

$\text{OH}^+][\text{H}^+] = 7.0)$ and of the dimeric form ($\log \left(\frac{[\text{CuL}(\text{OH})_2^{2+}]}{[\text{CuL}(\text{OH})^+]^2} \right) = 2.2$) fall in the range of values reported by Gustafson and Martell¹⁹ for a series of related bidentate ligands.

A similar hydrolysis reaction appears to take place in glycylglycine-Cu(II) titrations at high pH values. The postulated structure (XIII) has one molecule of water coordinated to the Cu(II) ion. A reaction resulting in the formation of a monohydroxo chelate is therefore possible. Dimerization of the monohydroxo chelate probably does not occur because of the negative

(19) R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 519 (1959).

charge of the $\text{CuL}(\text{OH})^-$ (XIV), in accordance with the generalizations discussed previously for dimerization of Cu(II) chelates.²⁰

The structure suggested for the Cu(II)-histidylhistidine peptide chelate contains no water molecule coordinated to Cu(II). The absence of an appreciable tendency toward hydrolysis is confirmed by the steep inflection of the titration curve of Fig. 1 at $a = 5$ followed by a high pH buffer region at pH values of 10 or above.

(20) S. Chaberek, R. C. Courtney, S. J. Westerback, H. Hyytiainen, and A. E. Martell, *ibid.*, **79**, 3036 (1957).

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Interaction of Alkylolithium Compounds with Base. Complex Formation between Ethyllithium and Triethylamine in Benzene

BY THEODORE L. BROWN,¹ R. L. GERTEIS, D. A. BAFUS, AND J. A. LADD

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Solutions of ethyllithium with varying quantities of added triethylamine in benzene have been studied using dielectric constant and freezing point lowering measurements. The results demonstrate that interaction between the two solute species does occur and provide evidence that a number of related equilibria are involved. It is proposed that, at low ratios of base to alkylolithium, coordination of base occurs to the intact alkylolithium hexamer. As the base:hexamer ratio increases, the hexamer dissociates into coordinated dimer. The species $(\text{RLi})_2(\text{base})_2$ is formed initially, but may be further solvated at higher base concentrations. It is further proposed that the equilibria postulated also characterize alkylolithium solutions in other bases, notably ether. Infrared, n.m.r., and kinetic data are consistent with the proposed equilibria.

The structures of alkylolithium compounds in the vapor^{2,3} and solid states,⁴ and in hydrocarbon solutions,^{3,5} are reasonably well established at this time. There remains, however, an uncertainty as to the form in which the compounds exist in basic, solvating media. The effect of small quantities of a Lewis base on the reactivity of alkylolithium compounds in hydrocarbon solutions,⁶⁻⁸ particularly in connection with anionic polymerization reactions,⁹⁻¹³ is a related problem which has attracted considerable interest in recent years.

It is well known that the alkylolithium compounds are much more reactive in ether than in hydrocarbon media.¹⁴ Since this reactivity extends to reaction with the solvent itself, attempts to determine the degree of association in ether by ebulliometry have not been notably successful.^{15,16} Further, the danger of contamination from oxygen or water vapor is enhanced in this type of experiment.

Infrared spectra of alkylolithium compounds in basic solvents have been reported.¹⁷⁻¹⁹ The behavior of

the 500 cm^{-1} band, which exhibits a large ^6Li - ^7Li isotope shift, is quite interesting.¹⁷ It seems very likely that this band is due largely to carbon-lithium stretching-bending in the polymeric species; it should therefore be quite sensitive to the state of the alkylolithium compound. The band appears at 530 cm^{-1} in hydrocarbon solvent and is shifted to lower frequencies in ether (492 cm^{-1}), benzene plus ether (511 cm^{-1}), and benzene plus triethylamine (520 cm^{-1}). The fact that the bands do shift appreciably demonstrates that interaction with base does occur. On the other hand, the shifts are smaller than one would expect if the interaction led to complete disruption of the polymeric alkylolithium species. It is possible, even probable, that in the presence of base the polymer is partially disrupted, with some form of multicenter bond persisting in the resulting complex. But a complete disruption of the polymer to give solvated monomer complexes should result in a drastic shift to lower frequency of the 500 cm^{-1} band.²⁰ The infrared data therefore indicate some self-association of alkylolithium compounds in basic solutions.

Indirect evidence relating to interaction of alkylolithium compounds with bases has also been obtained from kinetic studies.^{6,9,13}

(17) (a) A. N. Rodinov, T. V. Talalaeva, D. N. Shigorin, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **136**, 369 (1961); (b) A. N. Rodinov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, *ibid.*, **143**, 371 (1962).

(18) R. West and W. H. Glaze, *J. Am. Chem. Soc.*, **83**, 3580 (1961).

(19) A. N. Rodinov, T. V. Talalaeva, D. N. Shigorin, G. M. Timofeink, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **151**, 1131 (1963).

(20) In the limiting case of a solvated ion pair, the carbon-lithium stretching force constant should be very low, its magnitude determined by the degree of "intimateness" of the ion pair.

(1) Alfred P. Sloan Research Fellow.

(2) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

(3) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

(4) H. Dietrich, *Acta Cryst.*, **16**, 681 (1963).

(5) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

(6) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

(7) D. Y. Curtin and W. J. Koehl, *ibid.*, **84**, 1967 (1962).

(8) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

(9) A. V. Tobolsky and C. E. Rogers, *J. Polymer Sci.*, **40**, 73 (1959).

(10) F. J. Welch, *J. Am. Chem. Soc.*, **82**, 6000 (1960).

(11) D. J. Kelley and T. V. Tobolsky, *ibid.*, **81**, 1597 (1959).

(12) M. Morton, *Rubber Plastics Age*, **42**, 397 (1961).

(13) S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **40**, 1564 (1962).

(14) G. E. Coates, "Organometallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 7-18.

(15) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

(16) Ref. 14, p. 20.

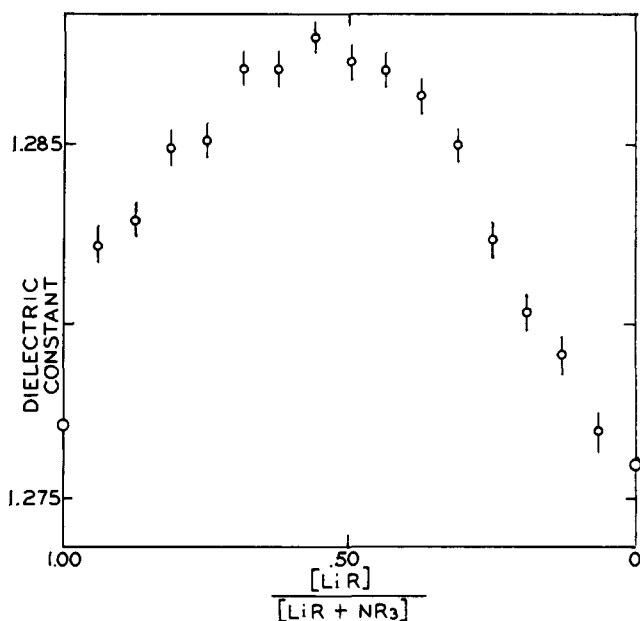


Fig. 1.—Dielectric constant vs. triethylamine:ethylithium ratio in dilute benzene solution.

The researches mentioned are representative of a very large body of work which relates in one way or another to the question of complex formation between alkyllithium compounds and bases. It seems clear that there is a need for information of a more direct character relating to association in these systems. We report here a study of the interaction of ethyllithium with triethylamine in benzene solution. The base was chosen for its moderately high base strength and low reactivity with ethyllithium.

Discussion

The electron-deficient nature of the alkyllithium polymeric species^{8,21} implies that they may possess some Lewis acid character. One of the first questions, then, in studying the interaction of an alkyllithium compound with a base is whether an observed interaction occurs without disruption of the polymeric framework.

Figure 1 shows the result of a dielectric constant study of ethyllithium–triethylamine solutions. Various volume ratios of ethyllithium and triethylamine solutions of nearly identical concentrations (0.1153 *N*, computed as monomer, and 0.1144 *N*, respectively) were taken; the total initial concentration is essentially constant, and the experiment therefore amounts to a Job's method analysis.^{22,23} The data exhibit some scatter, but the general shape of the curve was

(21) Assuming an idealized D_{3d} symmetry for the hexamer, the six atomic orbitals contributed by the six carbon atoms form symmetry orbitals of species A_{1g} , E_g , A_{2u} , and E_u . The lithium 2s-orbitals and two of the sets of lithium 2p-orbitals, also each generate the same reducible representation. The third set of lithium 2p-orbitals forms symmetry orbitals of species A_{2g} , E_g , A_{1u} , and E_u . In forming the bonding molecular orbitals of the hexamer, the largest contribution from lithium no doubt arises from s-orbital contribution. There should, however, be a considerable participation from the lithium 2p-orbitals. The six electron pairs which bond the alkyl groups and lithium atoms together are placed in bonding molecular orbitals of symmetry A_{1g} , E_g , A_{2u} , and E_u , leaving a number of vacant orbitals at approximately the energy of the 2s-orbital of lithium.

(22) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 29–32, 72.

(23) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 47.

found in replicate experiments to be quite reproducible. A distinct maximum was found in all cases, demonstrating that a complex of some kind is indeed formed.

The sensitivity of the dielectric constant measurement as an empirical index of base interaction is dependent on the polar nature of the complex or complexes formed. Neither of the reactants in the present case is very polar. The amine–alkyllithium interaction should result in the formation of a polar coordinate bond. It is possible, however, that if more than one base molecule interacts with a given alkyllithium species, the individual bond polarities may partially cancel as a result of the geometry.

As a second experimental approach to this system we have measured the freezing point lowering of solutions containing ethyllithium and triethylamine. Table I lists the results of a freezing point lowering study of ethyllithium in benzene. The reactive nature of the compound presents problems in obtaining data of high precision, but the results leave little doubt that ethyllithium exists predominantly as hexamer over a wide concentration range. Similar results were obtained for cyclohexane solutions. Analogous results have been reported quite recently for solutions of *n*-butyllithium in benzene and cyclohexane.²⁴

TABLE I

AVERAGE DEGREE OF ASSOCIATION OF ETHYLLITHIUM IN BENZENE SOLUTION

\bar{m} (monomer)	\bar{n}
0.0198	5.72
0.0201	6.29
0.0430	5.83
0.0632	5.57
0.0686	6.29
0.0789	6.42
0.0979	6.17
0.106	6.64
0.150	6.01
0.153	5.64
0.172	5.89
0.227	6.35

$$\bar{n} \text{ av.} = 6.07$$

$$\sigma = 0.35$$

Addition of triethylamine to ethyllithium solutions results in an increase in N , where

$$N = \frac{B_t + H_t}{\text{observed molality}}$$

The observed molality is determined from the freezing point lowering; B_t and H_t represent the total initial concentrations of triethylamine and ethyllithium (computed as hexamer), respectively. Table II shows the value of N obtained for a number of solutions encompassing a wide range of amine:hexamer ratio.

The relationship between freezing point lowering and molal concentration is the same linear function for either the base or hexamer alone in benzene. Values of N differing significantly from one are therefore ascribable to some form of interaction between the two

(24) D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, **59**, 2058 (1963).

species. This is, of course, to be expected. Of greater interest is the rather rapid increase in N with increasing base concentration, to values in excess of 1.5. A number of equilibria which merit consideration can be ruled out on the basis of these data, at least insofar as being the predominant equilibrium.

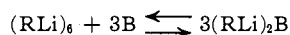
TABLE II

RESULTS OF FREEZING POINT LOWERING MEASUREMENTS OF SOLUTIONS CONTAINING ETHYLLITHIUM AND TRIETHYLAMINE

H_t^a	B_t^b	Ratio	S^c	N	N_{calcd}
0.0167	0.0109	0.652	0.0208	1.33	1.22
0.0163	0.0218	1.34	0.0286	1.41	1.36
0.0160	0.0326	2.04	0.0330	1.47	1.46
0.0167	0.0375	2.24	0.0339	1.60 ^d	1.48
0.0156	0.0436	2.79	0.0384	1.53	1.52
0.0153	0.0545	3.56	0.0446	1.56	1.55
0.0150	0.0654	4.36	0.0532	1.51	1.54
0.0162	0.0941	5.80	0.0723	1.53	1.54
0.0136	0.111	8.17	0.0833	1.49	1.39
0.0156	0.153	9.81	0.115	1.46	1.37
0.0150	0.250	16.7	0.190	1.39	
0.0139	0.350	25.2	0.283	1.29	
0.0136	0.393	28.9	0.319	1.27	

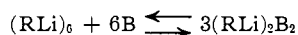
^a H_t = initial concentration of $(C_2H_5Li)_6$. ^b B_t = initial concentration of triethylamine. ^c S is the molality of the solution computed from the freezing point lowering. ^d This datum not included in calculation of K_1 , K_2 , and K_3 .

Eastham and Gibson have proposed, on the basis of the effect of ether on the reactivity of n -butyllithium, that a complex of the form $[Et_2O(RLi)_2]$ is formed on addition of ethyl ether to a hydrocarbon solution of the lithium reagent.⁶ While the dielectric constant results do not entirely rule out an analogous complex with triethylamine, the freezing point data do. Even if it is assumed that the reaction



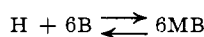
proceeds to completion, the maximum value which N may attain is 1.33, at a B_t/H_t ratio of 3. N values significantly higher than this are observed.

If the predominant complex-forming reaction were

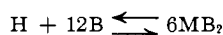


an N value as high as 2.33 might be obtained if the reaction were to proceed to near completion. But N should then maximize at a B_t/H_t ratio somewhat greater than 6, whereas it attains a maximum value at a lower ratio, between 3 and 4.

Formation of solvated monomer species may also be ruled out as a single, predominating equilibrium. For example the reaction



where H = hexamer, M = monomer, and B = amine, cannot lead to a value of N greater than 1.17, in contradiction with experiment. The reaction

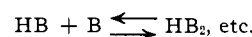
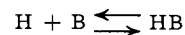


while it may produce sufficiently high values for N , should result in a dielectric constant maximum at a

2:1 amine:RLi ratio. Further the maximum N should occur at a B_t/H_t ratio of twelve or higher, again in contradiction with experiment.

There does not appear to be any one equilibrium which is capable of satisfactorily accounting for all the data. It is possible, however, to propose a set of successive equilibria which follow upon one another in a reasonable way as the amine:hexamer ratio is changed. The proposed equilibria cannot be tested quantitatively except in certain ranges of concentration but, insofar as comparison is possible, agreement with the observed properties of the system is seen.

The rapid rise in N with increase in amine concentration at lower B_t/H_t ratios is suggestive of equilibria of the form



with equilibrium constants K_1 , K_2 , etc. The N data have been analyzed in terms of the assumption that three such successive equilibria are sufficient to describe the system. Values of B_t/H_t ratio up to ten were employed, and the calculations were performed using a modified formation constant program.²⁵ The values computed for the successive formation constants, in units of l./mole, are:

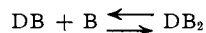
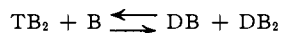
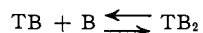
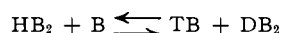
$$\begin{aligned} \log K_1 &= 1.70 & \sigma &= 0.44 & K_1 &= 50 \\ \log K_2 &= 1.33 & \sigma &= 0.56 & K_2 &= 21 \\ \log K_3 &= 1.78 & \sigma &= 0.28 & K_3 &= 60 \\ \log \beta_3 = \log K_1 K_2 K_3 &= 4.81 & \sigma &= 0.04 & \beta_3 &= 6.5 \times 10^8 \end{aligned}$$

The standard deviations (σ) are also shown; the large values of σ are due in part to the low precision of the N data, particularly at lower B_t/H_t ratios, and in part also to systematic factors discussed below.

The calculated constants reproduce the N values well for lower amine:hexamer ratios (column 6 of Table II), but predict values which are too low for solutions of higher ratios. Further, the unrealistically large value for K_3 is indication that even in the range of B_t/H_t considered, there must be other equilibria involved. As a general rule, the equilibrium constants of successive reactions decrease monotonically in value, and by a factor of perhaps 3 to 4. On this basis, if K_1 is realistic, and we believe it is, K_2 appears to be a reasonable value. On the other hand K_3 should be quite small. We propose, therefore, that the first two equilibria are important in the system, but that other processes occur at higher amine:hexamer ratios.

As a rather formal way of seeing how coordination to the hexamer might occur, it is helpful to consider the hexamer structure as an octahedral arrangement of lithium atoms, with alkyl groups bonded to six of the eight faces of the octahedron (Fig. 2).³ Coordination of base may then occur at the two vacant faces which are on opposite sides of the molecule. The coordination weakens the hexamer framework bonding, so that the following equilibria follow readily on addition of further base

(25) W. J. Randall, D. F. Martin, and T. Moeller, *Proc. Chem. Soc.*, 340 (1961). We are indebted to Mr. W. J. Randall for providing us with a copy of his program.



where H = hexamer, T = tetramer, D = dimer, and B = base species.

We have not attempted to be all inclusive in listing possible equilibria; suffice it to say that the system is potentially very complex. The most important point

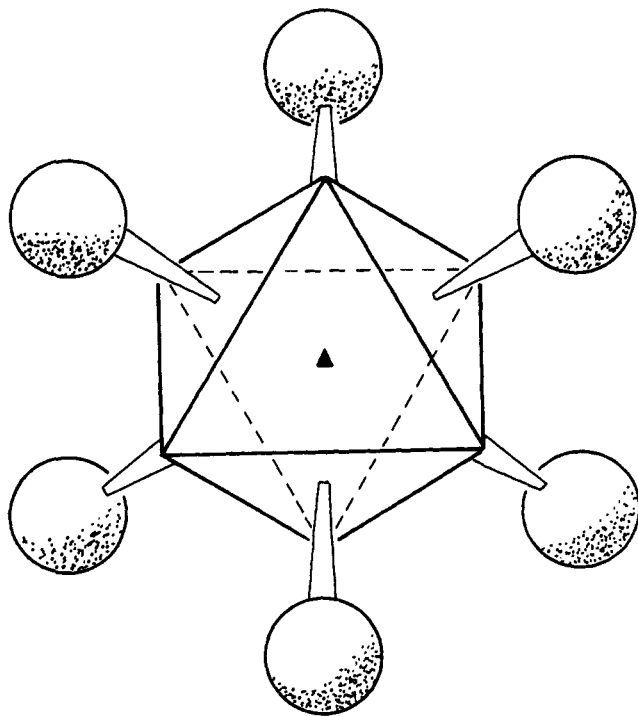
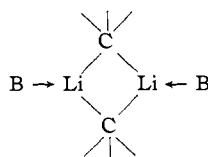


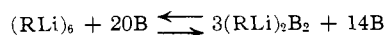
Fig. 2.—A schematic drawing of the alkyl lithium hexamer structure. The stippled spheres represent bridging carbon atoms; the lithium atoms are located at the corners of the octahedron. An S_6 axis passes through the centers of the two blank faces, shown by the small triangle.

is that the species ultimately arrived at in excess base is the solvated dimer, $(\text{RLi})_2\text{B}_2$. The structure we propose for this species is



Three-center bridge bonds connect the two alkyl lithium monomers. The properties of the bridge bond are presumably not unlike those of the four-center bond of the hexamer. In solutions of high base concentration there may be additional solvation of the dimer to give perhaps species of the form $(\text{RLi})_2\text{B}_4$, but in any case the dimer structure is maintained.

At amine:hexamer ratio of about 20, the reaction



will probably have proceeded far to the right. At this

amine:hexamer ratio, therefore, the N value should approach 21/17, or 1.23. The observed value of 1.35 (interpolated from the data in Table II) is somewhat higher than this, possibly indicating higher solvation of the dimer.

While a detailed comparison is not possible, the equilibria proposed are in general consistent with the dielectric constant results, insofar as agreement can be tested. The predominant species at high $B_t:H_t$ ratios is the 1:1 complex, $(\text{RLi})_2\text{B}_2$. To the extent that this species possesses polar character it contributes to a maximum in the dielectric constant for a 1:1 ratio. At lower $B_t:H_t$ ratios the predominant species should be HB and HB_2 . The maximum in the dielectric constant curve may therefore be shifted to lower than 1:1 ratio as a result of contributions from these species, as well as from TB, TB_2 , and DB.

The proton n.m.r. spectra of ethyllithium in toluene, triethylamine, and ether are tabulated in Table III.

TABLE III

PROTON MAGNETIC RESONANCE SPECTRA OF ETHYLLITHIUM IN VARIOUS SOLVENTS

Solvent	τ_{CH_2}	τ_{CH_3}	J_{ax}
Toluene	10.83 ± 0.02	8.60 ± 0.03	8.2 ± 0.2
Triethylamine	11.06 ± 0.08		8.3 ± 0.2
Diethyl ether	11.10 ± 0.05		8.4 ± 0.2

The chemical shift values and coupling constants vary to a remarkably small degree with change in solvent. We believe that these data are more in consonance with the presence of association and multicenter bonding in the base solutions than with solvated ion pair formation. Fraenkel²⁶ has suggested from the similar chemical shift values of ethyllithium, ethylmagnesium bromide, and (presuming upon a comparison of the methyl compounds) diethylmagnesium that the alkyl groups may be present in the form of solvated ion pairs in all of these compounds. But the data in Table III show that the methylene chemical shift for ethyllithium is quite insensitive to solvation effects. The methylene chemical shift difference between ethylmagnesium bromide and ethyllithium in ether (0.37 p.p.m.) is larger than the change in chemical shift of the methylene group in ethyllithium in going from toluene to ether solution (0.27 p.p.m.). Furthermore, one would expect that the ^{13}C -H coupling constant in methyl derivatives would be relatively insensitive to the metal atom if the compounds were in the form of ion pairs. But the ^{13}C -H coupling constant measured by us for methyl lithium in ether is 98 c.p.s., which is quite different from the value of 107.7 c.p.s. obtained for ethylmagnesium bromide. Furthermore, the τ -value observed by us for the methyl lithium resonance is 11.94, whereas we obtain a value of 11.40 for the methyl resonance of dimethylmagnesium. There is, of course, a rapid exchange of alkyl groups in a solvent such as ethyl ether; this is evident from studies of solutions containing mixed organomethyl compounds^{27,28} and from the absence of asym-

(26) G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, 767 (1963).

(27) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).

(28) R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *ibid.*, **85**, 1191 (1963).

metry effects where they are to be expected if exchange were slow.²⁶

The ⁷Li resonance of ethyllithium in ether occurs at a chemical shift of -1.00 p.p.m. from a 70% aqueous solution of hydrated lithium bromide as external standard. This is the same as the chemical shift for the ⁷Li resonance of ethyllithium in benzene.³ For lithium aluminum hydride in ether the ⁷Li resonance appears at +0.78 p.p.m. from the same standard. Now lithium aluminum hydride is very probably present in ether in the form of ion pairs. The fact that the lithium resonance of ethyllithium in ether is very close to the value it exhibits in benzene solution, rather than to the value shown by LiAlH₄, suggests at least that ion pairs are not the prevalent species for ethyllithium in ether. There is, unfortunately, a paucity of data relating to the effects of structure and solvent on the ⁷Li resonance. Until more is known the data we present here are subject to only tentative interpretation.

Application to the Results of Kinetic Studies.—There are no compelling reasons for believing that the equilibria between an alkyl lithium compound and ether²⁹ are qualitatively any different from those involving triethylamine. The ether is presumably a weaker base,³⁰ and it may be that disruption of the hexamer occurs at a higher base:hexamer ratio. Any structure proposed for a dimer must involve each lithium in a minimum of two molecular orbitals which are of fairly low energy. The only argument for existence of a dimer in a basic solvent which is at all supportable must rest on the existence of a Li-C-Li bridge bond. Assuming the usual three-center bond model,³¹ we are left then in the dimer itself with a nonbonding bridge MO and two atomic orbitals per lithium atom which remain vacant. Assuming for the sake of illustration a 2sp² hybridization of the lithium orbitals, two of the sp² orbitals on each lithium are employed in forming the bridge bonds, leaving a third sp² hybrid and a 2p-orbital vacant on each lithium. A bonding arrangement of this kind is most likely to be effective if the third sp²-orbital on each lithium is employed in complex formation with the solvent. Indeed it may be said that such complex formation is necessary to provide the driving force for dissociation of the hexamer.

The result obtained by Eastham and Gibson,⁶ a rapid increase in reactivity of *n*-butyllithium with addition of ether to an ether:RLi ratio of 1:2, can be understood in terms of the equilibria we have proposed. Coordination of a molecule of base to the hexamer, though it does not result in dissociation, should result in an increase in lability of the adjacent alkyl groups. Addition of the second molecule of base should increase this lability even further. Additional interaction results in the formation of solvated dimers, which need not differ markedly in reactivity from the HB₂ species. One might expect, then, that at a base:hexamer ratio of somewhat above 2:1, corresponding to a base:monomer ratio of somewhat above 1:3, a process of solvation will have occurred which results in a considerable activation of all alkyl groups. Changes

in the rate constant beyond this point may be due to general medium effects, or to a difference in reactivity of the solvated hexamer as compared with the other solvated species, notably the dimer. Eastham and Gibson's result is thus plausibly accounted for.

The situation with regard to the effect of ether or other bases on the kinetics of propagation steps in anionic polymerization reactions is somewhat different. Morton and co-workers have shown that propagating chains terminated in C-Li are dimeric in hydrocarbon.¹² The lower degree of association can be attributed to considerable steric effect of the chains. Whether addition of base causes dissociation of the chain dimers into solvated monomers is probably still open to question, but the indications at present are that it does. In any case, base:RLi ratios of 1:1 or 2:1 are to be expected in these systems as observed.

Experimental

Materials.—Ethyllithium was prepared by methods described previously,³ or was obtained as a solid in a saturated benzene solution from Lithium Corporation of America. Freshly recrystallized material was employed in all experiments. Triethylamine (Eastman Organic Chemicals) was distilled from barium oxide, then fractionally distilled under an argon atmosphere. Reagent grade benzene was thoroughly flushed with argon, then dried over sodium wire.

¹³CH₃I in about 50% enrichment was obtained from Bio-rad Laboratories, Richmond, Calif. It was treated with ethyllithium in benzene solution to produce methyl lithium.³² The solid product was filtered, washed with pentane, and dissolved in ether for determination of the proton resonance spectrum.

Dimethylmagnesium was prepared by methods previously described.^{14,33} All preparations were found to be free of magnesium halide.

All experiments involving alkyl lithium compounds were performed in a glove box under nitrogen atmosphere. Removal of traces of oxygen and water was effected by a procedure described elsewhere.³⁴ Infrared spectra of solutions containing ethyllithium (those employed in the dielectric constant and freezing point lowering work) were examined to ensure absence of bands indicative of decomposition.³ The concentrations of ethyllithium solutions were determined by decomposing aliquot samples with water and titrating to phenolphthalein end point with standard 0.01 *N* hydrochloric acid. Conversion to molality was made using the density of benzene at 25°, 0.872 g./cm.³, after density determinations confirmed that ethyllithium (and triethylamine) solutions in benzene do not differ significantly in density from the solvent itself.

Dielectric Constant Measurements.—A drawing of the cell employed in the dielectric constant measurements is shown in Fig. 3. The cell possesses a volume capacity of about 20 ml. and an electrical capacitance of about 50 pf. in air. Cooling liquid (Ethyl Cellosolve) from a constant temperature circulating bath is brought into the box through a wall fixture, circulated through the cell jacket, and returned to the bath without coming in contact with the box atmosphere. The cell contents are thus thermostated at 25.00 ± 0.05°.

The cell leads were rigidly positioned so that the cell could be filled, emptied, rinsed, and dried, without altering the lead capacitances. The dielectric constant measurements were made with a heterodyne beat apparatus. The variable frequency oscillator of this apparatus is a Franklin oscillator similar to that described by Le Fèvre.³⁵ We have replaced the 1H4-G tube by a 12AU7, grounded the cathode, and changed the grid resistor to 5 megohms. The oscillator circuit is remarkably

(32) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957). Recent work in our laboratory indicates that methyl lithium prepared in the manner described is not pure, but consists of a 1:1 complex of methyl and ethyllithium. The same complex is found on reaction of ethyllithium with dimethylmercury. Details will be published elsewhere.

(33) S. J. Storer and E. I. Becker, *J. Org. Chem.*, **27**, 1868 (1962).

(34) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

(35) R. J. W. Le Fèvre, I. G. Ross, and B. M. Smythe, *J. Chem. Soc.*, **277** (1950).

(29) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

(30) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

(31) R. E. Rundle, *J. Phys. Chem.*, **61**, 47 (1957).

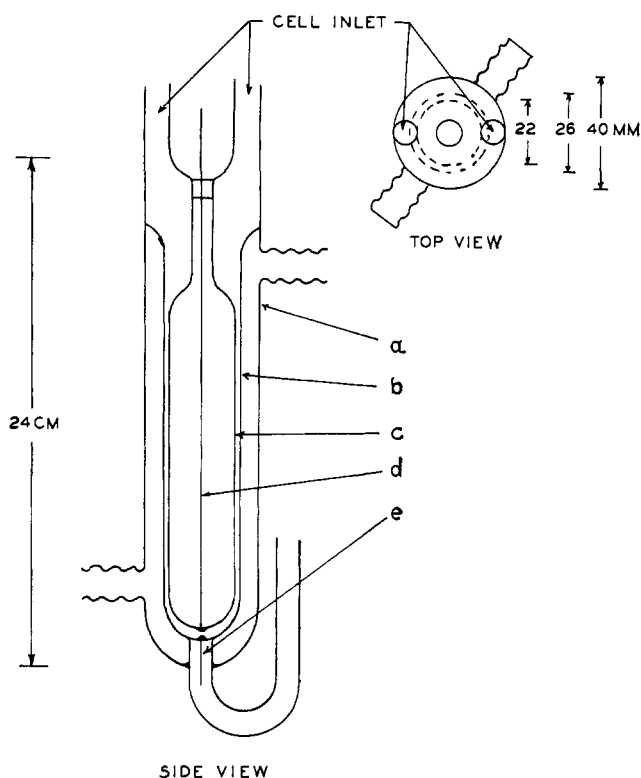


Fig. 3.—Cell used for dielectric constant measurements: a, constant temperature jacket; b, outer electrode surface (silvered); c, inner electrode surface (silvered); d, Pt wire connection to inner electrode; e, Pt wire connection to outer electrode.

stable when operated on a well-regulated B^+ supply. It is superior in stability to the circuit described by Chien,³⁶ and is doubly advantageous in that the 6A8 tube employed in the Chien circuit is now obsolete.

The crystal-controlled fixed frequency oscillator is operated at 100 kc.

Freezing Point Lowering Apparatus.—The freezing point lowering measurements were made with an apparatus which possesses a number of novel features. The cell which holds the solution is attached through a 24/40 standard taper joint to an assembly which contains the thermistor element, the temperature sensor. The assembly also acts as the stirrer (Fig. 4). Stirring is accomplished through operation of an electronically actuated a.c. solenoid which alternately lifts and drops the assembly.

The thermistor is Model 33A7 produced by Victory Engineering Corp., Union, N. J. It is held in place by potting it in a thin-walled glass well with Wood's metal. It forms one arm of a resistance bridge, with 5.0 K ten-turn precision potentiometers as the other three arms. The bridge is brought into balance, with approximately equal resistance values in all arms, at the freezing point of the solvent. The variable resistances are adjusted to produce a freezing point indication at the proper position in the output display; no further changes in bridge settings are made in subsequent measurements on the solutions.

Bridge current is supplied through a variable resistor from a lead-acid storage battery. With the bridge in approximate balance, *i.e.*, at the freezing point of the solvent, the current is adjusted to a desired value. It is important not to employ a high bridge current in circuits of the type described, inasmuch as Joule heating of the thermistor element may occur and produce spurious output. We have employed a value of 145 μ a. in our work.

The output of the bridge is amplified by a Minneapolis-Honeywell Model OMM-2HLA-9R d.c. amplifier. A wide range of gain settings is available, and one may be chosen which fits the range of freezing points expected. The output of the amplifier is displayed on a West Instrument Corp. "Marksman" recorder, with a 50-mv. scale. With a proper selection of bridge

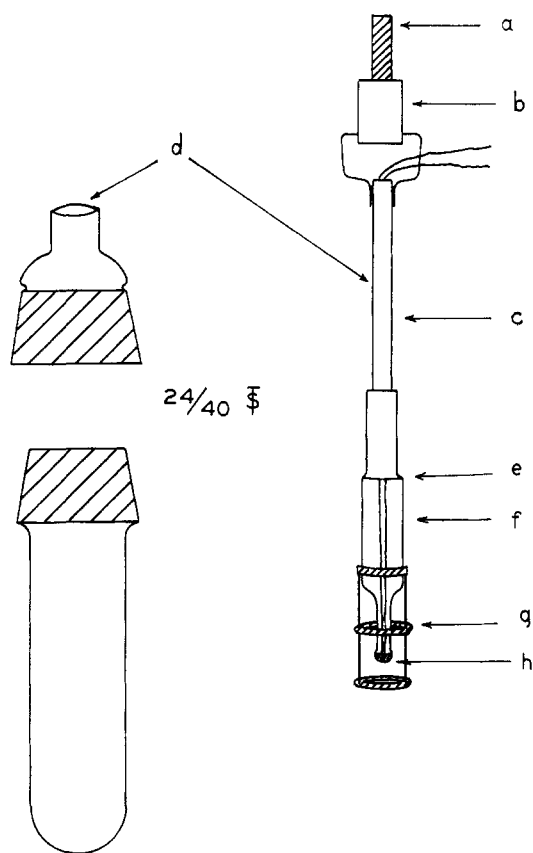


Fig. 4.—Freezing point lowering cell: a, soft iron core for solenoid lifting; b, Teflon block; c, 0.25-in. brass tube; d, thermistor assembly fits loosely in the glass neck in region shown by arrow (A soft latex rubber sleeve is used to join the glass neck to the brass tube); e, Kovar seal; f, glass; g, copper stirring rings; h, thermistor imbedded in Wood's metal in a thin-walled glass bulb.

current and amplifier gain, chart presentations of 5×10^{-4} $^{\circ}$ C./chart division are easily attained. Much lower scales, are of course, attainable. The noise level resulting from thermal gradients during stirring, mechanical effects, etc., is on the order of 1×10^{-4} $^{\circ}$ C. in a freezing benzene solution.

The cell was cooled in our experiments by placing it in a brass cold well within the glove box. Ethyl Cellosolve is circulated through the jacket of the well from a refrigerated circulating bath, thermostated to within 0.5° of the desired temperature. The circulating fluid does not come into contact with the box atmosphere. It was found that for the particular configuration in use, the best results were obtained when the temperature of the circulating fluid was maintained about 3° below the expected freezing point; however, the temperature differential is not critical.

In practice the freezing point lowering curve is obtained for each solution a number of times. Supercooling to the extent of 0.05 to 0.1° is usually observed. The linear portion of the time-temperature curve is extrapolated back to the original cooling line to obtain the correct reading. The apparatus and method described are far superior to the Beckmann thermometer in determining freezing points. Its major advantage, aside from greater sensitivity, is rapid response (time constant of less than 1 sec.) which results from the low heat capacity of the temperature sensor.

Calibration of the instrument for determination of molality is accomplished by measuring the output voltage at the freezing point as a function of molality for solutions of a variety of different solutes. Typically, compounds such as *p*-chlorobenzonitrile, diphenyl, anthraquinone, 1,5-dichloroanthraquinone, 9-fluorenone, and hexachlorobenzene are employed. It was found that solutions of all these compounds follow the same linear relationship between output voltage and molality in the concentration range 0–0.20 *m*. Because of imperfect impedance

(36) J. Y. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

matching, it was necessary to calibrate each gain setting of the amplifier separately.

Examination of a number of triethylamine solutions revealed that at concentrations above about 0.2 *m* the relationship between output voltage and molality deviates from linearity. Appropriate corrections were made for this effect in computing the values of *N* in Table II.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained on a Varian Associates Model A-60 instrument. The ethyllithium chemical shift measurements were made with respect to the center of the solvent meth-

ylene absorption in triethylamine and ether and converted to τ -values by separate measurement of the τ -values of the solvent absorptions. In toluene solutions the ring proton absorption was employed as intermediate reference.

The ⁷Li spectra were obtained in the manner described previously.³

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Hydrolysis of Xenon Hexafluoride and the Aqueous Solution Chemistry of Xenon^{1,2}

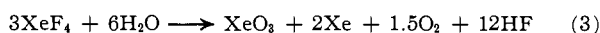
By E. H. APPELMAAN AND J. G. MALM

RECEIVED JANUARY 10, 1964

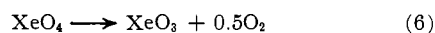
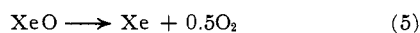
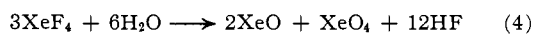
Both XeF₄ and XeF₆ hydrolyze in water to produce aqueous solutions of nonvolatile XeO₃ molecules. These solutions are stable, but they are strongly oxidizing, rapidly liberating chlorine from strong HCl. The Xe–Xe(VI) potential is estimated to be 1.8 v. in acid and 0.9 v. in base. The XeO₃ molecule is a weak acid, forming HXeO₄[−] above pH 10.5. In strongly basic solution Xe(VI) disproportionates to give xenon gas and octavalent xenon, while in such solutions ozone oxidizes Xe(VI) nearly quantitatively to Xe(VIII). Sodium and barium salts of Xe(VIII), perxenates, have been characterized, with typical compositions Na₄XeO₆·2.2H₂O and Ba₂XeO₆·1.5H₂O. A salt of mixed oxidation state, K₄XeO₆·2XeO₃, has also been observed. Aqueous solutions of sodium perxenate evolve oxygen slowly to give Xe(VI). The reaction becomes almost instantaneous below pH 7. Octavalent xenon is an extremely powerful oxidizing agent, rapidly oxidizing iodate to periodate and Mn⁺² to permanganate. The Xe(VI)–Xe(VIII) potential is estimated at 3.0 v. in acid and 0.9 v. in base. In basic solution Xe(VIII) is present as the ion HXeO₆^{−2}. Below pH 10 the principal species becomes H₂XeO₆^{−2}. Both Xe(VI) and Xe(VIII) have characteristic, pH-dependent, ultraviolet absorption spectra which can be attributed to the several species present.

Introduction

The three well-characterized xenon fluorides have been shown to react with water according to the following equations^{3–5}



Thus when XeF₆ is hydrolyzed, the xenon is quantitatively retained in solution as aqueous hexavalent xenon, while when XeF₄ is hydrolyzed, one third of the xenon is so retained. The stoichiometry of reaction 3 can be explained by a mechanism such as⁵



Divalent xenon has never been identified in aqueous solution, but reaction 6 is consistent with our knowledge of aqueous Xe(VIII).^{5,6}

In addition to these reactions, XeF₆ reacts with strong base to precipitate solid compounds containing

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) F. B. Dudley, G. Gard, and G. H. Cady, *Inorg. Chem.*, **2**, 228 (1963).

(4) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).

(5) J. G. Malm, B. D. Holt, and R. W. Bane, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167 ff.

(6) E. H. Appelman, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 185 ff.

octavalent xenon.⁵ The nature of this reaction will be discussed in our paper. We will also discuss in detail the properties of aqueous Xe(VI) and Xe(VIII).

Experimental

Preparation and Hydrolysis of Xenon Hexafluoride.—The XeF₆ was prepared as described elsewhere.⁷ It was distilled *in vacuo* and condensed on the bottom of a glass bulb. For the preparation of pure aqueous XeO₃ the bulb also contained magnesium oxide. The bulb was sealed off from the vacuum line and opened by means of a break-seal. The solution used for the hydrolysis was then added carefully to the frozen fluoride.

Preparation of Pure XeO₃.—Approximately 5 g. of xenon hexafluoride was hydrolyzed in about 100 ml. of water in the presence of at least 1.5 g. of MgO per gram of XeF₆. At least this much MgO was needed to neutralize rapidly all the HF produced. The resulting slurry was agitated until it was slightly alkaline and was then filtered through a sintered glass filter of medium porosity. To remove magnesium the solution was passed through a column of hydrous zirconium phosphate⁸ which had been washed with 2 *M* HNO₃ or HClO₄. Residual fluoride was then removed by passage through a column of hydrous zirconium oxide⁸ which had been converted to the nitrate form by exhaustive washing with 0.1 *M* HNO₃. The final product was a solution *ca.* 0.1 *M* in xenon(VI) and *ca.* 0.005 *M* in acid.

Other Materials.—Sodium perchlorate was prepared by neutralization of sodium carbonate followed by recrystallization. Mallinckrodt primary standard grade potassium iodate served as an iodometric standard, and N.B.S. potassium acid phthalate served as an acidimetric standard. Ozone was prepared from commercial oxygen by the usual silent discharge method.⁹ Commercial "pre-purified" nitrogen was used and all other chemicals were commercial products of reagent grade. Distilled water was redistilled first from alkaline permanganate, then from dilute sulfuric acid, and finally once more without additive before being used in these studies.

(7) J. G. Malm, I. Sheft, and C. L. Chernick, *J. Am. Chem. Soc.*, **85**, 110 (1963).

(8) Manufactured by Bio-Rad Laboratories, Richmond, Calif.

(9) See, for example, D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 262.