$$\underset{\mathbf{5}}{2\text{RMgX}} \rightleftharpoons (C_2H_5)_2Mg + MgBr_2 \qquad (5)^{39}$$

absorption in the region of the C–Mg absorption of diethylmagnesium in diethyl ether was observed. The expected shift in the n.m.r. spectrum upon the addition of amine to a solution of ethylmagnesium bromide in tetrahydrothiophene was not observed and remains anomalous.

The large negative values observed for the entropy of activation (Table VIII) indicate that there is a considerable degree of order in the transition state. Previous work by Swain,[21] who studied the reaction of *n*-butylmagnesium bromide with benzonitrile in ethyl ether and found a value of −34 e.u., indicates that a high entropy of activation is characteristic of this type of reaction. The only real difference in the values presented in Table VIII is in the case of diglyme. In this solvent there seems to be a considerable degree of solvent participation in the ground state as well as in the transition state, resulting in a less negative value for the energy of activation. No linear relationship exists between the values of ΔH^* and ΔS^*.

It is well known that magnesium halide can be precipitated from solutions of Grignard reagents by the addition of 1,4-dioxane to these solutions. Attempts to measure the position of the equilibrium (5) were futile from the start since the precipitation of magnesium halide would result in displacement of the equilibrium.[40] We have been able to obtain magnesium bromide from solutions of ethylmagnesium bromide without the aid of a precipitant. Hamelin, *et al.*,[41,42] have studied crystallization from solutions of ethylmagnesium bromide in a number of solvents and have found that the bromide content of these solids was high in all cases except when ethyl ether was the solvent. The solvents employed by Hamelin were anisole, isopropyl ether, ethyl ether, *n*-butyl ether, and tetrahydrofuran. These data indicate only that an equilibrium similar to 5 involving magnesium bromide exists in solutions of ethylmagnesium bromide. It seems likely in view of the limited solubility of magnesium bromide in most of these solvents and in view of the infrared spectra of these solutions (at least in diethyl ether and tetrahydrofuran), which show no absorption in the region of absorption of diethylmagnesium solutions, that the equilibrium constant for this reaction is small. Ashby and Becker[14] have reported a compound, $C_2H_5Mg_2Cl_3$, which they obtained by crystallization of a solution of ethylmagnesium chloride in tetrahydrofuran. We have not observed any material having a similar composition in solutions of ethylmagnesium bromide. The difference between these two solutions may be the result of the effect of the halogen upon the constitution of the reagent.

Since we have shown that the degree of association of ethylmagnesium bromide increases with increasing concentration, the failure to take this phenomenon into account may lie at the origin of much of the seemingly contradictory information reported for the degrees of association of various Grignard reagents in various solvents.

Acknowledgment.—We are glad to acknowledge generous support of parts of this work by the National Science Foundation under its Grant NSF-G-14558 (A. A. S.)

[39] The nature of **5** is unspecified.

[40] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 104–109.

[41] R. Hamelin and S. Goypiron, *Compt. rend.*, **246**, 2382 (1958).

[42] R. Hamelin and S. Hayes, *Bull. soc. chim. France*, 692 (1961).

Relationship between Structure and Solubility of Organic Lithium Compounds

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It has been found that organic lithium compounds with branching along the main chain of the organic moiety have increased solubility in hydrocarbon solvents such as benzene, heptane, and pentane. For example, branched-chain lithium alcoholates such as lithium isobutoxide and *sec*-butoxide have excellent solubility in *n*-heptane (*ca.* 50 wt. %), while the normal isomer is soluble only to the extent of about 5%. Conversely, straight-chain lithium alcoholates such as the *n*-butoxide have excellent solubility in alcohols (*ca.* 50%), while the branched chain isomers have very low solubility (less than 5%). This behavior has also been found to a lesser extent with disubstituted lithium amides. Association of the organic lithium compounds with concomitant micelle formation is offered as one explanation for such behavior.

The effect of molecular oxygen on excess butyllithium is to convert it to lithium *n*-butoxide.[1] Hydrocarbon solutions of *n*-butyllithium which have been oxidized retain this lithium *n*-butoxide in solution as a vanadium pentoxide inactive impurity.[2] This observed solubility of lithium *n*-butoxide in hydrocarbon solutions of *n*-butyllithium led us to an examination of the solubility properties of various lithium alcoholates in hydroxylic as well as aprotic solvents. There are very few references to any actual solubilities of lithium alcoholates in the chemical literature. Dermer,[3] in a review article on the metallic salts of alcohols, indicates that lithium ethoxide is soluble in alcohols, partially soluble in organic solvents, and insoluble in liquid ammonia. Jones and Thomas[4] describe the preparation of lithium ethoxide from lithium chloride and sodium ethoxide in ethanol, taking advantage of an apparent inverse temperature–solubility relationship of lithium

[1] C. Walling and S. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955).

[2] P. F. Collins, C. W. Kamienski, D. L. Esmay, and R. B. Ellestad, *Anal. Chem.*, **33**, 468 (1961).

[3] O. C. Dermer, *Chem. Rev.*, **14**, 385 (1934).

[4] J. H. Jones and J. S. Thomas, *J. Chem. Soc.*, **123**, 3284 (1923).

ethoxide in this solvent. Cram and co-workers[5] prepared lithium *t*-butoxide in *t*-butyl alcohol and dioxane. The reported concentration of this alcoholate in the two solvents is 26 wt. % and 3 wt. %, respectively. Simonov and co-workers[6,7] mention the fact that lithium *t*-butoxide, lithium isopropoxide, lithium isobutoxide, and lithium 3-pentanolate are readily soluble in ordinary organic solvents, but give no values. The authors also cite a previous work by Dubovitskii and Nogina (no reference given) in which they found the degree of association of a 0.088 *N* lithium *t*-butoxide solution in cyclohexane to be fivefold. They[8] also mention the fact that cryoscopic molecular weight measurements on the above-mentioned alkoxides in cyclohexane and benzene indicate an association number of 5 at 1 mole % concentrations and 3 at 0.5 mole % concentrations. These compounds were all found to be crystalline solids which could be sublimed without decomposition *in vacuo* (5×10^{-2} mm.) at 100–150°.

Golovanov and co-workers[9] state that ebullioscopic molecular weight measurements show that lithium *t*-butoxide has an association number of 6.4 ± 0.7 in cyclohexane solutions and 9.4 ± 0.9 in benzene solutions. The authors assumed the simplest associate of lithium *t*-butoxide to be a trimer in the form of a planar or nearly planar six-membered ring. The hexamer and nonamer could then be represented as composite "storied structures" of two or three trimers.

Results

It has been found that, in general, branched-chain organic lithium compounds have good solubility in hydrocarbon solvents, but poor solubility in hydroxylic solvents. Conversely, the straight-chain organic lithium compounds have excellent solubilities in hydroxylic solvents, but poor solubility in hydrocarbon solvents.

Figure 1 graphically illustrates this relationship as it pertains to various lithium alcoholates. Table I lists the solubilities of various lithium alcoholates in the more common solvents. We have found that those alcoholates exhibiting good hydrocarbon solubility also exhibit good solubility in ethers such as tetrahydrofuran. The opposite was found to be true of those alcoholates with low hydrocarbon solubility. Note that the results we obtained for lithium *t*-butoxide solubility differ considerably from those obtained by Cram.[5]

Figure 2 depicts this relationship still further by showing the increase in solubility of these branched-chain alcoholates in heptane with an increase in temperature. Note that little or no increase in solubility occurs with increasing temperature in the case of the straight-chain alcoholates in heptane.

TABLE I

SOLUBILITIES OF LITHIUM ALCOHOLATES IN SOME COMMON SOLVENTS

Compd.	Solvent	Concn. Moles/l.	Concn. Wt. %	Temp., °C.
Lithium methoxide	Methanol	2.90	12.7	0
		2.88	12.6	25
		2.86	12.5	40
		2.17	10.3	71
	Ethyl ether	0.04		25
	Pentane	0.00		25
	Heptane	0.00		26, 62, 83
Lithium ethoxide	Ethanol	2.40		26
		3.45		50
		3.50		70
	Ethyl ether	0.035		25
	Pentane	0.09		25
	Heptane	0.05		26
		0.05		45
		0.05		72
Lithium *n*-propoxide	*n*-Propyl alcohol	2.89		25
	Heptane	0.12		23
		0.12		41
		0.15		65
Lithium isopropoxide	Isopropyl alcohol	0.02		23
		0.05		41
		0.62[a]		70
	t-Butyl alcohol	0.26		30
	Heptane	3.78		23
		4.00		40
		4.65		60
Lithium *n*-butoxide	*n*-Butyl alcohol	5.14		26
	n-Hexane	0.66		25
	n-Heptane	0.25		25
Lithium isobutoxide	Isobutyl alcohol	0.13	1.3	22
		5.0[b]		75–80
	Ethyl ether	2.11		23
	Tetrahydrofuran	2.30		27
	n-Heptane	4.33	45.3	23
Lithium *sec*-butoxide	*sec*-Butyl alcohol	0.28	2.8	20
	n-Heptane	7.98	81.0	25
Lithium *t*-butoxide	*t*-Butyl alcohol[c]	0.15	1.5	23
	Ethyl ether	0.28		23
	Tetrahydrofuran	2.45	22.1	20
	n-Heptane	0.84		5
		0.99	11.4	23
		1.42		49
		2.38		77
		3.50		92
Lithium cyclohexanolate	Cyclohexanol	0.26		32
		0.30		90
		0.31		106
	n-Heptane	0.02		25
		0.04		50
		0.06		75

[a] Solution not saturated. Clear samples of filtrate from mixtures more concentrated in alkoxide than 0.8 mole/l. were difficult to obtain at lower temperatures owing to crystallization of the mixtures. [b] Lithium isobutoxide forms solid crystalline masses with molar isobutyl alcohol to alkoxide ratios of from 1.7 to 1 (6.4 moles of lithium isobutoxide per liter of solution) to about 10:1 (*ca.* 1 mole of alkoxide per liter of solution). Liquefaction of these masses to yield clear solutions occurs at 75–80°. [c] Lithium *t*-butoxide also forms solid crystalline masses with *t*-butyl alcohol, but these complexes do not form clear solutions on heating to reflux.

Figure 3 is a plot of the apparent solubility of lithium *n*-butoxide in *n*-heptane against the concentration of *n*-butyllithium also present in the solution. The apparent solubility of lithium *n*-butoxide in *n*-heptane was found to increase with an increase in *n*-butyllithium concentration in a directly proportionate manner. However, this effect was noted only when the *n*-butyllithium concentrations were equal to or greater

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(5) D. J. Cram, A. Langemann, W. Lwowski, and K. Kopecky, *J. Am. Chem. Soc.*, **81**, 5760 (1959).

(6) A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, *Proc. Acad. Sci. USSR Phys. Chem. Sect.* (Eng. Transl.), **136**, 1, 119 (1961).

(7) A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, *ibid.*, **141**, 1, 894 (1961).

(8) A. P. Simonov and D. N. Shigorin, *Dokl. Akad. Nauk SSSR*, **141**, 665 (1961).

(9) I. B. Golovanov, A. P. Simonov, A. K. Priskunov, T. V. Talalaeva, G. V. Tsareva, and K. A. Kocheshkov, *ibid.*, **149**, 835 (1963).

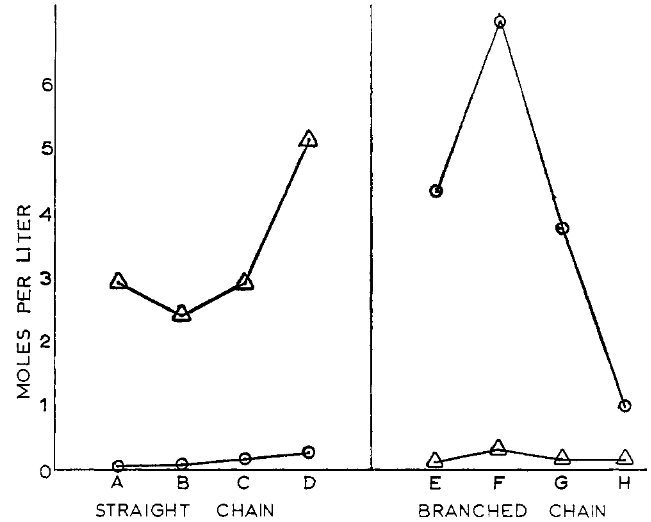

Figure 1.—Solubility of various C_1 to C_4 lithium alcoholates at room temperature: A, lithium methoxide; B, lithium ethoxide; C, lithium *n*-propoxide; D, lithium *n*-butoxide; E, lithium isobutoxide; F, lithium *sec*-butoxide; G, lithium isopropoxide; H, lithium *t*-butoxide; O, *n*-heptane; △, respective alcohols.

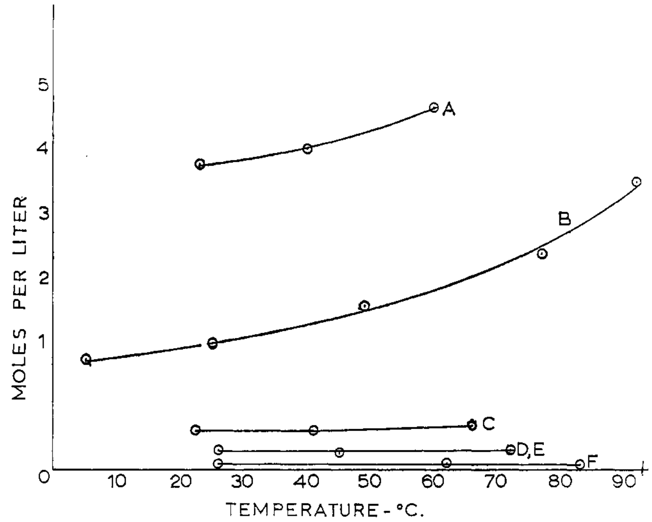

Figure 2.—Solubility of lithium alcoholates in *n*-heptane *vs.* temperature: A, lithium isopropoxide; B, lithium *t*-butoxide; C, lithium *n*-propoxide; D, lithium ethoxide; E, lithium cyclohexanolate; F, lithium methoxide.

than the lithium *n*-butoxide concentrations. Precipitation was observed in the solutions at molar alcoholate–organolithium ratios of 1:1 and above.

Figure 4 shows the equivalent solubility–temperature relationships for some of these alcoholates in their respective alcohols. The lowest homolog of the series, lithium methoxide, shows an inverse solubility–temperature relationship with an analysis of the solid phase showing it to be a disolvate below 40°, and solvate free above 40° (see break point in the curve). We have found that lithium ethoxide, the next higher homolog, has an increasing solubility–temperature relationship, in direct contrast to the results of Jones and Thomas.[4]

Lithium isopropoxide and lithium isobutoxide also show an increase in solubility with temperature. However, these branched-chain alkoxides exhibit a peculiar behavior when mixed with their respective alcohols at ordinary temperatures. We have found that lithium isopropoxide, lithium isobutoxide, and lithium *t*-butoxide formed solid, crystalline masses with the evolution of heat when we attempted to dissolve them in their respective alcohols. This effect appeared to be concentration dependent and was most striking with molar solvent-to-alkoxide ratios between 2:1 and 10:1. When the solvent-to-alkoxide ratios were raised to above 10:1, the crystalline masses began to liquefy and the solubility of the alkoxide in its alcohol was found to be surprisingly low (approximately 0.1 mole/l.). For example, it was found that, when the molar ratio of isobutyl alcohol to lithium isobutoxide in the mixture was varied from 1.7:1 (mixture approximately 6 *M* in lithium isobutoxide) to 11:1 (mixture approximately 1 *M* in lithium isobutoxide), all of the resultant products were crystalline (monoclinic) masses with consistencies which varied from hard solids which could be powdered (1.6–6 *M* range) to very thick slurries (1–1.6 *M* range) (see Table II). On heating the solid mixtures to *ca.* 75–80°, they liquefied completely. At an isobutyl alcohol to lithium isobutoxide molar ratio of 11:1, it was found by analysis of an aliquot of the clear filtrate from the slurry that the actual solubility of lithium isobutoxide in isobutyl alcohol was only 0.13 mole/l. (1.3 wt. %) at 22° (Figure 4, curve A).

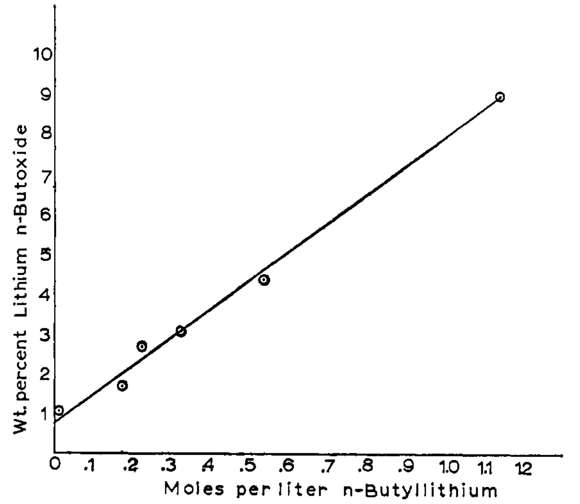

Figure 3.—Variation of lithium *n*-butoxide solubility in *n*-heptane with *n*-butyllithium concentration at 25°.

TABLE II

APPEARANCE AND MELTING POINT OF "CRYSTALLIZED" LITHIUM ISOBUTOXIDE–ISOBUTYL ALCOHOL MIXTURES

Molar ratio of isobutyl alcohol to lithium isobutoxide in mixture	Approximate concn. (moles/l.) of alkoxide in mixture	Appearance of mass	M.p. range, °C.
11	1.0	Thick slurry	Clear solution at 75–80°
10	1.1	Thick slurry	Clear solution at 75–80°
9	1.2	Semisolid[a]	Clear solution at 75–80°
8	1.4	Semisolid[a]	Clear solution at 75–80°
7	1.6	Solid	75–80[b]
6	1.8	Solid	75–80[b]
5	2.2	Solid	75–80[b]
4	2.7	Solid	75–80[b]
3	3.5	Solid	75–80[b]
1.7	6.4	Solid[c]	75–80[b]

[a] Some free liquid observable. [b] Sealed tube. [c] Hard solid which can be powdered.

A similar situation was found with lithium isopropoxide in isopropyl alcohol. Curve E of Figure 4 was obtained by mixing 4 g. of lithium isopropoxide with 100 ml. of isopropyl alcohol (high dilution) and determining the solubility of the saturated solution at different temperatures. In the 25–45° range the solubility remains low (0.02–0.05 mole/l.), but at 70° all of the alkoxide dissolves to give a clear solution. More concentrated mixtures of lithium isopropoxide in isopropyl alcohol gave crystalline masses at lower temperatures which liquefied on heating to *ca.* 80°.

However, it was found that, when an alcohol other than the respective alcohol of the alkoxide was employed, no crystallization occurred even with alcohols having a high degree of chain branching. For example, when lithium isopropoxide was mixed with *n*-propyl alcohol or *t*-butyl alcohol in the 1–6 *M* concentration range only fluid slurries resulted which exhibited a low order of solubility of the lithium isopropoxide.

A similar pattern of solubilities based on the structure of the hydrocarbon moiety has also been observed with lithium alkylamides with some general differences (see Table III and Figures 5 and 6). For example, lithium di-*n*-propylamide is less soluble in amine solvents than lithium *n*-propoxide is in *n*-propyl alcohol (compare Figures 1 and 6). Lithium isopropoxide is also much more soluble in *n*-heptane than is lithium diisopropylamide. In addition to this a gelation effect occurs at higher temperatures with lithium diisopropylamide in heptane.

Table III

Solubilities of Lithium Alkyl Amides in Amines and in *n*-Heptane

Compd.	Solvent	Concn. Moles/l.	Concn. Wt. %	Temp., °C.
Lithium dimethylamide	Dimethylamine	3.27	...	−10
	n-Heptane	0.09	0.66	25
Lithium diethylamide	Diethylamine	3.83	37.8	25.5
	n-Heptane	0.05	0.57	25
Lithium di-*n*-propylamide	Di-*n*-propylamine	0.97	...	19
		1.78	...	40
		2.25	...	55
	n-Heptane	0.07		27
		0.12		65
		0.16		75
Lithium diisopropylamide	Diisopropylamine	0.37	5.55	25
		0.48	7.24	42
		0.92	13.6	62
	n-Heptane	0.20	3.13	20
		0.32	4.90	40
		1.12	17.6	55
	(Reversible gelation occurs at higher temp.)			
Lithium dicyclohexylamide	Dicyclohexylamine	0.19	...	28
		0.44	...	53
		0.70	...	75
	n-Heptane	0.11		23.5
		0.33		52
		1.05		78
Lithium 2-aminoethylamide	Ethylenediamine	2.32	...	25
	n-Heptane	0.04[a]	...	21

[a] Essentially the same at 47 and 75°.

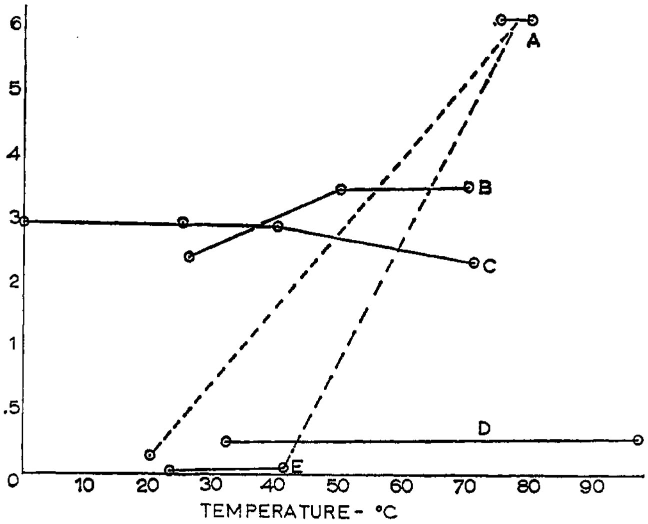

Figure 4.—Solubility of some lithium alcoholates in their respective alcohols *vs.* temperature: A, lithium isobutoxide; B, lithium ethoxide; C, lithium methoxide; D, lithium cyclohexanolate; E, lithium isopropoxide.

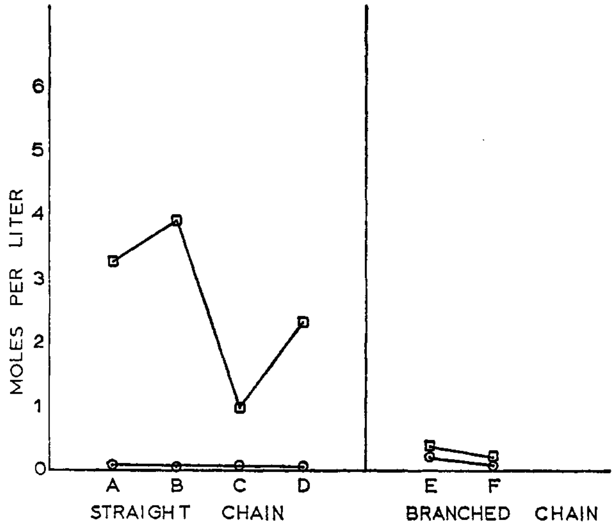

Figure 5.—Solubility of various lithium alkylamides at room temperature: A, lithium dimethylamide (−10° in dimethylamine); B, lithium diethylamide; C, lithium di-*n*-propylamide; D, lithium 2-aminoethylamide; E, lithium diisopropylamide; F, lithium dicyclohexylamide; O, *n*-heptane; □, respective amine.

Discussion of Results

The striking difference in the solubility characteristics of the straight-chain and branched-chain lithium alkoxides appears to indicate that the structure of these two types of alkoxides is different. Some precedent for this difference in structure can be found in the literature dealing with other metallic alkoxides. Bradley,[10] in an examination of isomeric Al, Fe, Ti, Zr, Ce, and Th amyl oxides, found that a decrease in the degree of polymerization of these alkoxides was caused by the progressive branching of the amyl group from primary to secondary to tertiary isomers, and he concluded that a steric effect was operative. He also found that this effect was more marked with small metal atoms than with larger ones.

Other properties found included an increase in volatility and solubility in organic solvents with an increase in chain branching in the alkoxide and a decrease in the degree of polymerization with an increase in the donor power of the solvent (but not with an

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(10) D. C. Bradley in "Progress in Inorganic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., pp. 303–361.

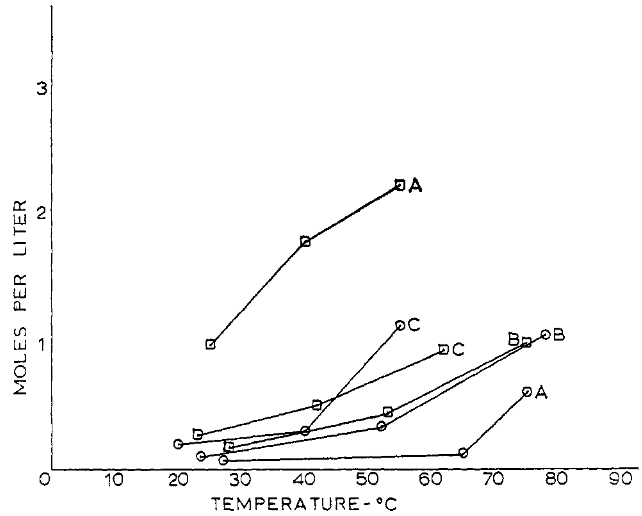

Figure 6.—Solubility of some lithium alkylamides *vs.* temperature: A, lithium di-*n*-propylamide; B, lithium dicyclohexylamide; C, lithium diisopropylamide; ○, *n*-heptane; □, respective amine.

increase in dielectric constant). Bradley's explanation for these properties was based on the effects of two opposing tendencies. One tendency is that of the metal to expand its coordination number by intermolecular bonding with oxygen causing the formation of relatively nonvolatile and insoluble compounds. The opposite tendency is the screening or steric effect of the alkyl groups which interferes with the coordination process to a degree depending on their size and shape. This screening effect prevents intermolecular bonding and more volatile and soluble alkoxides result.

The fact that the dielectric power of a solvent had less of an effect on the degree of polymerization of tantalum alkoxides than did solvent donor power indicated to Bradley that the polymer molecules were held together with covalent rather than electrostatic intermolecular bonds. The degree of polymerization of these alkoxides was not lowered greatly by an increase in the temperature of the solvent medium.

N.m.r. spectral analysis corroborated Golovanov's[9] hypothesis that the O–Li bonding in branched-chain lithium alkoxides takes place *via* multicentered orbits involving "loose" delocalized electrons. The alkyl groups in the associates did not interact with each other and the oxygen-atom environment around the lithium was symmetrical. The author depicts the structure as one involving a framework of O–Li groups surrounded by "umbrellas" of methyl groups. On the other hand, n.m.r. data indicated that in the straight-chain lithium alkoxides such as the *n*-butoxide, a strong interaction of alkyl radicals takes place and the oxygen-atom environment of the lithium nucleus is unsymmetrical. This indicates that for these straight-chain types, a donor–acceptor interaction plays the basic role in complex formation. As in the case of the metallic alkoxides studied by Bradley,[10] this effect should result in larger polymers (possibly linear) for the straight-chain lithium alkoxides than for their branched-chain analogs. Unfortunately, thus far, no one has determined the degree of association or "polymerization" of the straight-chain lithium alkoxides as has been done with the branched-chain analogs.

If it can be assumed that the straight-chain alkoxides do form larger "associated" polymers than their branched-chain analogs then, in the case of lithium *n*-butoxide, for example, we must be dealing with a polymeric alkoxide of relatively high molecular weight perhaps in the order of 1000–2000 or even greater. This, coupled with a linear structure in which O–Li bonds are exposed, should result in a lower solubility of the straight-chain alkoxides in hydrocarbon solvents as was observed by Bradley with other metallic alkoxides. Our experimental results bore this out, the solubility of all the straight-chain lithium alkoxides in hydrocarbons being very low. The fact that a rather flat temperature–solubility curve was obtained in hydrocarbon solvents indicates the very small influence of temperature on depolymerization of the associated, straight-chain polymeric alkoxides in these solvents, quite similar to what was observed by Bradley with other metallic alkoxides. Some additional evidence for this can be found in infrared data obtained by Simonov[11] which demonstrated association in both vapor and crystals of these alkoxides. It is interesting to note that the more hydrocarbon-soluble organolithiums can apparently break down the polymeric, straight-chain alkoxides and by association bring them into solution. We have observed this phenomenon with the *n*-butyllithium–lithium *n*-butoxide system while Bafus has observed it with the ethyllithium–lithium ethoxide system. Bafus[12] proposes that in the bonding scheme for ethyllithium hexamer, each lithium atom is bonded to three methylene carbon atoms by three four-centered bonds, while each methylene carbon atom is bonded to three lithium atoms by one four-centered bond. One of the sp^3 orbitals of hybridized lithium proposed as taking part in forming the four-centered bonds is free (extending away from the polymer) and can interact with a base such as lithium ethoxide. That we were able to obtain excellent solubility of the straight-chain alkoxides in alcoholic solvents, but not in ethereal solvents, would tend to indicate that the bonding between the molecules in the associated polymers is more ionic than covalent, the dielectric constant of the solvent playing a greater role than the solvent's donor power contrary to the results of Bradley with other metallic alkoxides. Hydrogen bonding must also play some role in the solubility pattern of the straight-chain alkoxides. Kecki and Witanowski[13] have recently shown by n.m.r. studies that the hydrogen bonds in the lithium methoxide–methanol system are much stronger than in pure methanol. No splitting of the OH signal of methanol was observed in the n.m.r. spectra of the methoxide solutions. The authors postulated proton transfers in the chain polymers, and considered the system as one in which there is some deficit of protons resulting in strong molecular attractions.

Thus, the fact that the solubility behavior of the branched-chain lithium alkoxides is so different from that of the straight-chain analogs must be due to a considerable difference in their structures. It is somewhat easier to explain the solubility behavior of the

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(11) A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, *Bull. Acad. Sci. USSR Div. Chem. Sci.* (Eng. Transl.), **6**, 1056 (1962).

(12) D. A. Bafus, Ph.D. Thesis, University of Illinois, 1962, University Microfilms, Inc., Ann Arbor, Mich.

(13) Z. Kecki and J. Witanowski, *Roczniki Chem.*, **37**, 881 (1963).

branched-chain alkoxides in hydrocarbon solvents than in alcoholic solvents. In hydrocarbon solvents, not only are the associated polymers smaller than in the straight-chain analogs but alkyl "umbrellas" shield the central –O–Li framework and present a more hydrocarbon-like exterior, amenable to solution by these solvents. However, there is some difficulty in explaining the "crystallization" effects observed when the branched-chain alkoxides are mixed with their respective alcohols. If we again consider that the bonding in branched-chain alkoxides is multicentered and that the central O–Li framework is shielded by an outer sheath of alkyl groups, we might suppose that solubilization of the alkoxides by alcohols could not take place owing to the inability of these solvents to act as donors for the lithium atoms or to hydrogen bond with the oxygen atoms in the framework. This we have found to be so since the solubility of all the branched-chain alkoxides is low in alcoholic solvents. Thus, one is left with the possibility of the formation of a gel-like structure due to trapping of solvent molecules in the framework of the alkoxide polymer. This is also difficult to rationalize since the spherical structure of the associated micelles of alkoxide would not be expected to trap solvent as readily as would the larger, more linear structures in straight-chain alkoxides; yet, no such gel-like material forms when straight-chain alkoxides are mixed with either alcohols or hydrocarbons.

The significant amount of heat liberated when "crystallization" takes place (25 → 40°) as well as the rather narrow fusion range and high degree of crystallinity in these solid masses in the 1–6 M concentration range definitely indicates either the formation of huge, solid, externally-solvated alkoxide micelles or simply crystallization of the alcohol itself due to simple nucleation by alkoxide or to the formation of alcohol micelles similar in structure to the alkoxide itself. Another factor which lends credence to the latter hypothesis is that, although these alkoxides form crystalline masses in combination with their own alcohols, they do not form them in combination with other alcohols, be they branched or unbranched. For example, lithium isopropoxide forms a hard, crystalline mass which can be powdered when mixed with two to three times its weight of isopropyl alcohol, but, when mixed with the same quantities of *n*-propyl alcohol or *t*-butyl alcohol, only fluid slurries result. In both systems, the solubility of lithium isopropoxide is very low (*i.e.*, 0.1–0.2 mole/l.).

The fact that this crystallization phenomenon appears to occur only in the parent alcohol in which the solubility of the alkoxide is low, but not in solvents such as *n*-heptane, tetrahydrofuran, and ethyl ether in which solubility is good, or in other alcohols where solubility is poor, appears to limit this crystallization to "like" solute and solvent molecules. The solute alkoxide must possess a certain degree of symmetry, due to its unique structure, which induces this crystallization to occur. It is hoped that X-ray diffraction studies will help to elucidate the nature and mode of formation of the crystalline species involved.

The much lower degree of solubility of branched-chain lithium dialkylamides such as lithium diisopropylamide in hydrocarbon solvents compared with that of the branched-chain alkoxides might be explained as indicating the inability of these amides to form associated complexes involving multicenter bonding. This could be due to both the steric hindrance of two alkyl groups on one nitrogen and to the decreased ability of nitrogen to participate in multicentered bonding owing to its lower electronegativity. The somewhat poorer solubility of the straight-chain alkylamides in their respective amines compared with the solubility of straight-chain alkoxides in their respective alcohols is probably due to both a lower dielectric constant and a lower hydrogen-bonding power for the amine solvent compared with the alcoholic solvent, again based on the lower electronegativity of nitrogen *vs.* oxygen.

Experimental Section

A. Preparation of Lithium Alcoholates in *n*-Heptane.—In general the following scheme described for the preparation of lithium *t*-butoxide was employed for the preparation of lithium alkoxides in hydrocarbon media and for their isolation.

A solution of 14.8 g. (0.20 mole) of *t*-butyl alcohol (Eastman White Label, dried over Linde Molecular Sieves, No. 5A) in 100 ml. of *n*-heptane (Phillips Petroleum Co., 99 mole %; dried over Linde Molecular Sieves, No. 5A) was added to a suspension of 2.0 g. (0.29 g.-atom) of lithium metal (wire, $^1/_8$-in. diameter), cut in small pieces, in 100 ml. of *n*-heptane.

The mixture was vigorously stirred and refluxed under an argon atmosphere for 3 days. The above mixture was filtered to remove a small amount of unreacted lithium metal and subsequently distilled. A volume of 75 ml. of solvent containing any unreacted *t*-butyl alcohol was distilled off, leaving approximately 90 ml. of a light yellow colored solution. On cooling to room temperature and standing overnight, this solution deposited large, well-formed monoclinic crystals. The supernatant solution was found to be 0.987 M in base and to have a density of 0.695 g./ml. at 23°. Calculating for lithium *t*-butoxide content, we obtained a solubility value of 11.4% at 23°. On cooling this solution to 5°, crystals were again deposited, but these redissolved on warming to room temperature.

The isolated crystals formed above were washed once with dry, unsaturate-free *n*-pentane, and blown dry under an argon stream. A weight of 2.4346 g. of these crystals was found to contain 0.03051 mole of base, yielding neut. equiv. 79.80 (theory for lithium *t*-butoxide, 80.05), purity 99.7%. These crystals were also found to be soluble in *n*-pentane, toluene, and tetrahydrofuran. They did not melt below 200° (sealed tube).

In the preparation of the straight-chain alkoxides it was found necessary to employ a large excess of the alcohol (*ca.* 100%) in order to obtain clear solutions of the product and to thus ensure complete reaction of the lithium metal.

Infrared examination revealed no free alcohol present in these alkoxides as determined by the absence of a band at 2.8 μ.

B. Preparation of Lithium Alcoholates in Their Respective Alcohols.—The following scheme, described for the preparation of lithium isobutoxide in isobutyl alcohol, was generally employed for the synthesis of all the alkoxides in their respective alcohols.

A weight of 2.0 g. of lithium metal (as a 0.5-in.-diameter rod) was cut into small pieces, as in method A, and added to 100 ml. of isobutyl alcohol (Fisher certified reagent, dried over 5A Molecular Sieves). The mixture was stirred and heated to reflux until all the metal had disappeared and clear colorless solution had cleared up.[14] On allowing the solution to cool, a solid mass of crystals formed in the flask (crystallization appeared to begin somewhere between 70 and 75°). A volume of 200 ml. of isobutyl alcohol was added to thin out the mixture so that it could be stirred. After stirring the mixture for 1 hr., a clear colorless sample of the solution was obtained by filtration and was analyzed for base content. The solution was found to be 0.13 M in base

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(14) Clear, homogeneons solutions which began to crystallize at 75–80° were obtained with solvent–alkoxide ratios as low as 1.7 to 1. The melting points of the crystalline solids with ratios varying from 1.7 : 1 to 7 : 1 were all found to be approximately 75–80° (sealed tube, see Table II).

and had a density of 0.81 g./ml. at 22°. Calculating for lithium isobutoxide content, we obtained a solubility value of 1.3 wt. % at 22°.

Lithium *n*-butoxide, unlike the isobutoxide, did not crystallize from its *n*-butyl alcohol solution on cooling to room temperature. Its solubility in *n*-butyl alcohol was subsequently found to be greater than 5 moles/l. Lithium methoxide, ethoxide, and *n*-propoxide were also found to be quite soluble in their respective alcohols at room temperature.

C. Solubility of Lithium *n*-Butoxide in *n*-Heptane Solutions Containing *n*-Butyllithium.—The following experimental scheme was employed. About 100 to 200 ml. of a certain required molarity of *n*-butyllithium solution in pure grade *n*-heptane was accurately measured out and transferred to a three-necked, round-bottom, argon-swept flask equipped with a mechanical stirrer, reflux condenser (argon inlet tube at top), and a 10-ml. buret fitted (at its lower end) with a rubber stopper and its upper end with an argon-inlet tube. The required amount of Fisher certified reagent *n*-butyl alcohol needed to convert half the *n*-butyllithium to lithium *n*-butoxide was then added slowly to the stirred, cooled *n*-butyllithium solution. The mixture was allowed to stir for about a 0.5-hr. period and was then allowed to stand overnight. Precipitation was complete by this time. A sufficiently large sample (about 35 ml.) of the clear solution was then filtered off into a graduated dropping funnel, through a sintered-glass filter tube (Ace Glass Co., E porosity), to obtain analyses for *n*-butyllithium[2] and total base concentrations. The remainder of the mixture in the flask was then transferred to a graduated dropping funnel under argon to determine the total volume of salts and solution. Initial *n*-butyllithium concentrations were 2.54, 1.05, 0.78, 0.51, and 0.38 *M*. In all cases addition of one-half of the equivalent amount of *n*-butanol resulted in the formation of a precipitate.

The following amounts of reagents were employed in each of five determinations: (1) 87.5 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane and 11.60 ml. (9.4 g., 0.127 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 2.54 *M*); (2) 100 ml. of 1.05 *M* *n*-butyllithium solution in pure *n*-heptane and 4.80 ml. (3.89 g., 0.0525 mole) of *n*-butyl alcohol, (initial *n*-BuLi concentration = 1.03 *M*); (3) 26.8 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 3.65 ml. (2.96 g. 0.04 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 0.78 *M*); (4) 17.5 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 2.32 ml. (1.88 g., 0.025 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 0.51 *M*); (5) 13.0 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 1.73 ml. (1.4 g., 0.019 mole) of *n*-butyl alcohol (initial *n*-butyllithium concentration = 0.38 *M*).

In addition to the above, one run was made in which an equivalent amount of *n*-butyl alcohol was added to an *n*-butyllithium solution. *n*-Butyl alcohol (8.12 ml., 6.59 g., 0.089 mole) was added to 30.6 ml. of *n*-butyllithium in *n*-heptane diluted to 100 ml. with pure *n*-heptane.

Structure–Property Relations for Some 4-Substituted 2-Nitroanilines[1]

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The pK_A values at 25° of 12 4-substituted 2-nitroanilines in perchloric acid have been measured and quantitatively related to Hammett σ values. The value of the reaction constant for the series does not conform with Jaffé's assumption for a constant *ortho* effect. The variation is discussed. The electronic spectral data correlate with σ and a fair correlation was obtained between ν_B and ν_A. The polarographic reduction half-wave potentials for the series at the dropping mercury electrode have been obtained. It appears that no $\rho\sigma$ relationship exists. The attempted polarographic oxidation of the series using a rotating platinum electrode was unsuccessful. The N–H fundamental frequencies and intensities have been determined for 10 members of the series. The asymmetric frequencies, symmetric frequencies, band intensities, and half-band widths individually correlate with σ. The Hückel molecular orbital treatment is applied to four members of the series and linear relationships exist between π-electron densities and σ and between β coefficients and σ.

The Hammett equation has been successfully employed in deriving quantitative relationships between structure and chemical reactivity.[3a] Also, certain physical properties, *e.g.*, half-wave potentials from polarographic reactions,[3b] electronic spectral excitations,[4–6] infrared absorption frequencies,[3c] and electron densities calculated by molecular orbital theory,[3d] have been correlated with Hammett substituent constants.

Essentially, this article is a study of the applicability of the Hammett equation to acidity, electronic spectral excitations, polarographic reduction potentials, infrared N–H absorption frequencies and band intensities, and electron densities calculated by HMO theory of a series of 4-substituted 2-nitroanilines.

The 4-substituted 2-nitroanilines provide an excellent series for such a study. The nitro group ensures that the electronic spectrum of importance to this study will appear in the easily accessible visible or near-ultraviolet region. The presence of the nitro group *ortho* to the amino group is advantageous in that it chelates with the amino group, thereby preventing molecular association, and it is sufficiently removed from the 4-substituent that no steric interaction can take place. Furthermore, the presence of the nitro group is convenient for the determination of polarographic half-wave reduction potentials. Finally, the amino group provides for a suitable study of the substituent effect on N–H stretching frequencies.

Results and Discussion

The Correlation of the Acidity and Electronic Spectra of 4-Substituted 2-Nitroanilines with Substituent Constants.—It has been previously shown for 2,4-dinitrophenylhydrazones[4,5] that differences ($\Delta\nu$) between wave numbers of visible spectra of neutral and alkaline solutions are quantitatively related to Hammett[7a] and Taft[8] substituent constants. More recently, it has

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(1) Abstracted in part from the Ph.D. Dissertation of J. O. S., Texas A & M University, Aug. 1964.

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