Aggregation of *n*-butyllithium in basic solvents

Kinetic experiments which we report here provide substantial evidence that in 100% tetrahydrofuran (THF) solution at 22° *n*-butyllithium is predominantly *at least* trimeric. In contrast evidence has been reported and interpreted as establishing that *n*-alkyllithium compounds exist as solvated dimers in the presence of basic solvents, examples being *n*-butyllithium in diethyl ether[1] and ethyllithium in triethylamine[2]. In view of the correspondence between the behaviors of diethyl ether, triethylamine and THF, such different extents of aggregation would not be expected.

Rates of metalation of triphenylmethane by organolithium compounds in THF solution can be measured spectroscopically[3]. The reaction was shown[3] to be first order in $(C_6H_5)_3CH$, but is found to be of variable order in organolithium reagent.

The explanation for the one-sixth kinetic order dependence found for *n*-butyllithium addition to olefins[4–9] and metalation of fluorene[10] in hydrocarbon solution is believed to be that the reactive form of *n*-butyllithium is monomer which exists in equilibrium with a predominance of relatively unreactive hexamer. Colligative measurements establishing hexamer as the predominant *n*-butyllithium species in hydrocarbon solution[11] support this mechanism. Under similar circumstances in THF solution (*i.e.*, *n*-butyllithium predominantly in the form of a relatively unreactive aggregate in equilibrium with a more reactive less associated* form) the rate law would be $k[RLi]_t^{1/n}[(C_6H_5)_3CH]$ where $k = k_2K(1/n)^{1/n}$. The extent of aggregation s n and K is the equilibrium constant for $(1/n)\ (RLi)_{na} \rightleftharpoons (RLi)_a$.

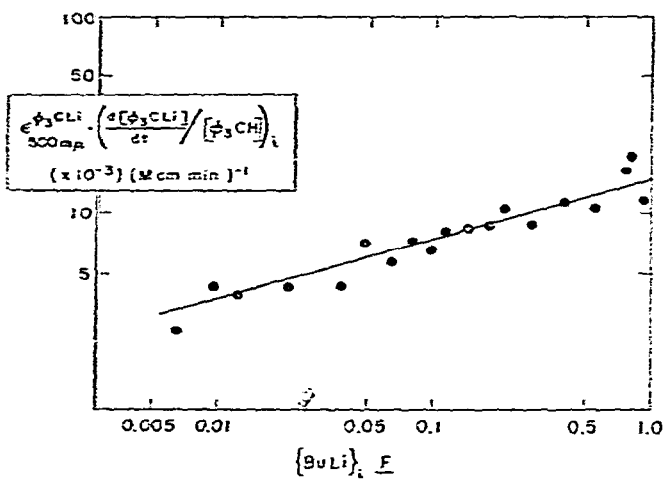

Fig. 1. Kinetic dependence of reaction rate on *n*-butyllithium concentration.

From the slope of a plot of log rate *vs.* log $\{RLi\}_t$ the minimum* average extent of aggregation can be determined. Regression analysis establishes that the slope of Fig. 1 is 0.33_2 or $n = 3$. It can be said with 95% certainty that the true value of n is

* A fractional kinetic order does not establish that the reactive species is monomer but shows that the less associated species is $1/n$ the size of the larger aggregates. A kinetic scheme not involving this equilibrium can be visualized but it would also require the organolithium compound be aggregated to an extent equal to n.

between 3.9 and 2.6*. This kinetic behavior requires *n*-butyllithium to be on the average predominantly at least trimeric in THF solution if the reactive *n*-butyllithium species is monomer. If the reactive species is dimer the predominant form of *n*-butyllithium in THF must be hexamer.

Eastham *et al.* have concluded on the basis of kinetic data[12], dielectric measurements[13] and other physical measurements[1] that *n*-butyllithium exists in diethyl ether solution as a solvated dimer having stoichiometry 1/2 $Et_2O/n\text{-}C_4H_9Li$. Brown[2] has concluded from freezing point measurements and continuous variation analysis of ethyllithium solutions that the predominant species in excess triethylamine is also a solvated dimer, but of stoichiometry 1/1, *i.e.* $(EtLi)_2(Et_3N)_2$. Brown has interpreted his findings to support those of Eastham. Although their experiments are well conceived, the interpretation given to the acquired data does not appear to be the only possibility. Eastham's measurements are evidence that there is a significant change in the *n*-butyllithium species in hexane–ether solution when the ratio $Et_2O/n\text{-}C_4H_9Li$ is 0.5, but do not establish that the species is a monosolvated dimer. For example, a disolvated tetramer could also fit the majority of his observations. The freezing point lowering observed by Eastham[1] for a 2/1 mole ratio of *n*-butyllithium/Et_2O in cyclohexane, instead of demonstrating 100% monosolvated dimer, could be indicative of other situations, *e.g.* a predominance of monosolvated trimer (0.17 molar) in equilibrium with free Et_2O (0.08 molar) or monosolvated hexamer (0.08 molar) with Et_2O (0.17 molar). Brown concludes that species other than a solvated ethyllithium hexamer are required to explain the freezing point lowerings obtained in the presence of triethylamine. He considers a solvated tetramer but without obvious justification concludes the predominant species is a solvated dimer. Although a solvated dimer is a logical extension, the predominance of a dimeric species in triethylamine is not established by Brown's colligative measurements. In addition Job's method of continuous variation on which Brown relies to support a dimeric species[2] does not give reliable results with systems composed of more than a single equilibrium[14]. Presumably, as recognized by Brown, the interaction between Et_3N and ethyllithium in hydrocarbon solution involves several equilibria.

Determination of aggregation by the kinetic experiments reported here is less subject to alternative interpretation. There appears to be no explanation other than *at least* trimeric association of *n*-butyllithium in THF for the fractional kinetic order found for *n*-butyllithium metalation of triphenylmethane in THF. It seems unlikely that *n*-butyllithium would be less associated in diethyl ether or triethylamine than in THF[13].

Crystal structure determination of ethyllithium[15] and methyllithium[16] by three dimensional X-ray, indicate a preference of alkyllithiums to associate into dimers which further associate to tetramers. On the other hand colligative measurements (vapor pressure lowering) show *n*-butyllithium to be hexameric in hydrocarbon solution[11]. A high stability for the alkyllithium hexamer is indicated by its predominance even in the vapor of ethyllithium[17]. Interpretation of the 1/3 kinetic order

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* The probability that this data belongs to a set for which n is 2 is extremely small. The probability that the true value of n is 4 is $\sim$ 0.05. Small amounts of impurities (*i.e.*, adsorbed on the glass walls, etc.) would tend to bias the data toward a larger slope, *i.e.*, smaller n. Thus, although the precision indicates only a low probability of $n = 4$ a consideration of the effect of impurities makes $n = 4$ a real possibility.

of *n*-butyllithium in THF as indicating the predominant species is hexamer in equilibrium with a reactive dimer would be consistent with the demonstrated stability of the hexamer and the preference for dimers. However, by analogy with the previous findings for *n*-butyllithium[8-10] in hydrocarbon solution, the preferred interpretation of the fractional kinetic order is that the predominant *n*-butyllithium species in THF solution are trimers (or tetramers) in equilibrium with reactive monomer.

Similar kinetic measurements of the rate of metalation of triphenylmethane by other organolithium compounds establish that the extent of aggregation in THF solution depends on the structure of the organolithium compound. Benzyllithium and allyllithium are indicated to be monomeric*. Phenyllithium is dimeric and vinyllithium is at least trimeric**. Details of these metalation kinetic studies will be published soon.

A referee has pointed out that if the predominant *n*-butyllithium species is dimer and *the reactive entity* is *free ion* a 1/4 kinetic order would be obtained. The general scheme is as follows:

$$1/n(\mathrm{RLi})_n \underset{K_1}{\rightleftharpoons} \mathrm{RLi} \underset{K_2}{\rightleftharpoons} \mathrm{R}^- + \mathrm{Li}^+$$

$$\frac{d[(C_6H_5)_3CLi]}{dt} = k'[RLi]^{1/2n}[(C_6H_5)_2CH_2]$$

where $k' = k'_2 K_1^{1/2} K_2^{1/2} (1/n)^{1/2n}$

In view of the low inherent stability anticipated for the *n*-butyl anion and the concentrations of *n*-butyllithium [5×10^{-3}–5×10^{-1} *F*] used it is almost sure that in these experiments the free *n*-butyl anion is not the predominantly reactive species. The following evidence supports this belief. The dissociation constant (K_d) for ion-pair to free ions for the resonance stabilized polystyryl anion in THF is $\sim 2 \times 10^{-7}$ *M* and, although free styryl anion is ~ 400 times as reactive as polystyryllithium ion-pair[21]***, only at concentrations $< 5 \times 10^{-5}$ *F* does reaction via free ions dominate over that of ion-pairs. For lithium cyclohexylamide in cyclohexylamine K_d 10^{-12} *M* and in the exchange reaction between hydrocarbons and lithium cyclohexylamide it was concluded that no significant amount of reaction involves free ions[22]. Since neither *n*-butyl or cyclohexylamide anion is capable of resonance stabilization, it seems unlikely that *n*-butyl anions are kinetically significant species in these metalation reactions. If free ions were the kinetically active species in these metalations, they would probably be most significant with benzyllithium and show a 1/2 order dependence. The experimentally found first order dependence is consistent with ion-pairs.

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* This is in agreement with the analogous polystyryllithium[18] in THF and polyisoprenyllithium[19] in THF.

** An identical dependence is found for the addition of vinyllithium to 1,1-diphenylethylene in THF solution[20].

*** The importance of resonance for ion-pair dissociation in THF is indicated by the finding that $NaClO_4$ dissociates to a lesser extent than polystyrylsodium[21].

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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 olefins[1–5]. 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 low[1–3], 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:

$$(\mathrm{RLi})_n \rightleftharpoons n\ \mathrm{RLi} \qquad (1)$$

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

$$\mathrm{RLi} + \mathrm{S} \longrightarrow \text{product} \qquad (2)$$

$$rate_i = k[S_i][(RLi)_i/n]^{1/n} \qquad (3)$$

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