Nuclear Magnetic Resonance Study of a Lithium-exchange Reaction

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WE are engaged in an n.m.r. study of reactions of the following type:

$$M^+X^- + M^+ \overset{k}{\rightleftarrows} M^+ + X^-M^+ \quad (1)$$

where M^+ designates an alkali-metal ion and X^- a paramagnetic aromatic anion. We expected to see two effects in the n.m.r. spectra of the metal ion nuclei:[1]

(i) a broadening of the n.m.r. peak, due to the fact that the metal nucleus experiences a magnetic pulse upon association with a paramagnetic anion,

(ii) a shift of the resonance peak if the reaction rate (k) is fast.

The magnitude of the broadening will be determined by the magnitude and duration of the magnetic pulses and thus might yield information concerning the electronic structure of the ion pairs (M^+X^-) and the kinetics of the exchange reaction. The direction of the shift can be used to determine the sign of the metal ion hyperfine splitting in the paramagnetic ion pair.

We report measurements on the system Li^+/fluorenone$^-$–LiBr in tetrahydrofuran (THF). This system is of particular interest since e.s.r. experiments by Hirota[2] have demonstrated that the Li hyperfine splitting of Li^+/fluorenone$^-$ in 1,2-dimethoxyethane (DME) varies with temperature and changes sign at −5°. In the solvent we used (THF) the curve of the Li hyperfine splitting against temperature runs parallel to the curve shown by Hirota for DME; the zero Li splitting is reached here at −30°. To explain the sign reversal it was assumed that the net spin density *at* the alkali nucleus consists of negative and positive contributions, brought about by different mechanisms, each with a different temperature dependence.[3] This could lead to the observed sign reversal of the hyperfine splitting. We expected that the n.m.r. experiments could yield more detailed information concerning the mechanisms involved.

The results of the n.m.r. measurements of the ^{7}Li line-width as function of temperature and fluorenone^{-} concentration are summarised in the Figure. The line-width increases with increasing temperature and increasing concentration of fluorenone^{-}. That this broadening can be attributed unambiguously to the effect of reaction (1) is demonstrated by the ^{7}Li line-width variation in the presence of diphenylpicrylhydrazyl (DPPH) (Figure, curve VI) and the decrease in line-width when fluorenone^{-} is further reduced to the dinegative ion (Figure, curves III and IV). Within the limits of the experimental accuracy (± 1 c./sec.) we did not observe a shift of the resonance line of ^{7}Li in solutions of 1M-LiBr in THF with fluorenone^{-} in concentrations up to 0·1M over the temperature region $-100°$ to room temperature.

The Figure shows that there is no direct correlation with the data of the e.s.r. experiments; the line-broadening is *not* governed by the magnitude of the metal ion hyperfine splitting. We attribute the observed line broadening to the effect of quadrupole interaction in the ion pair. Association of Li^{+} and fluorenone^{-} can give rise to an electric field gradient at the nucleus as a result of two effects: first of all by polarization of the Li *s*-electrons by the charge densities in the aromatic ion and secondly by an electron transfer from the aromatic ion to a Li 2*p*-orbital. Internal movements of the ion pair as well as tumbling of the ion pair as a whole then will give quadrupole relaxation of the ^{7}Li nuclear spin, contributing to the line-width. Our experimental finding that the line-width as a result of the exchange reaction does not show a minimum at $-30°$ does not necessarily contradict the assumption that there are different mechanisms contributing to the spin density at the nucleus which cancel each other at $-30°$; a zero value of the spin density at the Li nucleus does not imply that the field gradient at the Li nucleus is zero, too. The line-width variation with temperature might reflect the field gradient variation at the nucleus.

An alternative explanation might be that the ^{7}Li nuclear spins are completely dephased by the quadrupole interaction upon association (strong pulse limit). In that case the line broadening is determined by the lifetime of the free Li^{+} ions only, thus by the concentration of the fluorenone^{-} and the magnitude of the rate constant (*k*) of the exchange reaction. In agreement with this explanation is the observed dependence of the line-broadening on the concentration of fluorenone^{-} and on the temperature. Experiments with ^{6}Li, which has an extremely small quadrupole moment, will be performed in order to verify the validity of this explanation.

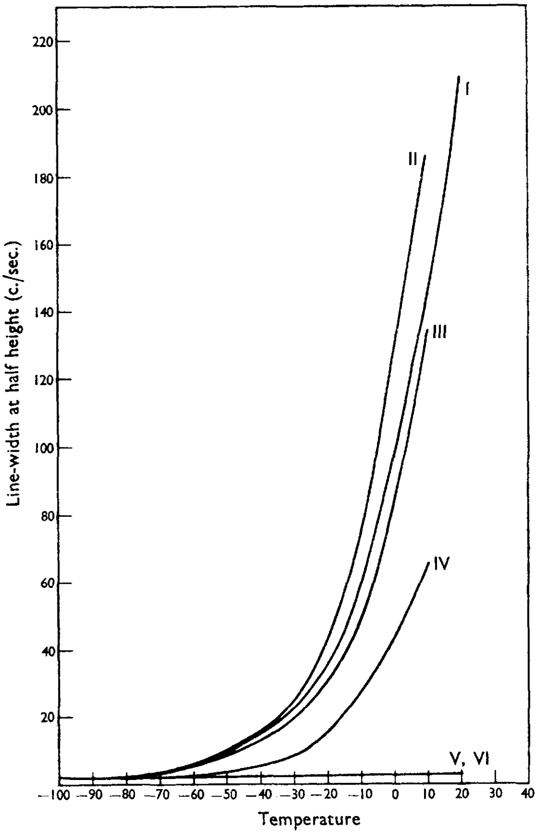

FIGURE. ^{7}Li *resonance line-width at half peak height (c./sec.) against temperature. (Measuring frequency:* 15·1 *Mc./sec.)*

I–IV *represent a solution of* 5 × 10^{-3}M-*fluorenone and* 1M-LiBr *in* THF *progressively reduced with* Li.

II *represents the curve for maximum fluorenone^{-} concentration.*

V *represents a solution of* 1M-LiBr *in* THF.

VI *represents a solution of* 1M-LiBr *and* 7·5 × 10^{-3}M-DPPH *in* THF.

The absence of a shift of the ^{7}Li resonance line indicates that the Li^{+} exchange rate is slow compared with the hyperfine splitting in c./sec. An approximate upper limit for the exchange rate at

$-80°$, calculated for a maximal fluorenone$^-$ concentration of 0·1M, is 10^7 mole^{-1} sec.$^{-1}$.

Further experiments with other aromatic ions and alkali metals are in progress.

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[1] E. de Boer and C. MacLean, *J. Chem. Phys.*, 1966, **44**, 1334.
[2] N. Hirota, *J. Amer. Chem. Soc.*, 1967, **89**, 32.
[3] E. de Boer, *Rec. Trav. chim.*, 1965, **84**, 609.