A CALORIMETRIC STUDY OF THE INTERACTION BETWEEN n-BUTYLLITHIUM AND SOME ELECTRONDONORS

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Received February 20th, 1980

Solvation of n-butyllithium with some ethers and amines was investigated by employing thermometric titration at the initial temperature 303 K. The highest enthalpy changes appear in the reaction of n-butyllithium with dimethoxyethane and N,N,N',N'-tetramethylethylenediamine ($\Delta H = -48.0$ and -51.3 kJ/mol respectively), the lowest are observed in the reaction with diethyl ether and anisole ($\Delta H = -10.2$ and -4.3 kJ/mol respectively). Anomalies in the temperature dependence of these reactions were observed for tetrahydrofuran and dimethoxyethane. The respective entropy changes were calculated for some electrondonors. The replacement of one electrondonor in the complex by another was examined thermometrically.

Complexation of aliphatic organolithium compounds (RLi) with electrondonors (donors, D) has already been studied by various physicochemical methods which may shed some light on this process[1]. Since, however, the parameters of chemical equilibria in the system RLi–D–inert solvent depend considerably on the type and concentration of the individual components, the published results can difficultly be transposed on a comparable basis. In spite of this, several general conclusions may be drawn. RLi with an unbranched and short aliphatic chain, *e.g.* n-butyllithium (BuLi), forms a hexameric associate in a nonpolar solvent. If a donor is present in the system, the degree of association drops to $n = 4$ and m donor molecules are bound on the tetramer by coordination bonds; at the same time, m increases with the basicity of the donor and its value varies between 1 and 4 (refs[2,3]).

These reactions have been rather poorly investigated with respect to thermochemistry. A change in enthalpy accompanying the interaction between BuLi and tetrahydrofuran (THF) in hexane was measured by adiabatic calorimetry[4]. The value found, $\Delta H = -30.9$ kJ/mol, consists of a contribution of the endothermal dissociation of BuLi hexamer to tetramer and of that of the exothermal coordination of the donor. The authors arrived to a conclusion that the exothermal complexation of BuLi tetramer with THF is reflected more pronouncedly only at a ratio of the initial analytical concentrations of the donor and organometallic compounds $R = [D]_0 : [BuLi]_0$, which is higher than 0·3. Further work done by the same team[5] also concerns the complexation of BuLi with various donors. While in the reaction with triethyl amine ($\Delta H = -7{\cdot}1$ kJ/mol), triethylphosphine ($\Delta H = -4{\cdot}2$ kJ/mol) and tetrahydrothiophene ($\Delta H = -2{\cdot}1$ kJ/mol) ΔH was virtually independent on R, for THF the same dependence was more complicated. For $R < 0{\cdot}5$, ΔH was $-31{\cdot}4$ kJ/mol, while for $R > 0{\cdot}5$ it quickly decreased as much as to $\Delta H \sim -2{\cdot}0$ kJ/mol. The authors explain this finding in a way opposite to the preceding paper. At low R values the exothermal coordination of the donor predominates, while at a higher R a strongly endothermal dissociation competes with this process. Both these papers allow a conclusion to be drawn that the absolute value of the overall reaction enthalpy is reduced with increasing steric hindrances of heteroatoms in the donor molecule. In the series of various RLi, those organometallic compounds react with donors possessing an especially high exothermal effect which prior to their interaction with the donor were associated to a tetramer (*e.g.*, t-butyllithium)[6].

Results of the published calorimetric studies of these reactions are sometimes difficult to interpret. At the same time, the method itself may provide very useful information on the system. Hence, the aim of this study consisted in obtaining new experimental data and in comparing them with the results of ref.[3] which deals with the determination of the parameters of equilibrium complexations of BuLi with various donors in benzene.

EXPERIMENTAL

Chemicals

The purification of benzene, the purification and drying of compounds used as donors and the preparation of n-butyllithium were performed as described earlier[3].

Design of Calorimeter

Dewar vessel (volume *c.* 50 ml) immersed in a water thermostating bath was provided with a ground stopper and an inserted glass vessel containing a titration agent (donor or its solution in benzene). The vessel was immersed in the titrated solution, and its contents could be dosed with a special capillary into the titrated solution, either continuously or at once, using a defined overpressure of argon. A teflon capillary was introduced to the bottom of the reaction space and used in the dosage and removal of solutions. A glass bead thermistor (Pramet, Šumperk) provided with contacts with teflon insulation was employed as the temperature detector. The voltage obtained on the resistance bridge with the thermistor introduced into one of its branches was strengthened and recorded with a recorder. The volume of the titrated solution was *c.* 30 ml, that of the titration agent was 2 ml.

Measurement

The reaction space and the vessel containing the titration agent were dried by rinsing several times with a BuLi solution in benzene and washed with dry benzene. The required amounts of the individual reaction components were dosed against a stream of argon. After thorough thermostating, the donor (or its solution) was transferred under pressure into the magnetically stirred titrated solution, either continuously (some 3 ml within 3 min) or at once. Experiments in which the donor was dosed gradually are referred to below as thermometric titrations. The calorimeter was tested by means of the neutralization titration of a 0·003 mol l^{-1} NaOH solution with a 0·25 mol l^{-1} H_2SO_4 solution at the initial temperature 303 K with visual indication of the equivalence point using phenolphthalein. These experiments served to verify the fast response of the detector to changes in temperature, linear character of the dosage and the quality of stirring. The apparatus was calibrated by means of the resistance heating of each resulting reaction mixture after completed titration. Each time the heat measured was $Q = UIt$ [J], causing the same response of the recorder as that obtained in the reaction between BuLi and the donor. For all measurements the heat thus determined was corrected to the respective enthalpies of mixing obtained by "blank tests", *i.e.* by repeating the same operations with solutions in the absence of organometallic compounds at the given temperature. The enthalpy of mixing exceeded 10% of the measured reaction enthalpy only for triethyl amine.

RESULTS AND DISCUSSION

The thermometric titration curves in the form of the dependence of $-\Delta H$ on $R = [D]_0 : [BuLi]_0$ for the individual donors at the initial temperature 303 K are shown in Fig. 1. The $-\Delta H$ values corresponding to $R = 1$ are given in Table I. The position of the bend on these titration curves remained essentially unchanged even at changed rates of dosage (with the exception of anisole and triethyl amine), which means that the course of the reactions is controlled by the rate of dosage (at least up to $R = 1$) and not by one of the slow equilibrium processes. For triethyl amine (TEA), N,N,N',N'-tetramethylethylenediamine (TMEDA) and diethyl ether (DEE) the bend lay near $R = 1$, and the temperature did not change after the equimolar ratio of components in solution had been reached. For dimethoxyethane (DME), the temperature increased also at $R = 1$ very pronouncedly, and this increase was now independent of the rate of dosage of the further donor. Hence, also on reaching $R = 1$ further exothermal unknown reactions take place in the system. For THF and 1,4-dioxane, the bend was observed at R much lower than unity. This phenomenon will be discussed later. The rise in temperature during the interaction between BuLi

TABLE I

$-\Delta H$ Values at $R = [D]_0 : [BuLi]_0 = 1$ in Benzene ($T = 303$ K)

Value	DME	TMEDA	THF	TEA	DEE	1,4-Dioxan	Anisol
$[BuLi]_0$, mol/l	0·107	0·187	0·135	0·182	0·182	0·247	0·135
$-\Delta H$, kJ/mol[a]	48·0	51·3	20·0	12·5	10·2	12·3	4·3

[a] Related to 1 mol of BuLi monomer.

and anisole did not exhibit any distinct bend and was independent of the rate of dosage. This is due to a very slow and reluctant complexation, as suggested also by the very low value of the change in enthalpy. The weak efficiency of this donor may be assigned to the mesomeric effect of the aromatic ring, which reduces the electron density on the oxygen atom.

If only a single reaction occurs in the system, *viz.*, a sufficiently fast complexation with a relatively high equilibrium constant, the composition of the complex may be derived directly from the position of the bend. In the case of the reaction between BuLi and averagely strong and weak donors, however, the complexation equilibria are not shifted to the side of the complexes so much as to satisfy this assumption[3]. Moreover, complexation is preceded by an equilibrium dissociation of the BuLi hexamer, which may considerably distort the situation. It follows from earlier measurements revealing the composition of the complex at various R by means of cryoscopy[2] and GLC (ref.[3]) that at $R = 1$ four donor molecules are bound on one tetrameric BuLi unit only in the case of such extraordinarily strong donors as *e.g.* TMEDA or quinuclidine. The bend of the titration curve at a certain R then means only that at higher R complexation does not take place to any major extent, and the composition of the complex remains unchanged. It may be inferred that in several papers in which the composition of the complex was derived from a change in the dependence of a certain quantity on R (*e.g.*, relative permittivity[7] or chemical shifts

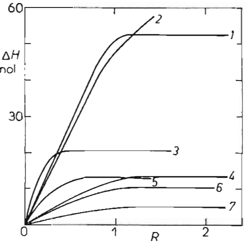

FIG. 1

Dependences of $-\Delta H$ on $R = [D]_0 : [\mathrm{BuLi}]_0$ in Thermometric Titrations in Benzene ($T = 303$ K)

1 TMEDA, *2* DME, *3* THF, *4* TEA, *5* 1,4-dioxane, *6* DEE, *7* anisole.

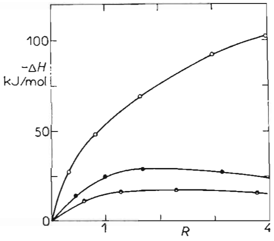

FIG. 2

Dependences of $-\Delta H$ on $R = [\mathrm{D}]_0 : [\mathrm{BuLi}]_0$ in Benzene ($T = 303$ K); the Amount of the Donor Corresponding to the Experimental Points was Added at Once

○ DME, $[\mathrm{BuLi}]_0 = 0{\cdot}179$ mol/l, ● THF, $[\mathrm{BuLi}]_0 = 0{\cdot}175$ mol/l, ◓ TEA, $[\mathrm{BuLi}]_0 = 0{\cdot}180$ mol/l.

in NMR spectra[8]) the low value of the equilibrium constants of chemical reaction in this system was not sufficiently taken into account.

The $-\Delta H$ *vs* R dependences in Fig. 2 at the initial temperature 303 K were obtained by adding a certain amount of donor corresponding to the given R at once each time to the solution of pure BuLi in benzene. $-\Delta H$ has somewhat higher values for all R's than in the case of "real" thermometric titrations. Hence, the route employed for the reaction is also of some importance. In the case of a sufficiently slow thermometric titration, additional solvation of the already existing complex of dissociated BuLi takes place after the addition of another drop. At each moment the system is close to equilibrium, and $-\Delta H$ obtained approaches the actual equilibrium enthalpy values. In the other experimental procedure (Fig. 2), the adequacy between $-\Delta H$ obtained and the total reaction enthalpy depends on the ratio of the rates of dissociation and complexation. It is possible to say that from the curves in Fig. 1 more precise values of $-\Delta H$ at $R = 1$ result than from Fig. 2. At the higher R the shape of the curves in Fig. 1 is partly distorted by thermal loss.

Using the $-\Delta H$ values determined in this study by thermometric titrations (Table I) and earlier data on these equilibria[3], it is possible to estimate the respective entropy changes. In ref.[3], the equilibrium constants and stoichiometric coefficients for a general reaction

$$(\mathrm{BuLi})_6 + m\,\mathrm{D} \rightleftharpoons (6/n)\ (\mathrm{BuLi})_n\,.\,(mn/6)\,\mathrm{D} \qquad (A)$$

($T = 303$ K, in benzene; THF, TEA, DME and TMEDA used as donors) were calculated at a given R (for $R < 1{\cdot}5$) and a known overall BuLi concentration $[\mathrm{BuLi}]_0$, overall donor concentration $[\mathrm{D}]_0$ and concentration of the free donor $[\mathrm{D}]_f$. These data can be employed for the evaluation of the concentration of free BuLi and of the complex C. Calculations of the entropy changes are restricted below

TABLE II

K_a, ΔG^0, ΔH^0 and ΔS^0 Values for the Reaction of Chosen Donors with BuLi at $R = [\mathrm{D}]_0 : [\mathrm{BuLi}]_0 = 1$ in Benzene ($T = 303$ K)

Donor	K_a	$-\Delta G^0$ kJ/mol[a]	$-\Delta H^0$ kJ/mol[a]	ΔS^0 kJ/deg mol[a]
DME	247	13·88	288	—0·905
TMEDA	339 340	32·08	307	—0·907
THF	1 563 400	35·93	120	—0·277
TEA	67·6	10·62	75	—0·212

[a] Related to mol of BuLi hexamer.

to a single case, *viz.*, a system where $R = 1$. The mole fractions x of all components in equilibrium were calculated (including also the concentration of the solvent, because the reaction is accompanied by a change in the molar number). The equilibrium constant of reaction (A) expressed for a standard state of the pure component at the temperature of the system is

$$K_a = K_\gamma \,.\, x_{\mathrm{C}}^{(6/n)} / x_{(\mathrm{BuLi})_6} \,.\, x_{\mathrm{D}}^{m} \,. \qquad (1)$$

To estimate K_a, it is sufficient to assume that the active coefficients are roughly unity, and hence $K_\gamma \doteq 1$. A change in the standard free enthalpy for reaction (A) is $\Delta G^0 = -RT \ln K_a$ [kJ/mol]. From Table I reaction enthalpies can be read off for the initial temperature 303 K and $R = 1$, related to 1 mol of monomeric BuLi. After multiplying by six, the reaction enthalpy similarly to K_a corresponds to the reaction described in terms of the equilibrium (A). The standard change in entropy in the reaction (A) can then be calculated from $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$ [kJ/mol . . deg]. The results are summarized in Table II. In all these cases entropy decreases during the reaction. The decrease is however much more pronounced for bidentate donors (TMEDA and DME) which are able to bind BuLi associates intermolecularly, thus forming greatly ordered structures.

The reaction between THF, a very efficient donor according to earlier data[2,3],

TABLE III

—ΔH Values in Replacement Titrations in Benzene ($T = 303$ K)

D_1[a]	D_2[b]	$[\mathrm{BuLi}]_0$ mol/l	R_1[c]	$-\Delta H$[d] kJ/mol
TEA	THF	0·185	1·0	8·5
THF	TEA	0·185	1·0	13·1
THF	DEE	0·153	0·166	7·4
		1·185	4·0	0·0
DEE	THF	0·185	1·0	10·4
DEE	DME	0·180	1·0	69·5
DME	DEE	0·180	1·0	0·0
THF	DME	0·217	0·166	61·2
		0·217	13·0	18·6
DME	THF	0·185	1·0	0·0
DME	TMEDA	0·185	1·0	11·4
TMEDA	DME	0·185	1·0	12·7

[a] D_1 is the donor being replaced, [b] D_2 is the replacing donor, [c] $R_1 = [D_1]_0 : [\mathrm{BuLi}]_0$, [d] per 1 mol of monomeric BuLi.

and BuLi is accompanied by a surprisingly low change in enthalpy (Table I). Since the bend on the calorimetric titration curve was investigated for THF already at $R \sim 0{\cdot}3$, it may be assumed that at higher R's a strong endothermic reaction competes with further complexation, so that the eventual thermal effect is low. A similar conclusion was derived for THF also by authors of ref.[5]. In this case (and in that of 1,4-dioxane) the inflexion on the titration curve does not indicate the completion of complexation. After the comparison of data published till now[1,2], it is possible to explain these facts by the following hypothesis: At low values of R the fast coordination of one or two molecules of THF (or 1,4-dioxane) on the BuLi hexamer takes place, without its dissociation. This complex is relatively very stable. With increasing R slow dissociation of the complex to tetramer units occurs and tetramers bind simultaneously further molecules of donor. The change of enthalpy in this phase of interaction is very low. If we use the other way of measurement (Fig. 2), not the kinetics of interaction, but only the total enthalpic effect is investigated.

Further data on the complexation efficiency of the individual donors were obtained by a calorimetric investigation of the replacement of one donor in the complex with another. In the solution being titrated, a certain donor D_1 was reacted at 303 K with BuLi in benzene at a certain ratio of the reaction components $R_1 = [D_1] : : [BuLi]_0$. After a time sufficiently long for this reaction to proceed completely to equilibrium (~30 min), the solution was titrated with another donor D_2. In the following titration the donors exchanged their respective roles. The measured ΔH allows us to estimate whether D_2 is able to replace D_1 in the complex, and to what extent. The results are summarized in Table III. The Table shows that bidentate donors are so efficient as to be able to replace readily the weaker D_1 (DEE) from complexes formed at $R_1 \sim 1$, while an opposite process at the same R_1 does not virtually occur at all (but for THF the validity of this statement is restricted by the reasoning outlined above). Quite obviously, the efficiency and rate of replacement decrease considerably at $R_1 > 1$.

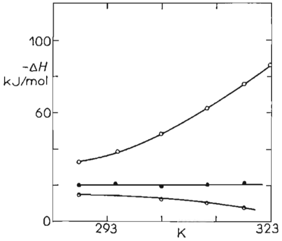

FIG. 3

Dependences of $-\Delta H$ on T in Benzene at $R = [D]_0 : [BuLi]_0 = 1$

○ DME, $[BuLi]_0 = 0{\cdot}179$ mol/l; ● THF, $[BuLi]_0 = 0{\cdot}175$ mol/l; ◒ TEA, $[BuLi]_0 = = 0{\cdot}180$ mol/l.

Measurements of the $-\Delta H$ *vs* T dependence for the ratio $R = 1$ (Fig. 3) has revealed for DME that $-\Delta H$ distinctly rises with temperature, while for THF this quantity is virtually temperature-independent, and for TEA it slightly decreases. In all cases the rate of the reaction between BuLi and donors increased with temperature. Since the formation of coordination bonds is always exothermal, with increasing temperature equilibrium (*1*) is shifted to the left. It is possible to assume that at the higher temperatures (> 283 K) DME decays in the presence of BuLi. This decomposition reaction will be investigated in one of our following studies.

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Translated by L. Kopecká.