1,4,7,10-Tetraoxacyclododecane. An Aprotic Solvent for the Alkali Metals

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Summary Sodium was found to dissolve in 1,4,7,10-tetraoxacyclododecane forming stable and highly concentrated blue metal anion solutions in the presence of added lithium chloride, while potassium, rubidium, and caesium form metastable blue solutions.

We report preliminary observations concerning the dissolution and some properties of alkali metals in 1,4,7,10-tetraoxacyclododecane (12-crown-4). We found that sodium, potassium, rubidium, and caesium dissolve in 12-crown-4 to give blue solutions with metal-dependent stability. Studies of the unique physical and chemical properties of metal solutions[1] formed upon the dissolution of the active metals in such solvents as ammonia,[1,2] hexamethylphosphoramide (HMPA),[3] and various amines[4] and ethers[5] are currently, and have been, the subject of a great deal of interest. So far no ether-type solvent (without the aid of a metal ion complexing agent)[1a] has been reported to dissolve sodium to the extent found in the present study.

The 12-crown-4 used in this study was obtained from Aldrich Chemical Company, Inc. and was further purified by at least two high-vacuum distillations from sodium metal. All metal solutions were prepared in borosilicate glass systems using high vacuum techniques (*ca.* 5×10^{-6} Torr). A Cary 17 recording spectrophotometer was used to record optical spectra using borosilicate cells of 1.0 mm nominal path length.

When liquid 12-crown-4 was poured on previously distilled sodium metal, a dark blue solution formed immediately upon contact at room temperature. When the blue solution was removed from contact with the metal, the blue colour persisted for several days. The optical absorption spectrum of the blue sodium solution showed only the presence of a peak located in the visible region at *ca.* 660 ± 20 nm. This band is characteristic of the metal anion, Na^-. The solubility of sodium in 12-crown-4 was determined to be at least 1.6×10^{-2} M at room temperature. In this experiment, degassed water was added to the blue solution (reaction complete upon mixing) and the evolved hydrogen was measured.

A dark blue solution formed immediately upon contact of 12-crown-4 with K at room temperature. The optical absorption spectrum of the K solution showed two maxima: one peak located in the visible region at *ca.* 890 ± 20 nm and another broad band at 1800 ± 200 nm. The former band can be assigned to the metal anion, K^-, while the latter can be assigned to solvated electrons. The potassium solutions appeared not to be as stable as the sodium solutions. Rubidium and caesium dissolved in 12-crown-4 to yield transient blue solutions, the colour of which was too short-lived for the optical spectra to be obtained at room temperature.

The markedly different stabilities observed for the different metal solutions were not totally unexpected since metal-dependent stabilities have been observed in other solvents.[1,3-5] It should be noted that stability of the metal solutions in the present study increases with decreasing anion size or increasing solvation.

The equilibrium for the sodium–12-crown-4 solution can be described by equation (1). Addition of LiCl to a sodium

$$2Na(s) \rightleftharpoons Na^+ + Na^- \qquad (1)$$

metal solution resulted in a marked increase in the Na^- concentration. Optical data indicated that the Na^- concentrations in these solutions were much greater than 0·1 M. After addition of the LiCl, a precipitate, presumedly NaCl, was observed. This experiment is consistent with 12-crown-4 complexing Li^+ and shifting the equilibrium of equation (1) to the right by removing Na^+ ion *via* the precipitation.

Metal anions are expected to be strong bases by virtue of their electron pair and their resulting chemical behaviour should resemble that of the hydride ion. As stated above, Na^- reacts with water upon mixing and the reaction can be depicted by equation (2). Also, Na^- in 12-crown-4 reacted

$$Na^+Na^- + 2H_2O \rightarrow H_2 + 2NaOH \qquad (2)$$

with triphenylmethane upon mixing to give a dark red solution. The probable reaction can be written as in equation (3). It should be noted that triphenylmethane

$$2Ph_3CH + Na^+Na^- \rightarrow 2Ph_3C^- + 2Na^+ + H_2 \qquad (3)$$

does not react with dilute solutions of sodium in ammonia[6] which consist predominantly of solvated electrons[2] and very little, if any, Na^-. We also added NH_3 to a solution of Na^- in 12-crown-4 and found that ammonia readily bleached the blue solution. Hydrogen and NH_2^- (determined with the aid of Nessler's reagent) were found to be products of this reaction and suggest that the net reaction is that shown in equation (4). Equation (4) shows that ammonia

$$Na^+Na^- + 2NH_3 \rightarrow 2NaNH_2 + H_2 \qquad (4)$$

acts as an acid in liquid 12-crown-4 and equations (2), (3), and (4) demonstrate that Na^- is indeed a strong base. In order to demonstrate the reducing power[7] of the Na^-, 0·242 mmol of benzene was added to 12·76 ml of a blue sodium–12-crown-4 solution in contact with an excess of the metal. After mixing for 2 h, 10·79 mmol of ethyl alcohol was added. Gas chromatographic analysis after separation showed that 60% of the benzene was converted into the cyclohexa-1,4-diene.

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