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NMR STUDIES OF ^{7}Li CHEMICAL EXCHANGE BETWEEN PHENYLLITHIUM AND *p*-TOLYLLITHIUM: THE DEGREE OF ASSOCIATION OF PHENYLLITHIUM IN DIETHYL ETHER SOLUTION

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SUMMARY

An investigation of the temperature dependence of the ^{7}Li NMR spectra of equimolar mixtures of phenyl- and *p*-tolyllithium in ether solution reveals that only two species exist in rapid equilibrium, the kinetics of which are consistent with a bimolecular mechanism having an Arrhenius activation energy of 29.5 ± 8 kJ/mol. The results are consistent with monomeric aryllithium molecules rather than dimeric as has been suggested on the basis of ebullioscopic measurements.

INTRODUCTION

Examination of the nuclear magnetic resonance spectra of solutions of the pure organolithium compounds[1-3] and of their mixtures with other lithium[4-7] or organometallic compounds[8-10] has provided a considerable insight to their structures and to the chemical exchange processes which are prevalent in these systems. The utility of ^{7}Li NMR spectra in this connection has been particularly well established and we report here the results of a study of ^{7}Li chemical exchange in mixtures of phenyl- and *p*-tolyllithium in diethyl ether solution.

There is no information currently available which is specifically concerned with chemical exchange in aryllithium systems, but Seitz and Brown have studied[9] the mixed systems phenyllithium/diphenylmagnesium and phenyllithium/diphenylzinc. The particular system studied in this work was chosen because the ^{7}Li chemical shifts of the individual components have been shown[11] to differ most among a series of variously substituted phenyllithiums and this criterion leads to the determination of the most reliable activation energies for such exchange processes[12].

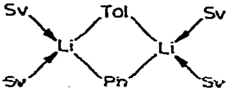
EXPERIMENTAL

Details of the preparation and handling of these reactive compounds have been described previously[11]. Solutions of phenyllithium and *p*-tolyllithium in anhydrous ether were first prepared individually and their concentrations estimated by spectral integration of the solute and solvent proton resonances. Samples for analysis were then made up by combining appropriate volumes of these solutions to provide equal concentrations of the two aryllithiums.

The ^{7}Li NMR spectra of these samples were obtained over a range of temperatures at 38.9 MHz using a Varian HA100 spectrometer. A capillary containing 70% methanolic lithium bromide solution provided the reference signal and chemical shifts were measured by the audio-sideband technique.

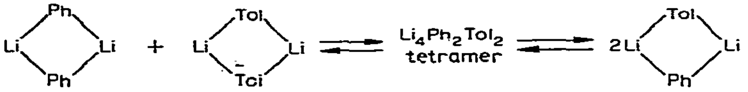
RESULTS AND DISCUSSION

Ebullioscopic measurements[13,14] have suggested that phenyllithium is dimeric in ether solution and it is reasonable to conclude that a substituted phenyllithium such as *p*-tolyllithium would exhibit the same associative characteristics. Thus, in a solution containing an equimolar mixture of these two compounds, the existence of a mixed dimer is to be expected:



Tol = *p*-tolyl
Ph = phenyl
Sv = solvent

There are two schemes by which such a mixed species could be produced: SchemeA, by an associative method:



Scheme B, by a dissociative method:

$$Li_2Ph_2 \rightleftarrows 2LiPh$$

$$Li_2Tol_2 \rightleftarrows 2LiTol$$

$$LiPh + LiTol \rightleftarrows Li_2PhTol$$

The latter scheme is the more likely since the strong Lewis base character of diethyl ether favours dissociation of these electron-deficient compounds (ethyllithium is predominantly hexameric in hydrocarbon solvents[15] but is probably tetrameric in ether[5]). Nevertheless, if the predominant species in solution is a dimer, then rapid chemical exchange would lead to dimers of the type Li_2Ph_2, Li_2PhTol and Li_2Tol_2 in the appropriate statistical proportions, *i.e.* 1/2/1 when equimolar amounts of phenyl- and *p*-tolyllithium are mixed. Thus, at low temperatures where chemical exchange is effectively stopped, ^{7}Li resonance signals corresponding to the three different species should be observed. Our results are completely inconsistent with this picture. At room temperature, the ^{7}Li resonance spectrum of an equimolar mixture of phenyllithium and *p*-tolyllithium in ether consists of a single, relatively sharp signal whose chemical shift is intermediate between that of the individual components. Upon lowering the temperature, the line broadens and eventually splits into a doublet at ~212°K. A further slight splitting was observed on decreasing the temperature further (Fig. 1) but no intermediate signal corresponding to a mixed species appeared.

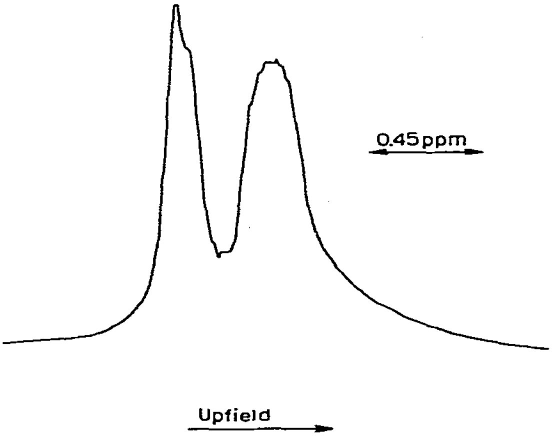
An analysis of the exchange was therefore carried out on the basis of a two-site equilibrium. At each temperature, the observed ^{7}Li spectrum was compared with a series of calculated line-shapes[16] and the best fit provided a value of τ, the mean lifetime of a ^{7}Li nucleus before exchange. Values of the transverse relaxation times (T_2) and of the chemical shift difference between the resonances in the limit of no exchange ($\delta\omega$) which were needed for the calculation were determined from the spectrum at the lowest temperatures.

Figure 2 shows an Arrhenius plot of $-\log \tau$ *vs.* $1/T$ for two equimolar solutions of phenyllithium and *p*-tolyllithium, the overall concentrations being 0.67 and 1.03 *M* respectively. From the slope of the graph, an Arrhenius activation energy of 29.5 ± 8 kJ/mol was determined which is not uncharacteristic of a bimolecular process. The observed concentration dependence also supports this conclusion. In comparison, Brown and co-workers report activation energies of $\sim$49 kJ/mol for ^{7}Li exchange between phenyllithium and phenyllithium complexes of diphenylmagnesium and diphenylzinc, the kinetics being consistent with a unimolecular process[9].

The results obtained here are therefore most readily interpreted in terms of a bimolecular exchange process of the type:

$$\text{*LiPh} + \text{LiTol} \rightleftarrows \text{LiPh} + \text{*LiTol}$$

which involves the monomeric aryllithiums. The ebulliometrically determined degree



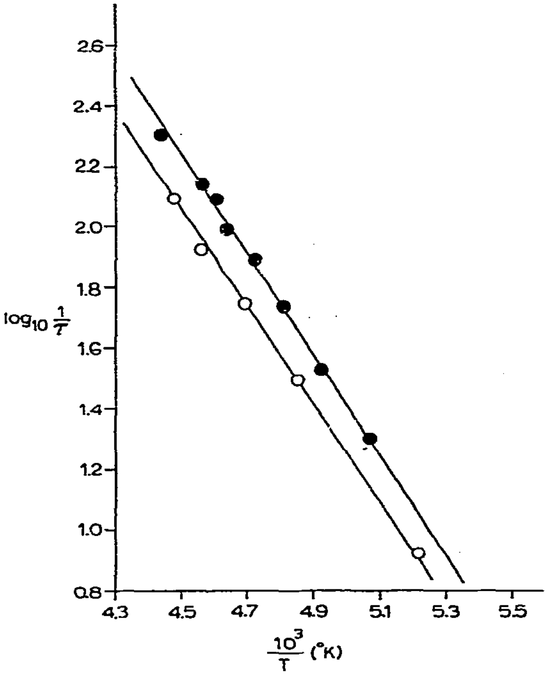


Fig. 1. The ^{7}Li nuclear magnetic resonance spectrum of an equimolar mixture of phenyl- and *p*-tolyllithium in diethyl ether solution at 174°K.

Fig. 2. An Arrhenius plot of $-\log \tau$ *vs.* $1/T$ for the ^{7}Li spectra. The overall concentrations were 0.67 *M* (○) and 1.03 *M* (●), respectively.

of association of phenyllithium in ether solution must then be in error and this is not surprising in view of the reactive nature of these electron-deficient compounds towards oxygen and water vapour as well as towards oxygenated solvents such as ether and tetrahydrofuran.

The existence of aryllithium compounds as monomers in ether solution is also more in keeping with our previous results concerning the ^1H and ^7Li chemical shifts in these systems[11]. There it was found that the introduction of a methyl or chloro substituent onto the aromatic ring of phenyllithium led to upfield shifts of the resonances of the protons *ortho* to the metal while the ^7Li resonance moved downfield and this was explained in terms of the magnetic anisotropy of the carbon in the C–Li bond. The magnitude of this effect experienced by the lithium nucleus is governed by the factor $R^{-3}(1-3\cos^2\theta)$ where R and θ are the polar coordinates of the lithium with respect to the carbon as origin and to the magnetic field direction as axis (see Fig. 3 of ref. 11). Assuming phenyllithium to be dimeric with a LiCLi bridging angle[17] of between 66–70°, θ takes on values of 55–57° which are very near to the unique value of $\theta = 54°44'$ where the above mentioned factor is zero. Whereas the $(1-3\cos^2\theta)$ term may be very small when $\theta = 55$–$57°$, the fact that the lithium atom is directly bound to the anisotropic carbon means that R is also relatively small, which tends to offset the angular factor. Nevertheless, the fairly large shifts observed in the ^7Li resonance on substitution compared with those of the ^1H resonances are more consistent with a monomeric species where $\theta = 90°$.

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