Nuclear Magnetic Resonance Studies of Lithium Exchange between Organolithium Compounds and Lithium Halides in Ether Solutions

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WE report studies which demonstrate the occurrence of ready lithium exchange between "ostensibly" organic-bound lithium of organolithium reagents and inorganic lithium of lithium halides.[1] At room temperature the lithium-7 n.m.r. spectrum[2] of a mixture of methyl-lithium and lithium bromide in tetrahydrofuran (THF) solution consists of a sharp single line having a chemical-shift value between that of pure methyl-lithium and pure lithium bromide.† The spectra reproduced in the Figure illustrate that this single lithium resonance line is an average value resulting from rapid lithium exchange between the organic and inorganic lithium,[3] for three ratios of methyl-lithium to lithium bromide.

Exchange is sufficiently slow at $-100°$ for

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† Chemical shifts (δ) are relative to external 0·5M-LiBr in THF. δ (methyl-lithium) = $+41$ Hz. in THF at $-100°$ and is of half-width (Δ) $\sim$3 Hz. Δ (LiBr) <1 Hz. δ values are reproducible to ±1 Hz. Δ values are probably accurate to $\pm0·5$ Hz.

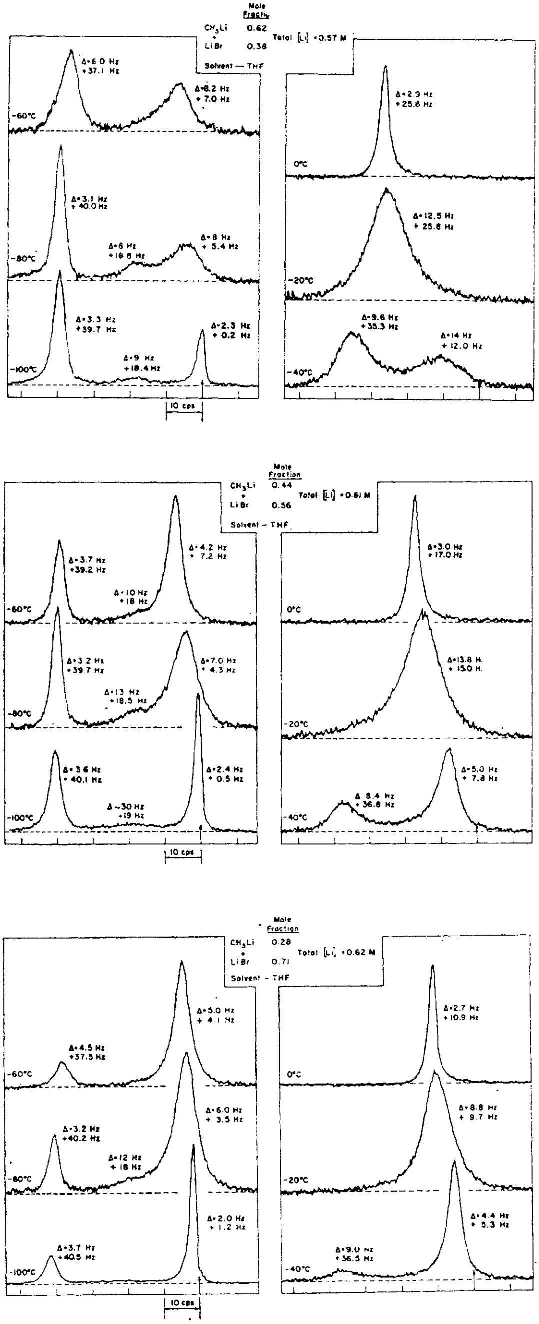

FIGURE. *Temperature dependence of lithium–7 n.m.r. spectra of methyl-lithium–lithium bromide mixtures for three molar ratios, in THF solution.*

resonances typical of the individual methyl-lithium and lithium bromide components to be resolved. With increasing temperature, the rate of lithium exchange between the different magnetic environments increases, causing the separate resonance lines to broaden, coalesce, and finally exchange-narrow. The spectra of pure methyl-lithium or pure lithium bromide remain sharp throughout this temperature interval. Of particular interest is the fact that under slow exchange conditions a definite, although broad, lithium resonance of intermediate chemical shift is evident. Its chemical shift value is essentially invariant with the methyl-lithium–lithium bromide ratio. The proton spectrum of methyl-lithium is not affected by lithium bromide.

Methyl-lithium is tetrameric and lithium bromide is also aggregated in THF[4] or ether[5] solution. The species producing the intermediate lithium resonance is suggested to be a mixed aggregate of methyl-lithium and lithium bromide in which rapid intra-aggregate lithium exchange is occurring,[6] although inter-aggregate lithium exchange is comparatively slow. Relative areas of the methyl-lithium and lithium bromide resonance envelopes at the different methyl-lithium–lithium bromide ratios, as well as the chemical-shift value, indicate the mixed species is of 1 : 1 stoicheiometry. Another feature is that with decreasing temperature the methyl-lithium resonance sharpens before that of lithium bromide. This implies a difference in the rate of exchange of the mixed species with each of the pure components. Providing intra-aggregate exchange remains rapid, the resonance of the mixed species should sharpen with decreasing temperature, since the inter-aggregate exchange rate decreases. The apparent broadening of the resonance of the mixed species between −80° and −100° may be due to a slowing of the intra-aggregate exchange rate in this temperature range, resulting in lifetime broadening, or could arise from a decrease in the relative concentration‡ of the mixed species with decreasing temperature.

An explanation given for the observed influence of lithium halides on the kinetic behaviour of organolithium reagents is the formation of mixed organolithium–lithium halide complexes.[7] Isolation of a 1 : 1 methyl-lithium : lithium halide complex is reported.[5a] The evidence given here constitutes the first direct observation of these mixed species in solution. Their relative importance at temperature above those producing slow exchange conditions is still open.

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‡ An exchanging species present in a relatively low concentration will have a shorter lifetime for a given exchange rate than will the species present in the larger amount.

Ready lithium exchange also occurs with mixtures of lithium bromide and phenyl-lithium or benzyl-lithium, from which we infer that this exchange is common to all types of organolithium species. The rate of lithium exchange with these organolithiums is substantially faster than it is with methyl-lithium. Even at −100° exchange is rapid and the spectrum is a broadened average resonance line. Other lithium salts such as lithium chloride, lithium tetraphenylboride, and lithium alkoxides undergo exchange with organic lithium. Exchange behaviour is analogous in diethyl ether.

The lithium-7 n.m.r. spectrum of mixtures of the two organolithium reagents, methyl-lithium and benzyl-lithium, which have appreciably different lithium chemical shifts, also clearly show the occurrence of ready lithium exchange.[8] The temperature dependence of this exchange is similar to that of methyl-lithium–lithium bromide and not like that of benzyl-lithium–lithium bromide. Apparently, the removal of methyl (or lithium) from the methyl-lithium environment is rate-determining. At slow exchange conditions, the spectrum of an equimolar mixture of methyl-lithium and benzyl-lithium shows a lithium resonance attributable to a mixed aggregate[9] of magnitude approaching that of the remaining pure components, and which sharpens with decreasing temperature.

It is of interest to note that from the reported configurational stability of 1-methyl-2,2-diphenylcyclopropyl-lithium[10] in the presence of an excess of lithium iodide in ether solution and the configurational stability of *cis*- and *trans*-1-propenyl-lithium in the presence of lithium bromide in ether solution[11] that lithium exchange occurs with retention of configuration.

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[1] Evidence for lithium exchange between a lithium ketyl (radical-anion) and lithium bromide was recently reported (G. W. Cauters, H. Van Willigen, and E. DeBoer, *Chem. Comm.*, 1967, 566). In such radical anions the lithium is presumably associated with the π-electron orbitals whereas the organic lithium described here is presumably bonded to carbon through σ molecular orbitals.

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[9] M. A. Weiner and R. West, *J. Amer. Chem. Soc.*, 1963, **85**, 485.

[10] M. Aronoff, Ph.D. thesis, Florida State University, 1965, p. 70; communicated to us by Prof. H. M. Walborsky.

[11] D. Y. Curtin and J. W. Crump, *J. Amer. Chem. Soc.*, 1958, **80**, 1922.