Solvent Effects in Organic Chemistry. XIV. Complexing of Sodium Ion by Various Common Solvents as Ligands in Acetone Solutions[1]

Sir:

The alkali and alkaline earth metals are of much greater importance to organometallic chemistry and biochemistry than all other metals. However, it is only quite recently that the coordination chemistry of their cations has begun to develop. Results available so far[2-4] indicate that such ion–ligand interactions are highly sensitive to the size and charge of the ion and the nature and shape of the ligand molecules. Therefore, a good quantitative comparison of typical ligands might pay high dividends in suggesting better systems to control organometallic reactions and better theories for understanding ion transport through membranes.[5-7] We present here preliminary measurements of an extensive systematic study of complexing between Na^+ and a wide variety of solvents as ligands at high dilution in acetone at 25°. Typically six increments of 10^{-3} mol of ligand are added to an excess (3×10^{-2} mol) of sodium tetraphenylboron in 200 ml of carefully dried acetone in a solution calorimeter.[2] For our purposes this salt is completely dissociated[8] under these conditions. We assume that the entire difference (ΔH_{obsd}) between the observed molar heat of solution of a ligand in pure, dry acetone and in the acetone solution of sodium tetraphenylboron is due to interaction between the ligand and the sodium ion.

These values do not actually represent the molar heat of formation of a 1:1 complex, since the complexing reaction is not driven completely to the right.

$$\mathrm{Na^+} + \text{ligand} \rightleftharpoons \text{complex} \tag{1}$$

Since

$$\Delta H_{\mathrm{obsd}} = [\text{complex}]\Delta H_{\mathrm{comp}} \tag{2}$$

and

$$[\text{complex}] = K_{\mathrm{comp}}[\mathrm{Na^+}][\text{ligand}] \tag{3}$$

the K_{comp} is needed for calculation of ΔH_{comp}. Equations 2 and 3 show that both K_{comp} and ΔH_{comp} can be determined from ΔH_{obsd} at different concentrations of Na^+ and ligand.

Such a treatment yields values for glyme ($\Delta G^\circ_{\mathrm{comp}} = +0.08$ kcal/mol, $\Delta H^\circ_{\mathrm{comp}} = -3.5$ kcal/mol, $\Delta S^\circ_{\mathrm{comp}} = -12.0$ eu) and for tetraglyme ($\Delta G^\circ_{\mathrm{comp}} = -2.53$ kcal/mol, $\Delta H^\circ_{\mathrm{comp}} = -6.0$ kcal/mol, $\Delta S^\circ_{\mathrm{comp}} = -11.7$ eu); note that $\Delta S^\circ_{\mathrm{comp}}$ is almost identical for these two quite different ethers.

Although we wish to emphasize that ΔH_{obsd} is not a direct measure of either ΔH_{comp} or the extent of complexing, we believe that it is a rough qualitative guide to the structural factors which contribute to sodium ion binding.

The preliminary results in Tables I, II, III, and IV suggest the following.

Table I

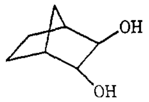
Compound	ΔH_{obsd}, kcal/mol
Acetone	0.00
Hydroxy Compounds	
Water	-0.52 ± 0.03
Methanol	-0.16 ± 0.01
Ethanol	-0.08 ± 0.02
$HOCH_2CH_2OH$	-0.92 ± 0.04
$CH_3OCH_2CH_2OH$	-0.69 ± 0.02
cis-1,2-Cyclohexanediol	-0.50 ± 0.07
trans-1,2-Cyclohexanediol	-0.47 ± 0.07
exo-2,3-Dihydroxynorbornane 	-0.25 ± 0.05
1,2-Propanediol	-0.73 ± 0.02
1,3-Propanediol	-0.20 ± 0.03
2,3-Butanediol	-0.52 ± 0.02
1,4-Butanediol	-0.05 ± 0.03
1,5-Pentanediol	-0.08 ± 0.02
1,3-Cyclohexanediol	-0.14 ± 0.09
1,4-Cyclohexanediol	-0.01 ± 0.10
1,2-Ethanedithiol	-0.02 ± 0.01

Table II. Ethers

Compound	ΔH_{obsd}, kcal/mol
Tetrahydrofuran	-0.08 ± 0.007
Methylal	-0.03 ± 0.008
$CH_3OCH_2CH_2OCH_3$ (glyme)	-0.45 ± 0.02
cis-1,2-Dimethoxycyclohexane	-0.22 ± 0.011
trans-1,2-Dimethoxycyclohexane	-0.11 ± 0.013
exo-2,3-Dimethoxynorbornane	-0.51 ± 0.01
1,2-Dimethoxypropane	-0.21 ± 0.012
Trimethoxymethane	-0.02 ± 0.01
1,2,3-Trimethoxypropane	-0.26 ± 0.01
1,2,3,4-Tetramethoxybutane (tetramethylerythritol)	-0.19 ± 0.03
1,2,3,4,5-Pentamethoxypentane (pentamethylarabinitol)	-0.52 ± 0.04
1,2,3,4,5,6-Hexamethoxyhexane (hexamethylmannitol)	-0.52 ± 0.02
$CH_3O(CH_2CH_2O)_2CH_3$ (diglyme)	-0.83 ± 0.03
$CH_3O(CH_2CH_2O)_3CH_3$ (triglyme)	-2.58 ± 0.05
$CH_3O(CH_2CH_2O)_4CH_3$ (tetraglyme)	-4.82 ± 0.06
$CH_3O(CH_2CH_2O)_5CH_3$ (pentaglyme)	-6.09 ± 0.08
Methyl α-D-tetramethylglucoside	-0.15 ± 0.011
Methyl β-D-tetramethylglucoside	-0.14 ± 0.03

(1) Water is an unusually good monodentate ligand for Na^+ even at high dilution in an inert medium.

(2) Compounds with two hydroxy, alkoxy, or amino groups on adjacent carbon atoms are markedly superior to those with other spacing between groups.

(3) The simple accumulation of methoxy groups on adjacent carbon atoms is not as effective as are ether oxygens interspersed at regular intervals between ethylene linkages as in the glyme series.[4] Our order of complexing closely parallels that observed by other workers.[4,9,10]

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(1) Supported by grants from the National Science Foundation (GP-31565X) and the Office of Saline Water (14-30-2570).

(2) See references in: E. M. Arnett and T. C. Moriarity, *J. Amer. Chem. Soc.*, **93**, 4908 (1971).

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(5) R. J. P. Williams, *Quart. Rev., Chem. Soc.*, **24**, 331 (1970).

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(9) H. E. Zaugg, *J. Amer. Chem. Soc.*, **83**, 837 (1961).

(10) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

Table III. Cyclic Ethers

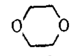
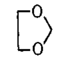
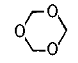
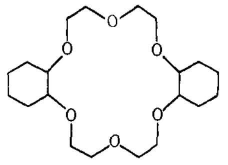
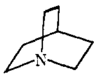
Compound	ΔH_{obsd}, kcal/mol
Tetrahydrofuran 	−0.08 ± 0.007
1,4-Dioxane 	−0.06 ± 0.003
1,3-Dioxolane 	−0.08 ± 0.003
Trioxane 	−0.04 ± 0.06
Triacetonemannitol	−0.21 ± 0.10
Dicyclohexyl-18-crown-6 ether 	−5.99 ± 0.36

Table IV. Amines

Compound	ΔH_{obsd}, kcal/mol
Primary amines react with system	
Diethylamine	−0.68 ± 0.03
Triethylamine	0 ± 0.02
Quinuclidine 	−0.26 ± 0.05
N,N,N′,N′-Tetramethyl-1,2-propanediamine	−0.71 ± 0.02
N,N,N′,N′-Tetramethylethylenediamine	−0.75 ± 0.01
Pyridine	−0.16 ± 0.004

(4) The cyclic polyethers show that the orientation of vicinal oxygen atoms in the proper conformation is important; note the low value for vicinal oxygens in 1,3-dioxolane.[9]

(5) Table V shows that by themselves acetate ester groups are very poor ligands for Na^{+} under our conditions, although an accumulation of them has some additive effect. However, comparison of glycerol diacetate with glycerol triacetate shows that the cooperative effect of a hydroxyl group and a vicinal acetate is superior to three vicinal acetates (in glycerol triacetate) or a lone hydroxyl group in ethanol. It is well known that completely acetylated cellulose is a poor reverse osmosis membrane material compared to the partially hydrolyzed polymer.[4,5] The data in Table V suggest that the hydrolyzed material might also complex cations better than the completely acetylated form. Comparison of acetylated glucose, maltose, and cellobiose suggests again that a cooperative effect between acetate and ether linkages could assist in binding sodium to cellulose acetate.

Table V. Esters

Compound	ΔH_{obsd}, kcal/mol
Ethyl acetate	−0.02 ± 0.006
Ethylene diacetate	0
Glycerol triacetate	−0.03 ± 0.016
Glycerol diacetate	−0.15 ± 0.005
Glucose pentaacetate	−0.014 ± 0.08
Maltose octaacetate	−0.60 ± 0.11
Cellobiose octaacetate	−0.62 ± 0.14

Table VI. Other Assorted Solvents with Ligand Groups

Compound	ΔH_{obsd}, kcal/mol
Acetonitrile	+0.06 ± 0.01
Dimethyl sulfoxide	−0.34 ± 0.01
N,N-Dimethylformamide	−0.23 ± 0.01
N,N-Dimethylacetamide	−0.30 ± 0.01
Hexamethylphosphoramide	−0.58 ± 0.02

The relatively high values for DMSO and the amides shown in Table VI accord with their use as dipolar aprotic solvents.[9]

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Received March 20, 1972

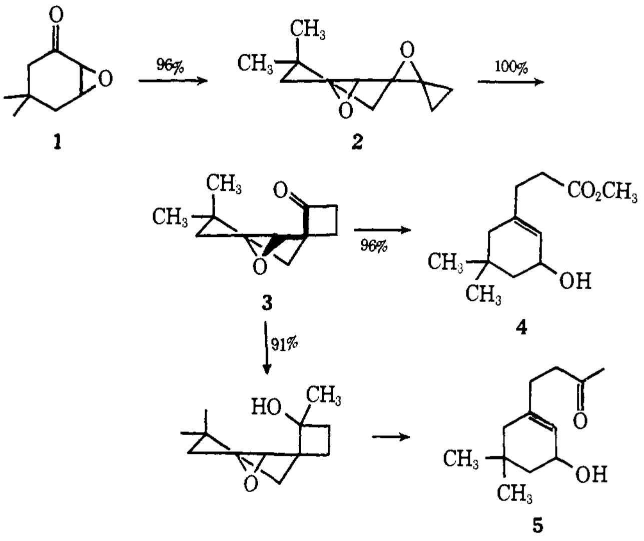
New Synthetic Reactions. Secoalkylation

Sir:

The Michael reaction constitutes one of the most useful synthetic reactions.[1] In essence, it involves the incorporation of alkyl groups as $C^{+}CC(=O)$ fragments. We wish to report a new alkylation reaction in which the electronic sense of the Michael acceptor is reversed, that is, introduction of alkyl groups utilizing $C^{-}CC(=O)$ as the synthetic unit. Application of this method led to a new annelation procedure complementary to the widely employed Robinson procedure.

Scheme I outlines the approach. Spiroannelation of α,β-epoxy ketone **1**[2] with diphenylsulfonium cyclopropylide, generated reversibly from potassium hydroxide and diphenylcyclopropylsulfonium fluoroborate,[3]

Scheme I. Secoalkylation of 2,3-Epoxy-5,5-dimethylcyclohexanone



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(1) For general discussions see E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, 10, 179 (1959); H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972, pp 595–623.

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