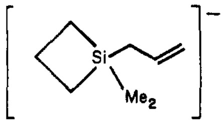
addition of allyl anion to $(CH_3)_3SiF$. The subsequent reaction (eq 7) of **7** with the fluorinated silane clearly indicates that Si–C bond formation occurs in adduct **7** and is consistent with the expected higher F^- affinity of $(CH_3)_3SiF$ compared to $(CH_3)_3SiC_3H_5$. Allyl anion also adds to **1** giving adduct **8**, which we believe is the first report of a silicon anion bearing five carbon substituents.



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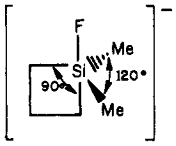
Our results are consistent with the trigonal-bipyramidal (tbp) geometry for these pentavalent silicon anions in which strain in the four-membered ring is relieved by allowing it to span one equatorial and one apical position (see structure **9**). The results



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are also in accord with the enhanced reactivity of strained cyclosilanes in nucleophilic reactions in solution[1,16] for which a similar explanation has been given and lend support to the intermediacy of such ions in chemical reactions of silanes. We had expected that **3** would have a much higher F^- affinity than either **1** or **2** because strain could be relieved in both rings; it turns out, however, that these F^- affinities are quite close to each other (probably <3 kcal/mol). We suggest that this is because F in the adduct of **3** must take an equatorial position if both silacyclobutanes are to span equatorial and apical positions. This is not a favorable orientation for F, whose apicophilicity is large.[17]

A simple mechanistic description of the reactions of F^- with silacyclobutanes would be a competition between the unimolecular fragmentation of an excited F^- adduct and the stabilization of that adduct by nonreactive collisions with He carrier gas. It is expected that direct anion addition will result in adducts which have excess energy due to Si–F bond formation. This mechanism predicts that the product distribution (adduct vs. ring cleavage) in reactions like (1) and (2) will be dependent on He pressure. We find that the reaction of F^- with **1** proceeds on approximately every collision with $k_{\text{exp}} = (2.1 \pm 0.4) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[18] Both k_{exp} and the product distribution of this reaction remain constant over the pressure range 0.20–0.50 torr. Similar experiments with argon as the carrier gas gave identical kinetic results. Apparently this simple mechanism does not adequately describe the reactions reported. One possible explanation is that in these reactions adduct formation and ring cleavage proceed through energetically or structurally different intermediates.

We are presently continuing our studies of the kinetics and energetics of the formation of pentacoordinate silicon anions as well as further mechanistic studies of gas-phase anion reactions with silanes.

Acknowledgment. This work was supported by The Council on Research and Creative Work of the University of Colorado Graduate School and grants from the National Science Foundation, the Army Research Office, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. R.D. expresses thanks to the University of Michigan, Chemistry Department, for the hospitality extended during sabbatical leave.

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(17) Emsley, J.; Hall, D., "The Chemistry of Phosphorus"; Wiley: New York, 1976.

(18) The collision rate is calculated by using the Langevin model $k = 2\pi q(\alpha/\mu)^{1/2}$. For the reaction of F^- with **1**, $k_{\text{collision}} = 1.97 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} when an estimated α of 11.3 Å^3 is used, based on comparison to similar compounds.

Thermodynamics of Solution of Nonpolar Gases in a Fused Salt. "Hydrophobic Bonding" Behavior in a Nonaqueous System

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Water is frequently considered to be a unique liquid. Its crucial role in biochemical systems is surely without parallel. It is often considered that its biochemical primacy derives from its abiliy to promote aggregation of the nonpolar chains of many amphipathic molecules, such as phospholipids, to produce biomembranes. This relationship of their organizing ability in biochemical systems to the unusual thermodynamics of solution of nonpolar compounds in water has been articulated persuasively by a number of authors, particularly Kauzman[1] and Tanford,[2] following the seminal paper of Frank and Evans[3] which drew attention to the peculiar thermodynamic situation and attempted to relate it to changes in the three-dimensional structure of water evoked by the introduction of nonpolar solutes.

In this preliminary report we will show thermodynamic properties of solution which are highly reminiscent of their behavior in water for several nonpolar gases in pure, anhydrous ethylammonium nitrate—a fused salt which is liquid down to 12 °C. Table I compares the Henry's law constant, standard free energy, enthalpy, and entropy for solution of krypton, methane, ethane, and *n*-butane in the fused salt (FS) and corresponding values for solution in water and cyclohexane (CX). The derived properties for transfer to CX from FS and H_2O are also listed in parentheses. Clearly, the magnitudes of the three principal thermodynamic properties are closely parallel in both polar media and are sharply differentiated from those in the nonpolar one. Although the range of free energies is slightly larger for solution in water than in FS, the range of enthalpies and entropies is larger for solution in the salt, and it is these latter properties which are often considered to be the primary manifestations of hydrophobic effects.[1-3] Other important thermodynamic properties for transfer demonstrate that the familar pattern of a large loss of free energy dominated by an increase in entropy which is associated with the transfer of nonpolar solutes from water to nonpolar solvents is recapitulated for transfer from FS to CX. The entropy and enthalpy changes are smaller for the fused-salt solutions, and the Barclay–Butler $\Delta S^\circ_s/\Delta H^\circ_s$ slope, which originally served to differentiate aqueous solutions[3] from those in other media, is intermediate for FS, between those in CX and H_2O.

Clear evidence for micelle formation has also been obtained from the observation of critical micelle concentrations of several surfactants (including CTAB) in FS, by both surface tension and light scattering measurements.[4]

We do not as yet have information comparing these properties with those for solution in other fused salts. It would be rash to speculate at this time on what structural or physical factors are behind the similarities in behavior of the aqueous and FS systems. In addition to the presumed high polarity and internal pressure,

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(1) Kauzman, W. *Adv. Protein Chem.* **1959**, *14*, 1.

(2) (a) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes."; Wiley: New York, 1980. (b) *Science* **1978**, *200*, 1012. (c) *Proc. Natl. Acad. Sci., U.S.A.* **1979**, *76*, 4175.

(3) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.

(4) Evans, D. F.; Cassassa, E. Z.; Roman, R., in preparation.

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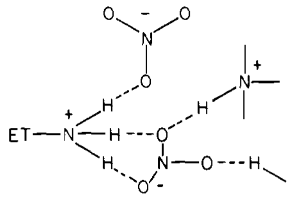
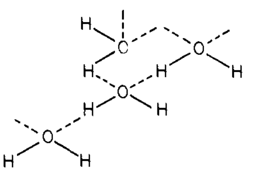
Table I. Thermodynamics for Solution of Nonpolar Gases in the Fused Salt Ethylammonium Nitrate (FS),[a] Water,[b] and Cyclohexane (CX)[c] at 25 °C[d]

		H_{25}, atm	ΔG°_s, kcal mol^{-1}	ΔH°_s, kcal mol^{-1}	ΔS°_s, gibbs mol^{-1}
Kr	FS	3131 ± 59	4.813 ± 0.108 (−1.634)	−1.771 ± 0.072 (0.940)	−22.08 ± 0.27 (8.63)
	H_2O	22250	5.932 (−2.753)	−3.752 (2.921)	−32.48 (19.03)
	CX	214.2	3.179	−0.831	−13.45
CH_4	FS	4750 ± 110	5.024 ± 0.073 (−1.635)	−0.057 ± 0.058 (−0.531)	−17.04 ± 0.15 (3.70)
	H_2O	39890	6.279 (−2.890)	−3.297 (2.709)	−32.11 (18.77)
	CX	305.3	3.389	−0.588	−13.34
C_2H_6	FS	1291 ± 19	4.269 ± 0.004 (−2.048)	−3.669 ± 0.002 (1.048)	−26.62 ± 0.01 (10.38)
	H_2O	29900	6.107 (−3.886)	−4.722 (2.101)	−36.32 (20.08)
	CX	42.39	2.221	−2.621	−16.24
C_4H_{10}	FS	396 ± 11	3.611 ± 0.135	−5.714 ± 0.105	−31.27 ± 0.295
	H_2O	45520	6.355	−6.206	−42.13

[a] This study. [b] H_2O data from: Wilhelm, E.; Battino, R.; Wilcock, J. W. *Chem. Rev.* 1977, 77, 219. [c] CX data from: Wilhelm, E.; Battino, R. *Ibid.* 1973, *73*, 1. [d] Thermodynamic properties for transfer of each gas from FS or H_2O to CX are given in parentheses.

or cohesive energy density, of FS, we note that this primary ammonium nitrate is well disposed to generate a three-dimensional hydrogen-bonded network to form a highly cross-linked liquid reminiscent of water, represented crudely here:





Other unknown factors may be the deciding ones. Further research should eliminate some explanations easily and help to define the range of similarities between H_2O and FS more sharply. We are currently investigating the heat capacity behavior and extending our studies of micelle formation by surfactants in the fused-salt medium.

The results presented here, and others to be reported later, demonstrate that, in terms of solution thermodynamics and response to surfactants, water is not alone among highly polar hydrogen-bonded media in manifesting behavior previously referred to as "hydrophobic". Tanford[2c] has pointed out that in terms of its inability to dissolve nonmetallic solutes, mercury is extraordinarily "solvophobic".

The experimental techniques and apparatus for determining Henry's law constants at 15, 25, and 40 °C, upon which these results are based, have been described previously.[5] The vapor pressure of FS was unmeasurably low with our apparatus, and linear van't Hoff plots were obtained.

Acknowledgment. This work was supported by NIH Grant No. AM-16143-07 to D.F.E. and a NIH Fellowship to G.W.S.

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(5) Arnett, E. M.; Chawla, B. *J. Am. Chem. Soc.* **1979**, *101*, 7141. Pressure measurements were made to the nearest ±0.1 mm by using a Texas Instruments Co. Bourdon gage positioned immediately below a bath, thermostated to ±0.001 °C, in which the entire Henry's law apparatus was immersed. The purity of the gases was >99.9% and they were allowed to equilibrate with the stirred container of FS for at least an hour after constant pressure was achieved.

Book Reviews

Statistical Mechanics of the Liquid Surface. By Clive A. Croxton. John Wiley & Sons, Somerset, N.J. 1980. xxii + 345 pp. $75.00.

With the great progress that has been made in the statistical-mechanical theory of bulk fluids, it is only natural to attempt to apply these same theoretical ideas to the treatment of fluid–fluid interfaces. The appearance of an interface introduces the grave complication that the system is no longer, in the average, translationally isotropic, so that, e.g., the radial distribution function $g(r_1,r_2)$ becomes a function of position. While this question was explored by Fowler and Kirkwood and Buff (indeed, its thermodynamic aspects were anticipated by Gibbs), Croxton makes clear that we have not reached a final theory of the liquid surface. Indeed, as the author makes clear, there is not yet universal agreement to what qualitative features characterize molecular distributions near an interface. Perhaps one obtains a quasi-regular layering of the superficial molecules; perhaps capillary waves are a necessary part of the description of the surface, but neither of these results is at all certain.

Croxton succeeds in communicating the excitement of a still-evolving part of science. After an introduction to classical statistical mechanics, with especial reference to interfaces, results for different types of liquids are dealt with. Nonelectrolyte fluids, liquid metals, liquid helium, and liquid water rate their own chapters, as do the more difficult liquid crystal and polymer-at-interface systems. Molecular dynamics and Monte-Carlo calculations have greatly advanced the theoretical understanding of bulk fluids; computer calculations on explicitly finite systems are more ambiguous. Theoretical material on surfaces of electrolyte solutions and of systems near critical points has deliberately been omitted. While this is a true monograph, the four-hundred references extend up through 1979. The author's critical and interpretational comments on the literature are those of one who has read and understood the papers and not those of one who has skimmed the abstracts. In summary, this is a highly literate volume which belongs in the personal library of every researcher who is interested in the field.

George D. J. Phillies, *The University of Michigan*