Electron Spin Resonance Study of an Unusually Tight Ion-pair

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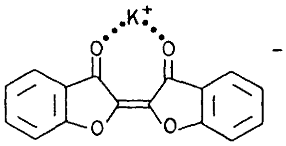
Summary The existence of an unusually tight ion-pair formed between potassium ion and oxindigo anion radical is demonstrated by e.s.r. spectroscopy.

ELECTRON spin resonance spectra of anion radicals generated by the reduction of the neutral molecules with alkali metals often exhibit additional hyperfine splittings as a result of the interaction between the unpaired electron and the metal nucleus.[1] This evidence is taken to confirm the existence of an ion-pair although its exact structure (*i.e.*, whether it is a solvent-separated or tight ion-pair) cannot always be known with certainty. For a given anion radical, the metal splitting depends on the co-ordinating ability of the solvent, the dielectric constant of the medium and temperature.

We report here an unusually tight ion-pair formed by the reduction of *trans*-oxindigo with potassium in ethereal solvents. The analysis of the e.s.r. spectrum of oxindigo anion radical was first reported by Heineken, *et al.*;[2] however, these workers did not investigate the dependence of metal splitting on temperature or solvent. As the Figure shows, the potassium hyperfine splitting remains virtually unchanged over a temperature range of 80 K. More surprisingly, the *same* splitting is observed in three solvents of different dielectric constants: 1,2-dimethoxyethane, tetrahydrofuran, and dioxan. To our knowledge, this system represents the tightest ion-pair reported in the literature.

It is tempting to postulate the following *cis* configuration (**1**) for the ion-pair, although direct evidence is lacking. An alternative structure is with the potassium ion above the plane of the oxindigo. This arrangement would better facilitate the interaction of the ion-pair with the solvent molecules and still retain the same symmetry. No metal splittings were observed when thioindigo and selenoindigo were reduced with potassium in the same solvents.



(1)

An attempt was made to perturb the ion-pair structure by the addition of a small amount of ethanol.[3] However, the radical anions were unstable in the presence of ethanol and rapidly decomposed to form diamagnetic species.

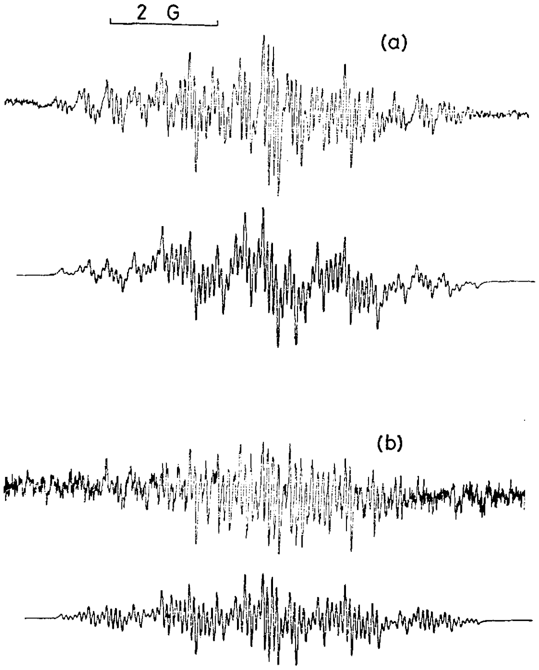


FIGURE. Experimental (lower trace) and calculated (upper trace) e.s.r. spectra of oxindigo anion radical generated by reduction with potassium in 1,2-dimethoxyethane at (a) room temperature and (b) 213 K. The hyperfine splitting constants of protons (0·34, 0·51, 1·36, and 1·53 G) and potassium (0·086 G) remain constant over the temperature range.

The potassium metal splitting can be removed by treating the ion-pair with the crown ether 2,2,2-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) without any change in the proton hyperfine splittings. However, the free anion radical is unstable and decomposes within a few minutes. From the known binding constant of K^+ 2,2,2-cryptate,[4] we can set an upper limit of 20,000 for the binding constant for the potassium-oxindigo ion-pair.

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