The rates of ethanolysis, acetolysis, and formolysis of 2-cyclopropylethyl brosylate and isoamyl brosylate are virtually identical, indicating little or no rate enhancement by cyclopropane.[6] The apparent m value[7] (calculated from the rates in formic and acetic acids) for 2-cyclopropylethyl brosylate is 0.34, and for isoamyl brosylate $m = 0.33$ at 75° (ethyl tosylate has $m = 0.37$ at 75°[7]). The insensitivity of the relative rates of cyclopropylethyl and isoamyl brosylates to changes in solvent ionizing power and solvent nucleophilicity suggests that both compounds solvolyze by the same mechanism.[8] The apparent m value is typical for primary arenesulfonates,[7] and it is probable that the transition states for both of these reactions involve a large degree of nucleophilic assistance by solvent (high N character[9]).

Formolysis product analyses (0.13 M brosylate, 0.14 M sodium formate) were determined from the crude formate ester mixtures by gas chromatography. Preliminary analyses at ten half-lives of solvolysis indicate that approximately 75% of the product is 1,3-pentanediol diformate (identified by nmr spectra and comparison with an authentic sample) and that less than 15% cyclopentyl formate is formed.[2f,10] An nmr spectrum of the formolysis reaction mixture using the same concentrations as reported[2f] shows that at least 80% of the cyclopropane hydrogens are retained at 75% reaction, indicating that the products are largely determined by ring opening of 2-cyclopropylethyl formate.[11] The maximum extent of rearrangement to cyclopentyl formate, etc.,[2f,10] is therefore 25% or less. The similar kinetic behavior of II and III and the formation of cyclopropylethyl formate as the predominant kinetic product indicate that participation by cyclopropane is relatively unimportant in this system.[12]

Cyclopropane is thus a less effective neighboring group than an olefin (allylcarbinyl brosylate is seven times more reactive than n-butyl brosylate[8]).[13] However, in the norbornyl system, I, cyclopropane is 10^3 times more effective than a double bond. It is concluded that either (a) the norbornyl system is strained, and the apparent rate enhancement reflects the difference in strain of I and the corresponding olefin, or that (b) the geometrical requirements for effective cyclopropane orbital overlap with a carbonium ion center are more stringent than the requirements for double bond participation.[16,17] If the cyclopropane-ring bonds are considered to be bent orbitals with a high degree of p character, these orbitals are in effect turned in toward each other on the cyclopropane ring and are therefore less available for overlap with a nearby center than are the orbitals of a double bond. These hypotheses are currently being tested further.

[6] The rates could not be determined in trifluoroacetic acid buffered with sodium trifluoroacetate as the cyclopropane protons in the nmr spectrum disappear completely before 10% solvolysis occurs.

[7] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[8] K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

[9] S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[10] Sauers and Ubersax[2f] isolated (in relative yields) 2-cyclopropylethanol (35%), cyclopentanol (36%), methylallylcarbinol (12%), and crotylcarbinol (17%) after $LiAlH_4$ reduction (aqueous work-up) of the crude formate esters obtained from formolysis (0.33 M brosylate, 0.71 M sodium formate) after ten half-lives.

[11] 2-Cyclopropylethanol in buffered formic acid gives predominantly 1,3-pentanediol diformate.

[12] M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968), have observed a rate enhancement in the 2-cyclopropylethyl system when methyl groups are substituted on the cyclopropane ring. We are grateful to Professor Dewar for sending us his manuscript prior to publication.

[13] Cyclopropane is also less effective than a double bond in the related neopentyl system. Acetolysis of 2-cyclopropyl-2-methylpropyl brosylate is eight times faster than the isopropyl analog[14] at 74.6°, whereas acetolysis of 2,2-dimethyl-3-butenyl brosylate is 95 times faster than its saturated analog.[15] Complete details will be published later.

[14] E. N. McElrath, R. M. Fritz, C. Brown, C. Y. Leftall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).

[15] R. S. Bly and R. T. Swindell, *ibid.*, **30**, 10 (1965).

[16] Nonbonded repulsive interaction of hydrogens on a cyclopropane ring with hydrogens attached to a carbonium ion center in the transition state for participation has recently been invoked[17] to explain the lack of rate enhancement by cyclopropane in a related system. Although the geometry may be different in the cyclopropylethyl system (the stereochemistry of cyclopropane participation is unknown), nonbonded interactions may, in part, prevent cyclopropane assistance in the transition state.

[17] G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968).

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Nuclear Magnetic Resonance Study of Alkali Ion Solvation

Sir:

In recent years spectroscopic techniques have been frequently applied to the studies of ionic solvation in aqueous solutions and in nonaqueous solvents. Far-infrared spectroscopy has been used for the investigation of alkali metal ion solvation in tetrahydrofuran[1,2] and in dimethyl sulfoxide.[3] While this technique is very useful for numerous nonaqueous systems, it is limited by the transparency of the solvents in the investigated spectral region, as well as by the solubilities of the inorganic salts.

A useful extension of our studies of solvation appears to be in the application of nmr spectroscopy. This technique has been widely used for the studies of solvation of, primarily transition metal ions in various solvents and has been recently reviewed in the literature.[4]

While our investigation was in progress, a communication by Schaschel and Day[5] appeared which reported similar work but in a different nonaqueous system. We wish to report here studies on the solvation of lithium, ammonium, and sodium salts by dimethyl sulfoxide.

All salts were dried under vacuum to constant weight before use. Dimethyl sulfoxide was purified first by vacuum distillation over granulated barium oxide, followed by repeated fractional crystallization. Physical properties of purified DMSO agreed well with the literature values. 1-Pentanol was kept over anhydrous

[1] W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966).

[2] (a) W. F. Edgell, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. R149; (b) W. F. Edgell, J. Lyford, and J. Fisher, Abstracts 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, No. S136; (c) W. F. Edgell, personal communication.

[3] B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967).

[4] J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

[5] E. Schaschel and M. C. Day, *J. Am. Chem. Soc.*, **90**, 503 (1968).

calcium sulfate and then slowly distilled. The middle fraction, bp 138°, contained less than 0.01% water as determined by Karl Fischer titration.

Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer operating at 37°. All measurements were made with tetramethylsilane as an internal standard.

The technique employed was a classical mole-ratio study in which the concentration of the alkali salt was held constant and the DMSO concentration was varied over a wide range. The shift of the DMSO proton signal was measured in each solution. In order for a study of this type to be meaningful, three conditions must be obeyed. An inert solvent must be available which will dissolve all solution components, a measurable parameter must exist which is a function of solvate concentration, and the formation constant of the solvate must be sufficiently large so that a limiting value of the parameter may be obtained. In this case the parameter was the proton nmr signal of a DMSO molecule. Its position in the nmr spectrum is dependent on whether or not it is included in the solvation shell of an ion, *e.g.*, coordination of DMSO to a cation will result in a decrease in electron density around the proton nuclei resulting in a downfield shift of their resonant frequency.

Unlike the somewhat unusual salt, sodium tetrabutylaluminate, chosen by Schaschel and Day,[5] typical alkali metal salts are not appreciably soluble in truly inert solvents such as the one chosen for their study, cyclohexane. Since such inert solvents did not dissolve appreciable amounts of common alkali metal salts, it is necessary to select a solvent with a minimal interaction toward DMSO and the alkali metal ions.

1-Pentanol represents a good compromise of the various requirements. It will appreciably dissolve alkali metal salts and, although it may hydrogen-bond to the DMSO, this interaction is much weaker than that between DMSO and a metal cation. Far-infrared spectral data[6] demonstrate that the interactions between alkali metal cations and alcohols are considerably weaker than those between the alkali cations and DMSO. Fortunately, the mole-ratio data obtained provides a built-in check of the "inertness" of the solvent and indicates that it is in fact sufficiently unreactive for the purposes of this investigation.

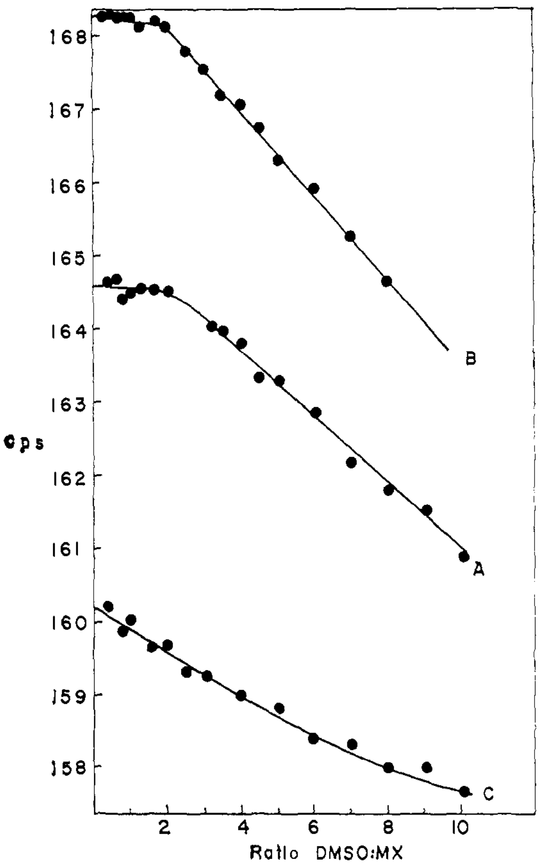

Figure 1. Chemical shift of DMSO protons *vs.* DMSO/MX mole ratio: A, $LiClO_4$; B, LiI; C, blank.

Figure 1 illustrates the results of our study. Curve A is a mole-ratio plot of the DMSO–$LiClO_4$ system where the lithium perchlorate concentration was kept at 0.704 *M*. Curve B is a similar plot for 0.70 *M* lithium iodide while curve C shows the magnitude of the shift induced by 1-pentanol over the same range of concentrations of DMSO but without the presence of Li^+ ion. The shift for pure DMSO is 156 cps downfield from TMS. Both with $LiClO_4$ and with LiI a clear break at the DMSO/Li^+ ratio of 2:1 is evident. It can be seen that although the alcohol has some effect on the proton signals of DMSO, it does not invalidate the indicated stoichiometry. It would be helpful to correct curves A and B for the DMSO–1-pentanol interaction, but to do this quantitatively we would need to know the formation constant of the Li^+–DMSO solvate. We can, however, make a reasonable approximation that while the DMSO/Li^+ ratio is $\leqslant 2:1$ essentially all of the DMSO present in solution is coordinated to the lithium ion. A subtraction of curve C from curves A or B would actually accentuate the break at 2:1 mole ratio.

At mole ratios greater than 2:1 some of the observed shift will be due to interaction with the alcohol so that a "correction" may be legitimately applied. As can be seen from Figure 1, the effect of such a correction would always be to enhance the break and in no way remove or decrease its clarity. We feel, therefore, that although 1-pentanol is not an ideal solvent for this type of study, it does not induce a sufficient error to invalidate the conclusions. It appears, therefore, that nmr studies of alkali metal ion solvation can be carried out even in solvents which are not totally inert toward the reacting components, provided that the interaction between the latter predominates.

Extending the same approach to ammonium thiocyanate (the most soluble of ammonium salts in our system), we find that the maximum solubility is only 0.50 *M*. The mole-ratio plot is shown in Figure 2 (curve A). It can be seen that there is a strong interaction with noticeable inflection at a mole ratio of 2:1. The decreased clarity of the break as compared to that obtained from Li^+ may be indicative of a lower force constant for the ammonium ion–DMSO interaction, or it may merely represent increased competition with the alcohol due to the lower concentrations of salt and DMSO employed.

The study of sodium iodide was limited to solutions with a maximum concentration of 0.22 *M*. At higher concentration a solid solvate DMSO–NaI precipitated.[6] The mole-ratio plot (Figure 2, curve B) differs sig-

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(6) B. W. Maxey and A. I. Popov, to be published.

nificantly from those for Li^+ or NH_4^+ in that its slope is much less, indicating a strong interaction even at mole ratios as high as 9:1. There seems to be some indication of a break at 1:1 mole ratio which would agree with the results of Schaschel and Day,[5] but in our system the break is much less pronounced and may not be significant. It seems reasonable to assume that while sodium ion is solvated by DMSO, in our system the stoichiometry is much less well defined than in the case of lithium. This observation is in accord with the usual behavior of Li^+ and Na^+ ions in solutions.

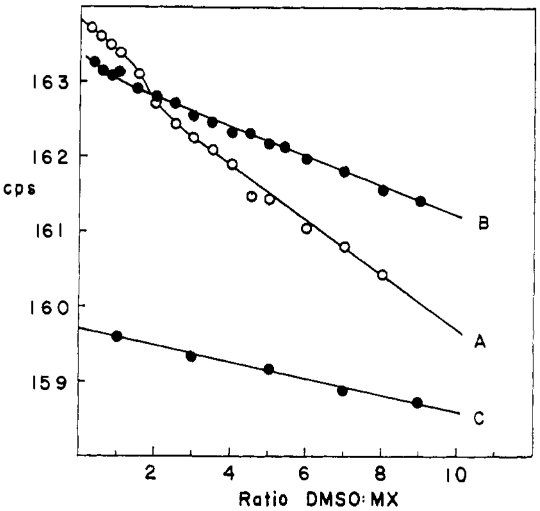

Figure 2. Chemical shift of DMSO protons *vs.* DMSO/MX mole ratio: A, NH_4SCN; B, NaI; C, blank.

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Tellurium in the Formal Electropositive Oxidation State One-Half in Acidic Chloride Media

Sir:

We are investigating the redox chemistry of tellurium in molten acidic chloride salt media and report here strong evidence that a polynuclear tellurium ion with the formal electropositive oxidation state one-half occurs in solution. We also have evidence for another polynuclear tellurium ion with an electropositive oxidation state but have not as yet established its formal oxidation number. Our experimental approach has been like that used to study the lower electropositive oxidation states of bismuth in molten salt solutions.[1]

Small amounts of elemental tellurium react with dilute solutions of $TeCl_4$ in the molten $AlCl_3$–NaCl eutectic to yield purple solutions having the spectrum shown in Figure 1. (In Figure 1 the absorbance has been corrected for overlap by the spectrum of $TeCl_4$ in the ultraviolet.) As long as the mole ratio $Te/TeCl_4$ is less than 7, the absorbance of these solutions is proportional to the amount of elemental tellurium added and only slightly affected by changing the temperature. When the $Te/TeCl_4$ mole ratio is increased to 7 and beyond, the absorbance at the principal band peak passes through a maximum and starts decreasing. The mole ratio of 7 at which this change occurs is independent of temperature and the initial $TeCl_4$ concentration over substantial ranges, and the estimated error in the value of this mole ratio is less than 1%.

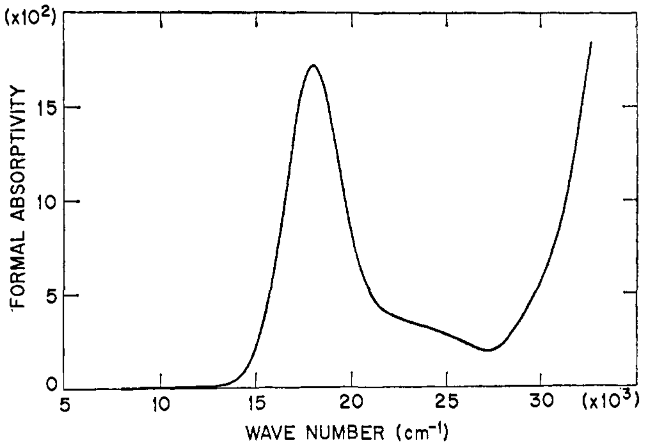

Figure 1. Adsorption spectrum of Te_{2n}^{n+} in the molten $AlCl_3$–NaCl eutectic.

We conclude that up to the mole ratio 7, only one entity is formed, and that it has the stoichiometry

$$7\text{Te} + \text{Te}^{4+} = \frac{4}{n}\text{Te}_{2n}^{n+}$$

At the mole ratio 7, virtually all of the tellurium is present as Te_{2n}^{n+}, and at higher mole ratios another tellurium entity is formed with a formal oxidation number between $^1/_2$ and 0.

We have not established the exact value of n in Te_{2n}^{n+}, but present data indicate it is not very different from 2, so that our best guess at the moment is that Te_4^{2+} is formed. This estimate of n is based on studies of two sets of inhomogeneous equilibria analogous to those previously described for bismuth.[1] An even value of n seems plausible because of the expectation that an even number of bonding electrons is involved. Our data give no information on whether or not this entity is bound in any way to chlorides or chloroaluminates.

As an interesting side experiment, we fused together Te, $TeCl_4$, and $AlCl_3$ in the mole ratio 7:1:4 and obtained a dark purple (almost black) product which we zone-melted without evidence of segregation; samples from different parts of the bar melted sharply at 228 ± 0.5° and gave the same X-ray powder patterns. Possibly this is a compound (stoichiometric composition Te_2AlCl_4) which contains Te_{2n}^{n+}.

It seems likely that Te_{2n}^{n+} is related to Se_4^{2+}, reported by Barr, Gillespie, Kapoor, and Malhotra[2] earlier this year.

Research continues on determining the value of n for Te_{2n}^{n+} in solution and the identity of the products

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[1] N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965); N. J. Bjerrum and G. P. Smith, *ibid.*, **3**, 165 (1967); N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967); H. L. Davis, N. J. Bjerrum, and G. P. Smith, *ibid.*, **6**, 1172 (1967); N. J. Bjerrum, H. L. Davis, and G. P. Smith, *ibid.*, **6**, 1603 (1967); N. J. Bjerrum and G. P. Smith, *ibid.*, **6**, 1968 (1967).

[2] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).