KINETICS OF INVERSION OF LITHIUM AND ALUMINUM ORGANOMETALLIC REAGENTS

Gideon Fraenkel, Don T. Dix and Marianne Carlson

Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

Recent nmr studies of organometallic reagents (Li, Mg, Al, and Zn derivatives) have stimulated interest in the nature of the inversion process occurring at carbon bonded to a metal (1-5). Although the kinetics of this phenomenon have been investigated for a few organometallic derivatives in diethyl ether (4,5), the mechanistic interpretations advanced are still incomplete. Now, we report the kinetic studies of the inversion rate of lithium and aluminum organometallic reagents in various solvents.

As previously described (1,2,5) in certain organometallic compounds, $\underline{1}$, where R^* contains an asymmetric center, the nmr line shape for the α- hydrogens is governed by the rate of inversion. Employing this method, we now report kinetic studies on inversion in 2-

(a) $\underset{\sim}{1}$
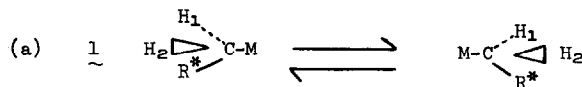
methylbutyllithium and triisohexylaluminum.

2-Methylbutyllithium, $\underline{2}$, was prepared in several solvents by reacting the mercury compound with lithium dispersion. At low temperatures the α-hydrogens in this latter reagent gave an nmr pattern which was AB of ABX. With increasing temperature the pattern collapsed to A_2 of A_2X. Hence rates of inversion were obtained from the nmr spectra (2,5). Reagent $\underline{2}$ gave single nmr spectra; thus there is no evidence for slow exchange among chemically shifted species, though it is still possible that fast exchange without inversion might give rise to a single average ABX spectrum.

Activation parameters and kinetic orders for inversion in 2-methylbutyllithium are listed in Table 1. In pentane, toluene, and ether the inversion process is first order in contained RLi. It is known (6,7) that organolithium compounds are aggregated in solution, the association number being from four to six. The kinetic dependence may be explained either as due to local carbon lithium bond ionization within the aggregate or to an exchange of

TABLE 1

Activation Parameters for Inversion

Conc. 1 M, R = 2-methylbutyl
R'= isohexyl

Solute	Solvent	$\Delta H^{\ddagger a}$ kcal	$\Delta S^{\ddagger b}$ e.u.	$1/\tau^c 25^\circ$C. sec.$^{-1}$	Kinetic Order
RLi	n-pentane	4.5	-38	17	1.0
RLi	ether	8.0	-23	125	1.0
RLi	toluene	10.5	-20	5	
RLi+ t-BuLi	n-pentane	5.5	-36	11	
RLi+ TMED	n-pentane	7.4	-19	265	
R'$_3$Al	toluene	28.0	+22.5	$1.5 \cdot 10^{-3}$	1.0
R'$_3$Al	ether	too slow to measure			

(a) ± 0.8 kcal   (b) ± 5 e.u.   (c) Accuracy 5%

lithium among several sites within the aggregate. Both of these processes could result in first order inversion. We distinguish among these possibilities as follows. Addition of t-butyllithium to the RLi solutions in pentane undoubtedly introduces t-BuLi into the RLi aggregates. The inversion rate for such a sample should be quite different in the case of the intra-aggregate exchange than for pure RLi. On the other hand, bond dissociation followed by recombination of the same atoms should yield results similar to those for RLi alone. Inspection of Table 1 shows that the latter is the case.

Koeppl, Sagatys and Miller have calculated inversion barriers for CH_3^- of 6 to 10 kcal (8). These values lie in the range of enthalpies of activation reported here. Tentatively we prefer the bond dissociation mechanism. However, not enough is known about electrical conditions within the RLi aggregates or solvation by basic substances to permit more detailed conclusions.

Basic substances increase the rate of inversion in RLi, increase $\Delta H^\ddagger$, and increase $\Delta S^\ddagger$. Diethyl ether as solvent has about the same effect as one equivalent of tetramethylethylenediamine.
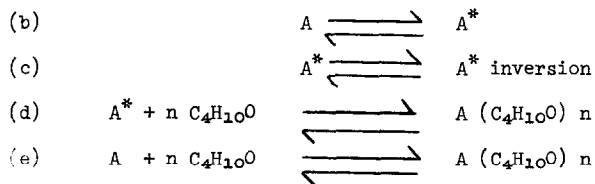
The behavior of the trialkylaluminum compound is quite different.   Roberts et. al. (4)
found trineohexylaluminum in diethyl ether to be configurationally stable over a 120°C.
temperature range in contrast to dineohexylzinc although both metals possess the same
electronegativity on the Pauling-Haissinsky scale (9).   We observed the same result for the
case of triisohexylaluminum in ether, but upon examining solutions of this derivative in
pentane and toluene in the absence of ether we found the inversion rate relatively fast.
The activation parameters are listed in Table 1.

The kinetic dependence of inversion was found to be first order.   Lardicci and co-workers
reported tris-2-methylbutyl-aluminum to be monomeric in benzene (10).   We suggest tentatively
that aluminum carbon bond heterolysis or bond stretching followed by one or more inversions
is responsible for the results reported here.

Solutions of triisohexylaluminum in pentane with various amounts (0.1 to 1.0 mole %) of
diethyl ether added were also studied.   Surprisingly the inversion rate was very slow
throughout the range of ether concentrations.   The nmr parameters for triisohexylaluminum
in ether and pentane are quite different.   These solutions undoubtedly contained at least
two species with different chemical shifts.   However, down to ~65° C. no extra peaks or line
broadening characteristic of slow exchange among species could be detected.   Hence while
inversion is slow, aluminum ether exchange is fast on the nmr time scale.

Mole (11) has reported that pyridine slows down the carbon metal bond exchange in
organoaluminum compounds.   Interestingly pyridine increases the rate of inversion in triiso-
hexylaluminum.

These effects can be accomodated by the following scheme, where $A = R_3Al$.

$$\text{(b)} \qquad A \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{3cm}{0pt}}} A^*$$

$$\text{(c)} \qquad A^* \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{3cm}{0pt}}} A^* \text{ inversion}$$

$$\text{(d)} \qquad A^* + n\ C_4H_{10}O \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{3cm}{0pt}}} A\,(C_4H_{10}O)\,n$$

$$\text{(e)} \qquad A\ + n\ C_4H_{10}O \underset{\longleftarrow}{\overset{\longrightarrow}{\rule{3cm}{0pt}}} A\,(C_4H_{10}O)\,n$$

Triisohexylaluminum coordinated to ether is assumed to invert slowly.   The symbol A^* represents
a partially ionic intermediate containing a stretched carbon-metal bond.   The latter can
lengthen enough to accomplish inversion or complex with ether in a highly favorable
equilibrium (K_d large).   In this way a small amount of ether could cause a large decrease in
the overall rate of inversion (12).

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12. Similar schemes involving aggregates of R_3Al could also be written. However, these are not considered since R_3Al is most likely monomeric under our conditions.