INTERACTION OF ALKYLLITHIUM COMPOUNDS WITH BASE

COMPLEX FORMATION BETWEEN ETHYLLITHIUM AND LITHIUM ETHOXIDE IN HYDROCARBON SOLVENTS

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Bases such as ethers or amines produce very marked effects upon the reactivity of alkyllithium compounds in hydrocarbon solution[1-4]. The effect of lithium alkoxides upon the reactivity of alkyllithium compounds has not been subjected to systematic study. Since they are frequently present in alkyllithium solutions as an impurity, it is important to have some knowledge of how they interact with the alkyllithium compounds. We have examined the effect of lithium ethoxide on various properties of ethyllithium solutions in hydrocarbon solvents.

EXPERIMENTAL

Lithium ethoxide was prepared by addition of a stoichiometric quantity of absolute ethanol to a dispersion of lithium metal in benzene. After stirring for three hours or longer, the solvent was removed under vacuum; the solid product was washed repeatedly with cyclohexane to remove traces of benzene, mineral oil and unreacted ethanol.

Ethyllithium was obtained as a solid under saturated benzene solution from Lithium Corp. of America. It was recrystallized from cyclohexane before use. Solutions of ethyllithium of known concentration in cyclohexane were allowed to stand in contact with solid lithium ethoxide for periods from one to twelve hours, with occasional shaking. The solutions were filtered, after which aliquots were removed. After decomposition with water, the aliquots were titrated with standard acid to determine total base concentration. Since the concentration of ethyllithium is known, the total base concentration and the known ethyllithium concentration are employed to yield the ethoxide concentration. As a check on this procedure, the optical densities of all solutions were measured at 923 cm^{-1} in the infrared spectrum. Ethyllithium absorbs strongly at this frequency[5]; an accurate graph of optical density *vs.* concentration was used to determine the ethyllithium concentration in the solutions. It was found that very prolonged contact of the solutions with solid lithium ethoxide sometimes resulted in loss of ethyllithium from the solution, probably through incorporation into the solid. These solutions were not included in the analysis of the data, although when the ethyllithium concentration determined from the infrared was employed, the results for these were in agreement with the other data.

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Infrared spectra were determined with a Beckman IR-7 spectrophotometer. The solution spectra were obtained in 1.0 and 0.4 mm fixed-thickness solution cells, calibrated by the interference fringe technique[6].

Nuclear magnetic resonance spectra were obtained as described elsewhere[7]; a Varian Associates model A-60 was employed in obtaining proton spectra, and a model Dp-60 for the ^7Li spectra. The ^7Li spectra were obtained with a 15.1 Mc r.f. unit.

TABLE I

FREEZING POINT LOWERING DATA FOR ETHYLLITHIUM–LITHIUM ETHOXIDE SOLUTIONS IN CYCLOHEXANE

$[(C_2H_5Li)_6]$	$[C_2H_5OLi]$	*R*	*Observed molality*	*N*
0.0183	—	0	0.0194	0.945
0.0183	0.0054	0.29	0.0195	1.21
0.0183	0.0107	0.585	0.0188	1.54
0.0183	0.0208	1.14	0.0192	2.04
0.0183	0.0264	1.44	0.0187	2.39
0.0183	0.0496	2.70	0.0196	3.46
0.0183	0.0574	3.14	0.0207	3.66
0.0146	0.0774	5.30	0.0191	4.82
0.0204	—	0	0.0210	0.960
0.0204	0.0423	2.07	0.0240	2.61
0.0204	0.0629	3.08	0.0232	3.59
0.0204	0.0711	3.48	0.0247	3.70
0.0204	0.0755	3.70	0.0242	3.96
0.0204	0.0755	3.70	0.0253	3.79
0.0204	0.0820	4.01	0.0249	4.12
0.0204	0.0864	4.23	0.0250	4.27
0.0204	0.0936	4.58	0.0254	4.50
0.0204	0.128	6.26	0.0269	5.50
0.0204	0.129	6.31	0.0274	5.45
—	0.0328	—	0.0144	2.29
—	0.1734	—	0.0372	4.67

The freezing point lowering apparatus and procedures have been described elsewhere[8]. Cyclohexane solutions of a number of organic substances were employed in obtaining a calibration curve of molality *vs.* freezing point. Ethyllithium and lithium ethoxide molarities, as determined by titration and infrared spectral measurements, were converted to molality by assuming that the densities of the solutions are the same as for pure cyclohexane. Since only dilute solutions were involved, this assumption introduces negligible error.

RESULTS AND DISCUSSION

The results of freezing point lowering measurements of cyclohexane solutions containing ethyllithium and lithium ethoxide are given in Table 1. From measurements of a large number of cyclohexane solutions we have established that ethyllithium is hexameric in this solvent over a wide range of concentration. The data are therefore presented in terms of the variables employed previously[8] in discussing the interaction of ethyllithium with triethylamine. We define the quantity

$$N = \frac{[H] + [B]}{\text{observed molality}}$$

where [H] represents the initial concentration of ethyllithium, calculated as hexamer, and [B] the initial concentration of lithium ethoxide. The observed molality is that determined from the freezing point lowering experiment. The values of N are given in Table 1 for each solution, and graphed in Fig. 1 as a function of the ratio $R = [B]/[H]$.

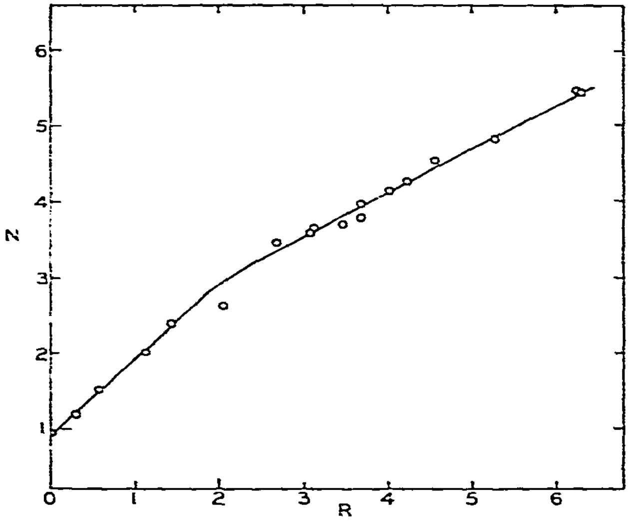

Fig. 1. Freezing point lowering data for ethyllithium–lithium ethoxide solutions.

It is evident that the observed molality increases very little, if at all, upon addition of ethoxide to ethyllithium solution, for R values from 0 to 2. At higher R values a slight increase in molality with increasing R is noted. These results require (*a*) that association does occur between ethyllithium and lithium ethoxide, and (*b*) that disruption of the ethyllithium hexamer does not occur. The relation between N and R in the region of R values from 0 to 2 is consistent with the equilibria

$$(C_2H_5Li)_6 + \frac{1}{n}(C_2H_5OLi)_n \rightleftharpoons (C_2H_5Li)_6C_2H_5OLi \qquad (1)$$

$$(C_2H_5Li)_6C_2H_5OLi + \frac{1}{n}(C_2H_5OLi)_n \rightleftharpoons (C_2H_5Li)_6(C_2H_5OLi)_2 \qquad (2)$$

If these two equilibria proceeded to completion, N would vary linearly from a value of 1 at $R = 0$ to a value of 3 at $R = 2$. The line through data in this region approaches this limiting condition closely.

At R values above 2 the data fall on a line with slightly lower slope. The continuous increase in N as a function of R, to R values of six or higher, can be explained in terms of formation of lithium ethoxide clusters which are coordinated to the hexamer. We have proposed previously[3] that the hexamer contains two sites at which coordination might occur. Assuming that monomeric lithium ethoxide coordinates initially to these sites, subsequent attachment of lithium ethoxide may occur by formation of aggregates at each site. The binding of ethoxide at the hexamer presumably occurs by interaction of an unshared electron pair on the oxygen with a vacant orbital of the hexamer framework. The same type of interaction may occur with an aggregate of lithium ethoxide units. It may, however, be weaker because of the aggregate formation, so that some dissociation results. A slight amount of dissociation of the aggregates would account for the lower slope of the relationship between N and R at higher R values. In summary, equations for the proposed equilibria, in addition to eqns. (1) and (2) are as follows [we use the symbols defined above, and write B-H-B for the species $(C_2H_5Li)_6(C_2H_5OLi)_2$ to indicate that coordination occurs at two different sites]:

$$B\cdot H\cdot B + \frac{1}{n} B_n \rightleftharpoons B_2\cdot H\cdot B \tag{3}$$

$$B_2\cdot H\cdot B + \frac{1}{n} B_n \rightleftharpoons B_2\cdot H\cdot B_2 \tag{4}$$

$$B_2\cdot H\cdot B_2 + \frac{1}{n} B_n \rightleftharpoons B_3\cdot H\cdot B_2 \quad \text{etc.} \tag{5}$$

Ethoxide must be present in the form of a complex with ethyllithium hexamer, with a small amount of free ethoxide present in solution, probably as aggregates containing two or more $LiOC_2H_5$ units. It has been reported[9-11] that lithium alkoxides are associated in solution with degrees of association from 3 to 9. We have made a few measurements on lithium ethoxide in cyclohexane solution (lower portion of Table 1) which indicate a varying degree of association as a function of concentration.

The proton resonance spectra of a number of ethyllithium–lithium ethoxide solutions in benzene were measured. The center of the methylene proton quartet of ethyllithium shifts linearly from 486 cps relative to benzene at $R = 0$ to 477 cps in the vicinity of $R = 2$; it remains in the range 477–479 cps at higher values of R.

Lithium ethoxide exhibits strong absorptions at frequencies of 1059 cm^{-1} and 1116 cm^{-1}. The optical densities of these bands were measured for a number of ethyllithium–lithium ethoxide solutions with R values ranging to about 6. Beer's law relationships were obtained for both bands. The equilibria which occur in the solutions thus do not markedly perturb the spectra of either ethyllithium or lithium ethoxide, an indication that major structural changes do not occur. The spectral results are thus consistent with the model proposed.

The presence of lithium ethoxide in solutions of ethyllithium causes very marked effects in the ^7Li NMR spectrum. The ^7Li resonance of ethyllithium in toluene at room temperature is a moderately sharp line, with a width at half-intensity of about 2 cps. The linewidth increases with decrease in temperature as a result of quadrupolar relaxation of the ^7Li nuclear spin[7] ($I = {}^3/_2$). In the presence of even very small concentrations of lithium ethoxide, the line is broadened considerably. The broadening is approximately proportional to the concentration of ethoxide. There is, with higher concentrations of ethoxide, a shift toward higher field, but in all cases, only a single symmetric absorption is observed. Although the ^{7}Li chemical shift in lithium ethoxide is not known, the magnitude of the upfield shift with increase in ethoxide concentration suggests that it is at least ten cps upfield from the ethyllithium resonance. Despite the extreme broadening of the line, therefore, it appears very probable that an exchange of lithium nuclei occurs, such that only a single resonance is seen. The broadening can be attributed to a very rapid relaxation of the ^{7}Li nuclear spins in the ethoxide sites due to a high field gradient[10]. The apparent linewidth in the case of rapid exchange is a weighted average of characteristic linewidths in the various sites. Attempts to observe a slowing-down of the rate of exchange at lower temperatures were unsuccessful, because the resonance line becomes very broad.

The exchange of lithium between ethoxide and ethyllithium is not surprising in terms of the model proposed for interaction of bases with alkyllithium hexamer. Coordination of oxygen on a face of the hexamer should cause the lithium atom of the alkoxide to lie in proximity to a lithium atom of the hexamer. Exchange can then occur through a transition state in which the lithium atoms become equivalently bonded to both oxygen and the adjacent alkyl groups. The equilibria expressed by eqns. (1) through (5) are likely to be rapid, so that effective averaging of all lithium resonances occurs.

The question of whether lithium ethoxide modifies the reactivity of ethyllithium in hydrocarbon solutions is interesting and important, since it must often occur that some ethoxide is present, albeit inadvertantly, in ethyllithium solutions. There is an important difference in the behavior of lithium ethoxide and triethylamine toward alkyllithium, in that the ethoxide does not appear to bring about extensive dissociation of the hexamer, whereas the amine does. If the very marked increase in reactivity caused by addition of ethers or amines to alkyllithium solutions in hydrocarbon solvents is due to a more facile dissociation of the hexamer, it is quite possible that lithium alkoxides may act not as catalysts but as inhibitors. A similar consideration may apply to the alkyllithium–lithium halide complexes reported by Glaze and West[12]. These complexes, which we conjecture are similar to the alkoxide complexes, appear to be of lower reactivity than the alkyllithium compounds themselves.

We hope to begin some kinetic studies in the near future with the aim of resolving some of these questions.

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SUMMARY

Freezing point lowering measurements have been carried out upon cyclohexane solutions containing mixtures of ethyllithium and lithium ethoxide. The results demonstrate that lithium ethoxide forms complexes with ethyllithium. The data are explained in terms of an initial coordination of two molecules of lithium ethoxide at two coordination sites of the hexamer. Subsequent attachment of ethoxide is presumed to occur by formation of clusters of lithium ethoxide at each of the two sites of binding

to hexamer. The infrared and proton NMR data are consistent with this model. The ^{7}Li nuclear resonance spectra of solutions containing both ethyllithium and lithium ethoxide exhibit only one absorption, which broadens and shifts to higher field with increasing ethoxide concentration. A rapid exchange of lithium nuclei between ethyllithium and lithium ethoxide is indicated.

Interaction of lithium ethoxide with ethyllithium does not appear to promote dissociation of the hexamer. In this respect, it differs from amines and ethers.

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