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On the mechanism of organolithium reactions in hydrocarbon solution

Numerous kinetic studies have been carried out on the reactions of organolithium compounds with olefins¹⁻⁵. These reactions may be the initiation step in "anionic" polymerization, as with styrene^{1,3}. Solvent plays an important role in affecting not only the rates but also the orders of the reactions. This communication deals with reactions occurring in hydrocarbon solvent.

While there is not unanimity, the prevalent understanding seems to be that the order of organolithium concentration in the rate expression for addition to olefin is low¹⁻³, on the order of 1/6. This low order holds over a wide RLi concentration range, from about 10⁻¹ to 10⁻⁴ M. The results have been interpreted in terms of the dissociation of an associated species:



The monomer, present in very low concentrations, is assumed to be the sole kinetically active species. Then, for reaction with substrate S:



$$\text{rate}_i = k[S]_i [(RLi)_i]_i^{1/n} \quad (3)$$

where subscript *i* refers to initial conditions. It is well established that the shorter chain *n*-alkyllithium compounds exist in hydrocarbon predominantly as hexamer^{6,7}, and that the only other species of comparable stability is the tetramer^{8,9}. The appearance of an apparent 1/6th order in the kinetics studies was understandably taken as good evidence for the correctness of the mechanism, and acceptance of the scheme

represented in eqns. (1)–(3) is almost unanimous among workers in this area. The mechanism is, however, quite unsupported by data other than the kinetic results, which are subject to alternate interpretation. Data which are presently available indicate, on the contrary, that the proposed mechanism may be incorrect.

It has been shown¹⁰ that intermolecular exchange of ethyl groups between bonding sites in toluene solutions of ethyllithium at 30° occurs with a rate constant $k_e = 1/\tau_e \leq 10 \text{ sec}^{-1}$. The rate-determining step which leads to intermolecular exchange is most probably



since this involves breaking the smallest number of bridge bonds, and because only one relatively high energy species (dimer) is produced. If the monomer is the kinetically active species, it must be produced, therefore, from dissociation of the dimer:



These considerations alone would lead one to expect a reaction order of 1/4 rather than 1/6, although there might be complications from a parallel dissociation of tetramer. But the available experimental data indicate that, in fact, the dimer cannot be dissociating rapidly enough to produce active monomer. To proceed further, it is necessary to have some feeling for the magnitudes of the rates and concentrations involved. Typically¹⁻⁵, for $[(\text{RLi})_6] \sim 10^{-4} M$, $S \sim 10^{-1} M$, $rate_i$ is on the order of $10^{-7} \text{ mole} \cdot \text{l}^{-1} \cdot \text{sec}^{-1}$. It is clear that step (4) produces dimer more rapidly than it is consumed, since the rate of dimer formation is given approximately by

$$\frac{d[(\text{RLi})_2]}{dt} \sim 3 k_e [(\text{RLi})_6] \sim 3 \times 10^{-7} \text{ mole} \cdot \text{l}^{-1} \cdot \text{sec}^{-1}$$

Morton and Fetters^{11, 12} have reported that polyisoprenyllithium (mol. wt. $\sim 2.5 \times 10^5$) is dimeric in hydrocarbon solution, with an enthalpy of dissociation of 37 kcal/mole*. If a similar value is assumed for dissociation of the short chain dimer—and there is no obvious reason why it should be smaller—a rate constant k_d for step (5) can be estimated. Let $k_d < 10^{14} \exp(-\Delta H_d/RT)$, where the pre-exponential term has been very generously estimated¹³. The rate of production of monomer is then $R_m < k_d [(\text{RLi})_2]$. $[(\text{RLi})_2]$ is presumably less than 1/10 of $[(\text{RLi})_6]$; say $10^{-5} M$. Then R_m is about $10^{-17} \text{ mole} \cdot \text{l}^{-1} \cdot \text{sec}^{-1}$, which is ten orders of magnitude slower than the observed initial rates! The argument is essentially unchanged if it is assumed that dissociation proceeds in two steps. What assumption about the enthalpy of dimer dissociation are necessary to increase R_m to an acceptable value of about $10^{-5} \text{ mole} \cdot \text{l}^{-1} \cdot \text{sec}^{-1}$? Retaining the very generous estimate for the pre-exponential term, ΔH would have to be about 20 kcal/mole or less. It seems very unlikely that ΔH_d could be this low. Preliminary estimates from ⁷Li NMR temperature dependence studies of the activation energy for reaction (4) are about 16–18 kcal/mole. But this step involves—in a formal sense—

* The dissociation of dimer was evaluated by Morton and Fetters from viscosity data. Their procedure is rather unusual, but the results obtained appear to be reliable. From the values reported for ΔH and K_d , a value of ΔS_d at 298°K of 90 e.u. is calculated. Although at first glance this seems unrealistically high, linear extrapolation of entropy–enthalpy data for systems of the form $A \rightleftharpoons B + C$ and $A_2 \rightleftharpoons 2 A$ ¹⁴⁻¹⁷ yields a rough ΔS value of about 85 ± 12 e.u. for ΔH value of 37.5 kcal/mole.

breaking two 4-center bonds to form two 3-center bonds¹⁹. This should require considerably less energy than breaking the two 3-center bonds to form two 2-center bonds. If the crude assumption is made that stabilization of multicenter bonding, arising from the increased delocalization of electrons, is proportional to the number of centers, ΔH_d should be on the order of 32–36 kcal/mole, which is in the range of Morton and Fetter's result.

The enthalpy of activation for exchange of methyl groups between bridging and terminal positions in trimethylaluminum dimer is 15.6 kcal/mole²⁰. This exchange process involves rupture of only one half of the dimer bonding. The heat of dissociation of trimethylaluminum dimer is reported to be about 20.2 kcal/mole²¹. A larger energy for dissociation of alkylaluminum dimer is to be expected. As an indication of this, it may be pointed out that trialkylaluminum compounds are not associated in ether or other basic solvents²². Studies in our laboratories by Mr. L. M. SEITZ of the ⁷Li NMR resonances of ether solutions containing methyl- and ethylaluminum reveal, by contrast, that the alkylaluminum compounds are strongly associated, and that the association is tetrameric at temperatures of about –50° and lower. A relatively strong bridge bonding in the polymeric alkylaluminum moieties is indicated.

As a further indication of the energetics involved, in the mass spectrum of ethylaluminum vapor at 87° and 0.08 mm Hg pressure (corresponding to a concentration of about 4×10^{-6} moles/liter), there is no evidence of even free dimer, let alone monomer⁸. This implies that the enthalpy change required to produce monomer is very large; the enthalpy of activation for production of monomer must be correspondingly large. Trimethylaluminum under similar conditions would be extensively dissociated. We conclude, therefore, on the basis of the available data, that *monomeric alkylaluminum is probably not the kinetically active species in reactions of alkylaluminum compounds in hydrocarbon solution*. Furthermore, there is no evidence to support the hypothesis that monomeric alkylaluminum is the kinetically important species in basic solvents such as ether or THF. Until such evidence is forthcoming, identification of a fractional reaction order with the inverse of the association number of an organoaluminum reagent is inappropriate.

In searching for alternative mechanisms²³, it is important to recognize that in the addition of RLi to an olefin, or in a metallation reaction, a new organoaluminum compound is produced. It can, through association with the remaining reactant, profoundly affect the kinetics of the reaction. Furthermore, the possibility of a complex-forming equilibrium with a nucleophilic substrate must also be kept in mind.

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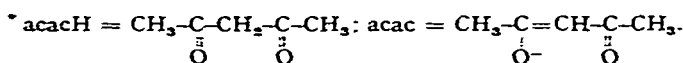
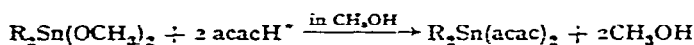
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Organometal complexes

II. Organotin and organolead bis(acetylacetonates)

Many stable complexes have been obtained by the reaction of dialkyltin dihalides with 8-hydroxyquinoline^{1,2}, 2,2'-bipyridine^{2,3} and 1,10-phenanthroline^{2,3}. Although these complexes have been reported to have a chelate structure containing hexa-coordinated tin, further stereochemical study seems to be rather difficult, for the ligands are too complicated². Infrared, Raman and NMR spectra studies have suggested that dimethylbis(acetylacetonato)tin^{1,5} or -lead⁴ have the methyl groups in *trans*-configuration. In order to study the electronic effect of substituents on tin on the acetylacetonate ligand through the tin atom, we have prepared a series of disubstituted bis(acetylacetonato)tin compounds (Table I).

Diorganobis(acetylacetonato)tin compounds were obtained by the reaction of the diorganotin dichloride and sodium methoxide in methanol, followed by the addition of acetylacetone.



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