = -56$ cal/mol/deg; this value falls in the region of heat capacities of activation for most alkyl bromide hydrolyses.[6]

$\bar{H}_g$ and $\bar{S}_g$ represent the partial molal enthalpy and entropy of the substrate in the "ground state" at concentration $[C_1]$. n is found to be 4 in the case of the apparent molal enthalpy and effectively 2 for apparent molal excess entropy of the *tert*-butyl alcohol. That is, in the activation process it is the substrate, divested of the alcohol species which occupied through "hydrophobic bonding" four sites, that ultimately reacts with water. These alcohols hinder access to the reaction site, as demonstrated by molecular models: adamantyl bromide can be enveloped by four *tert*-butyl alcohols completely cutting off the C–Br site from access to water. The OH groups on the four alcohols are free to hydrogen bond to water, and to other TBA's in secondary solvation shells. The reason for the entropy corrections involving only $2\phi S_2^{\text{e}}$ instead of 4 must be that in solution the main source of changes in entropy in the reorganization of the solvent shell is rotational freedom and changes from TBA–TBA H bonds to water–alcohol bonds. Apparently only two of the alcohols enveloping the adamantyl bromide suffer such changes. The mechanism outlined above is a modification of the one proposed recently by Koren and Perlmutter-Hayman[5] in their paper interpreting the source of a heat capacity of activation in solvolyses. The corrected enthalpies of activation are given in Table I. Consider the two equilibria: monomer, dimer TBA equilibrium

$$2\text{ROH} \rightleftharpoons (\text{ROH})_2 \qquad \text{(I)}$$

$$\text{AdBr(ROH)}_{n'} \rightleftharpoons \text{AdBr(ROH)}_{n'-n} + n\text{ROH} \qquad \text{(II)}$$

n must not be looked on as a solvation number; it is simply the effective number of TBA's removed from the vicinity of the reaction center on activation. The *total* solvation shell is of course variable with composition.

The hydrophobic bonding of four C–$(CH_3)_3$ groups to adamantyl bromide is energetically equal to that of two pairs of TBA's hydrophobically bonded to each other. In the activation process, then, in order for water to have access to the C–Br reaction site, a desolvation, releasing 4 TBA's from AdBr into the aqueous phase, must occur. This process is equivalent to shifting the monomer–dimer equilibrium of eq I. The energy associated with such processes (in this case, the negative of a heat of dilution) has been shown to be ϕL_2.[1a] It is this function which we find properly "corrects" the observed enthalpies of activation to a constant value representing the enthalpy of activation for solvolysis in pure water. Energetically it is the hydrophobic, nonpolar surface contacts that make the greater contribution to the heats of dilution and hence to the variations in the enthalpy of activation with solvent composition.

The corrections of the entropies of activation found by substituting the average enthalpy of activation (i.e., $\Delta H^{\ddagger}$ at 38 °C) proved to be more informative of the mechanism than anticipated. In fact, the $\Delta S^{\ddagger}_{26\,°\text{C}} = \Delta S^{\ddagger}_{50\,°\text{C}}$ cannot be corrected for the cosolvent effect. This is a consequence of using $\Delta H^{\ddagger}_{38\,°\text{C}}$ in the Eyring equation along with $k_{26\,°\text{C}}$ or $k_{50\,°\text{C}}$ instead of the enthalpies at 26 °C and 50 °C. The correct enthalpies to be used in the Eyring equation are those which take into account the fact that the apparent molal enthalpies of *tert*-butyl alcohol are strongly temperature dependent. Instead of $\Delta H^{\ddagger}_{38\,°\text{C}}$ we substituted:

$$\Delta H^{\ddagger}_{26\,°\text{C}} = \Delta H^*_{\text{corr}} + 4\phi L_2(26\ °\text{C}) \qquad (6)$$

$$\Delta H^{\ddagger}_{50\,°\text{C}} = \Delta H^*_{\text{corr}} + 4\phi L_2(50\ °\text{C}) \qquad (7)$$

The resulting calculated entropies (Table III) are now quite different at the two temperatures and can be corrected to the corresponding entropies of activation for solvolysis in pure water

Table V. The Observed and Calculated $\Delta(\ln k)$ at 26 °C and 50 °C for 1-Adamantyl Bromide in t-BuOH-H_2O

A. 26 °C

$X_{t\text{-BuOH}}$	$1/RT(\Delta\phi L_2)$	$1/R(\Delta\phi S_2^{\text{e}})$	$\Delta(\ln k)_{\text{calcd}}$	$\Delta(\ln k)_{\text{obsd}}$
0.08	−2.206	−2.783	3.258	3.241
0.10	−1.496	−1.928	2.128	2.369
0.15	−0.519	−0.689	0.698	0.965
0.20				

B. 50 °C

$X_{t\text{-BuOH}}$	$1/RT(\Delta\phi L_2)$	$1/R(\Delta\phi S_2^{\text{e}})$	$\Delta \ln X_2$	$\Delta(\ln k)_{\text{calcd}}$	$\Delta(\ln k)_{\text{obsd}}$
0.08	−1.1027	−1.857	−0.915	2.528	2.710
0.10	−0.7621	−1.288	−0.693	1.858	1.992
0.15	−0.2826	−0.453	−0.288	0.799	0.819
0.20					

Table VI. Rate Constants for Solvolysis of Cyclohexyl Bromide in *t*-BuOH–H$_2$O

X_2	$k_{26\,°\mathrm{C}}$, s^{-1}	$k_{50\,°\mathrm{C}}$, s^{-1}
0	(3.434 ± 0.08) × 10^{-6}	(9.374 ± 0.002) × 10^{-5}
0.05	(6.217 ± 0.05) × 10^{-7}	(9.774 ± 0.005) × 10^{-6}
0.08	(9.965 ± 0.05) × 10^{-8}	(1.959 ± 0.010) × 10^{-6}
0.10	(5.019 ± 0.06) × 10^{-8}	(1.075 ± 0.008) × 10^{-6}
0.15	(2.121 ± 0.08) × 10^{-8}	(5.115 ± 0.010) × 10^{-7}

at 26 °C and 50 °C (Table IVA,B). These corrected entropies are given by:

$$\Delta S^*_{\mathrm{corr}} = \Delta S^* - 2\phi S_2^{\mathrm{e}} \text{ at } 26\ °\mathrm{C} \qquad (8)$$

$$\Delta S^*_{\mathrm{corr}} = \Delta S^* - 2\phi S_2^{\mathrm{e}} + 2R \ln X_2 \text{ at } 50\ °\mathrm{C} \qquad (9)$$

If these average corrected entropies at 26 °C (10.46 ± 0.66) and at 50 °C (6.18 ± 0.29) represent the activation entropies for solvolysis in water (in the solvolysis of cyclohexyl bromide where measurements in water could be made $\Delta H^*_{\mathrm{corr}}$ and $\Delta S^*_{\mathrm{corr}}$ are demonstrated to be *the* values found in water), one can calculate a heat capacity of activation for solvolysis of adamantyl bromide in water:

$$\Delta C_p^*(\ln T_2/T_1) = \Delta S^*_{T_2} - \Delta S^*_{T_1} = -56 \text{ cal mol}^{-1} \text{ deg} \qquad (10)$$

a value in satisfactory agreement with those reported for alkyl bromide hydrolyses.[6]

As demonstrated in Table I, the differences in enthalpies of activation with composition are quantitatively accounted for by the differences in the apparent relative enthalpies of the *tert*-butyl alcohol which selectively solvates the adamantyl bromide; the "cosolvent-corrected" enthalpies of activation represent the enthalpy of activation in the solvent water. We may conjecture that the heat capacities of activation would show a similar cosolvent dependence. The changes in ΔH^* with temperature, then, will be reflections of an intrinsic ΔC_p^* (for solvolysis in water) and a ΔC_p^* due to changes in ϕL_2 with temperature. By introducing into the Eyring equation the $\Delta H^*_{26\,°\mathrm{C}}$ and $\Delta H^*_{50\,°\mathrm{C}}$ given by eq 6 and 7 and the k's at 26 °C and 50 °C, we compute ΔS^* at each composiion at 26 °C and 50 °C. These ΔS^*'s are both composition dependent and temperature dependent. Corrections for solvent composition (by use of ϕS_2^{e} and $\phi S_2^{\mathrm{e}} + R \ln X_2$) give ΔS^*'s in water which are temperature dependent. These permit the calculation of ΔC_p^* for solvolysis in water—a value in reasonable accord with those reported for alkyl bromides in the literature. The fact that the entropies of activation at 26 °C are corrected by eq 8 and those at 50 °C by eq 9 argues strongly for the conclusion that quasi-phase separation (microheterogeneity) is involved in the activation process at 50 °C but not at 26 °C. They suggest that part of the ΔC_p^* arises from this entropy effect.[13,19a] Support for this view was found in the effect of salts on the binary solvent system. The addition of NaBr caused phase separation at 50 °C but not at 26 °C, and this phase separation could be reversed by changing the temperature. On the other hand, the addition of NaCl caused phase separation at both temperatures. This suggests that the carbonium ion pair produces a quasi-phase separation in the activation process and the correction introduced in eq 9 thermodynamically correctly represents "unmixing" of the solvent pair in activation—a dramatic "solvent reorganization". Further support for this interpretation of the entropy is found in Symons and Anderson's NMR observations that the change in the proton shift, $\Delta\delta$, with respect to the solvent alone, in aqueous *tert*-butyl alcohol solutions containing salts, varies from negative to positive values as the temperature increases from 26 °C to 50 °C. A negative $\Delta\delta$ represents a low-field shift of the water proton and water structure promotion, while a positive $\Delta\delta$ represents a high-field shift of the proton and a structure breaking. Lucas[8] has concluded that $(n\text{-Bu})_4\mathrm{NBr}$ is a structure promoter at 25 °C but at 51 °C the effect is reversed. This means that at higher temperatures the bigger cation should act as a stronger structure breaker. We can conclude that in the solvolysis of 1-adamantyl bromide at low temperatures the structure promoting power of the alkyl chain has overcome the structure breaking power of the bromide ion; at higher temperatures the structure breaking properties of the bromide ion predominate.[10,12]

Table VII. Observed and Corrected Enthalpies of Activation for Cyclohexyl Bromide in *t*-BuOH–H$_2$O

X_2	$\Delta H^\ddagger_{\mathrm{obsd}}$(38 °C), kcal/mol	ϕL_2(38 °C), cal/mol	$\bar{L}_{\mathrm{w}}$(38 °C), cal/mol	ΔH^*(38 °C), kcal/mol
0	25.82 ± 0.37[a]	0	0	25.82 ± 0.37
0.05	21.41 ± 0.13	−2180	−78.7	25.61 ± 0.13
0.08	23.19 ± 0.20	−1405	−120.0	25.76 ± 0.10
0.10	23.88 ± 0.20	−1113	−126.3	25.86 ± 0.20
0.15	24.83 ± 0.60	−685	−150.0	25.90 ± 0.60
			mean	25.81 ± 0.10[b]

[a] Maximum estimated error based on k. [b] Average of the errors from the mean.

$\Delta \ln k$ was also calculated from the thermodynamic quantities of the alcohol as in previous publications (Table V):

$$\Delta \ln k = -\frac{1}{RT}\Delta(\Delta H^*) + \frac{1}{R}\Delta(\Delta S^*)$$

$$\Delta(\Delta H^*) = 4\Delta(\phi L_2)$$

$$\Delta(\Delta S^*) = 2\Delta\phi S_2^{\mathrm{e}} \text{ at } 26\ °\mathrm{C}$$

$$\Delta(\Delta S^*) = 2\Delta\phi S_2^{\mathrm{e}} - 2\Delta R \ln X_2 \text{ at } 50\ °\mathrm{C}$$

Cyclohexyl Bromide. Mechanism. The substitution of bromine at the secondary carbon of cyclohexyl bromide is expected to be different from that at the bridgehead carbon of 1-adamantyl bromide. However, cyclohexyl bromide is also solvated by *tert*-butyl alcohol and reacts with water. The desolvation of alcohol molecules and a subsequent attack of water at the reaction site of cyclohexyl bromide are proposed as the reaction mechanism.

$$\mathrm{RBr(C_1)} \xrightleftharpoons{K_{\mathrm{eq}}} \mathrm{RBr(C_2)} + n(t\text{-BuOH})_x$$

$$\mathrm{RBr(C_2)} + m\mathrm{H_2O} \xrightarrow[k_2]{} \mathrm{ROH} + \mathrm{HBr(H_2O)}_{m-1}$$

$\mathrm{C_1}$ represents the solvated complex of cyclohexyl bromide in the "ground state", RBr(1); and $\mathrm{C_2}$ represents the solvated complex after *tert*-butyl alcohol species are released from the solvation shell of $\mathrm{C_1}$. $\mathrm{C_2}$ is assumed to be present in a fast equilibrium with $\mathrm{C_1}$ and reacts with water once it is formed, i.e., in a *slow* $\mathrm{S_N2}$ step.

Then, rate = $k_{\mathrm{obsd}}[\mathrm{C_1} + \mathrm{C_2}] = k_2[\mathrm{C_2}][\mathrm{H_2O}]^m$ and, $K_{\mathrm{eq}} = [\mathrm{C_2}][t\text{-BuOH}]^n\gamma_\phi{}^n/[\mathrm{C_1}]$. Let $M_{\mathrm{w}} = [\mathrm{H_2O}]$ and $M_2 = [t\text{-BuOH}]$, which are very large compared with either $[\mathrm{C_1}]$ or $[\mathrm{C_2}]$, and can be assumed constant throughout the reaction: γ_ϕ is the activity coefficient of *t*-BuOH, based on apparent molal excess functions.[1] Let $K' = [\mathrm{C_2}]\gamma_\phi{}^n/[\mathrm{C_1}]$ and then $k_{\mathrm{obsd}} = k_2K'(\gamma_\phi)^{-n}(M_{\mathrm{w}})^m$ and $\ln k_{\mathrm{obsd}} = \ln k_2 + \ln K' - n \ln \gamma_\phi + m \ln M_{\mathrm{w}}$. Since the change in M_{w} in the temperature range makes negligible contribution, a differentiation of the above equation with respect to $(1/T)$ gives:

$$\Delta H^*_{\mathrm{obsd}} = \Delta H^*_{(k_2)} + \Delta H°_{\mathrm{C_2}} + n\phi L_2$$

since

$$\Delta H°_{\mathrm{C_2}} = \bar{H}°_{\mathrm{C_2}} - \bar{H}°_{\mathrm{C_1}}$$

$$\Delta H^*_{k_2} = (\bar{H}^* - \bar{H}°_{\mathrm{C_2}}) - m\bar{L}_{\mathrm{w}}$$

therefore $\Delta H^*_{\mathrm{obsd}} = (\bar{H}^* - \bar{H}°_{\mathrm{C_1}}) + n\phi L_2 - n\bar{L}_{\mathrm{w}}$. We define again $\Delta H^* = (\bar{H}^* - \bar{H}°_{\mathrm{C_1}})$, the "solvent corrected" enthalpy of activation and

$$\Delta H^*_{\mathrm{obsd}} = \Delta H^* + n\phi L_2 - m\bar{L}_{\mathrm{w}}$$

the $\Delta H^*_{\mathrm{obsd}}$ data calculated from k_{obsd} agree with the above equation and give $n = 2$, $m = 2$ over the mole fraction studies (Table VII).

Therefore, the hydrolysis of cyclohexyl bromide is of an $\mathrm{S_N2}$ mechanism and water molecules are involved in the activation process. The two *tert*-butyl alcohol molecules (or an alcohol dimer)

Table VIII. Calculated Entropies of Activation for Cyclohexyl Bromide in *t*-BuOH–H$_2$O (Method B)

X_2	$\Delta H^\ddagger_{26\,°\mathrm{C}}$, kcal/mol	$\Delta H^\ddagger_{50\,°\mathrm{C}}$, kcal/mol	$\Delta S^\ddagger_{26\,°\mathrm{C}}$, eu/mol	$\Delta S^\ddagger_{50\,°\mathrm{C}}$, eu/mol
0	26.43	25.21	4.84 ± 0.48*	0.90 ± 0.52[a]
0.05	20.27	22.72	−19.70 ± 0.69	−11.29 ± 0.42
0.08	22.37	23.75	−15.76 ± 0.63	−11.29 ± 0.56
0.10	23.24	24.37	−14.21 ± 0.81	−10.55 ± 0.70
0.15	24.43	25.04	−11.95 ± 0.78	−9.97 ± 0.75

[a] Maximum estimated error based on k and $\Delta H^\ddagger$. With use of $k'_{\mathrm{obsd}} = k/(M_{\mathrm{w}})^2$ for $X_2 = 0$: $\Delta S^\ddagger(26\,°\mathrm{C}) = -11.11$ eu/mol and $\Delta S^\ddagger(50\,°\mathrm{C}) = -15.01$ eu/mol.

Table IX. Corrected Entropies of Activation for Cyclohexyl Bromide in the *tert*-Butyl Alcohol–Water System for 26 °C and 50 °C

A. 26 °C

X_2	ϕS_2^{e}, eu/mol	$R \ln M_{\mathrm{w}}$	$\bar{S}_1^{\mathrm{e}}$, eu/mol	$R \ln X_1$	ΔS^*, eu/mol
0.05	−15.3	7.547	−0.33	−0.10	−11.42 ± 0.69
0.08	−10.76	7.284	−0.57	−0.17	−12.28 ± 0.63
0.10	−9.06	7.119	−0.63	−0.21	−12.27 ± 0.81
0.15	−6.60	6.739	−0.78	−0.32	−12.09 ± 0.78
				mean	−12.02 ± 0.28*

B. 50 °C

X_2	ϕS_2^{e}, eu/mol	$R \ln M_{\mathrm{w}}$	$R \ln X_2$	ΔS^*, eu/mol
0.05	−9.4	7.489	−5.954	−15.33 ± 0.42
0.08	−8.15	7.247	−5.02	−15.40 ± 0.56
0.10	−7.02	7.080	−4.58	−15.19 ± 0.71
0.15	−5.36	6.313	−3.77	−14.69 ± 0.75
			mean	−15.15 ± 0.23[a]

[a] Average deviation from the mean. $\Delta S^* = -15.15$ agrees with $\Delta S^\ddagger = -15.01$ eu/mol at $X_2 = 0$ (Table VIII). Since $\Delta S^*_{50\,°\mathrm{C}} - \Delta S^*_{26\,°\mathrm{C}} = \Delta C_{\mathrm{p}}^* \ln (T_2/T_1)$, $\Delta C_{\mathrm{p}}^* = (-15.15 + 12.02)/0.0772 = -40.5$ cal/(mol deg), which is in the range of ΔC_{p}^* obtained from ΔH^*. We can calculate from the Eyring equation $\Delta(\ln k) = -(1/RT)[\Delta(\Delta H^\ddagger{}_{\mathrm{obsd}})] + (1/R)[\Delta(\Delta S^\ddagger/_{\mathrm{obsd}})]$, which should be equal to the experimentally determined $\Delta(\ln k_{\mathrm{obsd}})$.

are removed from the reaction sphere to let water molecules come in and react with cyclohexyl bromide. From the relationships

$$\Delta G^\ddagger{}_{\mathrm{obsd}} = -RT \ln k_{\mathrm{obsd}} + RT \ln (k_{\mathrm{B}}T/h)$$

$$\Delta G^\ddagger{}_{\mathrm{obsd}} = \Delta H^\ddagger{}_{\mathrm{obsd}} - T\Delta S^\ddagger{}_{\mathrm{obsd}}$$

we obtain for the entropy of activation:

$$\Delta S^\ddagger{}_{\mathrm{obsd}} = \Delta S^* + mR \ln M_{\mathrm{w}} + n\phi S_2^{\mathrm{e}} - m\bar{S}_1$$

Both m and n should equal 2 in order to be consistent with the expression of enthalpy of activation. However, as the alcohol dimer returns to the bulk solvent system, the reorientation of the alcohol dimer involves only *one* hydrogen bond (the same argument is used for 1-adamantyl bromide), so $n = 1$ for ϕS_2^{e} in the above equation.

Furthermore, each of the two water molecules involved in the rate-determining process plays a different role: one solvates the "incipient" bromide ion and only $\bar{S}_1^{\mathrm{e}}$ instead of $\bar{S}_1$ is reflected in the entropy of activation; the other water molecule reacts with the substrate as a nucleophile to form the product; therefore $\bar{S}_1$ describes its entropy contribution and *one* $R \ln M_{\mathrm{w}}$ should be used in the above equation. Rewriting the above equation gives:

$$\Delta S^\ddagger{}_{\mathrm{obsd}} = \Delta S^* + R \ln M_{\mathrm{w}} + \phi S_2^{\mathrm{e}} - \bar{S}_1 - \bar{S}_1^{\mathrm{e}}$$

Both $\bar{S}_1$ and $\bar{S}_1^{\mathrm{e}}$ are small compared with the values of ϕS_2^{e}, ($R \ln M_{\mathrm{w}}$) and the precision of the data; therefore, we can write:

$$\Delta S^*_{26\,°\mathrm{C}} = \Delta S^\ddagger{}_{\mathrm{obsd}} - R \ln M_{\mathrm{w}} - \phi S_2^{\mathrm{e}}$$

However, at 50 °C, the same phenomenon as in the case of 1-adamantyl bromide occurs and

$$\Delta S^*_{50\,°\mathrm{C}} = \Delta S^\ddagger{}_{\mathrm{obsd}} - R \ln M_{\mathrm{w}} - \phi S_2^{\mathrm{e}} + R \ln X_2$$

$\Delta S^*_{26\,°\mathrm{C}}$ and $\Delta S^*_{50\,°\mathrm{C}}$ thus calculated are listed in Table IX. Since cyclohexyl bromide dissolves slightly in pure water, we have been able to study the rate of hydrolysis in pure water at both 26 °C and 50 °C. Stoichiometrically, two molecules of water are involved in the activation process; one forms the alcohol, the other solvates or pulls away the bromide ion. Define: $k'_{\mathrm{obsd}} = k_{\mathrm{obsd}}/(M_{\mathrm{w}})^2$ where k_{obsd} is the experimentally determined pseudo-first-order rate constant and $\Delta H^\ddagger = (\bar{H}^\ddagger - \bar{H}_{\mathrm{g}}) - 2\bar{H}°_{\mathrm{w}}$, $\Delta S^\ddagger = (\bar{S}^\ddagger - \bar{S} - \bar{S}_{\mathrm{g}}) - 2\bar{S}°_{\mathrm{w}}$.

Appendix

The origin of the ϕL term in the correction to $\Delta H^\ddagger$, given in ref 1, as applied to the solvolysis of adamantyl bromide is:

$$S + n_1A_1 = S(A_1)_{n_1} \qquad \text{with } K = K_1$$

$$S + n_2A_2 = S(A_2)_{n_2} \qquad K_2$$

$$\cdots$$

$$S + n_1A_1 + n_2A_2 = S(A_1)_{n_1}(A_2)_{n_2} \qquad K_{12}$$

etc.

S refers to the substrate (adamantyl bromide) and A_1, A_2, ... refer to the polymeric alcohol species which solvate the substrate (or form a clathrate cage about it through "hydrophobic bonding"). The activated complex must have four contacts of the polymers removed from the vicinity of the reactive site. Thus the equations of interest are:

$$S(A_i)_n = S(A_i)_{n-4} + 4A_i$$

$$\text{rate} = k\sum S(A_i)_{n-4} = kK\sum S(A_i)_n(A_i)^{-4} = k_{\mathrm{obsd}}\sum S(A_i)_n$$

where $\sum S(A_i)_n$ represents total substrate (AdBr) solvated by various polymeric alcohol species. $k_{\mathrm{obsd}} = kK\sum(A_i)^{-4}$, where K

Table X. Comparison of Observed Δln k and Calculated Δln k at 26 °C and 50 °C

A. 26 °C

$X_2 - X_2'$	$(-2/RT)\cdot\Delta(\phi L_2)$	$(1/R)\Delta(\phi S_2^{\mathrm{e}})$	$\Delta(\ln M_{\mathrm{w}})$	$(2/R)\Delta(\bar{S}_1^{\mathrm{e}})$	$\Delta(\ln k_{\mathrm{obsd}})$	$\Delta(\ln k_{\mathrm{calcd}})$
0.05–0.08	3.3496	−2.2849	0.1320	0.241	1.796	1.437
0.08–0.10	1.4206	−0.8556	0.083	0.067	0.715	0.715
0.10–0.15	1.9535	−1.2381	0.193	0.152	0.638	0.674

B. 50 °C

$X_2 - X_2'$	$(-2/RT)\cdot\Delta(\phi L_2)$	$(1/R)\Delta(\phi S_2^{\mathrm{e}})$	$\Delta(\ln M_{\mathrm{w}})$	$(2/R)\Delta(S_1^{\mathrm{e}})$	$\Delta(\ln X_2)$	$\Delta(\ln k_{\mathrm{obsd}})$	$\Delta(\ln k_{\mathrm{calcd}})$
0.05–0.08	1.7987	−0.580	0.1290	0.1057	−0.470	1.60	1.65
0.08–0.10	0.6818	−0.5687	0.089	0.5637	−0.470	0.600	0.710
0.10–0.15	0.9598	−0.835	0.041	0.156	−0.405	0.742	0.841

is the equilibrium constant for complex formation (cf. ref 5).

$$\left(\frac{\partial \ln (k_0/T)}{\partial T}\right)_{X_2,P} = \left(\frac{\partial \ln (k/T)}{\partial T}\right)_{X_2,P} + \left(\frac{\partial \ln K}{\partial T}\right)_{X_2,P} - 4\left(\frac{\partial \ln \sum A_i}{\partial T}\right)_{X_2,P}$$

$$\Delta H^{\ddagger} = \Delta H^* + \Delta H^\circ - 4\frac{(-M\phi L_{\mathrm{ROH}})}{\sum A_i = M} = \Delta H^* + \Delta H^\circ + 4\phi L_{\mathrm{ROH}}$$

An equivalent way to write the expression is:

$$k_{\mathrm{obsd}} = kK'\gamma_\phi^{-4}$$

$$RT \ln \gamma_\phi = \phi G^e = \phi L - T\phi S^e$$

The molecular origin of the apparent relative molal functions lies in the polymer equilibria among the alcoholic species and is shown below (see ref 1 and references therein).

The ϕL_{ROH} term is the phenomenological consequence of equilibria among all polymeric species of alcohol:

$$2A_1 = A_2;\ \Delta H^\circ{}_{11},\ K_{11}$$

$$A_2 + A_1 = A_3;\ \Delta H^\circ{}_{12},\ K_{12}$$

$$\cdots$$

$$A_i + A_j = A_{ij};\ \Delta H^\circ{}_{ij},\ K_{ij}$$

where all the ΔH_{ij}'s and K_{ij}'s are assumed equal. Gill and Farquhar have shown that

$$-M\phi L = K_{ij}(A_1)^2\Delta H^\circ{}_{ij} + 2K_{ij}(A_1)^3\Delta H^\circ{}_{ij} + \ldots$$

$$\mathrm{d} \ln (\sum A_{ij})/\mathrm{d}T = \frac{\partial(\sum A_{ij})K_{ij}/\partial T}{\sum(A_{ij})} - \frac{M\phi L_2}{\sum(A_{ij})}RT^2$$

$\sum(A_{ij})$ contains $(A_1 + 2A_2 + 3A_3 + 4A_4 + \ldots)$ moles of alcohol as measured in the laboratory in terms of the simple monomeric formula. The first term represents the change in composition with T at constant equilibrium constant; that is, it reflects the change in density of the solution with temperature, which in our experiments is small and relatively constant over the temperature interval.

$$\therefore\ \Delta H^{\ddagger}{}_{\mathrm{app}} = \Delta H^* + \Delta H^\circ{}_c + 4\phi L_{\mathrm{ROH}}$$

A similar expression can be deduced for the entropy correction.

Dimers of 5,15-Dioxoporphodimethenes with Direct Links between Methine Bridge Carbon Atoms†

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Abstract: Oxidation of zinc octaethylporphyrin with thallium(III) trifluoroacetate yields two dimeric 5,15-dioxoporphodimethenes with direct linkages between methine bridge carbon atoms C-10^1 and C-10^2. [Indexes 1 and 2 relate to the dioxoporphodimethene units throughout this paper.] One is the symmetric dimer in a gauche conformation; the other is an unsymmetric tautomer. Dehydrogenation of both dimers yields one product with a double bond between C-10^1 and C-10^2. This is probably the sterically most crowded tetrasubstituted olefin reported so far, and it produces a strong absorption band at 710 nm (zinc complex, 900 nm). Acetylation of monomeric and dimeric 5,15-dioxoporphodimethenes leads to a lactam, in which the methine bridge C-10 is connected with a central nitrogen atom. The reactions observed are interpreted with a reductone model for 5,15-dioxoporphodimethenes. 5-Oxo-10-hydroxyoctaethylphlorin was also isolated and characterized.

Chemical oxidation of metalloporphyrins, e.g., **1a**, leads to reactive oxyporphyrins, e.g., **1b**, in high yield.[1-5] Further oxidation occurs on the opposite methine bridge, and 5,15-dioxoporphodimethenes, e.g., **2a,b**, can often be obtained as stable end products.[2,3] Our interest in the chemistry of these compounds originates from the idea that they may behave as quinone analogues. We found it tempting to combine the known redox chemistry of quinones with the coordination and photochemistries of porphyrins. It particular we hoped that the keto groups could be hydrated. Irradiation of the porphodimethene chromophors should then allow some interesting photocleavages of the water adduct. The "porphoquinone" hypothesis was based on two experimental findings. (i) It was found earlier that metalloporphyrins react in a manner similar to that of benzene derivatives and that *meso*-hydroxyporphyrins have many properties in common with phenols.[4] We therefore deduced a possible chemical analogy between *p*-benzoquinone and 5,15-dioxoporphodimethenes. (ii) It was found that certain derivatives of dioxoporphodimethenes, which will be discussed in this paper, have a strong absorption band in the near infrared. These compounds were thought to be semiquinone-type dimers with a long wavelength charge-transfer band.

This paper is a very brief account of the failure of these hypotheses and a report on some faschinating new reactions of dioxoporphodimethenes. The structure elucidation of three thallium oxidation products of symmetric zinc octaethylporphyrinate (**1a**)[1-5] and their chemical reactions are described. They turned out to be comparable in complexity to the hydrogenation products of octaethylporphyrin described recently by Eschenmoser.[6] The reaction products, however, are quite different. Although we have obtained several preparations of our products in crystalline form, none of them were suitable for X-ray analysis.[7] Therefore we had to rely on spectroscopic data and

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† Dedicated to Professor Georg Manecke on the occasion of his 65th anniversary.

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