TEMPERATURE DEPENDENCE OF THE LITHIUM AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTRUM OF ETHYLLITHIUM

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(Received April 28th, 1964)

The exchange of alkyl groups between bonding sites in metal alkyl compounds is of interest in connection with bonding and structural considerations. The kinetic parameters of the exchange, and the effect of solvent on these, should provide some insight into factors of principal importance in determining the nature of the metal-carbon bond[1-3].

We wish to report here the results of an attempt to determine some of the features of alkyl group exchange in toluene solutions of ethyllithium. No information is currently available on self-exchange of alkyl groups in organolithium compounds. The only data which relates to exchange in hydrocarbon solutions of organolithium compounds is that of Weiner and West[4], who report the ^{7}Li spectrum of solutions containing both ethyl- and *tert*-butyllithium. In addition to showing the presence of mixed polymeric species, the spectrum contains a separate resonance due to *tert*-butyllithium. The average time between an exchange event, τ_e, between any two of the different prevalent species in solution is therefore long in relation to the chemical shift differences δ between the species ($2\pi\delta\tau > 1$). For a δ value of about 10 cps, τ_e is then about 0.01 sec or longer.

Proton NMR work, as well as chemical studies, have demonstrated considerable configurational stability of the lithium-bearing carbon in certain organic groups such as cyclopropyl or propenyl[5,6]. This must be distinguished from the exchange processes under discussion here, however, since exchange may occur by a path which does not result in loss of configuration.

We have examined the proton NMR spectrum of ethyllithium in toluene as a function of temperature for ethyllithium samples prepared from both ^{6}Li (96 % isotopic purity) and ^{7}Li (92.6 and 99 % isotopic purities). We have also studied the ^{7}Li NMR spectrum of LiC_2H_5, LiC_2D_5 and $LiC(CH_3)_3$ in toluene as a function of temperature.

EXPERIMENTAL

The procedures employed in preparing samples have been described elsewhere[7]. All samples were recrystallized from benzene before use. Isotopically enriched lithium metal (96 % ^{6}Li and 99 % ^{7}Li) was purchased from Union Carbide Nuclear Company, Oak Ridge, Tennessee. Ethyl bromide-d_5 was obtained from Volk Chemical Company, Skokie, Illinois. *tert*-Butyllithium in pentane solution was purchased from Lithium

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Corporation of America. A number of different samples, separately prepared, were studied in obtaining the data shown in Figs. 1, 2 and 3. The observation of a distinct difference in the methylene proton linewidths between normal abundance lithium (92.7 % ^{7}Li) and 96 % ^{6}Li samples is corroborated in the results obtained with a sample prepared from 99 % ^{7}Li. This sample was studied to eliminate the possibility that the linewidth difference is due to a paramagnetic impurity in the normal abundance metal which somehow survived recrystallization of ethyllithium. The sample prepared from the 99 % ^{7}Li metal showed the same behavior as samples prepared from natural abundance metal.

Solutions of ethyllithium in diethyl ether were prepared by dissolving ethyllithium, freshly recrystallized from benzene, in dried and distilled ether. The ether solution samples were made up at a temperature of perhaps 10° or less, and were kept at dry ice temperature in sealed NMR tubes until spectra were taken.

All spectra were measured on a Varian Associates Model DP-60 spectrometer. The proton resonances were measured at 60 mc. The ^{7}Li resonances were measured in part at 15.1 mc, in a field of about 9130 gauss, and in part at a 23.3 mc, in a field of 14092 gauss.

The proton resonance spectrum of ethyllithium in toluene was measured in pure absorption mode under slow passage conditions at various sample temperatures in the range 32 to —45°. Samples prepared from both ^{6}Li and ^{7}Li were studied. The width of the central line of the methyl group triplet, and an average value of the two central lines of the methylene group quartet were measured. Each estimate of linewidth is an average value obtained from at least seven scans through the absorption.

Proton linewidth measurements are not feasible at temperatures above +5 to 10°; the lines become quite narrow, and higher order splitting of the quartet and triplet patterns is discernable.

The ^{7}Li absorption linewidth was also measured under slow passage conditions at various temperatures. It was found that the ^{7}Li linewidth is appreciably wider if lithium ethoxide is present as an impurity. A large number of LiC_2H_5 samples were examined in obtaining the data shown in Fig. 3. Only one sample of LiC_2D_5 was prepared, but this showed no evidence of an impurity.

RESULTS AND DISCUSSION

The results of the proton linewidth measurements in the temperature range +4 to —40° are shown in Figs. 1 and 2. The nuclear spin system involved in this study is complex, and a number of factors must be considered in placing an interpretation on the proton linewidth results.

(*a*) Scalar coupling may occur between lithium and the protons. The nuclear moment of ^{7}Li is four times larger than for ^{6}Li; its spin is 3/2 as compared with 1 for ^{6}Li. $J_{\text{Li-CH}}$ is therefore 2.6 times larger for ^{7}Li than for ^{6}Li. Recent studies of M–H coupling in species of the form $M(C_2H_5)_3$ and $M(C_2H_5)_4^-$ ($M = B, N, C$) reveal M–H coupling constants in the range of 0 to 4.6 cps, with no discernable regularity in the relative magnitudes of the couplings to α and β protons[8,9]. The prevalent ethyllithium species in hydrocarbon solution is the hexamer[10]. In the model proposed for this species[7], each group is bonded equivalently to three lithium atoms, with roughly a 1/3 bond order for each carbon-lithium bond. It is to be expected, therefore, in light of the low bond order, and high degree of ionic character in the C–Li bond, that the lithium–proton coupling constants will not be large, perhaps on the order of 1 cps.

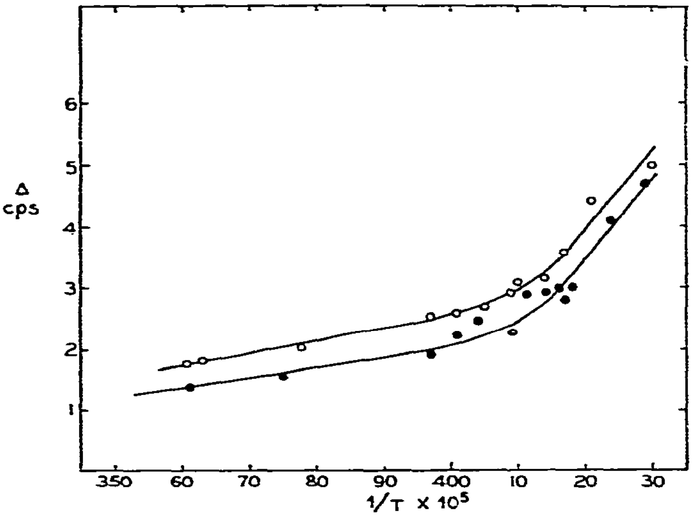


Fig. 1. Average linewidth at half-intensity of the central pair in the CH_2 quartet of ethyllithium in toluene at various temperatures. ●, ^{6}Li; ○, ^{7}Li.

(*b*) Exchange of alkyl groups may occur intermolecularly and/or intramolecularly. An intramolecular exchange would not serve to completely decouple the lithium and proton spins; instead, the effective J would be reduced to 1/2 the value for no exchange, and each proton would interact with six equivalent lithium atoms.

(*c*) Relaxation of the ^{7}Li spins via quadrupolar interactions may serve to decouple the proton–lithium spins. If the average lifetime of the lithium nuclei in a given spin state is sufficiently short, the lithium–proton scalar coupling might act as a mechanism for proton relaxation[11]. The effect is certain to be absent in ^{6}Li samples, in view of the small quadrupole moment of ^{6}Li.

In view of the expectation of small Li–CH coupling constants, it is not surprising that the proton lines are not split into a discernable multiplet structure. On the other hand, the distinctly broader linewidths for the proton absorptions in ^{7}Li samples, particularly in the methylene proton lines, is evidence that an Li–CH coupling does exist. It follows that intermolecular exchange of alkyl groups in the temperature range from $+4$ to $-40°$ is slow, *i.e.*, $2\pi J_{Li-CH}\tau_e$ is on the order of 1 or larger. Assuming $J_{Li-CH} = 1$ cps, τ_e is on the order of 0.1 sec or longer. The results do not permit a conclusion regarding intramolecular exchange.

The relatively short relaxation time of the ^{7}Li nuclei, as revealed by the ^{7}Li linewidth (*vide infra*), should result in a collapse of the ^{7}Li–CH coupling at lower temperatures[11]. But, since the proton multiplet structure arising from the coupling is not resolved in any case, broadening and partial collapse of the fine structure under the observed band envelope is not likely to be detected. The observation of a more or less constant difference in linewidth between the ^{7}Li and ^{6}Li methylene linewidths in the temperature range +4° to −30° is therefore not incompatible with the assumption of slow intermolecular exchange.

It is noteworthy that the difference in proton linewidths between the ^{7}Li and ^{6}Li samples is greater for the methylene absorptions than for the methyl. It appears from this that the Li–CH coupling constant is larger for the methylene protons than for the methyl.

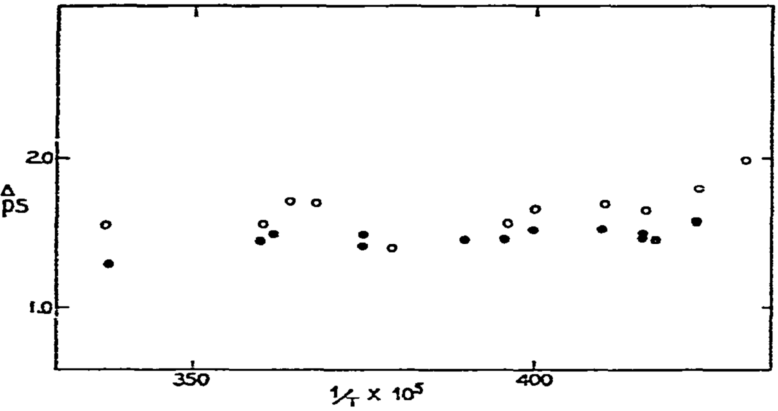
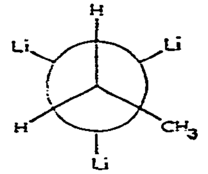


Fig. 2. Linewidth at half-intensity of the central line of the CH_3 triplet of ethyllithium in toluene at various temperatures. ●, ^{6}Li sample; ○, ^{7}Li sample.

The broadening of the methylene proton lines at lower temperatures is quite extensive. It is particularly interesting that the curves of linewidth *vs.* temperature for ^{6}Li and ^{7}Li ethyllithium show a comparable increase at about the same temperature. In light of the fact that the methyl linewidth does not undergo a similar increase, it does not appear that the effect results from an increase in solvent viscosity. It also does not appear to be caused by the lithium–proton scalar coupling, since the effect is present in both ^{6}Li and ^{7}Li spectra. Further, quadrupole relaxation of the ^{7}Li spin at the lower temperature should effectively erase an ^{7}Li–CH scalar coupling.

One explanation is that the ethyl group is capable, at higher temperatures, of rotation about the axis joining the methylene carbon to the hexamer. Assuming that the alkyl group is bonded to three equivalent lithium atoms, the situation can be represented as follows:



Under conditions of free rotation the methylene protons are subject to some averaged chemical environment. At lower temperatures the rotational motion is impeded. It seems reasonable to suppose that in these circumstances the methylene protons may interact sterically with the methyl groups of adjacent alkyl groups, so that magnetically non-equivalent environments are established.

To summarize, the proton data for ethyllithium in toluene at 4° and below indicate that intermolecular exchange probably proceeds at a maximum rate of perhaps 0.1 sec per exchange event per alkyl group or slower. The proton linewidths for diethyl ether solutions of $^7\mathrm{LiC_2H_5}$ remain narrow to —35°. We conclude that either the lithium–proton scalar coupling is very small, or intermolecular exchange is rapid, or both.

Fig. 3 shows a graph of the linewidth of the ^{7}Li resonance of $^7\mathrm{LiC_2H_5}$, $^7\mathrm{LiC_2D_5}$ and $^7\mathrm{LiC(CH_3)_3}$ in toluene as a function of η/T, where η is the solvent viscosity in centipoise units. The first point worthy of note is that the linewidths of the two ethyllithium samples do not coincide at room temperature, but that they appear to merge at lower temperature. This effect is nicely explained if it is assumed that a scalar ^{7}Li–CH coupling exists at room temperature. The ratio of the coupling constants $J_{\mathrm{Li-CH}}/J_{\mathrm{Li-CD}}$ is given by $\gamma(^1_1\mathrm{H})/\gamma(^2_1\mathrm{H}) = 6.5$, so that scalar coupling between lithium and the deuteron is much smaller than that between lithium and the proton. Thus, if a scalar coupling exists at room temperature, one expects that an unresolved multiplet structure will arise, and an apparently wider ^{7}Li linewidth will result in the $\mathrm{LiC_2H_5}$ sample. The fact that such a linewidth difference clearly does exist (Fig. 3) requires that intermolecular exchange be slow with respect to the Li–CH coupling. Assuming that the ^{7}Li–CH scalar coupling constant is on the order of 1 cps, τ_e is on the order of 0.1 sec or longer. The results do not permit a decision regarding the existence of intramolecular exchange.

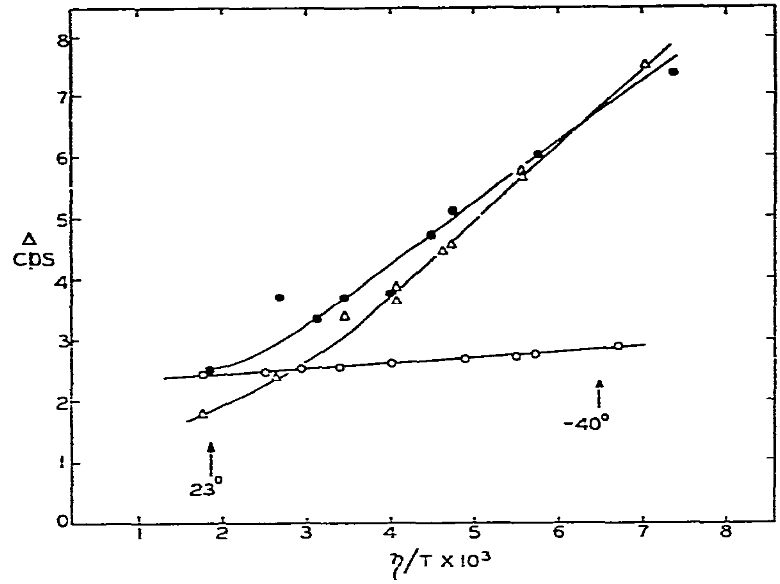


Fig. 3. Linewidth at half-intensity of ^{7}Li absorptions in toluene as a function of η/T, where η is solvent viscosity. ●, $^7\mathrm{LiC_2H_5}$; △ $^7\mathrm{LiC_2D_5}$; O $^7\mathrm{LiC(CH_3)_3}$.

The increasing linewidth of the ^{7}Li resonance in both ethyllithium samples is ascribed to quadrupolar relaxation. As the lifetime of the ^{7}Li nucleus in a given spin state becomes shorter at lower temperatures, the ^{7}Li–CH coupling is collapsed. At lower temperatures therefore, with quadrupolar relaxation predominating over other relaxation mechanisms, the ^{7}Li linewidths of the $^7\mathrm{LiC_2H_5}$ and $^7\mathrm{LiC_2D_5}$ samples should approach a common value. Within the limits of the experimental uncertainty, this is seen to be the case.

If quadrupolar relaxation is the predominant mechanism for relaxation of the ^{7}Li spin, the transverse and longitudinal relaxation times are equal, and are given by

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{10}\left(\frac{eQq}{\hbar}\right)^2 \tau_c \tag{1}$$

where $eQq/\hbar$ is the quadrupole coupling constant, and τ_c is the correlation time[12]. Assuming that the important correlation time is that for molecular rotation, and using the expression

$$\tau_c = \frac{4\pi\eta a^3}{3kT},$$

we obtain:

$$\frac{1}{T_1} = \frac{2\pi a^3}{15k}\cdot\left(\frac{eQq}{\hbar}\right)^2\cdot\left(\frac{\eta}{T}\right) \tag{2}$$

a is the radius of the cavity, presumed spherical, which the solute molecule occupies.

From the slope of the linear portion of the line for the ^{7}LiC$_2$D$_5$ sample we calculate an approximate value of the quadrupole coupling constant, $eQq/\hbar$, of 0.57 mc, using equation (1). It was assumed in the calculation that the hexameric species occupies a spherical cavity of radius a in the solution; $a^3 = 3/4\pi\cdot M/\rho N$, where ρ is the density of ethyllithium, 0.88 g/cm^3, $M = 216$ g/mole. Further, the calculated correlation time τ_c was divided by 10, as this is the approximate magnitude of correction which Moniz and Gutowsky[13] found to be necessary for a series of nitrogen compounds.

From the measured slope of the line for the *tert*-butyllithium sample, and assuming further that a tetrameric species prevails, with $\rho = 0.85$, and correcting for τ_c as above, an eqQ value of 0.14 mc is obtained.

The estimated values of eqQ are probably upper bounds; the correct values may be lower since the estimate of a factor of ten for the empirical correction to the Debye correlation time may be too large for solute species as large as the alkyllithium polymers.

In the models proposed for the hexamer and tetramer species[7,14], verified by recent X-ray studies[15,16], each lithium atom is bonded to three alkyl carbon atoms. The bonding carbon atoms form a roughly trigonal array about each lithium. The field gradient at the lithium nucleus is the result of the overall distribution of electrons and other nuclei in the near vicinity of each lithium, and depends not only on the polarity of the carbon–lithium bond, but upon relatively subtle geometrical factors. There is no cause, therefore, for alarm at the fact that the field gradient, and thus the quadrupole coupling constant, is much smaller in *tert*-butyllithium than in ethyllithium. Rather extensive molecular orbital calculations will be required before the various contributions to the field gradient have been properly assessed.

The ^{7}Li linewidth of ethyllithium in ether is narrower than in toluene; it varies from 1.6 cps at 26° to 2.8 cps at 42°. The range of η/T encompassed by this solvent is, however, quite small, so that useful conclusions regarding the functional relationship between linewidth and η/T cannot be drawn at present.

The NMR results, in summary, provide strong evidence that intermolecular exchange of alkyl groups between the prevalent polyhedral species present in hydrocarbon solutions of ethyllithium proceeds at a rate slower than $k = 1/\tau_c = 10\ \text{sec}^{-1}$. This result would seem to indicate that the polyhedral species (hexamer in the case of ethyllithium) is a strongly bound unit and not subject to facile dissociation into less associated species such as dimer. In this respect the NMR studies are in agreement with the mass spectral results for ethyllithium vapor[12]. No evidence was found in that study for the presence of species other than hexamer and tetramer at a temperature of about 87°.

ACKNOWLEDGEMENTS

This research was supported by a grant from the National Science Foundation, and by funds from the Alfred P. Sloan Foundation. The authors are indebted to Mr. O. Norton for assistance in obtaining the NMR spectra. Preliminary studies of this research were carried out by Dr. D. A. Bafus.

SUMMARY

Proton NMR linewidths have been measured for $^7LiC_2H_5$ and $^6LiC_2H_5$ in toluene solution in the temperature range +4 to −40°. The proton lines in samples prepared from ^6Li are narrower than in the ^7Li samples, indicating the existence of a scalar Li–CH coupling.

The ^7Li NMR linewidths have been measured as a function of temperature for LiC_2H_5, LiC_2D_5 and $LiC(CH_3)_3$ in toluene solution in the temperature range +23 to −42°. The results indicate a slow intermolecular exchange of alkyl groups in the entire temperature range. From the temperature dependences of the linewidths, quadrupolar coupling constants eqQ/h of 0.57 and 0.14 mc have been estimated for ethyllithium and *tert*-butyllithium respectively.

REFERENCES

1 E. G. Hoffmann, *Trans. Faraday Soc.*, 58 (1962) 642.
2 C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, 84 (1962) 912.
3 R. E. Dessy, F. Kaplan, G. R. Coe and R. M. Salinger, *J. Am. Chem. Soc.*, 85 (1963) 1191.
4 M. A. Weiner and R. West, *J. Am. Chem. Soc.*, 85 (1963) 485.
5 D. Seyferth and H. M. Cohen, *J. Organometal. Chem.*, 1 (1963) 15.
6 D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, 86 (1964) 883.
7 T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, 84 (1962) 1371.
8 A. G. Massey, E. W. Randall and D. Shaw, *Spectrochim. Acta*, 20 (1964) 379.
9 M. Frank-Neumann and J. M. Lehn, *Mol. Phys.*, 7 (1963) 197.
10 T. L. Brown, R. L. Gerteis, D. A. Bafus and J. A. Ladd, *J. Am. Chem. Soc.*, 86 (1964) 2135.
11 A. Abragam, *Principles of Nuclear Magnetism*, Oxford Univ. Press, 1961, p. 309.
12 Ref. 11, page 314.
13 W. B. Moniz and H. S. Gutowsky, *J. Chem. Phys.*, 38 (1963) 1155.
14 M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, 1 (1962) 654.
15 H. Dietrich, *Acta Cryst.*, 16 (1963) 681.
16 E. Weiss, *J. Organometal. Chem.*, 2 (1964) 314.
17 J. Berkowitz, D. A. Bafus and T. L. Brown, *J. Phys. Chem.*, 65 (1961) 1380.