Spectroscopic Studies of Ion Solvation. Interaction of Alkali and Alkaline Earth Cations and Protons with Electron Donors

Sir:

Studies[1] on the vapor phase complexes of alkali metal ions, protons, and other cations with electron donor molecules (ligands) such as H_2O, NH_3, and CH_3CN have provided valuable information on the binding of cations to ligands and have enabled us to examine models for the primary solvation sphere of cations in solution.[2] The low-frequency vibration bands characteristic of alkali and alkaline earth metal ions in solutions of polar solvents like ketones and amides have provided probes to study the primary solvation of cations.[3,4] We have for the first time employed electronic transitions of the coordinating ligands to study the solvation of group 1A and 2A cations. Electronic spectroscopy provides a direct probe to investigate the binding of cations to ligands, as well as the nature of equilibria involving cations coordinated by the ligand and solvent molecules. We have extended these studies to examine the interaction of protons with ligands.

Alkali and alkaline earth metal ions cause marked shifts of the n-π^* and π-π^* transitions[5] of ligands such as carbonyl and thiocarbonyl compounds, the magnitude of the shift depending on the cation and solvent. Among the group 1A cations, Li^+ causes the maximum spectral perturbation, while among group 2A cations, Ca^{2+} shows the maximum effect. Spectra of ligands like acetone, cyclopentanone, and benzamide recorded with varying concentrations of cations show progressive band shifts with increasing cation concentration and the presence of an isosbestic point (Figure 1). Thus, benzamide shows the isosbestic point at 227 nm with Li^+, Na^+, Mg^{2+}, Ca^{2+} in aqueous solution and at 225 nm in THF and methanol; cyclopentanone shows the isosbestic point at 282 nm with Li^+ in aqueous solution.

The isosbestic behavior and the spectral shifts (Figure 1) indicate equilibria[6,7] involving step-wise addition of ligands (L)[8] as follows.

$$M^{z+}(S)_m + L \rightleftharpoons M^{z+}S_{m-1}L + S(\text{solvent}) \quad (1)$$

$$M^{z+}S_{m-1}L + L \rightleftharpoons M^{z+}S_{m-2}L_2 + S \text{ etc} \quad (2)$$

$$M^{z+}SL_{n-1} + L \rightleftharpoons M^{z+}L_n + S \quad (3)$$

$$M^{z+} + nL \rightleftharpoons M^{z+}L_n \quad (4)$$

Equilibria 1 and 2 would be predominant at concentrations at which the ions are nearly fully solvated (up to 8 *M* in Li^+). Then it appears that further ligand binding occurs causing more pronounced shifts of the ligand spectrum. This would still retain the isosbestic point provided the spectrum of the ligand bound to the ion remains nearly the same in the presence or absence of a second lignad (or solvent) on the ion. At very high cation concentrations, the spectral shifts become more marked since all the solvent molecules would be involved in solvation and equilibria 3 and 4 would become predominant. Thus, the shifts in the case of Li^+ become very large above 8 *M*,[7] above 8 *M*, lithium salts are reported to cause large heat effects and perturbations of ligand vibrations in the case of amides.[9,10] The cation-induced spectral shifts vary with the solvent in the order, H_2O < CH_3OH < THF; this is probably related to the relative strengths of binding of the solvent and ligand molecules to the cations.

Acids like H_2SO_4 produce more marked spectral shifts of ligand absorption bands than alkali and alkaline earth metal ions (Figure 1). Single isosbestic points (281 nm for cyclopentanone and 231 nm for benzamide) are found at low to moderate concentrations of the acid[11] (<50% H_2SO_4) indicating the presence of an equilibrium similar to (1). The similarity of the spectral behavior of ligands in acid solutions and in the presence of group 1A and 2A cations suggests that protons can be treated just like other cations as far as the solvation equilibria are concerned. Spectral shifts become appreciable beyond 4.5 *M* H_2SO_4 at which composition the molar ratio of proton to water would be in the region 1:4–1:6. Coordination of protons by the ligands becomes significant above this acid concentration. At very high acid concentrations (>50% H_2SO_4), however, protonation occurs giving rise to carbonium ions and other products.

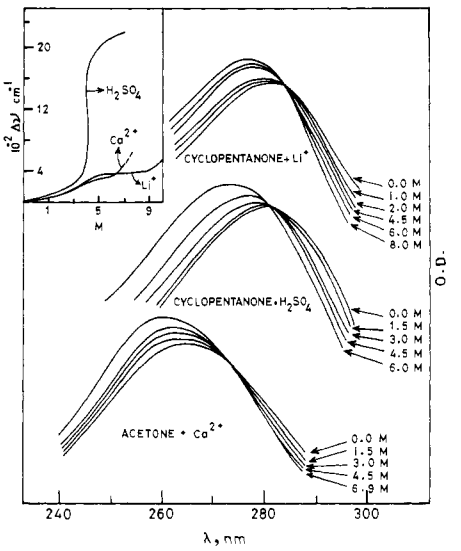

Figure 1. Effect of group 1A and 2A cations and protons on the n-π^* bands of cyclopentanone and acetone ($\sim 2.5 \times 10^{-2}$ *M*) in aqueous solution. In the insert the blue shifts of the n-π^* band of acetone are plotted against the concentration of cations or acid.

The spectral shifts which reflect the binding energies of the ligands are generally in the order, $H^+ > Li^+ \approx Ca^{2+} \geq Mg^{2+} > Na^+ > K^+$, a trend expected for neutral donor ligands.[8] Such an order is also predicted by molecular orbital calculations. Of all the cations, protons have the highest binding energy with ligands and the calculated binding energies vary in the order $HCONH_2 > CH_3OCH_3 > H_2O > H_2CO$. This order agrees well with the recently reported proton affinities.[12]

Interaction of amides with group 1A and 2A cations as well as protons is worthy of special mention in view of their importance to biology. Studies of the far-uv spectra of simple amides like DMF and of the near-uv spectrum of benzamide show that Li^+ and Ca^{2+} bind very strongly to the carbonyl group of the peptide bond. Isosbestic points due to equilibria 1–4 are clearly seen with amides as well. Such equilibria are also evidenced in moderately concentrated acid solutions (<50% H_2SO_4). The isosbestic point of benzamide in H_2SO_4 solutions (<50%) at 231 nm is distinctly different from the one at 247 nm reported by Liler[13] in highly concentrated H_2SO_4 solutions (>60%). The isosbestic point found by us at 231 nm appears to be due to equilibria 1–4. The spectral data are consistent with oxygen protonation[14] even in moderated concentrated acid solutions rather than nitrogen protonation.[13]

These studies serve to illustrate the usefulness of the study of the electronic spectra of ligands bound to group 1A and 2A cations or protons in understanding the mechanism of ion solvation. We are extending these studies to other systems and intend to publish a detailed report at a later stage.

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(6) In the case of Li^+, $n = 4$ with ligands like acetone, amides, amines, and so on; $m = 6$ if S is H_2O. It is likely that $n = 6$ with Ca^{2+} and Mg^{2+}. Well-defined crystalline 1:4 complexes of amides with Li^+, Na^+, and K^+ and 1:6 complexes with Mg^{2+} have indeed been characterized.[4]
(7) Around 8 *M* Li^+, the molar ratio of Li^+ to H_2O would be around 1:6. In the case of Ca^{2+} and Mg^{2+}, the shifts become appreciable beyond 6 *M* which corresponds to a molar ratio of M^{2+} to H_2O of 1:8.
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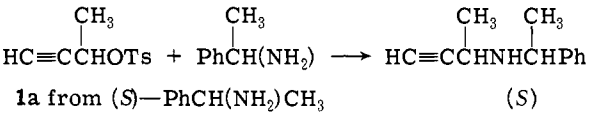
Synthesis of Chiral Allenic Alcohols and Nuclear Magnetic Resonance Determination of Their Enantiomeric Purities Using a Chiral Lanthanide Shift Reagent[1]

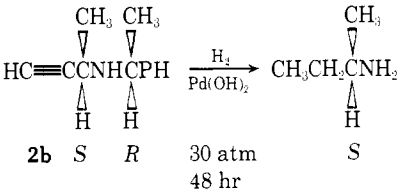
Sir:

A remarkable feature of the present knowledge of chiral allenes is the paucity of reliable information concerning their enantiomeric purities.[2] In the present paper we report on a general synthetic method for the preparation of chiral α- and β-allenic alcohols starting with a resolved acetylenic amine of the type **2** and the determination of the enantiomeric composition of these allenic alcohols using ^1H NMR spectroscopy in combination with the chiral lanthanide shift reagent tris(3-heptafluorobutyryl-*d*-camphorato)europium(III),[3] Eu(hfbc)$_3$. Prior to our report, chiral β-allenic alcohols have been accessible through Landor's method of asymmetric synthesis in which a 5-alkyl-pent-2-en-4-yn-1-ol is reduced with a chiral lithium aluminum hydride complex.[4] However, no similar method was available for obtaining chiral α-allenic alcohols.

Our synthetic approach rests upon a known procedure for the preparation of racemic α-allenic alcohols[5] and a new preparative method for racemic β-allenic alcohols.[6] A mixture of diastereomeric amines (**1**) was obtained from the separate reactions of (*S*)-(−)- and (*R*)-(+)-α-methylbenzylamine with the *p*-toluenesulfonate of *dl*-3-butyn-2-ol[7] (in MeOH, 3 days at 20°, yield 70%, bp 97–102°, 12 Torr). Two recrystallizations of the hydrochlorides from chloroform gave pure **2a** and **2b** in 75% yield (hydrochloride of **2a,** mp 217–218°, **2b,** mp 217°). The progress of the separations of the diastereomers in these mixtures could be followed from the ^1H NMR spectra[8] of the free amines. The propargylic protons gave rise to two quartets at δ 3.12 and 3.55 ppm with fine splitting caused by the acetylenic proton. The major signals (δ 3.55 ppm) were from the enantiomers having the least soluble hydrochlorides, i.e., **2a** and **2b.** The diastereomers were also separated by gas chromatography of the free amines. (OV-25 column, **2a** and **2b** had retention times of 8 min and their diastereomers 6.8 min.)



The catalytic reduction of **2b,** made from (*R*)-(+)-α-methylbenzylamine, gave (*S*)-(+)-2-aminobutane as the



levo hydrochloride,[9] $[\alpha]^{20}D$ −3° (*c* 5, EtOH) and the dextro benzamide,[10] $[\alpha]^{22}D$ +32.9° (*c* 5.19, EtOH). Therefore **2b** must have the *S* configuration at the propargylic carbon atom and **2a** the *R* configuration as shown in Scheme I.

Both enantiomers **2a** and **2b** were converted to their lithium alkynides and added to ethylene oxide (1.5 equiv of $LiNH_2$/2 equiv of ethylene oxide, −40°, 30 hr). The amino alcohols **3a** and **3b** were purified on a silica column (ether; yield 25 and 30% of oily **3a** and **3b,** respectively). The amine **2a** was also added to acetone via its Grignard derivative (2 equiv of EtMgBr was necessary for an acceptable yield) to give the amino alcohol **6** in 50% crude yield. The pure β-acetylenic amino alcohols **3a** and **3b** and the crude α-acetylenic amino alcohol **6** were quaternized with an excess of methyl iodide (acetone, K_2CO_3, 20°, 15 hr). The quaternary salts (**4a, 4b,** and **7**) were allowed to react with lithium aluminum hydride in THF; **4a** gave rise to (*S*)-(+)-3,4-hexadien-1-ol (**5a**),[4a] $[\alpha]^{22}D$ +12.0° (*c* 2.75, MeOH) approximately 30% yield from **3a; 4b** gave the levorotatory enantiomer **5b,**[4b] $[\alpha]^{22}D$ −11° (*c* 0.76, MeOH). The absolute configurations of **5a** and **5b** have been assigned by Landor[4] based on the stereospecific Claisen rearrangement of a chiral 1-butyn-3-yl vinyl ether and the Lowe-Brewster rule.[11]

From **7** there was obtained (+)-2-methyl-3,4-hexadien-2-ol (**8**), $[\alpha]^{22}D$ +32.9° (*c* 9.4, MeOH), in an overall yield of ca. 30% from **6** as determined by GLC. According to the Lowe-Brewster rule,[11] the dextrorotatory α-allenic alcohol **8** should be assigned the (*S*) configuration, which is in accord with the reasonable assumption that the stereochemical course of reactions **4a** → **5a** and **7** → **8** correspond. Assuming these assignments to be correct, since amine **3a** of known *R* configuration at the propargylic carbon gives the