

A STUDY OF THE INTERACTION OF OLIGOISOPRENYLLITHIUM AND OLIGOSTYRYLLITHIUM WITH SOME ELECTRONDONORS

Ivan K MÍNEK, Miroslav KAŠPAR and Jiří TREKOVAL

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The "cross" association between butyllithium (BuLi), on the one hand, and oligoisoprenyllithium or oligostyryllithium, on the other, was investigated thermometrically. Dependences of a change in the reaction enthalpy on the ratio of both components were compared with a theoretical assumption that the "mixed" associate consists of trimeric BuLi bound to the unassociated form of "living" oligomers. Thermometric titrations were used to investigate the interaction of "living" oligomers with tetrahydrofuran (THF), 1,2-dimethoxyethane, N,N,N',N'-tetramethylethylenediamine and triethyl amine. GLC analysis of the gas phase in equilibrium with solutions of electrondonors and "living" oligomers allowed the amount of free electrondonor to be determined at various ratios of the two components; the data were used in the determination of the stoichiometric coefficients of the equilibrium reactions under study. THF splits the associated forms of "living" oligomers and forms with them two types of complexes containing one or two THF molecules per one Li atom. All measurements were performed in benzene at 303 K.

A detailed elucidation of the mechanism of the anionic-coordination polymerization of dienes and styrene initiated with butyllithium (BuLi) in the presence of medium strong electrondonors (called further only donors — D) is complicated by several facts. Both the initiator and living oligomeric chains are associated in a nonpolar solution, and the presence of any donor may lower their degree of association and change the polarity of the C...Li bond. Each propagation step is a sequence of partial interactions of the active site with free initiator, donors and monomer¹. All reactions, including all phases of initiation, are equilibrium reactions and the equilibria can obviously be affected by a change in the concentration of any component during the polymerization.

For this reason, we investigated simple models, *i.e.*, interactions of living oligomers of styrene and isoprene (2-methyl-1,3-butadiene) with tetrahydrofuran (THF), 1,2-dimethoxyethane, N,N,N',N'-tetramethylethylenediamine, triethyl amine and BuLi at various initial molar ratios of both components. The determination of stoichiometric coefficients and equilibrium constants of these reactions is useful as it provides a view of the structure of active sites of oligostyryllithium and oligoisoprenyllithium before the accession of yet another monomer unit. Interactions in benzene

at 303 K were investigated by two methods. *viz.*, thermometrically and by GLC analysis of the gas phase in equilibrium with solutions of the compounds².

EXPERIMENTAL

Chemicals

Benzene was purified, donors were purified and dried, butyllithium and sec-butyllithium were prepared and the concentrations of organometallic compounds were determined by employing a procedure described earlier³. Styrene (Fluka) was predried with calcium hydride and after that distilled twice *in vacuo* over sodium. Isoprene (Fluka) was purified in a similar way (at normal pressure). Both monomers were stored under argon over calcium hydride in a freezing box. Trimeric oligostyryllithium and oligoisoprenyllithium were prepared by a slow dropwise addition of monomer solution in benzene to a vigorously stirred benzene solution of sec-butyllithium at room temperature. All operations were performed in argon atmosphere.

GLC Measurements

The amount of free donor in a solution of the living oligomer, donor and internal standard (toluene) was determined similarly to the preceding paper².

Thermometric Measurements

Thermometric titrations of living oligomers with solutions of donors or butyllithium were performed in a calorimeter described earlier³. It was reported in an earlier paper³ that the donor must be dosed sufficiently slowly so that at each moment of titration the system would be as close as possible to the equilibrium; as a result, the measured thermal effects would approach the equilibrium reaction enthalpies as much as possible. The given amount of the donor was therefore dosed for approx. 5–10 min. The interaction between living oligomers and BuLi was examined stepwise: a certain amount of BuLi solution was dosed, and after the mixture had reacted and the resulting solution had been thermostated again, another part of BuLi was added.

RESULTS AND DISCUSSION

Cross Association

The so-called cross association (association of active sites with the free initiator) is one of serious complications in the polymerizations investigated in this study⁴. It is important to know to what extent this association proceeds at various concentrations of active sites and initiator, and how many BuLi molecules on the average are bound on one active site.

The treatment of experimental data may be based on reported data on the association of both components before interaction. BuLi forms a hexamer in inert solvents⁵. Polystyryllithium (RS_mLi) is dimeric⁶⁻⁸. The degree of association of polyisoprenyllithium (RI_mLi) in a nonpolar medium, n , is still a subject of discus-

sion. Kinetic measurements have revealed that $n = 4$ (ref.⁹) and $n = 3 \div 4$ (ref.¹⁰). Kinetic data cannot however provide direct information on the state of the living polymer in the absence of the active components of the reaction system. Viscometric measurements gave $n = 2$ (ref.⁶); a similar value was obtained if viscometry and light scattering were used in parallel⁸. In another study, where light scattering was used⁷, it was reported that at higher concentrations $n = 4$, but decreases with decreasing concentration. These problems were discussed in detail in the most recent study¹¹ based on the two latter methods. The authors report that, if the associate of living chains is regarded as a linear polymer, n varies about two. If, on the other hand, the associate has the character of a starlike polymer, the molecular weight thus determined is lower than the real one, and at higher concentrations it may indeed hold that $n = 4$. At present, however, no definitive conclusions can be drawn in this matter.

The discontinuous procedure used in the thermometric measurement of the reaction between living oligomers and BuLi considerably impedes the possibility of tracing the formation of possible intermediates (cross associates with a different ratio of both components). Earlier experience³ makes it quite clear, however, that the formation of several types of associates cannot be recorded thermometrically even with much stronger interactions (*e.g.*, BuLi-tetramethylethylenediamine) having much higher equilibrium constants. If at various initial concentrations of the components, R,

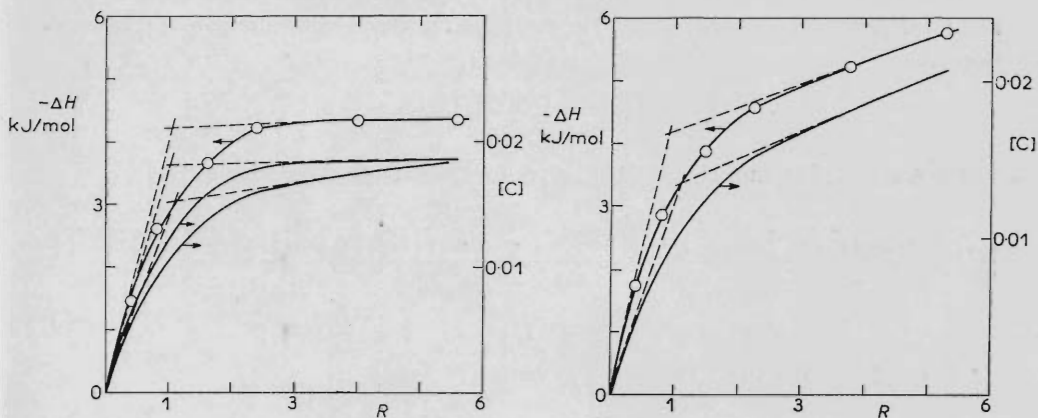
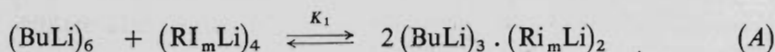


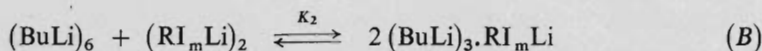
FIG. 1

Comparison of experimental thermometric dependences of $-\Delta H$ on the ratio of initial concentrations of reaction components ($R = [\text{BuLi}]_0 : [\text{RI}_m\text{Li}]_0$, or $R = [\text{BuLi}]_0 : [\text{RS}_m\text{Li}]_0$) with theoretical dependences of concentration of mixed associate ($[\text{C}]$, mol/l) on R (benzene, 303 K). *a* $[\text{RI}_m\text{Li}]_0 = 0.046$ mol/l, $K_1 = 16.2$ in reaction (A) $K_2 = 1.72$ in reaction (B); *b* $[\text{RS}_m\text{Li}]_0 = 0.046$ mol/l $K_2 = 1.0$ in reaction (C)

various individual associates are formed, the thermal effect of formation of one associate overlaps the effect of disappearance of the other. The bend on thermometric curves of the $-\Delta H$ vs. R dependence (the point of intersection of the respective broken straight line in Figs 1a and 1b) lies near $R = 1$ in both cases; however, as has been pointed out in the discussion of an earlier paper², in the case of equilibria with low equilibrium constants this finding does not mean that the associate eventually formed has the composition 1 : 1. In the reaction of BuLi with RI_mLi the dependences thus obtained may be described in terms of two hypothetical equilibrium reactions. One of them is based on the assumption that RI_mLi is tetrameric:



The proposed second reaction is based on viscometric measurements of Morton, Pett and Fetters¹², who for the interaction of RI_mLi with ethyllithium determined the equilibrium constant as 6.5. Similarly,



Using equilibria (A) and (B), it is possible to determine the theoretical form of the dependence of the concentration of the arising mixed associate, $[C]$, on R . Assuming that at each R a change in enthalpy is proportional to $[C]$, one can compare the form of the theoretical dependence $[C]$ on R for both equilibria and the experimental dependence of $-\Delta H$ on R . The equation for the equilibrium constant of reaction (A)

$$K_1 = [C]^2 / ([A]_0 - 0.5[C]) ([H]_0 - 0.5[C]), \quad (1)$$

where A is $(RI_mLi)_4$ and H is $(BuLi)_6$, gives for the explicit expression of $[C]$

$$[C] = \frac{0.5([H]_0 + [A]_0) \{1 - [(1 - 4(1 - 4/K_1) [H]_0 [A]_0 / ([H]_0 + [A]_0)^2]^{1/2}\}}{0.5 - 2/K_1} \quad (2)$$

At $R = 1.5$, it holds that $[H]_0 = [A]_0$; hence;

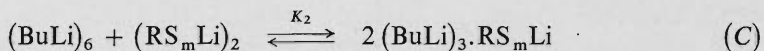
$$[C] = [H]_0 [1 - \sqrt{(4/K_1)}] / (0.5 - 2/K_1), \quad (3)$$

For simplicity's sake, one could consider *e.g.*, that $[H]_0 = 0.5$ mol/l. If $K_1 = \infty$ were valid, then at $R = 1.5$ all BuLi would be bound in a mixed associate, and $[C] = 2 [H]_0$. The dependence of $-\Delta H$ on R in the range $R < 1.5$ would be identical with the tangent of the experimental curve at the point $R = 0$. The actually measured

$-\Delta H$ amounts to only 64% of the hypothetical $-\Delta H$ value for $K_1 = \infty$. Also, the actual $[C]$ at $R = 1.5$ is 64% of the value obtained for the infinitely high K_1 , *i.e.* 0.64 mol/l. After substitution of these values for $[H]_0$ and $[C]$ into Eq. (3), we obtain $K_1 \approx 16.2$. Reaction (B) was treated quite similarly. At $R = 3$, $[RI_mLi]_0 = [H]_0$. The equilibrium constant is $K_2 \approx 1.72$.

A comparison between the dependence $-\Delta H$ vs R and $[C]$ vs R shows that also at a nonequimolar ratio of components in the cross associate the bend on the curves of equimolar initial concentrations of the compounds lies near $R = 1$. The resolution of the $[C]$ vs. R dependences for the derived values of K_1, K_2 is not so good as to show that one of them represents the experimental dependence $-\Delta H$ vs. R more adequately than the other. One can only state that if K_1 is applied, the theoretical curve fits better in with the experimental one in the range of higher R . Similarly to the RI_mLi being a mixture of the dimeric and tetrameric forms, a mixture of several types of associates may also be formed in the cross association.

The reaction of RS_mLi with $BuLi$ may be formulated similarly to reaction (B), *i.e.*,



The equilibrium constant $K_2 = 1.0$. Again, the theoretical and experimental dependences (Fig. 1b) are very similar (the dependence of $-\Delta H$ on $[C]$ is virtually linear). The equilibrium constant is lower than for equilibrium (B), which may express the higher sterical requirement of the living end of RS_mLi compared with RI_mLi .

At $R = 3$, the reaction enthalpy is -4.9 kJ/mol for RI_mLi and -4.3 kJ/mol for RS_mLi (related to 1 mol of the monomeric living oligomer). Hence, the energy gain in the cross association is very similar for both reactions. In both cases the interaction is weak, and any strong donor is likely to change the structure of these mixed associates very easily.

Interaction of Living Oligomers with Electronegative Donors Thermometric Measurements

The character of thermometric titration curves (after correction to the heats of mixing of donors and benzene) resembled that described in an earlier paper³. The reaction was exothermic up to $[D]_0 : [RI_mLi]_0$ (or $[D]_0 : [RS_mLi]_0$) being $0.7 \div 1.0$. After this value of R had been reached, no more heat was released, with the exception of interactions with 1,2-dimethoxyethane, where the temperature rose markedly even at $R > 1$. Hence, the situation in the case of 1,2-dimethoxyethane is quite identical with that observed in its interaction with $BuLi$ (ref.³). In this characteristic feature 1,2-dimethoxyethane differs also from tetramethylethylenediamine, which also is a bidentate donor. At $R > 1$ in the case of interactions of 1,2-dimethoxyethane,

the complexes already formed are probably destroyed. Also in the case of these interactions the position of the bend on the titration curves cannot be used in the estimation of the composition of the complex (*cf.* discussion in an earlier paper³).

The overall changes in the reaction enthalpy (related to 1 mol of unassociated living oligomer) are shown in Table I. If the absolute magnitude of $-\Delta H$ is the measure of the complex-forming efficiency of the donors (which is not always fulfilled because of the dissociations), in the interaction with RS_mLi THF is the strongest donor and triethyl amine is the weakest donor, while in the interaction with RI_mLi the strongest donor is tetramethylethylenediamine and the weakest is again triethyl amine. In all cases with the exception of THF the reaction between the donor and RI_mLi is more exothermal than that with RS_mLi . This phenomenon may again be due to the smaller steric accessibility of the living end of RS_mLi . The enthalpy data for the reaction between THF and the living oligomers discussed here may be compared with the recently published data¹³, the authors of which found, for the interaction of 0.02 RS_mLi with THF, that $-\Delta H = 18.2$ kJ/mol, and for the interaction of 0.02M $RILi$ with THF, that $-\Delta H = 13.8$ kJ/mol (at 298 K in benzene). Thus, the determined enthalpies are again higher for RS_mLi . It cannot be excluded that in the case of the pair $RI_mLi + THF$ the dissociation of RI_mLi proceeds to an especially high degree (*e.g.*, $(RI_mLi)_4 \rightleftharpoons 4 RI_mLi$), and there is a pronounced thermal competition between this reaction and exothermal complex-forming reactions. The small differences in the magnitude of enthalpies for the corresponding reaction components may be assigned to the fact that in ref.¹³ the authors measured $-\Delta H$ at $R \div 0.25$. At this ratio of the components the extent of the dissociation of the oligomer and of its complex-forming reaction certainly differs from that observed at $R = 1$. The absolute value of $-\Delta H$ in the case of interactions between triethyl amine and THF, on the one hand, and living oligomers, on the other, is somewhat lower than in the interaction with $BuLi$ ³. On the other hand, however, the enthalpy of the interaction

TABLE I

Reaction enthalpy changes $-\Delta H$ (kJ/mol — related to 1 mol of unassociated living oligomer) for interaction of RS_mLi or RI_mLi with donors in benzene at 303 K; $[RS_mLi]_0 = 0.055$ mol/l, $[RI_mLi]_0 = 0.06$ mol/l, $[D]_0 : [RS_mLi]_0 = 1$, $[D]_0 : [RI_mLi]_0 = 1$

Living oligomer	Tetrahydrofuran	1,2-Dimethoxyethane	Tetramethyl ethylenediamine	Triethylamine
RS_mLi	16.0	8.8	14.6	4.1
RI_mLi	13.0	16.6	18.7	9.0

between tetramethylethylenediamine and BuLi (ref.³) is much higher (50 ± 60 kJ/mol) than in all the reactions investigated in this study. Consequently, the formation of complexes of tetramethylethylenediamine with BuLi is extremely advantageous from the energy point of view, and the character of complex-forming reactions of this donor with the initiator and active propagation sites is different.

GLC Measurements

In an earlier paper², GLC analysis of the gas phase in equilibrium with solutions of the donor (D), BuLi and internal standard at various R was used in the determination of free donor $[F]_f$ at constant $[D]_0$. In this study the concentration of organo-

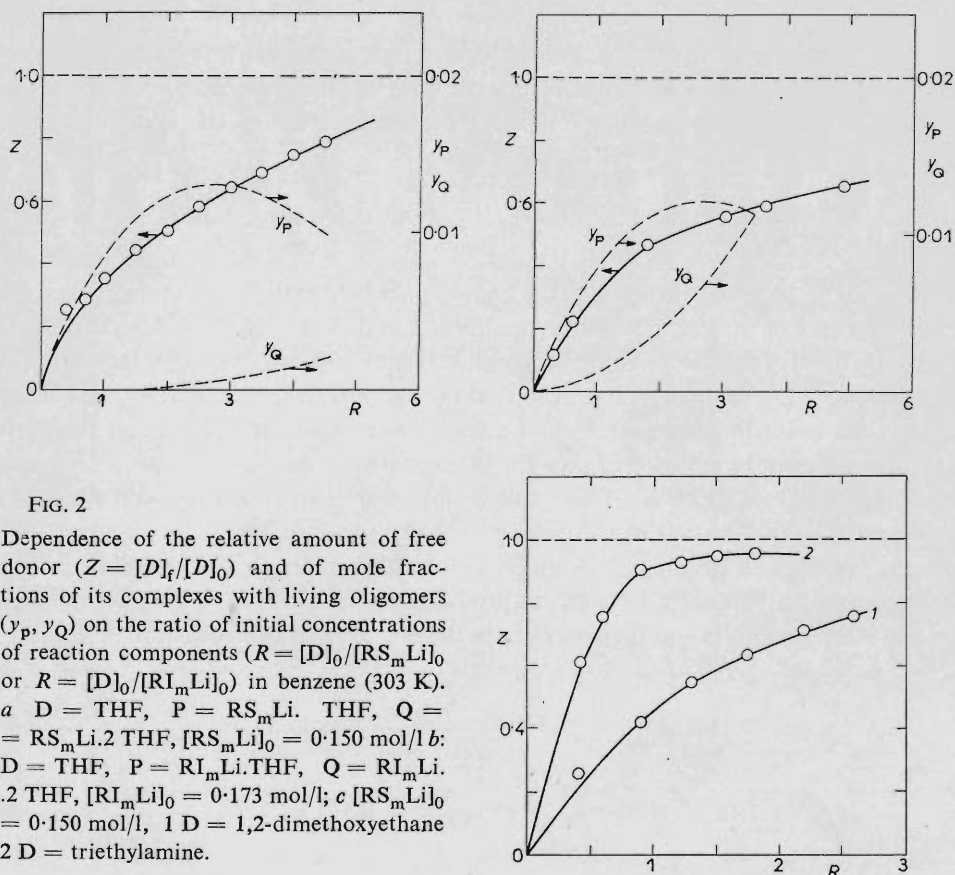
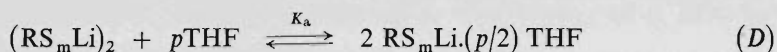


FIG. 2

Dependence of the relative amount of free donor ($Z = [D]_f/[D]_0$) and of mole fractions of its complexes with living oligomers (y_P, y_Q) on the ratio of initial concentrations of reaction components ($R = [D]_0/[RS_mLi]_0$ or $R = [D]_0/[RI_mLi]_0$) in benzene (303 K). *a* $D = \text{THF}$, $P = \text{RS}_m\text{Li}$. THF , $Q = \text{RS}_m\text{Li} \cdot 2 \text{ THF}$, $[RS_mLi]_0 = 0.150$ mol/l; *b*: $D = \text{THF}$, $P = \text{RI}_m\text{Li}$, THF , $Q = \text{RI}_m\text{Li} \cdot 2 \text{ THF}$, $[RI_mLi]_0 = 0.173$ mol/l; *c* $[RS_mLi]_0 = 0.150$ mol/l, $1 D = 1,2\text{-dimethoxyethane}$, $2 D = \text{triethylamine}$.

metallic compounds remained constant while $[D]_0$ varied. The form of the calibration curves, *i.e.* of the dependences of the relative heights of peaks of the donor compared with the peak of the internal standard at constant concentration on $[D]_0$ in the absence of living oligomers was described in an earlier paper². The dependences of $[D]_f : [D]_0$ (Z , relative amount of free donor) on R for the pairs THF + RS_mLi , THF + RI_mLi , 1,2-dimethoxyethane + RS_mLi and triethyl amine + RS_mLi are shown in Fig. 2; the interaction of tetramethylethylenediamine with living oligomers has not been studied so far, because this amine could not be separated in GLC on accessible columns at given concentrations. The results will be discussed separately for each reaction pair.

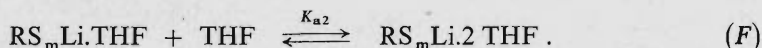
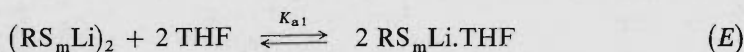
Reaction THF + RS_mLi . Assuming that only a single equilibrium reaction occurs in the system



the stoichiometric coefficient, p , can be determined using the known relative concentration of the donor. The equilibrium constant of this reaction expressed for the standard state of the pure components at the temperature of the system is given by

$$K_a = K_\gamma [(2/p)(x_{THF} - y_{THF})]^2 / \{ [x_B - (1/p)(x_{THF} - y_{THF})] \cdot y_{THF}^p \}, \quad (4)$$

where x denotes mole fractions of the compounds before the interaction, y denotes mole fractions of the compounds in equilibrium and B is $(RS_mLi)_2$. All mole fractions also involve the amount of the solvent. It is sufficient to assume, for the purposes of this paper, that the activity coefficients are roughly of the order of unity, and hence $K_\gamma \approx 1$. In order to determine K_a and p , experimental values of all molar fractions at various R must be substituted into Eq. (4), and p must be varied so that K_a remains constant (independent on R). These calculations were carried out using a programmable calculator. The pair of values of $p \approx 2.15$ and $K_a \approx 2060$ was obtained. The system investigated in this case is much simpler than the pair $BuLi + THF$. It can be assumed that the only interaction products are complexes of RS_mLi with one or two THF molecules and their amount in the mixture can be determined:



If $RS_mLi.THF$ is denoted with P and $RS_mLi.2THF$ is denoted with Q , the equilibrium

constants of reactions (E) and (F) are given by

$$K_{a1} = x_p^2 / (y_B \cdot y_{THF}^2) \quad (5)$$

$$K_{a2} = y_Q / (y_p \cdot y_{THF}) \quad (6)$$

It also holds that

$$y_Q = 0.5(x_{THF} - y_{THF} - y_p) \quad (7)$$

$$y_p = (x_{THF} - y_{THF}) / (1 + 2K_{a2}y_{THF}) \quad (8)$$

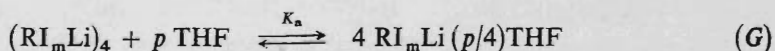
$$y_B = x_B - 0.5y_p - 0.25(x_{THF} - y_{THF} - y_p) \quad (9)$$

By substituting Eq. (8) into Eq. (9) and the two latter equations into Eq. (5), one obtains, after rearrangement,

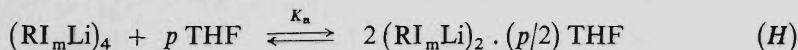
$$K_{a1} = \frac{(x_{THF} - y_{THF})^2 / (1 + 2K_{a2}y_{THF})^2}{\{x_B - 0.25(x_{THF} - y_{THF}) [1 / (1 + 2K_{a2}y_{THF}) + 1]\} \cdot y_{THF}^2} \quad (10)$$

Eq. (10) differs from Eq. (4) in terms containing K_{a2} . By varying K_{a2} , one must again obtain such a value of this quantity which would keep K_{a1} constant within the whole range of R . The respective calculations yielded $K_{a1} \approx 3 \cdot 10^5$ and $K_{a2} \approx 2.3$. The dependences of concentrations of complexes P and Q on R (Fig. 2a) according to Eqs (8) and (7) show that the amount of Q increases with increasing R , while the amount of P decreases at higher R . The highest concentration of P lies in the range $R = 2 \div 3$.

Reaction $THF + RI_mLi$. The data treatment (Fig. 2b) is again complicated by some confusion regarding the degree of association of RI_mLi . If the nonsolvated RI_mLi is dimeric, the reasonings may be exactly the same as in the case of RS_mLi . In the first stage of calculations we obtain $m \approx 3$ and $K_a \approx 45\,000$. After distinguishing the equilibria of type (E) and (F), we have $K_{a1} \approx 60\,000$ and $K_{a2} \approx 17$. The dependences of concentrations of P and Q on R demonstrate (Fig. 2b) that the concentration of complex Q is much higher in this case. This finding again illustrates the fact that RI_mLi is a stronger electron acceptor than RS_mLi . If RI_mLi is tetrameric before the interaction, it may be deduced that owing to THF, n of this living oligomer is lowered down to $n = 1$:



By applying the calculation procedure described above to the adequately rearranged Eq. (4), one obtains $p \approx 5.5 \div 6$ and $K_a \approx 10^6$. Similarly, if the equilibrium



predominates in the system, $p \approx 6$ and $K_a \approx 10^{10}$. It should be pointed out here that all the obtained values of K_a , K_{a1} and K_{a2} are only a rough estimate provided by approximate calculations.

The results show that by a formal treatment of the equilibria of type (D), (G) and (H) it is impossible to determine the degree of association of RI_mLi before or after the interaction. On the other hand, however, this procedure gives a comparatively reliable ratio of both components in the forming complex, which in all cases is about 1.5.

Reaction 1,2-dimethoxyethane + RS_mLi . 1,2-Dimethoxyethane is a weaker donor in the interaction with RS_mLi than THF. This follows already from a visual comparison of curves 1 in Figs 2a and 2c. In the interaction with organolithium compounds, dimethoxyethane undergoes destructive reactions. Mathematical data treatment was therefore abandoned in this case.

Reaction triethyl amine + RS_mLi . The interaction between these two compounds is very weak (Fig. 2c, curve 2). Formal treatment using an equation similar to Eq. (4) leads to low values of p ($\sim 0.2 \div 0.5$). Hence, a considerable amount of the complex of one molecule of triethyl amine with RS_mLi is formed only at high R .

CONCLUSIONS

Since thermometric measurements yielded the magnitudes of overall $-\Delta H$ (under conditions close to the equilibrium ones), and GLC provided the values of equi-

TABLE II

Thermodynamic constants for interactions of RS_mLi or RI_mLi with tetrahydrofuran in benzene at 303 K; $[\text{D}]_0 : [\text{RS}_m\text{Li}]_0 = 1$, $[\text{D}]_0 : [\text{RI}_m\text{Li}]_0 = 1$

Reaction system	Reaction	$-\Delta H^0$ kJ/mol	K_a	$-\Delta S^0$ kJ/mol K
$(\text{RS}_m\text{Li})_2 + \text{THF}$	D	32.0	2 060	-0.042
$(\text{RI}_m\text{Li})_2 + \text{THF}$	D	26.0	45 000	0.003
$(\text{RI}_m\text{Li})_4 + \text{THF}$	G	52.0	10^6	0.038
$(\text{RI}_m\text{Li})_4 + \text{THF}$	H	52.0	10^{10}	-0.059

librium constants, it is possible to estimate the standard entropy changes in interactions investigated by both methods:

$$\Delta S^0 = (\Delta H^0 + RT \ln K_a)/T. \quad (11)$$

At the same time, it is only necessary to recalculate $-\Delta H$ (Table I) so that it would correspond to the description of the reaction according to the respective equation for K_a . The results are summarized in Table II; the equilibria for which the particular tabulated quantities were calculated are also given. In all cases the entropy changes are lower than in the interaction of BuLi with the donors³.

The anionic coordination polymerizations of isoprene and styrene in the presence of donors still remain a complicated problem. Because of the equilibrium character of all the processes involved and their mutual competition, virtually each system under study must be characterized individually, with extreme caution and bearing in mind all effects that could be imagined. With respect to these findings, the investigation of model systems seems useful still, as it can provide valuable information on the actual character of the active sites.

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