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Abstract

Full Text

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MIXED COMPLEXES OF PHENYLLITHIUM, METHYLLITHIUM, *n*-BUTYLLITHIUM, AND LITHIUM HALIDE SALTS

We were interested in elucidating the role of lithium halide salts in stabilizing or lowering the reactivity of ethereal solutions of certain organolithium compounds. A number of examples are known of the reduced reactivity of RLi in the presence of lithium bromide. For example, "salt-free" phenyllithium, obtained from diphenylmercury and lithium in ether, is capable of metalating anisole (17%), whereas "ordinary" phenyllithium, from bromobenzene and lithium, does not react even after 48 hours. It should be noted that metalation of anisole by the phenyllithium–phenylsodium complex under the same conditions proceeds in 71% yield (⁀1). In the reaction of "salt-free" *n*-butyllithium (from *n*-C_4H_9Cl) with 1,1-diphenyl-2-chloroethylene at −35° for 2 hours, 80% tolane is formed, whereas with *n*-butyllithium synthesized from *n*-butyl bromide, the yield of tolane under the same conditions is 35% (⁀2).

At present, the ability of organolithium compounds to form complexes is well known; this imparts considerable distinctiveness to the chemistry of organolithium compounds. Aliphatic organolithium compounds, as shown for ethyllithium ([3-9]) and *tert*-butyllithium (⁀10), are associated in solutions, vapors, and crystals. *tert*-Butyllithium has been described as a tetramer, and ethyllithium from a tetramer to a heptamer ([1-9]). In solutions of benzene, hexane, and ether, according to ebullioscopic and cryoscopic data, *n*-butyllithium forms an associate from a pentamer to a heptamer. Methyllithium in ether is trimeric (⁀4); for dodecyllithium in benzene and cyclohexane, values from dimer to tetramer have been obtained. Benzyllithium in ether is close to a dimer, and phenyllithium is a dimer (⁀4).

Complex formation (association) of organic lithium compounds is usually associated with the possibility of forming multicenter electron-deficient orbitals at the expense of the electrons of the C—Li bond and the free 2*p*-orbitals of the lithium atom, analogous to the complex organic compounds of beryllium and aluminum ([5,7,8,10]).

It is of interest that the ability to form complexes is also retained in lithium halide salts, LiX (X = Cl, Br, J). At high temperature—in the vapor and in melts —these compounds are predominantly present as dimers ([11,12]). It is assumed that complex formation of lithium halide salts occurs through use of the lone

SovietRxiv

pair of electrons of the halide and the free orbitals of lithium, with the formation of bridges ([11,12]).

It is known that crystalline mixed complexes of organolithium compounds and halide salts (LiBr, LiJ) can be isolated. Previously we described similar methyllithium complexes of composition $CH_3LiLiX \cdot 2(C_2H_5)_2O$ ([13]) and, for aromatic compounds, of composition $2RLi \cdot LiBr \cdot 2(C_2H_5)_2O$, where R is phenyl, *p*-tolyl, and *m*-tolyl ([14]). The complexes can be isolated from ordinary reaction mixtures, in which RLi and LiX are present in approximately equal amounts, and also by mixing pure ethereal solutions of RLi and LiX. In the reaction of aliphatic organolithium compounds of the ethyllithium and *n*-butyllithium type and alkyl halides in inert media, crystalline complexes of composition $RLi \cdot nLiX$ (n from 1.4 to 6) are isolated, possessing reduced reactivity—

···reactivity in comparison with the starting *RLi* ([9]). The nature and structure of such *RLi* complexes with halide salts is still unclear.

In addition, organolithium compounds are capable of forming acceptor-donor type complexes with atoms possessing an unshared electron pair (O, N, S, etc.). The ease with which a variety of reactions proceed in ether and tetrahydrofuran media is explained by the formation of such "onium" complexes, which increase the polarity of the C—Li bond ([15]).

We have previously described unstable etherates of methyllithium ([13]) and paratolyllithium ([16]), as well as very stable etherates of α-naphthyllithium and mesityllithium ([16]).

Table 1

Association factors of *RLi* and *LiX* compounds in ethereal solutions

Substances	Total concentration, mol.%	Association factor
A. Phenyllithium	0.06—0.6	1.76—2.38
B. Phenyllithium	0.05—0.75	2.11—2.45
V. LiBr	0.05—0.25	2.04—2.35
G. LiJ	0.05—0.42	1.85—2.26
D. Phenyllithium + LiBr	0.05—0.63	2.74—3.40
E. Phenyllithium + LiBr	0.045—0.5*	2.95—3.11
Zh. Phenyllithium + LiBr	0.15—0.98*	3.91—4.18
Z. Phenyllithium + LiBr	0.10—0.54*	3.77—4.12
I. Phenyllithium + LiJ	0.03—0.29*	2.62—2.85
K. α-Naphthyllithium	0.022—0.21	1.84—2.20
L. Methyllithium + LiJ	0.33—2.25*	3.84—4.07
M. *n*-Butyllithium + LiBr	0.16—1.06*	4.60—5.35
N. *n*-Butyllithium + LiBr	0.18—0.89*	4.70—5.75
O. *n*-Butyllithium	0.11—0.37	5.55—6.25

* The total concentrations of the mixed solutions were calculated for arithmetic-average molecular weights.

Mixed complexes of RLi with other organometallic compounds are known. For example, a crystalline complex of ethyllithium and tert-butyllithium has been described ([17]), as well as mixed complexes of phenyllithium with organometallic compounds of the first group $[(C_6H_5)_2Li]^{\ominus}M^{\oplus}$, where $M = Na, K, Rb, Cs$; these compounds are more reactive than the starting RLi. Complexes with compounds of beryllium, zinc, magnesium, aluminum, and boron have been described ([4,18]). All these complex compounds possess different reactivities, depending on the RLi radical and the second component of the complex. If crystalline phenyllithium or its solutions, $[(C_6H_5)Li]Li$, rapidly decompose on exposure to air, the complex with triphenylboron is extremely stabilized and dissolves in water ([18]).

In the present work, phenyllithium, α-naphthyllithium, methyllithium, n-butyllithium, lithium bromide, lithium iodide, and also their mixtures in various ratios were investigated by the ebullioscopic method in ethereal solutions (under argon).

Crystalline phenyllithium was synthesized by an exchange reaction in benzene medium, by the action of ethyllithium on triphenylantimony ([18]) or on diphenylmercury ([9]). The washed crystals of phenyllithium, dried in vacuum, were analyzed and rapidly dissolved on cooling (0°) in ether dried over sodium in argon. The solution obtained was immediately used for ebullioscopic measurements of molecular weight and was analyzed. In both cases the association factor of phenyllithium proved to be close to 2 (see Table 1, A and B). The same result was previously reported by Wittig and Lange for a solution of phenyllithium obtained from diphenylmercury and lithium in ether medium, without isolation of C_6H_5Li ([4,15]).

We obtained ethereal solutions of lithium bromide and lithium iodide from pure etherates of these compounds, described by us earlier (13, 14). In both cases the association factor was also close to 2 (Table 1, B, C).

Thus, it has been shown that in ethereal solutions pure phenyllithium, lithium bromide, and lithium iodide are present in the form of dimers.

By mixing pure solutions of dimers of phenyllithium and lithium bromide, mixtures of 25 : 1 and 1 : 10 were obtained. The association factor, calculated from the total concentration ($C_6H_5Li + LiBr$), rose to 2.75–3.40 (Table 1, D and E). The significant increase in molecular weight shows that an admixture of lithium bromide to phenyllithium, or of phenyllithium to lithium bromide, does not destroy the original dimeric complex of LiBr or C_6H_5Li, but, as it were, catalyzes its further association. In the case of a mixture of phenyllithium and lithium bromide (1 : 1), deliberately prepared or taken immediately after completion of the reaction ($C_6H_5Br + 2Li$), the molecular weight increased still more and the association factor was close to that of a tetramer (3.85–4.36) (Table 1, Zh and Z). Consequently, when phenyllithium is obtained under ordi-

nary conditions, we are dealing with complex compounds probably consisting of combinations of dimers of phenyllithium and lithium bromide. Owing to the great strength of the dimeric complexes of lithium bromide and phenyllithium, it is most probable that in reactions in ethereal solutions it is not individual molecules of aromatic RLi and LiBr that enter into interaction, but their dimers or dimers of their etherates. In the case of equimolecular mixtures of phenyllithium and lithium bromide, formation is possible of a tetrameric complex from a dimer of phenyllithium and a dimer of lithium bromide, or of a mixture of hexamer (from 3 dimers) and dimers. The IR spectra of these solutions confirm preservation of the main bands in the KBr region both for phenyllithium and for lithium bromide. The crystalline complex that separates out, previously described as $2C_6H_5Li \cdot LiBr \cdot 2(C_2H_5)_2O$, should be assigned the composition $4C_6H_5Li \cdot 2LiBr \cdot 4(C_2H_5)_2O$, which corresponds to a hexameric complex. Its isolation from the ethereal solution can be explained by its lower solubility in comparison with other possible complexes (tetramers, dimers).

In measuring an ethereal solution of phenyllithium and lithium iodide (1 : 1), a total association factor of less than 3 was obtained, which indicates their weaker interaction with each other (Table 1, I). In measuring a solution of pure α-naphthyllithium (from the etherate (14)), over the entire region investigated the molecular weight was close to that of a dimer (Table 1, K). On adding a solution of dimeric lithium bromide or lithium iodide, the degree of association remains about 2, i.e., mutual complex formation is not observed, as we also noted earlier (13).

In measuring an ethereal solution of methyllithium and lithium iodide (1 : 1), obtained from methyl iodide and lithium, the degree of association was found to be about 4 (Table 1, L). This result confirms the formation of mixed complexes (13).

A solution of *n*-butyllithium, obtained at low temperature (−30°) from *n*-butyl bromide and lithium, was investigated. After completion of the reaction, the concentrated solution (1–1.5 N) is diluted with pure ether and immediately subjected to measurement and analysis (under argon). A total molecular weight close to that of a pentamer was obtained (Table 1, M). With a ratio of *n*-butyllithium to lithium bromide of 1 : 10, an association factor of the same order was found (Table 1, N). The absence of a sharp decrease in the association factor upon addition of a large excess of a solution of dimeric lithium bromide indicates the existence of mixed complexes in ether.

For an ethereal solution of salt-free *n*-butyllithium obtained from *n*-butyl chloride, an association factor of about 6 was obtained (Table 1, O), and for a benzene solution of *n*-butyllithium about 7.

The results obtained confirm the formation of mixed complexes of organolithium compounds with lithium bromide in ethereal solutions, which also explains the decrease observed in some cases in reaction-

of the ability of RLi to form complexes. The lower ability of RLi to form

SovietRxiv

complexes with lithium iodide is manifested in the ease with which side reactions proceed. The instability of ethereal solutions of α-naphthyllithium can also be explained by the absence of the stabilizing influence of lithium halide salts.

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