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Preliminary communication

THE NATURE OF THE COUNTERION IN BUTYLLITHIUM/POTASSIUM t-ALKOXIDE REACTION MIXTURES: AN ESR STUDY

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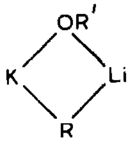
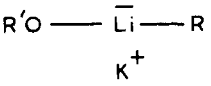
Summary

The ESR spectrum of the cycloheptatrienyl radical dianion, which is in equilibrium with the corresponding trianion generated by the reaction of cycloheptene with a 1/1 n-butyllithium/potassium ^{t}amyloxide mixture, is characteristic of the potassium rather than the lithium salt.

Mixtures of alkyllithiums with potassium tertiary alkoxides (diversely known as LICKOR reagents, Lochmann's base or Schlosser's base) were first used to synthesise potassium compounds [1], but later recognised [2—5] as very strong bases which are far more reactive than conventional butyllithium: electron donor complexes. Most of this work [1,6] indicates that potassium compounds are produced by such bases, although quench products with acetone behave like the lithium compounds [7]. Recent NMR investigations [8] also suggest that the counterion is potassium. Schlosser [2,4] has, however, pointed out that freshly prepared $LiR/KO^{t}R'$ mixtures are stronger bases than the corresponding KR compounds, implicating an active intermediate which may be a complex [4,9] (1) or a lithium "ate" species [10] (2).



(1)



$$R'O - \underset{K^{+}}{\overset{-}{Li}} - R$$

(2)

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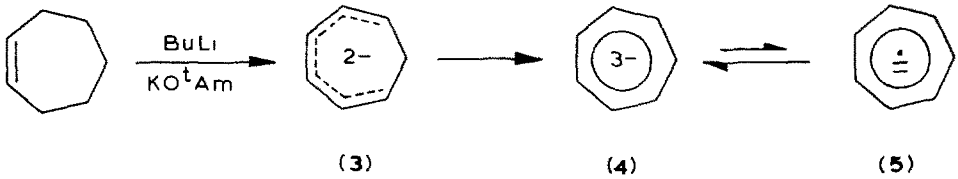
We now report an ESR investigation designed to observe counterion effects directly, and thus help to clarify the nature of LiR/KO^{t}R$'$ mixtures.

We previously reported [11] that reaction of cycloheptene with BuLi/KO^{t}Am under standard metallation-elimination conditions led to the cycloheptadienyl di-anion, (3). We now find that a larger excess of BuLi/KO^{t}Am gives some cycloheptatrienyl trianion, (4), in the final product [12].



SCHEME 1

The known equilibrium of the trianion with the corresponding radical dianion 4 [12] (Scheme 1) present an ideal opportunity to investigate the counter-cations in such media as the ESR spectra of the three radical dianion salts $[(Li^+)_2(5)^{2-}$, $(Na^+)_2(5)^{2-}$, and $(K^+)_2(5)^{2-}]$ show distinctive counter cation couplings [12,13]. We proposed to use the metal coupling in ESR spectra of the cycloheptene/"superbase" reaction medium as a probe of the counter-ions associated with the carbanionic species present.

Cycloheptene was thus treated with a 6-fold excess of BuLi/KO^{t}Am in hexane for 18 h and then refluxed for 12 h to produce 5. A portion of the reaction mixture was transferred to an ESR tube, cooled to −78°C, and treated with dry THF to obtain a homogeneous solution. The ESR spectrum obtained from this mixture was insensitive to changes in concentration, and is shown in Fig. 1. It is essentially identical to that published for the potassium salt of 5, a(7H) 3.52 G, ΔH_{pp} 3.0 G [13], and is quite different from simulations which were carried out of the spectrum of the lithium salt, a(7H) 3.52, a(2Li) 0.83 G [12a] with varying line width. Although our ESR measurements do not directly relate to the trianion but to the radical dianion with which it is in equilibrium, we believe that a change of counterion on oxidation is unlikely.

We therefore conclude that the counterion of delocalized carbanions produced by reactions of LICKOR in BuLi/KO^{t}Am systems is potassium, in accord with conclusions reached from NMR studies [8].

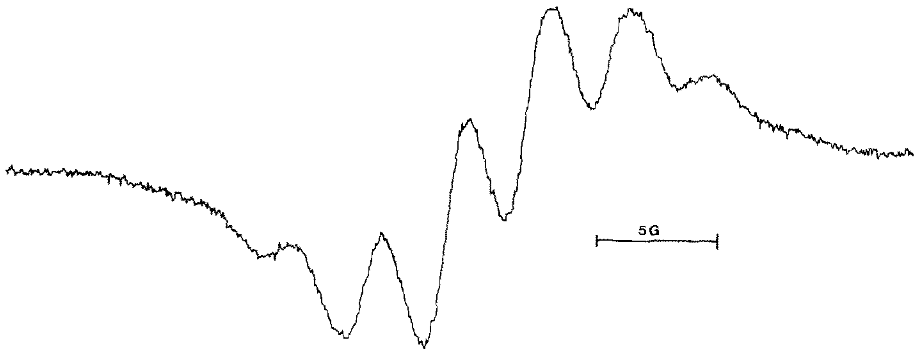


Fig. 1. The ESR spectrum obtained from a mixture of cycloheptene with BuLi/KO^{t}Am as described in the text.

This work does not, however, answer the fundamental questions of the nature of the active metallating agent in BuLi/KOR mixtures or of the detailed mechanism of the metallation. While there now appears to be a body of evidence that potassium salts of many hydrocarbon anions are favoured, this may be due to the preference of lithium as the counterion for anions containing oxygen [7]. The equilibrium in which the lithium counterions prefer to be associated with alcoholates is favoured thermodynamically [14]:

$$\mathrm{BuLi + KOR \rightleftharpoons BuK + LiOR}$$

None of the species in this equilibrium, however, is expected to be present as a monomer, so that some aggregated entity must be responsible for the extreme basicity. We are investigating the nature of this active species.

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