

Spectrophotometric Detection of Ion Pair—Crown Ether Complexes of Alkali Picrates

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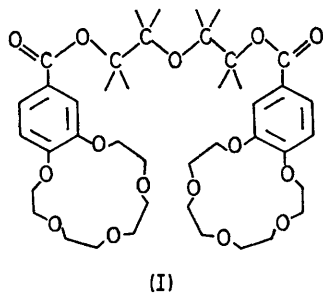
Summary Bathochromic shifts observed in the optical spectra of alkali picrates in tetrahydrofuran on addition of crown ethers and bis-(crown ethers) can be rationalized in terms of tight and loose ion pair-crown ether complexes.

WE have found that the optical spectra of picrate salts in low polarity media are sensitive to the interionic distance of the ion pair. In studying the structure of ion-pair solvation complexes the picrates have the advantage over previously used salts such as carbanions and radical anions^{1,2} of being

air and moisture stable, and permitting the use of a much wider range of solvents and cation chelating agents.

The usefulness of this spectrophotometric method was demonstrated by adding crown ethers³ to a tetrahydrofuran solution of sodium or potassium picrate. Complex formation constants were calculated from the overlapping spectra of the different ion-pair species. Conductance measurements showed that under our experimental conditions the fraction of free ions was always less than 0.1. Crown ethers used were dimethyldibenzo-18-crown-6, monobenzo-15-crown-5 (15C5) and a bis-crown ether of 15C5 (I).

Results show that in THF the alkali picrates are tight ion pairs with absorption maxima at 351 nm (Na), 357 nm (K), and 362 nm (Cs). Addition of crown ether causes a bathochromic shift. For example, on addition of dimethyldibenzo-18-crown-6 to a 10^{-3} M solution of sodium picrate a separated 1:1 ion pair complex is formed with an absorption maximum at 378 nm. The formation constant for the



complex is $4 \times 10^4 \text{ M}^{-1}$, much lower than found with the more delocalized fluorenyl carbanion.⁴ Addition of 15C5 to sodium picrate produces a crown co-ordinated tight ion-pair complex, $\text{Pi}^-\text{Na}^+\text{15C5}$, with λ_m at 357 nm. No change in this maximum is observed when a large excess of 15C5 is added. However, when the same crown ether is

added to potassium picrate the initially formed 1:1 tight ion pair complex (λ_m 362 nm) is converted into a 2:1 crown separated ion pair with λ_{max} at 381 nm. Isosbestic points appear at 360 nm and at 366 nm. The formation constant of the 1:1 complex is about 10^4 M^{-1} , while the equilibrium constant for the reaction $\text{Pi}^-\text{K}^+\text{15C5} + \text{15C5} \rightleftharpoons \text{Pi}^-\text{15C5}\text{K}^+\text{15C5}$ is $2.0 \times 10^2 \text{ M}$, about ten times lower than found for fluorenyl potassium.⁴ A 2:1 complex of 15C5 with K^+ has also been reported for other potassium salts, both in solution and in the solid state.^{5,6}

The observation of a 2:1 crown complex induced us to synthesize (I) from the acid chloride of 4'-carboxybenzo-15-crown-5 and diethylene glycol. On mixing this bis-(crown ether) with potassium picrate only one new species is formed with λ_m at 381 nm. The formation constant of this loose ion pair with the K^+ ion sandwiched in between the two 15C5 moieties was found to be $1.7 \times 10^5 \text{ M}^{-1}$. We are presently determining the effect of structure and length of the chain of this crown ether on the formation constant of the complex.

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