Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.18; H, 3.88.

2,3-Diphenylindenone Ozonide (XVI). The crystalline ozonide XVI was prepared by the method of Criegee.[8] On standing at 10° in benzene solution, it was completely converted to the anhydride XVII in 24 hr. In a similar solution irradiated with 3100–4000-A light the reaction was greatly accelerated and XVII was formed in quantitative yield after 1.5 hr.

Colligative Property Measurements on Oxygen- and Moisture-Sensitive Compounds. I. Organolithium Reagents in Donor Solvents at 25°

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Abstract: The differential vapor-pressure technique used to study solution colligative properties of oxygen- and moisture-sensitive compounds is described. Colligative measurements on organolithium reagents in tetrahydrofuran and diethyl ether at 25° are reported. Deviations from ideality are accounted for in terms of solute aggregation and solute–solvent interactions. The findings are that organolithium reagents may or may not be aggregated in these donor solvents at 25°. The data indicate a predominance of tetrameric methyllithium, dimeric phenyllithium, and monomeric benzyllithium, these species being representative of alkyl, sp^2 hybridized, and charge-delocalized reagents. These aggregate sizes agree with postulations of organolithium aggregation in tetrahydrofuran based on kinetic studies.

Kinetic studies of metalation[1–4] and olefin addition[5,6] by organolithium reagents in tetrahydrofuran (THF) solution at 22° revealed fractional reaction orders for certain of the organolithium species. These reaction orders of less than unity were interpreted to be a consequence of organolithium aggregation in THF solution,[2–6] a surprising result in view of the good solvating power of THF for such species.

No accounts are reported of colligative studies of organolithium compounds in THF solution. This report describes colligative property measurements made on organolithium solutions in pure donor solvents THF and diethyl ether.[6]

Previous colligative studies have established that alkyllithiums are aggregated in hydrocarbon solution.[7–9] Nevertheless, in the presence of basic solvents it was logical to expect that aggregation would be disrupted in favor of strong solvation by the basic solvents.[10] Pioneering ebullioscopic measurements on organolithiums in diethyl ether,[11] on the other hand, indicated methyllithium to be approximately trimeric and *n*-butyllithium pentameric, whereas both benzyllithium and phenyllithium were indicated to be dimeric. Later ebullioscopic experiments[12] also indicated phenyllithium to be dimeric in diethyl ether and *n*-butyllithium to be hexameric in this solvent. Ebulliometrically determined degrees of organolithium aggregation in ether solvents are, however, open to criticism[13] because of the possible reaction of the organolithiums with solvent at elevated temperatures.[14] Another point of view, deduced from freezing-point measurements of *n*-butyllithium in cyclohexane solution containing a small amount of diethyl ether[15] and ethyllithium in benzene–triethylamine mixtures,[16] is that alkyllithiums are dimeric in the respective donor solvents. These experiments in mixed solvents are, however, subject to alternative explanations.[2] Interpretation of recent low-temperature nmr studies on concentrated (~1 *M*) mixtures of methyllithium and ethyllithium in diethyl ether invoked tetrameric structures for alkyllithium species at −80°,[17] although it was not possible to rule out an alternative model based on trimeric species. Low-temperature findings may not reflect the behavior at room temperature.

The experiments reported here illustrate that certain organolithium species are aggregated in diethyl ether and THF at 25° in spite of the opportunity for solvent coordination. With other structure types more extensive solvation is apparently favored and the species are found to be monomeric in these solvents. The

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(17) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 2174 (1966).

technique used in these studies is that of vapor-phase osmometry,[18] also referred to as the differential vapor-pressure method.[18d] It has the advantage of permitting measurements at 25° over a range of formal organolithium concentrations $\{\mathrm{RLi}\}$. This method has been used recently in several other fundamental studies of polar and ionic species.[19] It has not, however, previously been applied to molecules that are oxygen and moisture sensitive, as are organolithiums. The usual practice is to suspend drops of solution and solvent on thermistors in the vapor above a bath of pure solvent. The difference between solvent activities in the pure solvent and solution causes solvent to condense on the solution drop until its temperature is elevated to a point that vapor pressure equilibrium is established with its environment. A sensitive thermistor bridge[18] is utilized to measure the resultant small temperature differential between the isolated solution and solvent drops.

Experimental Section

Apparatus. The system consists of a dual thermistor probe[20] fixed into the neck of a 100-ml glass vapor equilibration chamber. The unit has two side arms. One is connected to high vacuum and a dry argon supply, the other is closed off with a rubber syringe cap and is the introduction port for samples loaded in Hamilton gas-tight syringes. The unit is thermostated by placing it in an air bath, which is enclosed in a second air bath placed in a tank of water thermally regulated to ±0.01° in the vicinity of 25.0°.

Colligative Measurements and Calibration Procedure. Organolithium reagents in pure THF and diethyl ether were studied. Solvent is the conventional reference used in differential vapor-pressure measurements,[18] but measurements relative to a standard solution are equally satisfactory.[18c] In working with these air- and moisture-sensitive systems great advantage was found in using a methyllithium solution of approximately 0.1 *M* formal concentration as reference.[21] This relatively large "sink" of active species served to scavenge impurities and eliminate experimental difficulties originating in reaction of adventitious impurities with the organolithium solution droplet under investigation. At the start of an experiment the vapor equilibration chamber was pumped under high vacuum for 12 hr and then filled with dry argon and maintained at a slightly positive pressure. The cell was next rinsed with 5 ml of methyllithium reference solution which was then withdrawn. The cell was placed in the thermostating unit and 40 ml of methyllithium reference solution added. One hour proved to be ample time for establishment of vapor-pressure equilibrium in the system.[22] The full measurement routine[21] involved placing reference solution on both beads and balancing the bridge at 60 ohms after 4 min had elapsed at which time equilibrium was reestablished. A reference droplet was then immediately replaced by the sample under investigation, washing the thermistor with two to three drops of the test solution. The resultant temperature differential arising from equilibration of the solvent activities of the sample and reference solutions was measured as a resistance (ΔR) using a decade resistance unit (reading to 1000 ohms in 0.01-ohm steps) in the compensating arm of the Wheatstone bridge.[20] Readings of ΔR were recorded at 30-sec intervals over a period of at least 3 min.

The relationship between resistance (ΔR) and number of particles in solution was established by calibrating each solvent using *trans*-stilbene, triphenylmethane, and naphthalene as solutes. Solutions of these species were considered to act in an ideal manner. The bridge imbalance registered after 2 min was plotted as a function of solute mole fraction (X). With a reference other than pure solvent, observed ΔR (t = 2 min) readings were normalized[21] to give the values relative to pure solvent, as shown in Figure 4. Calibration plots were drawn up of normalized ΔR (ohms, t = 2 min) *vs.* X. In practice no real limitation was observed in the choice of reference solution. The same calibration plot of normalized ΔR (ohms, t = 2 min) *vs.* X was obtained for all three calibration hydrocarbons irrespective of whether the reference used was 0.10 *M* methyllithium, 0.33 *M* methyllithium, 0.025 *M trans*-stilbene, or pure solvent. System instability produced a maximum error in normalized ΔR (ohms, t = 2 min) of ±1.0 ohm. The high stability of methyllithium in both THF and diethyl ether[14] at 25° was a major determining factor in its convenient use as a reference in these measurements.

Materials. Methyllithium, phenyllithium, and benzyllithium were prepared as halide-free diethyl ether solutions from the corresponding disubstituted mercury compounds[11] and clean chunks of lithium metal as reported previously.[23] The preparative procedures furnished the organolithium reagents in high yield and uncontaminated by other substances such as lithium halide. Total alkali was determined by HCl titration. Only fresh organolithium solutions were used in which the total active lithium and total alkalinity were indicated to be equivalent by electronic, spectral, and glpc measurements. Possible complications arising from decomposition products were thus avoided. For example, with phenyllithium–THF solutions made from diphenylmercury, vapor above the solution was analyzed before and after ethanol quenching and the benzene:THF ratios determined (F & M Model 609 flame ionization gas chromatograph with 10 ft × 0.25 in. DEGS column at 50°). Direct comparison with standard benzene–THF solutions showed that a maximum 1–2% quenching occurred during syntheses.

These organolithium–THF solutions were initially prepared as diethyl ether solutions. The diethyl ether was pumped away and replaced by THF just prior to the use of the organolithium reagent. Glpc analysis established quantitative removal of the diethyl ether. For example, the remnant diethyl ether in a phenyllithium–THF solution amounted to a ratio phenyllithium:diethyl ether = 20.

Dimethylmercury (Eastman Organic Chemicals) was used without further purification. Diphenylmercury and dibenzylmercury were recrystallized from a methylene chloride–ethanol mixture. Methyllithium (from methyl chloride) in diethyl ether and *n*-butyllithium in hexane (obtained from Foote Mineral Co.) were also used. Repeated high vacuum pumping of these solutions and dissolving of the remaining reagent in THF or diethyl ether as required gave methyllithium–THF and *n*-butyllithium–diethyl ether solutions effectively free of diethyl ether and hexane, respectively. The quantitative removal of diethyl ether and hexane from the starting materials was demonstrated by glpc analysis. Diethyl ether was distilled from lithium aluminum hydride. THF was preliminarily dried over calcium hydride and then distilled from lithium benzophenone ketyl.

Naphthalene and triphenylmethane were recrystallized from ethanol. *trans*-Stilbene (Eastman Scintillation Grade) was used without further purification.

Results

The organolithium results were first treated in the form of normalized ΔR (ohms, t = 2 min) *vs.* $\{\mathrm{RLi}\}$, *M*. Using the calibrations, these data were transformed into plots of apparent solute mole fraction (X_{app}) *vs.* $\{\mathrm{RLi}\}$, *M*. Apparent degrees of organolithium aggregation (n_{app}) were then computed according to the equation

$$n_{\mathrm{app}} = \frac{S_{\mathrm{M}}\{\mathrm{RLi}\}(1 - X_{\mathrm{app}})}{(\rho - M_{\mathrm{RLi}}\{\mathrm{RLi}\})X_{\mathrm{app}}}$$

where S_{M} represents the solvent molecular weight,

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(18) (a) M. Davies and D. K. Thomas, *J. Phys. Chem.*, **60**, 763, 767 (1956); (b) H. C. Ehramtraut, "Proceedings 1961—International Symposium on Microchemical Techniques," N. D. Cheronis, Ed., Interscience Publishers, Inc., New York, N. Y., 1962; (c) A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961); (d) S. Bruckenstein and A. Sato, *J. Am. Chem. Soc.*, **87**, 698 (1965).

(19) W. L. Masterton and J. A. Scola, *J. Phys. Chem.*, **68**, 14 (1964); J. F. Coetzee and R. M. Lok, *ibid.*, **69**, 2690 (1965); B. Magyar, *Helv. Chim. Acta*, **48**, 1259 (1965); G. E. Boyd, A. Schwarz, and S. Lindenbaum, *J. Phys. Chem.*, **70**, 821 (1966).

(20) The thermistor probe and associated Wheatstone bridge circuitry is part of a Model 301 osmometer sold by Mechrolab, Inc.

(21) The procedure used in these studies is analogous to an earlier established technique, the full details of which have been reported[18c] under the subtitle "Internal Calibration."

(22) At 25° the thermistors are of closely matched resistance (~6000 ohms) with an approximate temperature coefficient of the resistance of −4%/degree. Thermal instability in the vicinity of the thermistors amounted to a temperature differential between the thermistors of less than 0.001°, equivalent to a bridge imbalance of ~0.2 ohm.

(23) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

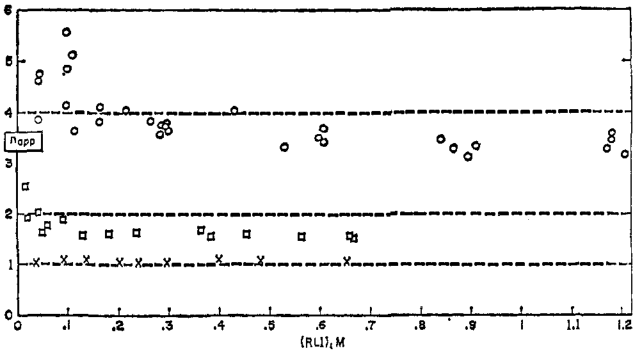

Figure 1. Apparent degree of organolithium aggregation (n_{app}) as a function of formal organolithium concentration {RLi}, *M* in THF at 25°: ○, methyllithium; □, phenyllithium; ×, benzyllithium.

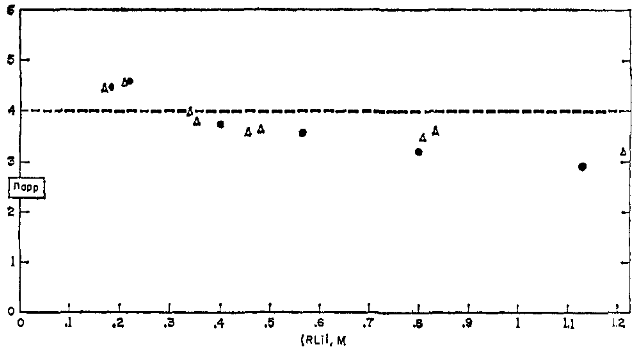

Figure 2. Apparent degree of organolithium aggregation (n_{app}) as a function of formal organolithium concentration {RLi}, *M* in diethyl ether at 25°: △, methyllithium; ●, *n*-butyllithium.

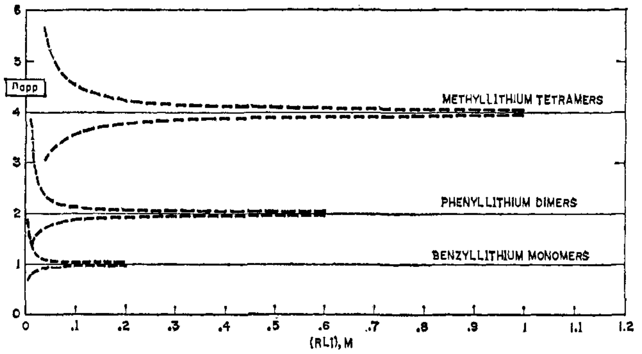

Figure 3. Boundaries (- - - -) of the expected asymmetric distribution of points resulting from differential vapor-pressure studies of hypothetical organolithium solutions in THF at 25°.

{RLi} the molar formal organolithium concentration, M_{RLi} the molecular weight of monomeric organolithium, X_{app} the experimentally determined apparent mole fraction of organolithium aggregates, and ρ the organolithium solution density in grams/liter at 25°. Measurements of densities of the organolithium solutions showed them to be within ±3% of that of pure solvent, 0.88 g ml^{-1} for THF and 0.70 g ml^{-1} for diethyl ether. In Figure 1 n_{app} *vs.* {RLi}, *M* is plotted for solutions of methyllithium, phenyllithium, and benzyllithium in THF at 25°. Figure 2 shows similar plots for methyllithium and *n*-butyllithium in diethyl ether.

Discussion

The colligative measurements shown in Figures 1 and 2 are interpreted as evidence that at 25°, over the formal concentration ranges studied, methyllithium in THF or diethyl ether and *n*-butyllithium in diethyl ether are on average tetrameric, phenyllithium is dimeric in THF, and benzyllithium in THF is monomeric. It is inferred that the aggregate size apparently shows little sensitivity to formal organolithium concentration over the range studied, indicating a predominance of a single structure. Absence of a distribution of species is also indicated by the kinetic and colligative studies of organolithium reagents in hydrocarbon solutions[24] as well as by kinetic studies in THF and diethyl ether solution.[3,6] The observed decrease of apparent aggregate size with increase in organolithium concentration is interpreted to be a consequence of negative deviation from ideal solution behavior. These deductions involve the assumption that deviations from ideality in the colligative properties of organolithiums in THF and diethyl ether at 25° are largely due to solute self-association and solute–solvent interactions. In the discussion which follows it is reasoned that reported colligative, spectroscopic, glpc, and kinetic data afford justification for this assumption.

Donor solvents such as THF and diethyl ether interact strongly with organolithium reagents.[25] In view of specific strong solvent–solute interaction negative deviation from ideality is the predicted behavior. The consequence of solute–solvent binding is that the vapor pressure of solvent is reduced more by a given number of particles than it would be were the solute–solute, solute–solvent, and solvent–solvent interactions equal. Thus a given number of organolithium particles would be expected to decrease the solvent vapor pressure to a level below that computed from Raoult's law.[26] Differential vapor-pressure measurements on such solutions would indicate an apparent number of solute particles in solution in excess of the number actually present. Consequently the calculated average degree of organolithium association (n_{app}) would be lower than the true value.

The individual measurements of effective aggregate size of the more highly aggregated species in Figures 1 and 2 show significant scatter at low concentrations. Experimental uncertainty in this particle concentration range is unfortunately considerable. The extent to which the uncertainty in normalized ΔR (ohms, $t = 2$ min) of ±1.0 ohm contributes to scatter in derived values for n_{app} can be assessed by considering as hypothetical cases ideal solutions of methyllithium tetramers, phenyllithium dimers, and monomeric benzyllithium in THF at 25°. If differential vapor-pressure measurements on these solutions were subject to an error of ±1.0 ohm in normalized ΔR (ohms, $t = 2$ min), then the plotted results n_{app} *vs.* {RLi}, *M*, would exhibit an asymmetric distribution about the concentration-independent lines $n_{\text{app}} = 4.0$, 2.0, and 1.0, respectively (Figure 3). In addition to this instrumental error,

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[24] R. C. P. Cubbon and D. Margerison, "Progress in Reaction Kinetics," Vol. 3, G. Porter, Ed., Pergamon Press Inc., New York, N. Y., 1965, pp 407–408.

[25] R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966).

[26] O. D. Bonner, K. W. Bunzl, and G. B. Woolsey, *J. Phys. Chem.*, 70, 778 (1966).

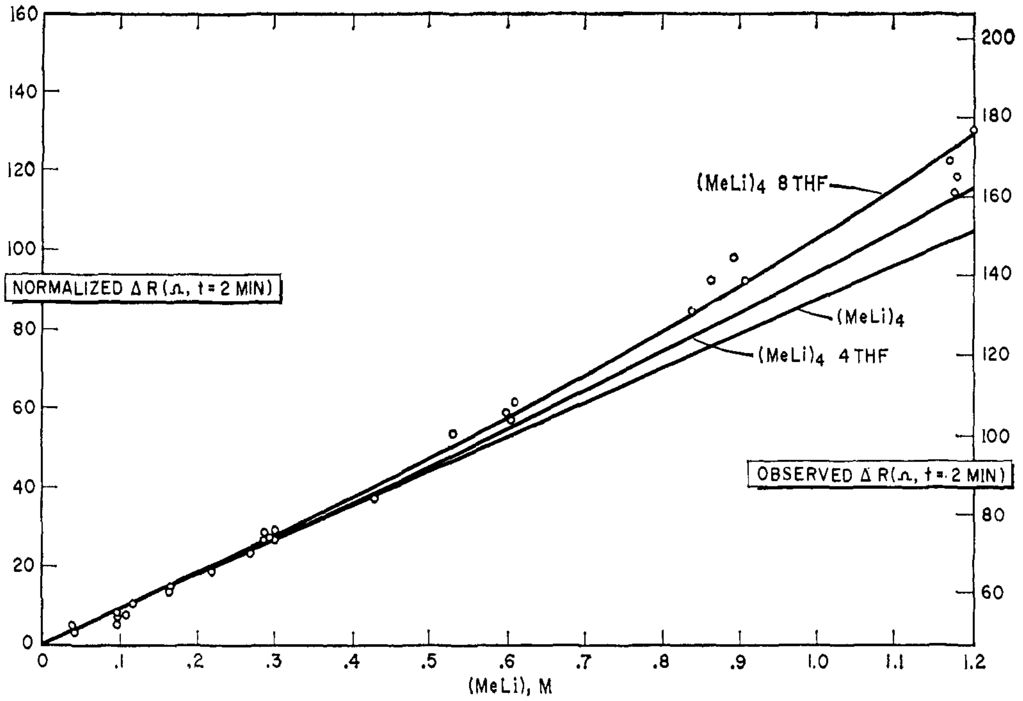

Figure 4. Colligative measurements on methyllithium in THF at 25° along with calculated model system traces for solvated methyllithium tetramers.

trace impurities may influence n_{app}.[17,27] We have initiated colligative studies to evaluate the effects of small amounts of water, oxygen, and lithium salts on aggregate size. Preliminary experiments show the work reported here was not influenced by trace impurities.

The organolithiums investigated in these colligative studies in THF and diethyl ether represent three different structural classes: alkyl, sp^2-hybridized, and resonance-stabilized organolithiums. In the first two types electrons of the carbon–lithium bond are presumably localized in σ orbitals. In these structures with such a localized charge dipole the balance between solvation and aggregation energies favors self-association. Multicenter electron-deficient bonding is thought to provide the forces responsible for aggregate formation.[8,10,28] In the latter case delocalization of the carbon–lithium bond electrons throughout the organic moiety is expected to promote solvation of the lithium cation and owing to a greater diffusity of charge decrease dipolar attractions. These factors apparently override the tendency for self-association in benzyllithium.[29]

The findings of these colligative measurements are in agreement with the previous interpretation[2-6] that the reaction order in organolithium reagent reflects its state of aggregation in the donor solvent THF. For example, studies of the kinetics of metalation of triphenylmethane by methyllithium[4,6] in THF at 22° establish that the reaction order ($1/n$) in methyllithium is 0.28 ± 0.04[30] over the {MeLi} range 0.01–0.6 M. A similar situation is found in the addition of methyllithium to 1,1-diphenylethylene (DPE) in THF ($1/n$ = 0.28).[6] Tetrameric association of methyllithium at 25° is in agreement with this fractional reaction order.[31] The reaction order in n-butyllithium is 0.33 for metalation of triphenylmethane under the same conditions.[2] The reaction of n-butyllithium with DPE in THF at 22° is very fast but the reaction was studied in diethyl ether[6] yielding a reaction order in n-butyllithium of 0.30. These values are consistent with the colligative measurements. The conclusion is that methyllithium and n-butyllithium are tetrameric in both THF and diethyl ether at 25°. This is contrary to the earlier conclusion, based on the interpretation of other kinds of physical measurements made on alkyllithiums in THF and diethyl ether,[15,16,32] that the predominant alkyllithium species is a solvated dimer in these solutions. Colligative measurements and the kinetics[1-6] of metalation and olefin addition reactions are in accord with benzyllithium being monomeric and phenyllithium dominantly dimeric in 100% THF and diethyl ether at 25°. Since there is correspondence between colligative and kinetic findings, it seems reasonable to suggest on the basis of kinetic studies[6] that allyllithium is monomeric in THF and diethyl ether at 25° whereas vinyllithium is trimeric or tetrameric, even though colligative data are not yet available for allyllithium and vinyllithium.

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(27) T. L. Brown, J. A. Ladd, and G. N. Newman, *J. Organometal. Chem.* (Amsterdam), 3, 1 (1965); W. H. Glaze and G. M. Adams, *J. Am. Chem. Soc.*, **88**, 4653 (1966).

(28) G. E. Coates, "Organo-Metallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 21.

(29) Although colligative measurements of benzyllithium in hydrocarbon solution are not practical owing to insolubility, the structurally analogous polystyryllithium was shown to be dimeric in benzene solution by viscosometric [M. Morton and L. J. Fetters, *J. Polymer Sci.*, **2A**, 3311 (1964)] and kinetic [S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962)] studies. Polyisoprenyllithium and polybutadienyllithium, the structural analogs of allyllithium, are also indicated to be dimeric in hydrocarbon solution (see Morton and Fetters above).

(30) Confidence limits, 95%, of the slope of log rate *vs.* log {MeLi} plot, see ref 2.

(31) The nature of the reactive species cannot be definitively deduced from reaction order alone. Readers are referred to a previous paper[2] for a discussion of the kinetic arguments relating reaction order ($1/n$) and degree of aggregation.

(32) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963); F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

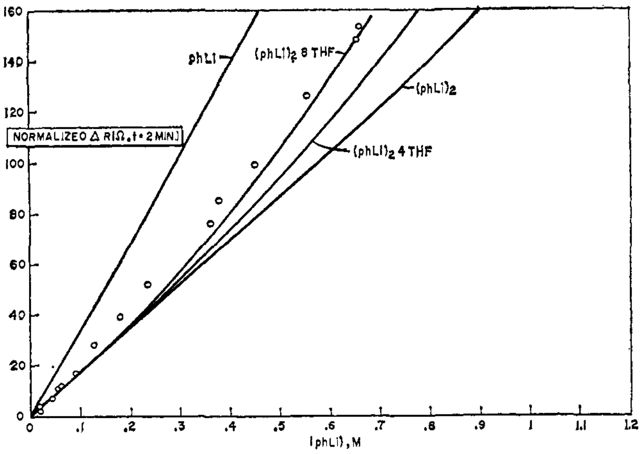

Figure 5. Differential vapor-pressure data for phenyllithium in THF at 25° and traces calculated for solvated phenyllithium dimer model systems.

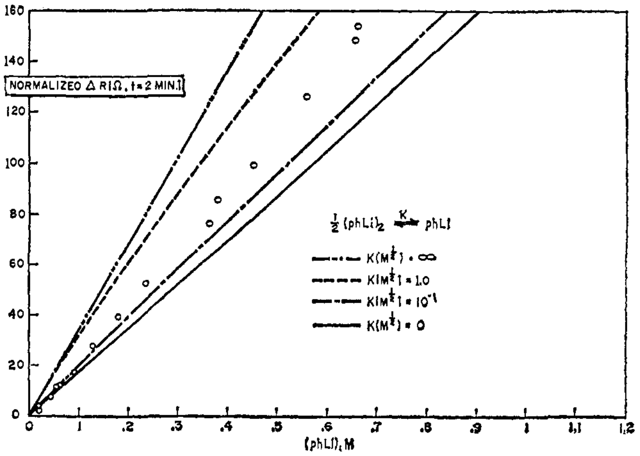

Figure 6. Colligative property measurements of phenyllithium in THF at 25° together with data calculated for the model system $0.5(\mathrm{PhLi})_2 \rightleftharpoons \mathrm{PhLi}$: —··—, $K = \infty$; – – – –, $K = 1.0\ M^{1/2}$; — · —, $K = 10^{-1}\ M^{1/2}$; ———, $K = 0$.

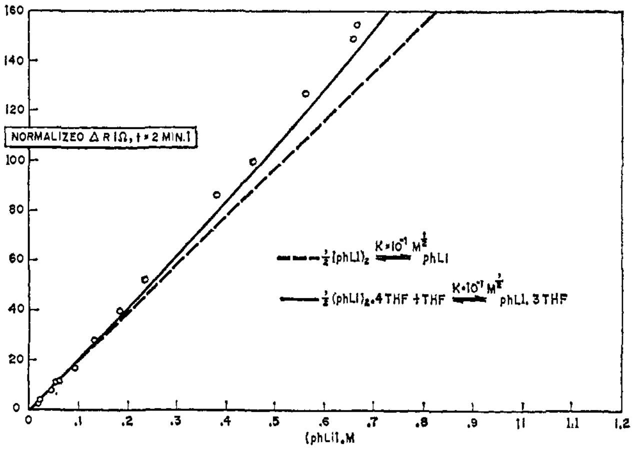

Figure 7. A comparison between colligative data for phenyllithium in THF at 25° and calculated model system traces.

By way of illustrating the effect that binding of THF by organolithium aggregates might have on the observed differential vapor-pressure measurements, comparisons were made between experimental findings and calculations based on simple model organolithium systems. These are illustrated in Figures 4–7. Solution ideality was assumed to prevail in the model systems. The expected normalized ΔR readings as a function of $\{\mathrm{RLi}\}$ were calculated for each model system.

Behaviors calculated for two discrete THF etherates of tetrameric methyllithium are compared in Figure 4 with experimental measurements of methyllithium in THF. They are in accord with the concept that solvent–solute interaction accounts for the decrease of effective aggregate size at higher concentration.

The colligative data for phenyllithium in THF at 25° are compared with values calculated for phenyllithium monomer, dimer, and THF solvated dimer units in Figure 5. In the latter two systems it is assumed that the dimer–monomer equilibrium constant (K) is sufficiently small that the monomer concentration is negligible throughout the formal phenyllithium concentration range considered. Agreement between experiment and these models is poor. An alternative consideration is that the equilibrium constant (K) for the dimer–monomer equilibrium is large enough so that the concentration of monomer is both significant and variable over the $\{\mathrm{PhLi}\}$ range 0.05–0.6 M in THF at 22°. Figure 6 illustrates that proper choice of K could approximate the data without invoking solvation. Nevertheless, the kinetic findings for phenyllithium in THF at 22°[3,6] indicate that $K \lesssim 10^{-1}\ M^{1/2}$, the probable value being $K \sim 10^{-1}\ M^{1/2}$. Using this value of K Figure 7 illustrates that the colligative data is in accord with this situation when discrete solvates are considered. Both colligative and kinetic observations are, therefore, consistent with a dominance of phenyllithium dimers.

These model systems illustrate that the observed trends in measured colligative data are in accord with expected solution properties of the organolithium reagents in donor solvents. They support the belief that the decrease in apparent aggregate size with increasing organolithium concentration arises from nonideal solution behavior. Those model systems which best approximate the experimental findings are considered to be likely representations of the species in solution.

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