then the implications for mechanistic studies are startling, and we will have to completely reexamine our definition of diradical intermediates and our simplistic view of nonconcerted reactions.[19]

**Acknowledgment.** We are indebted to A. Imamura, W. J. Hehre, and J. Lisle for computational assistance and discussions. This work was supported by the National Institutes of Health (GM 13468) and the National Science Foundation (GP 8013). Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The stay of one of us (R. G.) at Cornell was made possible by a grant from the Deutsche Forschungsgemeinschaft.

(19) Another area where we may have to face an intermediate simulated by a flat-topped potential surface is in some nonclassical carbonium ions.

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# Heat Capacities of Organic Compounds in Solution. II. Some Tetraalkylammonium Bromides[1]

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**Abstract:** Partial molar heat capacities of solution $\Delta C_{p_2}^\circ$ are reported for a series of tetraalkylammonium bromides. The process is transfer from the pure solid state to high dilution in water as measured by the integral heat method of Criss and Cobble. Heats of solution are shown to be extremely dependent upon the hydrophobic structure of the ion and upon the temperature. This gives warning against interpreting heats of solution for compounds of this type at a single temperature in simple terms. The corresponding heat capacity of solution for tetra-*n*-butylammonium bromide in ethanol is reported and results contrasting to those in water are discussed.

For a variety of good reasons, tetraalkylammonium salts occupy a special position in the development of modern solution theory. As a result they have been subjected to unusually extensive and systematic scrutiny by a battery of physical methods, with particular emphasis on their behavior in aqueous solution.[2] This combined effort has been described by Franks[3] as "a textbook example of how. . . water–solute interactions should be studied."

The very large partial molal heat capacity $\bar{C}_{p_2}$ of tetra-*n*-butylammonium bromide in aqueous solution reported by Frank and Wen[4] and recently confirmed by Ackerman[5] is often cited as powerful evidence that nonpolar groups enhance a degree of temperature-dependent structuredness on water molecules close to them. In our previous paper[6] concerning the determination of heat capacities of solution for a series of alcohols in water,[7] we described the application of Criss and Cobble[8] "integral heat of solution" method. A simple solution calorimeter described by us[9] was used to measure the temperature coefficient of the partial molal heat of solution ($\Delta \bar{H}_s$) for the solute from a pure liquid or solid state to high dilution in water. It, therefore, gives directly the difference in heat capacity ($\Delta C_{p_2}^\circ$) between the heat capacity of the pure solute [as a liquid ($C_p^L$) or gas ($C_p^G$) or solid ($C_p^S$)], and that of its partial molal heat capacity at infinite dilution, $\bar{C}_{p_2}$. This is defined formally as

$$\Delta C_{p_2}^\circ = \bar{C}_{p_2} - C_{p_2}^{L,\,G,\text{ or }S} \qquad (1)$$

In this paper, we will describe the result of applying this method to a series of crystalline tetraalkylammonium bromides in water at temperatures mostly between 10 and 50°. Our results may be compared with those from a similar study (published since the present paper was first submitted) by Sarma, Mohanty, and Ahluwalia,[10] which covers a wider series of salts but which was limited to two temperatures. Their paper also provides a bibliographical entrée to the field.

## Experimental Section

**Preparation and Purification of Chemicals.** With the exception of tetraisoamylammonium bromide [$(i\text{-Am})_4NBr$], the tetraalkylamonium bromides and other reactants were of Eastman White Label quality. Tetramethylammonium bromide ($Me_4NBr$) was recrystallized once from water. Tetraethylammonium bromide ($Et_4NBr$) was recrystallized once from isopropyl alcohol. Tetra-*n*-propylammonium bromide ($Pr_4NBr$), tetra-*n*-butylammonium bromide ($Bu_4NBr$), and [$(i\text{-Am})_4NBr$] were recrystallized once from a chloroform–ether mixture (10–15 volumes of ether added to the chloroform).

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* To whom correspondence should be addressed.

(1) This work was supported by a grant from the Office of Saline Water, U. S. Department of the Interior.

(2) J. E. Prue, A. J. Read, and G. Romeo in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968, p 155.

(3) F. Franks, see ref 2, p 40.

(4) H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(5) H. Rüterjans, F. Schreiner, U. Sage, and Th. Ackerman, *J. Phys. Chem.*, 73, 986 (1969).

(6) E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Amer. Chem. Soc.*, 91, 4028 (1969).

(7) D. M. Alexander and D. J. T. Hill, *Aust. J. Chem.*, **22**, 347 (1969).

(8) C. M. Criss and J. W. Cobble, *J. Amer. Chem. Soc.*, **83**, 3223 (1961).

(9) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, 87, 1541 (1965).

(10) T. S. Sarma, R. K. Mohanty, and J. C. Ahluwalia, *Trans. Faraday Soc.*, **62**, 2333 (1969).

[(*i*-Am)$_4$NBr] was prepared by refluxing equimolar mixtures of 1-bromo-3-methylbutane and triisoamylamine in acetonitrile for 48 hr. The product was crystallized by the addition of ether. The salt was then recrystallized from a chloroform–ether mixture. All the tetraalkylammonium bromides were dried in a vacuum oven at 50–60° for at least 24 hr. Sodium chloride (Baker Analyzed Reagent) was dried at 130° and was used with no further purification.

The purities of the tetraalkylammonium bromides were checked by means of a potentiometric titration with standard $AgNO_3$ using a silver indicator electrode and a glass electrode as reference.[11] The potential was monitored with a Beckman Model DR pH meter. Approximately 4 mmol of the bromide salt was dissolved in *ca.* $10^{-2}$ *M* $HNO_3$ and titrated with 0.100 *M* $AgNO_3$. Potential readings were taken at 0.50-ml increments near the equivalence point, and the end point was determined by the "analytical" method.[12] Analysis for these salts based on the correct formula weight were in the range of 99.7–100.3% compared to a test run with potassium bromide (Baker Analyzed Reagent) which gave analyses of 100.9 and 101.3%.

**Calorimetry.** A solution calorimeter was employed which was essentially the same as the one which we described elsewhere,[9] but with the following exceptions. The 2-K resistor of the complementary arm of the Wheatstone bridge was replaced by the thermistor of a twin calorimeter, instead of the usual base-line compensator. A Kepco Model ABC 40–0.5(M) power supply replaced the 6-V batteries. The 200-ml dewar flasks were placed in brass jackets for immersion in a 10-gal aquarium water bath. The Teflon head had two more holes drilled for the accommodation of a total of three solid-injection syringes.

Temperatures above ambient were maintained with a no. 20 constant temperature circulator (Bronwill Scientific Division/Will Corp.). Temperatures below ambient were maintained with a Forma Scientific Inc. "cold finger" in conjunction with the Bronwill circulator. The system was allowed to equilibrate overnight and the temperature inside the dewars varied a maximum of 1° from the start of a run to the end.

Plastic syringes containing approximately 0.3–2 mmol of sample (the amount depended upon the value of $\Delta\bar{H}_s$) were filled in a drybox and sealed with rubber septa. Three syringes were placed into each of two dewar flasks which contained 200 ml of solvent and were allowed to equilibrate. A heating curve was run prior to each injection, and the temperature was measured immediately after injection. After the contents of all six syringes were delivered, six more were placed in the same dewar flasks, and the runs repeated.

## Results

The partial molal heat of solution values ($\Delta\bar{H}_s$) at high dilution in water for NaCl and five tetraalkylammonium bromides at a series of temperatures are listed in Tables I–VI. Except for tetrapropylammonium bromide, our results for $\Delta C_{p_2}°$ agree within combined experimental error with those of Sarma, *et al.*,[10] although their values and errors are generally higher than ours. Our reported error limits are the standard deviations for six measurements at each

**Table I.** NaCl

| $\Delta\bar{H}_s$, kcal/mol | *t*, °C |
|---|---|
| 1.723 ± 0.043 | 6.1 |
| 1.686 ± 0.025 | 6.3 |
| 1.372 ± 0.030 | 14.6 |
| 1.331 ± 0.017 | 14.8 |
| 1.014 ± 0.042 | 24.3 |
| 0.981 ± 0.050 | 24.4 |
| 1.007 ± 0.067 | 24.6 |
| 0.882 ± 0.027 | 28.9 |
| 0.867 ± 0.027 | 29.5 |
| 0.667 ± 0.030 | 37.5 |
| 0.658 ± 0.034 | 37.7 |
| 0.602 ± 0.020 | 39.9 |
| 0.561 ± 0.036 | 40.6 |
| 0.387 ± 0.020 | 48.7 |
| 0.350 ± 0.034 | 48.9 |

**Table II.**[a] $Me_4NBr$

| $\Delta\bar{H}_s$, kcal/mol | *t*, °C |
|---|---|
| 5.972 ± 0.098 | 13.6 |
| 5.921 ± 0.015 | 22.8 |
| 5.896 ± 0.026 | 23.0 |
| 5.821 ± 0.099 | 29.9 |
| 5.789 ± 0.034 | 31.0 |
| 5.671 ± 0.076 | 40.9 |
| 5.695 ± 0.058 | 42.5 |
| 5.560 ± 0.055 | 47.9 |
| 5.641 ± 0.091 | 48.2 |

[a] Least squares intercept: $\Delta\bar{H}_s(25°) = 5.868 \pm 0.012$ kcal/mol; ($\Delta C_{p_2}° = -11.3 \pm 0.1$ cal/mol deg.

**Table III.**[a] $Et_4NBr$

| $\Delta\bar{H}_s$, kcal/mol | *t*, °C |
|---|---|
| 1.023 ± 0.073 | 10.3 |
| 0.985 ± 0.085 | 10.9 |
| 1.341 ± 0.018 | 23.7 |
| 1.426 ± 0.038 | 26.9 |
| 1.596 ± 0.024 | 30.8 |
| 1.625 ± 0.031 | 32.4 |
| 1.830 ± 0.065 | 40.0 |
| 1.889 ± 0.086 | 40.3 |
| 2.123 ± 0.101 | 49.6 |
| 2.241 ± 0.065 | 50.7 |

[a] Least squares intercept: $\Delta\bar{H}_s(25°) = 1.411 \pm 0.013$ kcal/mol; $\Delta C_{p_2}° = 30.0 \pm 0.9$ cal/mol deg.

**Table IV.**[a] $Pr_4NBr$

| $\Delta\bar{H}_s$, kcal/mol | *t*, °C |
|---|---|
| −2.35 ± 0.13 | 13.7 |
| −2.38 ± 0.11 | 13.8 |
| −1.49 ± 0.01 | 22.0 |
| −1.20 ± 0.06 | 25.4 |
| −1.04 ± 0.10 | 26.0 |
| −0.88 ± 0.14 | 28.0 |
| 0.77 ± 0.01 | 43.6 |
| 1.16 ± 0.10 | 46.6 |

[a] Least squares intercept: $\Delta\bar{H}_s(25°) = -1.18 \pm 0.01$ kcal/mol; $\Delta C_{p_2}° = 106 \pm 1$ cal/mol deg.

**Table V.**[a] $Bu_4NBr$

| $\Delta\bar{H}_s$, kcal/mol | *t*, °C |
|---|---|
| −5.64 ± 0.12 | 5.7 |
| −5.48 ± 0.19 | 5.8 |
| −3.86 ± 0.184 | 16.5 |
| −3.68 ± 0.151 | 16.6 |
| −2.93 ± 0.06 | 20.6 |
| −2.26 ± 0.120 | 25.3 |
| −2.18 ± 0.080 | 25.4 |
| −1.99 ± 0.111 | 26.5 |
| −1.62 ± 0.06 | 27.5 |
| 0.05 ± 0.147 | 37.7 |
| 0.10 ± 0.090 | 37.8 |
| 1.47 ± 0.109 | 46.2 |
| 1.63 ± 0.094 | 47.0 |
| 3.62 ± 0.088 | 58.2 |
| 3.89 ± 0.115 | 59.5 |

[a] Least squares intercept: $\Delta\bar{H}_s(25°) = -2.21 \pm 0.02$ kcal/mol; $\Delta C_{p_2}° = 176 \pm 1$ cal/mol deg.

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(11) C. N. Reilley and D. T. Sawyer, "Experiments for Instrumental Methods," McGraw-Hill, New York, N. Y., 1961.

(12) L. Meites and H. C. Thomas, "Advanced Analytical Chemistry," McGraw-Hill, New York, N. Y., 1958.

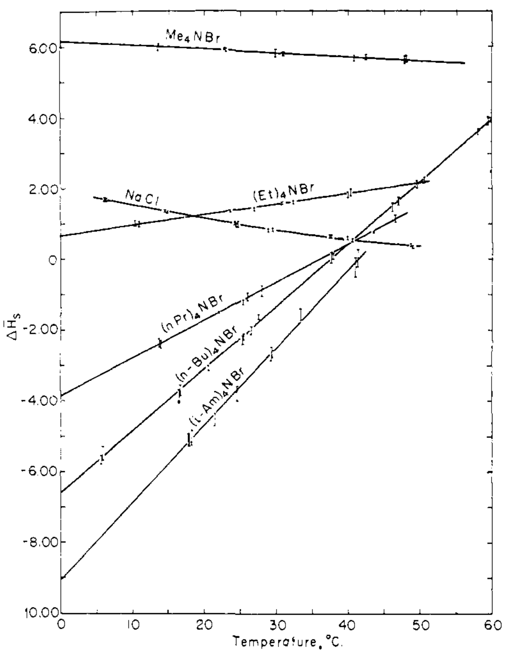

Figure 1. $\Delta\bar{H}_s$ values as a function of temperature for salts in Tables I–VI.

temperature. In Figure 1, these data are summarized and plotted. A linear variation of $\Delta\bar{H}_s$ with temperature is observed, or, stated differently, the heat capacities of solution ($\Delta C_{p_2}{}^\circ$) are constant within our experimental error over this temperature range.

Table VI.[a] $(i\text{-Am})_4NBr$

| $\Delta\bar{H}_s$, kcal/mol | $t$, °C |
|---|---|
| −5.10 ± 0.17 | 17.8 |
| −5.02 ± 0.20 | 18.3 |
| −4.53 ± 0.17 | 21.5 |
| −3.77 ± 0.20 | 24.6 |
| −2.65 ± 0.18 | 29.3 |
| −2.66 ± 0.09 | 29.5 |
| −1.55 ± 0.16 | 33.4 |
| −0.229 ± 0.275 | 41.1 |
| 0.037 ± 0.246 | 41.3 |

[a] Least squares intercept: $\Delta\bar{H}_s(25°) = -3.604 \pm 0.047$ kcal/mol; $\Delta C_{p_2}{}^\circ = 219 \pm 5$ cal/mol deg.

The apparent constancy of $\Delta C_{p_2}{}^\circ$ is unexpected in view of the work of Ackerman, *et al.*,[4] who reported definite temperature dependence of the partial molar heat capacities ($\bar{C}_{p_2}$) for a series of alkali halides and organic salts. Results by other workers cited in our first paper[6] also show considerable temperature dependence of $\bar{C}_{p_2}$ obtained from specific heat data. By eq 1, $\Delta C_{p_2}{}^\circ$ differs from $\bar{C}_{p_2}$ by the heat capacity of the pure solid ($C_p{}^S$), a nearly constant term for a given salt; hence, the variation of $\Delta C_{p_2}{}^\circ$ with temperature should be almost identical with that of $\bar{C}_{p_2}$. Two possible reasons for our failure to find a temperature variation for $\Delta C_{p_2}{}^\circ$ could be (a) that our calorimeter does not measure $\Delta\bar{H}_s$ with precision adequate to detect nonlinear temperature dependence over this range, or (b) that curvature in Ackerman's results were caused by solute–solute interactions. His method entails the measurement of the specific heats of relatively concentrated solutions (0.5–2 $m$) and an extrapolation to infinite dilution so that temperature-dependent heat capacity of dilution terms could be involved. In view of his difficulty in extrapolating apparent molal heat capacities to infinite dilution for tetra-*n*-butylammonium bromide, and the dramatic concentration effects observed by White and Benson[13] for potassium octanoate, we believe that explanation b (see above) is attractive and reasonable for the larger ions. The results of Sarma, *et al.*,[10] are not relevant to this point since they were determined at only two temperatures.

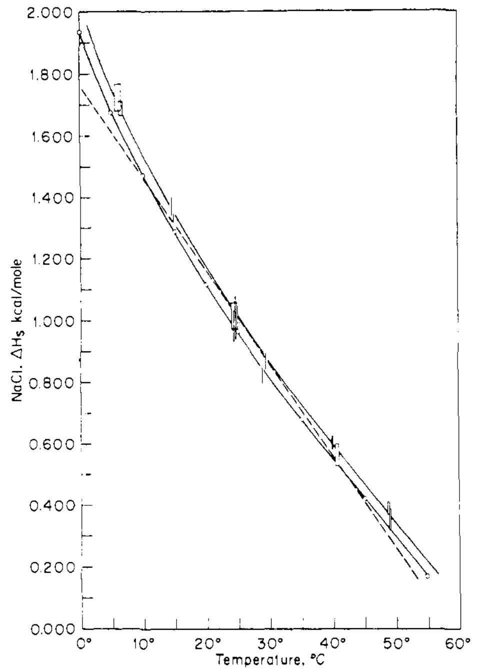

Figure 2. Comparison of $\Delta\bar{H}_s$ values for NaCl as a function of temperature: ⊙, values of Criss and Cobble; □, from this paper; ----, linear least squares fit of data from this paper.

We have tested the precision of our calorimeter over a 50° temperature range by measuring the heat of solution of NaCl as a function of temperature in comparison with the precise study of Criss and Cobble.[8] The NaCl data in Figure 1 are presented (including the temperature variation) together with Cobble's results in Figure 2. The curvature of his plot is identical with that of ours. The slightly larger endothermicity of our values relative to his is due to a concentration dependence.[14] Our final concentration was 0.03 $M$ while Cobble's was 0.02 $M$.

The linear temperature dependence of the Me$_4$NBr heats can be shown by a comparison with the NaCl data. Both results were treated with linear and quadratic least squares equations.[15] The quadratic fit reduced the standard deviation of the NaCl points ($s_L = \pm 0.059$ *vs.* $s_Q = \pm 0.025$ kcal/mol), while the Me$_4$NBr points remained practically unaffected ($s_L = \pm 0.030$ *vs.* $s_Q = \pm 0.029$ kcal/mol). The errors for the other salts, especially the three with largest cations,

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(13) P. White and G. C. Benson, *J. Phys. Chem.*, **64**, 599 (1960).

(14) V. P. Parker, N.S.R.D.S.—NBS2, National Bureau of Standards, April 1965.

(15) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951.

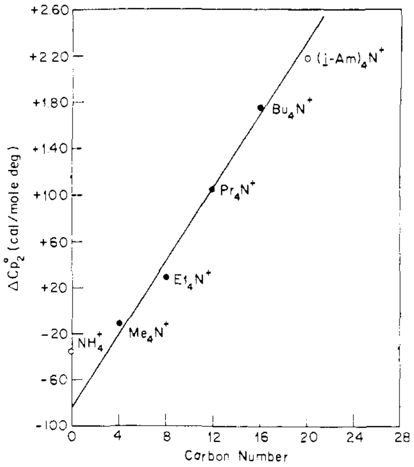

Figure 3. Plot of $\Delta C_{p_2}{}^\circ$ for straight chain tetraalkylammonium bromides *vs.* carbon number ($NH_4Br$ and ($i$-Am)$_4$NBr data were not used in drawing the correlation line shown).

are sufficiently great that the plots are experimentally indistinguishable from a straight line.

Conspicuously absent from the series reported here are results for tetra-*n*-amylammonium bromide. This salt dissolves so slowly in water, especially at high temperatures, that reliable enthalpies could not be measured.

## Discussion

**Thermodynamic Properties.** The process to which our thermodynamic properties apply is the transfer of 1 mol of solute from its pure liquid, solid, or gaseous state to high dilution in water at 25° (see eq 1). In view of the fact that the salts are all crystalline at this temperature and that lattice energies are determined by a variety of complex factors,[16] there is an extra degree of uncertainty in interpreting $\Delta P_2{}^\circ$ (where $P$ stands for any thermodynamic property) for the solution of these solids in water unless their sublimation properties are known. In contrast, some of the corresponding properties for common nonelectrolytes are relatively easy to handle since many of their heats of vaporization are accessible for referring heats of solution back to a gaseous standard state. Furthermore, in their pure liquid states they are sufficiently similar to most solvents (with the principle exception of water) that heats of mixing or heats of solution are usually small. Figure 1 is therefore interesting in view of the sign and magnitude of $\Delta \bar{H}_s$ for the solutes as a function both of molecular structure and of temperature. Obviously, the heats of solution in cool water of the bromides displayed there are related directly to their carbon number. Furthermore, the differentiation between them is dependent on the temperature of the solution, the greatest separation occurring at lowest temperature. As the temperature is raised, the heats of solution tend to converge so that in hot water we would expect to find a much less systematic arrangement of $\Delta \bar{H}_s$ within a smaller range of values.

These results suggest some kind of interaction between cold water and the hydrophobic portion of the ions and also suggest that this solvation interaction is disrupted at higher temperatures. The fact that these salts are so widely differentiated at low temperatures indicates that differences in their lattice energies are either small relative to their heats of solvation or are proportional to them. Since the pattern is so similar to that which has been reported for the alcohols, the prior alternative is more reasonable. We therefore consider that the heat capacities of these salts like those of the corresponding alcohols[6,7] are overwhelmingly dominated by a large exothermic contribution resulting from the interaction of the hydrophobic portion of the carbon chain with water at low temperature. The nature of the attractions which produce this exothermic development of structure is, of course, related directly to the whole controversy of the structure of water and how it is modified by solutes. The sign of $\bar{C}_{p_2}$ serves to dichotomize structure-breaking and structure-making solutes in water more sharply than any other thermodynamic property we know. All inorganic salts of which we are aware have negative partial molal heat capacities in water and all nonelectrolytes have positive ones. By this criterion, the tetraalkylammonium salts starting with tetramethylammonium behave like nonelectrolytes and the direct correlation of $\Delta C_{p_2}{}^\circ$ with carbon number is exactly analogous to that found in other nonelectrolytes of which the alcohols are the best documented examples.[6,7]

An important practical consideration which follows from the data represented in Figure 1 is the danger of interpreting heats of solution of nonelectrolytes or alkylammonium salts in water at a single temperature. Obviously, the heats of solution and (more important) the differences between them are very sensitive to temperature as well as to molecular structure.

**Concerning the Persistance of Clathrate Structure at High Dilution.** Jeffrey and his group have reported a systematic study of clathrate hydrates including some tetraalkylammonium salts.[17] In this series, tetra-*n*-butylammonium ion and tetraisoamylammonium ion have a particularly strong tendency toward the formation of clathrate hydrates. A number of authors have suggested that some of the properties of nonelectrolytes in aqueous solution might be interpreted in terms of a tendency to form icelike cages with the geometry of the clathrate even at high dilution in water. A result which bears on this notion is provided by comparison of tetraisoamylammonium bromide, which forms a very stable clathrate at 25°, with the other members of the series, which do not. One might suppose that the creation of a specially stable icelike cage around this ion at high dilution would lead to an abnormal $\Delta C_{p_2}{}^\circ$ value compared to the other members of the series. This is not observed in Figure 3. This result does not support the "clathrates at high dilution" model but should not be taken as overwhelming evidence against it. The particular stability of the tetraisoamylammonium bromide clathrate in its crystalline form may be due to some special geometrical contribution to the lattice energy as repeating units are placed side by side. This type of reinforcement would be lacking at high dilution and thereby remove the singularity in this case.

**$\Delta C_{p_3}{}^\circ$ in Ethanol.** The large magnitudes of $\Delta C_{p_3}{}^\circ$ for $R_4N^+$ salts in water provide strong evidence for

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(16) S. S. Chang and E. F. Westrum, *J. Chem. Phys.*, **36**, 2420 (1962).

(17) G. A. Jeffrey and R. K. McMullan in "Progress in Inorganic Chemistry," Vol. 8, F. A. Cotton, Ed., Interscience Publishers, New York, N. Y., 1967, p 43.

solute-induced water structuring especially when the salts of high carbon number are compared to alkali metal bromides. The self-consistency of this picture suggests the reasonable question, "How would analogous measurements compare in another solvent?" Being unaware of published results which could provide an answer, we measured $\Delta C_{\mathrm{p}_2}{}^\circ$ for tetra-*n*-butylammonium bromide in ethanol. Some of the results are displayed in Table VII and differ dramatically from those for the aqueous systems in Table V.

**Table VII.** Molal Heat of Solution of Tetra-*n*-butylammonium Bromide in Ethanol as a Function of Temperature and Concentration[a]

| 8° | | 22.3° | | 40.3° | |
|---|---|---|---|---|---|
| $M \times 10^3$ | Kcal/mol | $M \times 10^3$ | Kcal/mol | $M \times 10^3$ | Kcal/mol |
| 3.14 | +4.50 | 2.50 | +4.64 | 4.62 | +4.52 |
| 6.45 | +4.59 | 4.20 | +4.69 | 7.02 | +4.89 |
| 8.83 | +4.82 | 6.14 | +4.93 | 9.86 | +4.93 |
| 11.2 | +4.61 | 8.68 | +4.70 | 12.6 | +4.99 |
| 14.2 | +4.70 | 10.7 | +4.96 | 16.4 | +4.79 |
| 17.8 | +4.71 | 12.9 | +5.05 | 19.4 | +5.02 |

[a] These are representative values taken at the extremes and the middle of our temperature range. Approximately 40 similar results were obtained at 8, 17.4, 17.5, 22.7, 32.2, 32.6, and 40.0°.

First, and most important, we note the small temperature dependence of $\Delta \bar{H}_{\mathrm{s}}$ for solution of this salt in ethanol compared to that in water the apparent least squares average for $\Delta C_{\mathrm{p}_2}{}^\circ$ being 10.2 ± 2.3 cal/mol deg in the former case against 176 in the latter. It is also clear that molal heats of solution of this salt in ethanol are far more dependent on concentration than they are in water. The same is found for $\Delta C_{\mathrm{p}_2}{}^\circ$ since the temperature coefficient for the most dilute solutions in Table VII are clearly less temperature dependent than are those for the most concentrated. Decreasingly exothermic heats in response to increasing concentration are commonly a symptom of solute–solute interactions. In view of the absence of such a phenomenon in water, we attribute its appearance in ethanol to ion pairing. No enthalpies of ion pairing are known for cases such as this although Kay[18] reports very small temperature coefficients for ion pairing constants in methanol.

Applying Evans[19] value of $K_{\mathrm{assoc}} = 75$ for tetra-*n*-butylammonium bromide in ethanol at 22° to the present case, we may calculate that 14% of the ions at our lowest solute concentration ($2.5 \times 10^{-3}$ *M*) are paired. At the same temperature, 38% of the ions at the highest concentration ($1.3 \times 10^{-2}$ *M*) are paired. The less exothermic heat of solution at higher concentration is reasonable if we accept the proposition that bromide ions which are tightly paired are poorer hydrogen-bond acceptors than are dissociated ones.

Several suggestions could be made for the positive sign of $\Delta C_{\mathrm{p}_2}{}^\circ$ in ethanol. (1) Ethanol has some residual solute-induced structure (like that of water) which is temperature dependent. (2) At low temperatures the free bromide ions are better solvated through hydrogen bonding than at higher temperatures so that a temperature increase favors contact ion pairing. (3) The dielectric constant of ethanol, like most other solvents, has a negative temperature coefficient. This favors ion pairing at higher temperatures and more concentrated solutions are most sensitive to the effect. The latter explanation seems most reasonable to us.

(18) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69** 4208 (1965).

(19) D. F. Evans and P. Gardam, *ibid.*, **72**, 3281 (1968).

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# Homoallenic Participation. III. The Effect of a 2-Methyl Group

**Roger S. Macomber**

*Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.* *Received May 25, 1970*

**Abstract:** The preparation and acetolysis of 2-methyl-3,4-pentadien-1-yl tosylate (IIIb) and model compound 2-methyl-1-pentyl tosylate are reported. Compound IIIb undergoes acetolysis with accompanying return–rearrangement to the same rearranged tosylate afforded by 4,5-hexadien-2-yl tosylate (X). Both III band X yield essentially identical product mixtures, suggesting that both solvolyze through the same ion (manifold). The rates of acetolysis were followed titrimetrically; IIIb was found to solvolyze ~40 times faster than the model compound at 85°, and about one-fourth as fast as X. The results are discussed in the context of neighboring group participation.

Several recent publications, by our group[1] and others,[2–7] have shown that a β-allenic system (I) exhibits the same versatility in promoting solvolytic reactions (homoallenic participation) as does a similarly located double bond (homoallylic participation). Our

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(1) (a) T. L. Jacobs and R. S. Macomber, *Tetrahedron Lett.*, 4877 (1967); (b) *J. Amer. Chem. Soc.*, **91**, 4824 (1969).

(2) (a) R. S. Bly, A. R. Ballentine, and S. U. Koock, *ibid.*, **89**, 6993 (1967); (b) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969).

(3) R. Garry and R. Vessiere, *Bull. Soc. Chim. Fr.*, 1542 (1968).

(4) (a) M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2511 (1969); (b) *ibid.*, 2515 (1969); (c) *ibid.*, 3699 (1969); (d) C. Santelli-Rouvier, P. Archer, and M. Bertrand, *C. R. Acad. Sci., Paris, Ser. C*, **269**, 252 (1969).

(5) A preliminary report by Bertrand and Santelli[6] suggested that homoallenic participation in the hydrolysis of optically active 4,5-hexadien-2-yl tosylate proceeds with a high degree of stereospecificity to yield rearranged products, while unrearranged alcohol arises from a classical SN1 process. They also found[4a,c] that acetolysis of the same compound led to unrearranged acetate with some retained activity.