AN INVESTIGATION OF THE FORMATION OF COMPLEXES OF n-BUTYLLITHIUM WITH SOME ELECTRONDONORS

Ivan KMÍNEK, Miroslav KAŠPAR and Jiří TREKOVAL
Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

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The formation of complexes of n-butyllithium with triethyl amine, tetramethylethylenediamine, tetrahydrofuran and dimethoxyethane was investigated by using the GLC analysis of the gas phase over a solution of organometallic compounds and electrondonor and by the vapour pressure osmometry method (VPO) at 303 K in benzene. A simple general reaction scheme was proposed, involving dissociation of BuLi hexamer followed by coordination. The composition of the complex, its concentration and the equilibrium constant of coordinations were determined by GLC. These parameters were used in VPO measurements of the molecular mass of the complexes. With respect to the type of the electrondonor, the main types of the complexes contain one to four molecules of electronodonor.

Molecules of organolithium compounds exhibit a tendency towards mutual association. According to modern views[1], an equilibrium between the hexameric and tetrameric forms exists in nonpolar solutions of aliphatic alkyllithium compounds; it is shifted in favour of the tetramer with increasing steric requirements of the alkyl substituent.

The character of associated RLi changes markedly in the presence of an electrondonor (donor, D). Due to coordination, the C–Li bonds become polarized, and the associate decomposes. At the same time, the degree of association n decreases and a complex with m molecules of the donor is formed. Data on the numerical value of $r = m/n$ in the complexes were obtained, *e.g.*, by using ^{7}Li-NMR spectra and cryoscopy[2]. The authors[2] assume that the most important processes occurring in the system are the equilibria

$$(\mathrm{RLi})_6 + D \rightleftharpoons (\mathrm{RLi})_6\, D \tag{1}$$

$$(\mathrm{RLi})_6 D + 5D \rightleftharpoons 3/2\,(\mathrm{RLi})_4.4D\,. \tag{2}$$

At the ratio $R = [D]_0 : [\mathrm{RLi}]_0 \sim 1$ (where "o" means concentrations of the compounds before their mutual interaction), complex with the composition $r = 1$ prevails. With branched RLi and very weak D, r decreases. Views on the detailed course of reactions (*1*) and (*2*) differ considerably. Equilibrium (*1*) (or the reaction between

RLi hexamer and two molecules of *D*, the existence of which has been directly demonstrated by an X-ray structural analysis of the complex of cyclohexyllithium with benzene[3]) need not necessarily precede reaction (*2*). Similarly, equilibrium (*2*) may be achieved by several processes at various rates. Other measurements reveal[4,6] that the average values of r and n in complexes are respectively 0·5 and 2. The assumed dimeric form of the complex in these studies is only speculative and does not agree with some recent data[7,2]. On the other hand, $r = 0{\cdot}5$ was detected also, *e.g.*, using the kinetics of the reaction between RLi and alkyl halides[9] or ethers[10].

While the molecular structure of $(\mathrm{RLi})_n$ in nonpolar solvents has been sufficiently elucidated, the same cannot be said about the character of associates coordinated with donors. At the same time, however, the presence of a donor in the reaction systems affects very markedly all the parameters of reactions between RLi and substrates, and the mechanism of this action must be elucidated. In this study we therefore made another attempt to obtain some quantitative data on complex-forming processes so as to use *a priori* data as few as possible in the reaction scheme.

EXPERIMENTAL

Chemicals

Benzene, toluene (Lachema), decaline and heptane (Schuchard) were shaken several times with sulphuric acid and water, and after that dried with potassium hydroxide and calcium hydride and rectified twice over sodium in argon atmosphere. Triethyl amine (TEA) (Reachim), N,N,N',N'-tetramethylethylenediamine (TMEDA) (Fluka), 1,2-dimethoxyethane (DME) (Reachim) and tetrahydrofuran (THF) (Fluka) were predried with $LiAlH_4$ and rectified twice in an inert atmosphere.

n-Butyllithium was prepared as a *c.* 1M solution in benzene or heptane by reacting n-butyl chloride (Fluka) and lithium powder[11]. Its concentration was determined by double titration[13].

Gas Chromatography

The required amounts of solvent, donor and internal standard (toluene or decaline) were dosed into *c.* 30 ml vessels provided with a threeway cock so as to have some 20 ml of the gas phase over the solution. The vessels were thermostated to 303 K, with the solution being stirred with a magnetic stirrer. On reaching equilibrium between the liquid and gas phases (*c.* 1/2 h), *c.* 5 ml of the gaseous mixture was taken through a septum by means of a gas-tight syringe; the gas was simultaneously replaced with argon flowing through a side outlet of the three-way cock from a reservoir. The sample was analyzed on a Perkin–Elmer F-33 apparatus. The column was filled with poly(ethylene glycol) on Chromaton N-AW, the temperature of the injection zone was 423 K, the column temperature was 393 K. Nitrogen was the carrier gas; flame ionization detection was used. Since the volumes of the donor and internal standard in the sample corresponded to 10^{-6} l by the order of magnitude of the same compounds in the liquid phase, the sensitivity of the detector was quite sufficient for the given purpose. After the donor solution without the organometallic compounds had been analyzed, a certain amount of BuLi was added to the solution, and further GLC analysis was performed. A check test, carried out with the help of GLC — analysis of the samples from the liquid phase, showed that the loss of THF caused by the destruction reaction between THF and BuLi could not be detected even after 4 hours for $R = 1$. In the case of DME, the loss of approximately 5% of this donor was observed after 15 minutes for $R = 1{\cdot}2$. For $R = 0{\cdot}8$ loss of DME was negligible. For this reason, only values of [DME] for $R < 1$ were taken into account for calculations.

Vapour Pressure Osmometry (VPO)

These measurements were carried out using an apparatus manufactured at the Czechoslovak Academy of Sciences Development Workshops and adapted for inert conditions. Prior to each measurement, the apparatus was hermetically closed, heated to 370 K, and its cell was dried by repeated evacuation and filling with argon. After the last filling with argon and interruption of hermetization, the cell was cooled and kept under continuous insignificant overpressure of argon, which was let in through heat-isolated hoses and two washing bottles thermostated to 303 K, similarly to the cell. The first washing bottle contained a *c.* 1M solution of BuLi in benzene, the other was filled with pure dry benzene with which argon was saturated. The cell contained a small vessel with benzene, whose vapours saturated the cell space. The reference drop consisted of benzene, the measured drop was a solution of BuLi and *D* in benzene prepared in advance. The difference between the temperatures of the reference and measured drops on the thermistores was measured on the resistance bridge and read off on a mirror galvanometer after 4 min, when the system had virtually reached its equilibrium. The apparatus was calibrated by using solutions of naphthalene and anthracene in benzene. The average molecular mass of associated BuLi in benzene determined by employing this method was 380 (the theoretical mass of the hexamer molecule being 364).

RESULTS AND DISCUSSION

The GLC analysis of the gas phase in equilibrium with the given solution was employed in the determination of the free donor concentration, $[D]_f$. In earlier papers dealing with similar topics[8,12] GLC was applied in an arrangement where the donor carried by an inert carrier gas passed through a column with a RLi solution in an inert solvent fixed in the packing of the column. The measuring method used in this case, *i.e.* analysis of the gas mixture on usual columns, is much simpler. Using the known $[D]_f$ and some simplifying assumptions, it is possible to determine the concentration of the complex $[Q]$.

The validity of Raoult's law for solutions containing molecules of the donor and internal standard was verified by measuring the dependence of the ratio of peak heights of the donor and internal standard in samples taken from the gas phase on the varying concentration of one of these compounds in the liquid. These dependences were linear in all cases in the concentration range used (0·005–0·2 mol/l). The resolution of compounds on the chromatogram was good for THF, DME and TEA, while for TMEDA at lower concentrations the peaks of TMEDA and benzene coincided on all the columns available. For this reason, the reaction of this compound was examined in heptane, and a mixture of both decaline isomers was used as the internal standard.

Experimental results are presented in Fig. 1 as a dependence of the relative amount of the free donor in the sample ($Z = [D]_f : [D]_0$) on the concentration of BuLi. None of these dependences exhibits a discontinuity which would indicate a sharp change in the participation of the main reactions in the system (the scale $R = [D]_0 : [\text{BuLi}]_0$ is also shown in the figures).

With THF, the measurement was performed also in an opposite way: the donor was added to a certain amount of BuLi, while $[\text{BuLi}]_0$ remained virtually constant. A comparison between the results of both measurements (Fig. 2) reveals that both dependences of Z on R are similar, and the relative amount of the free donor in the system is virtually independent of the concentrations of BuLi and donor, depending only on their ratio.

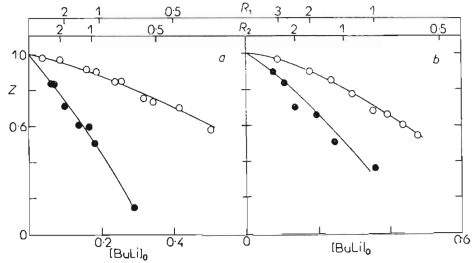


FIG. 1

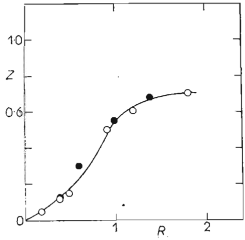
Dependence of the Relative Amount of Donor in the Liquid Phase

$Z = [D]_f : [D]_0$ on $[\text{BuLi}]_0$ (mol/l) and $R = [D]_0 : [\text{BuLi}]_0$ *a*: ○ DME; ● THF; $R_1 = [\text{DME}]_0 : [\text{BuLi}]_0$; $R_2 = [\text{THF}]_0 : [\text{BuLi}]_0$; *b*: ○ TEA; ● TMEDA; $R_1 = [\text{TMEDA}]_0 : [\text{BuLi}]_0$; $R_2 = [\text{TEA}]_0 : [\text{BuLi}]_0$.

FIG. 2

Dependence of the Relative Amount of Donor in the Liquid Phase

$Z = [\text{THF}]_f : [\text{THF}]_0$ on $R = [\text{THF}]_0 : [\text{BuLi}]_0$; ○ $[\text{THF}]_0 = 0{\cdot}175$ mol/l, $[\text{BuLi}]_0$ varied in the range 0·08—0·80 mol/l; ● $[\text{BuLi}]_0 = 0{\cdot}102$ mol/l, $[\text{THF}]_0$ varied in the range 0·03—0·20 mol/l.



Experimental data were evaluated assuming that none of the stoichiometric coefficients of main reactions was known. It was obvious, at the same time, that a system of several equilibrium reactions with the accuracy of experiments used and with such a low number of known data cannot be treated. Using the finding just mentioned, that the stoichiometry probably does not undergo any pronounced changes in the range of R used in the measurements, a single general equilibrium reaction was suggested in the first approximation:

$$(\mathrm{BuLi})_6 + mD \overset{K}{\rightleftarrows} (6/n)\left[(\mathrm{BuLi})_n \,.\, (mn/6)\, D\right] . \qquad (3)$$

The equilibrium constant of this reaction is:

$$K = \frac{\{(6/mn)([D]_0 - [D])_f\}^{6/n}}{\{(1/n)[\mathrm{BuLi}]_0 - (6/mn)([D]_0 - [D]_f)\} \,.\, [D]_f^m} , \qquad (4)$$

where $(6/mn)([D]_0 - [D]_f) = [Q]$ is the concentration of the complex.

In Eq. (*4*), $[\mathrm{BuLi}]_0$, $[D]_0$ and $[D]_f$ are known, while m, n and K remain unknown. One of the ways for finding out at what m and n K is constant in the range of $[\mathrm{BuLi}]_0$ used is to vary both these parameters and to substitute them into Eq. (*4*). A programmable calculator was used for this purpose. The second parameter was changed at a constant value of one of these quantities after certain increments, and the value of K was calculated for each of the experimental points.

The results of the calculations are summarized in Table I, where K and m are the average values for all the experimental points for which $R \leqq 1{\cdot}5$.

TABLE I

Average Values of the Equilibrium Constant K and m from Eq. (*4*)
Generally K for Eq. (*4*) has the dimension $(\mathrm{mol/l})^{(6/n) - 1 - m}$.

n		DME	THF	TEA	TMEDA
6	K	176	—	78	—
	m	2·45	—	1·6	—
4	K	62	15 000	25	3 900
	m	2·4	3·3	1·5	5
2	K	13·5	—	2·1	—
	m	2·3	—	1·5	—

Calculations showed that in those cases where $[D]_f$ decreases with increasing concentration of BuLi very quickly (for THF and TMEDA), no such m at which the calculated K would be constant could be found for $n = 6$. For $n = 2$, the calculated $r = m/n$ with these two donors was approximately two, which is an improbably high value. Hence, THF and TMEDA cause a decomposition of the BuLi hexamer into a tetrameric form during the coordination.

For all the n values used in the study, m evaluated for all donors in the calculations of K was not an integer number. This finding may indicate the formation of a major number of competitive complex. At $R > 1{\cdot}5$, K decreased gradually to one tenth of its original value, which may be due to experimental inaccuracies in this concentration range, or to testify to the fact that in this range Eq. (*3*) ceases to hold in its original form.

Investigation of the System by VPO

The GLC method, though providing the m/n value in the complex formed, does not however inform us directly about its molecular mass. With $[D]_f$, $[\text{BuLi}]_0$, $r = m/n$ and concentration of the complex being known, this quantity may be evaluated by using one of the methods based on colligative properties of solutions. The method of vapour pressure osmometry was chosen for measurements of the molecular mass of the complex; its advantage for the given purpose consists predominantly in the easy choice of the solution temperature.

We started by examining the behaviour of solutions of the individual donors in benzene ("blank tests"). It appeared that evaporation of donor considerably competed with the condensation of benzene in the measured drop. The dependences of the rise in temperature of the drop of solution of the donor on its concentration were virtually linear in all cases, and exhibited the largest slope for TMEDA and the smallest for THF. The rise in temperature of the drop of solution of the donor and BuLi had first to be corrected by using these blank tests and the known $[D]_f$ which could be determined by using the GLC results. The remaining observed rise in temperature of the measured drop is caused by the mixture of $(\text{BuLi})_6$ and a complex of unknown M_Q. The apparent (average) molecular mass of this mixture is M_{app}.

We can assume in the first approximation that complex Q' exists, with the molar concentration:

$$[Q'] = (6/mn)([D]_0 - [D]_f)\,. \tag{5}$$

Its molecular mass is

$$M_{Q'} = M_{(\text{BuLi})_n} + M_{m\text{D}}\,. \tag{6}$$

We can formally express the actual molecular mass of complexes formed M_Q as $M_Q = p\,.\,M_{Q'}$ and it holds that $M_Q\,.\,[Q] = M_{Q'}\,.\,[Q']$. The following relation is valid between the known quantities $[Q']$, $[\mathrm{BuLi}]_0$, M_{app} and the unknown M_Q:

$$M_Q = (M_{\mathrm{app}}\{(1/p)[Q'] + (1/6)[\mathrm{BuLi}]_0\} - \\ -(1/6)[\mathrm{BuLi}]_0 \cdot M_{(\mathrm{BuLi})_6}) \cdot \{(1/p)[Q']\}^{-1} . \quad (7)$$

We carried out the following calculations: Certain values of m and n were chosen from Table I and the competent concentration $[Q']$ was calculated from Eq. (5). This value was substituted into (7) and p was varied. As soon as we achieved for one of the suggested p, an $M_{Q'}$ value (from (6)) p times lower than M_Q (from (7)), the relation $M_Q = p(M_{(\mathrm{BuLi})_n} + M_{m\mathrm{D}})$ expressed the real molecular mass of the complexes formed.

Triethylamine. It was found with the help of the "optimization" process described above that the "best" values suggested were $n = 4$ a $p = 1$. The molecular mass thus determined is somewhat higher than those suggested, however, which means that the solution probably contains a mixture of the tetrameric and hexameric complexes. This finding is in good agreement with the view that TEA is relatively weak donor.

Tetrahydrofuran. According to GLC, only $n = 4$ can be considered for this compound. For $p = 1$, a comparatively good agreement was obtained between the suggested and calculated M_Q. Hence, in the presence of THF BuLi forms a comparatively strongly solvated tetramer.

TABLE II

M_Q Values Evaluated from Eq. (7) Depending on $R = [\mathrm{D}]_0 : [\mathrm{BuLi}]_0$

DME[b] ($n = 4, p = 2$)		THF ($n = 4, p = 1$)		TEA ($n = 4, p = 1$)	
R	M_Q	R	M_Q	R	M_Q
0·43	1 084	0·74	547	0·61	494
0·46	949	1·55	490	1·29	385
0·98	896	2·49	461	2·07	389
1·05	872	4·70	427	2·93	381
1·47	978	—	—	3·90	356
2·17	935	—	—	—	—
2·76	940	—	—	—	—
—	944[a]	—	494[a]	—	350[a]

[a] M_Q values substituted into Eq. (6), multiplied by p. [b] Values for DME are distorted by influence of unknown destruction reaction (see Experimental Part).

Tetramethylethylenediamine. In the case of this compound, any inaccuracy in corrections for blank tests in benzene introduces such a great error that evaluation of M_{app} becomes virtually impossible. Also, any attempts to replace benzene with toluene or heptane were unsuccessful, and attempts to calculate M_Q for this compound were abandoned.

It is obvious that calculations used above are rather clumsy. For monodentate donors (containing only one heteroatom), the VPO – method only checks the GLC results. We assume, in spite of this, that combination of these two methods will bring useful information about the composition of complexes of polydentate donors with organolithium compounds in the future.

In all these cases the degree of association of BuLi in the complex varies about $n = 4$. This corresponds to data reported earlier[2,7]. The coordination property of the donor is characterized by m determined by means of GLC. The higher m/n, the more basic the donor. Hence, of all the compounds under investigation the highest basicity is exhibited by TMEDA and the lowest by TEA (Table I).

The results reported in this study can be compared with data obtained by cryoscopy. The authors of ref.[2] also determined r in the complex formed, starting from the assumption that up to $R = 1$, dissociation of the BuLi hexamer proceeds in solution, in addition to coordination. At $R > 1$, this dissociation is complete, and coordination does not change the degree of association of BuLi any more. On this assumption, in cyclohexane at $R = 1$ 3·6 THF molecules and 2·1 TEA molecules are bound to one tetrameric BuLi unit. Both these values are higher than $m = 3{\cdot}3$ for THF and $m = 1{\cdot}5$ for TEA determined in this study by GLC. At the same time, however, authors of paper[2] found that the number of donor molecules bound to the associate of the organo metallic compounds strongly depends on the type of the solvent. In benzene, m is lower by approximately one third than in completely inert cyclohexane. This fact (similarly to temperature) may explain differences in the determined value of m. Relatively strong donors (except TEA) were selected for these measurements; the solvent used is also a weak donor. Hence, in this case BuLi may be coordinated predominantly in the tetrameric form also at R values much lower than $R = 1$.

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