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Effect of Electron-donor Solvents on the Reactivity of Lithium Alkyls

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The causes of and the relations governing the acceleration of reactions involving lithium alkyls by electron-donor solvents are discussed. The kinetic effect is due to a change in the polarity of the C-Li bond in consequence of the formation of complexes (of the donor-acceptor type) of the lithium alkyl and the solvent and a change in the state of lithium alkyl in solution.
The bibliography includes 115 references.

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I. INTRODUCTION

Despite the exceptionally wide applications of lithium alkyls in synthetic organic and polymer chemistry, it is still not quite clear how the state of lithium alkyls changes under the action of different solvents; the problem of the form in which lithium alkyls participate in reactions and of the ultimate mechanism of the change in the reactivity of lithium alkyls under the influence of electron-donor solvents remains controversial. These problems are discussed in the present review†.

I. EFFECT OF SOLVENTS ON THE DEGREE OF ASSOCIATION OF LITHIUM ALKYLS IN SOLUTION

The co-ordination unsaturation of organolithium compounds[1-3] is reflected in their characteristic capacity for association. Thus in hydrocarbon solvents ethyl- and n-butyl-lithium exist in the form of hexamers and t-butyl-lithium in the form of a tetramer (see Refs. 1 and 5). Branching or an increase in the length of the alkyl group R inhibit the association RLi.[4,6]

In connection with the problem of the effect of electron-donor solvents on the reactivity of lithium alkyls, information about their complexes with ethers[7-10], amines[11-13], and dialkyl sulphides[14] is of interest. The structure of such complexes has still not been adequately investigated and there are discrepancies in the data on their composition[10-12,15]. For example, Brown et al.[12] believe that, in benzene solutions containing a large excess of triethylamine relative to ethyl-lithium, a 1 : 1 complex is formed, which is a dimer of ethyl-lithium solvated by two molecules of the base. On the other hand, according to Eastham and coworkers[10,11,15], complexes of lithium alkyls and solvents with one electron-donor atom (triethylamine, ethyl ether, tetrahydrofuran) have a 2 : 1 composition, corresponding to a dimer of the lithium alkyl solvated by one molecule of the amine or ether, even in the presence of a large excess of the solvent. Complex formation with an electron-donor substance D can be represented by the mechanism[15]

$$[(RLi)_2]_n + n\,D \rightarrow n\,(RLi)_2 \cdot D. \qquad (1)$$

In the complex formation process, steric factors play an important role, which is very characteristic of the specific solvation of cations[16]. Thus although triethylamine is a stronger base than tetrahydrofuran (THF),[17,18] the steric hindrance to solvation[11,19,20] makes the complexes of RLi with triethylamine less stable and less polar than those with THF.[11]

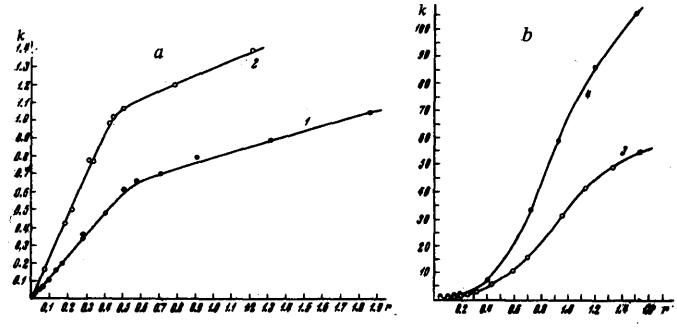


Figure 1. Determination of the composition of n-butyl-lithium solvate from data on the kinetics of the reaction between n-butyl-lithium and n-butyl bromide. Variation of k with r: *a*) for ethyl ether (*1*) and tetrahydrofuran (*2*); *b*) for 1,2-diethoxyethane (*3*) and 1,2-dimethoxyethane (*4*).

Information about the composition of complexes of lithium alkyls with electron-donor solvents can be obtained indirectly in some cases by studying the kinetics of reactions in which the lithium alkyls participate. For example, when the rate of reaction n-butyl-lithium with n-butyl bromide[21] (A) or 1-bromo-octane[22] (B) is studied, the curve relating the rate constant k to the molar ratio r of ether and the lithium alkyl in hexane solution shows an inflection of r = 0.5 (Fig. 1*a*). This indicates the formation of 2 : 1 complexes of n-butyl-lithium with ethyl ether or tetrahydrofuran.

When the reaction of A is carried out with addition of variable amounts of ethylene glycol ethers, each of which contains two oxygen atoms, the concentration dependence of the rate constant has a different form (Fig. 1*b*). The rate constant increases in proportion to the square of the concentration of the ether (c) up to r close to unity This can

† For an exhaustive list of the literature references on the properties and reactions of lithium alkyls, see Talalaeva and Kocheshkov[1].

be satisfactorily explained if it is supposed that in this case 1 : 1 complexes of n-butyl-lithium with the ethylene glycol ether are active in the reaction of n-butyl-bromide with n-butyl-lithium (see also Ref. 23). The different orders of reaction with respect to the ether (first in the case of ethers with one oxygen atom and second when the ether molecule contains two oxygen atoms, Fig. 2) correspond to different compositions of the complexes.

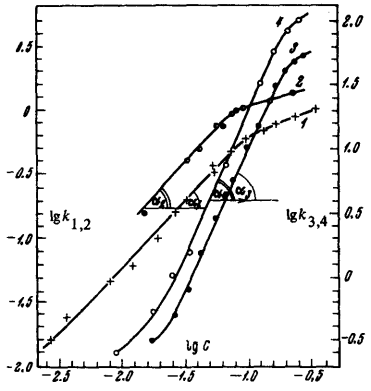


Figure 2. Determination of the order of the reaction between n-butyl-lithium and n-butyl bromide with respect to ethyl ether (*1*), tetrahydrofuran (*2*), 1,2-diethoxyethane (*3*), and 1,2 dimethoxyethane (*4*). (tan $\alpha_1 \simeq$ tan $\alpha_2 \simeq 1$; tan $\alpha_3 \simeq$ tan $\alpha_4 \simeq 2$).

Infrared spectra[4,6,24,25] and NMR (^{1}H and ^{7}Li) spectra[4,15,26] show that the degree of association of lithium alkyls in electron-donor solvents is lower than in hydrocarbon solvents. A reliable determination of the degree of association of lithium alkyls in ether solutions is complicated by the fact that lithium alkyls can react irreversibly with ethers[27-30]‡. Nevertheless, knowledge of the state of lithium alkyls in electron-donor solvents is important not only in understanding the characteristics of the kinetics and mechanisms of their reactions in these media but also because it throws light on the mechanism of the decomposition of association complexes under the action of electron donors.

The decomposition of association complexes is frequently represented by the equation

$$\frac{1}{n}(\mathrm{RLi})_n \rightleftarrows \mathrm{RLi}, \qquad (2)$$

which reflects the process occurring, albeit of course in a simplified form. In more realistic hypotheses[34,35] it is postulated that the dissociation of the organolithium complexes is stepwise and is represented by equations of the type

$$(\mathrm{RLi})_n \rightleftarrows (\mathrm{RLi})_{n-1} + \mathrm{RLi}. \qquad (3)$$

‡ The rate of decomposition depends on the structure of both reactants[24,27]. This reaction affects significantly the polymerisation processes initiated by lithium alkyls[31-33] and in principle can distort the kinetics of other reactions of lithium alkyls in the presence of ethers.

Thus it is suggested that association complexes of different composition are present in solution in equilibrium with one another and with the monomeric form of the lithium alkyl. This widely held view was objected to by Brown[36], who believes that not all the association complexes are stable in solution. On the basis of NMR (^{7}Li and ^{1}H) spectra, Brown concluded[26] that ethyl- and methyl-lithium have a tetrameric structure in ethyl ether at low temperatures. According to his experimental data for the kinetics of the intermolecular exchange of the alkyl groups of ethyl- and methyl-lithium association complexes in ethyl ether[26] and the association complexes of ethyl-lithium in toluene[37], the rate of this reaction in the hydrocarbon solvent is determined by the breakdown of lithium-alkyl hexamers:

$$(\mathrm{RLi})_6 \rightarrow (\mathrm{RLi})_4 + (\mathrm{RLi})_2, \qquad (4)$$

and in ethyl ether by the breakdown of the tetramer with formation of the dimer:

$$(\mathrm{RLi})_4 \rightarrow 2\,(\mathrm{RLi})_2\,. \qquad (5)$$

In another study[12] Brown investigated cryoscopically the mechanism of the successive breakdown of ethyl-lithium hexamers into tetramers and dimers following the addition of triethylamine to the benzene solution. According to Brown, in the region of low molar ratios of the electron-donor solvent (D) and lithium alkyl the solvation of the hexamer $[(\mathrm{RLi})_6 + 2\mathrm{D} \rightarrow (\mathrm{RLi})_6.2\mathrm{D}]$ does not result in its breakdown, but in the presence of an excess of the base the hexamer is completely dissociated into the solvated dimer.

Eastham and Gibson inferred the changes in the state of a number of lithium alkyls in different mixtures of an ether or amine with n-hexane from a study of the dielectric constant[10,11], the NMR spectra[10,15], or the vapour pressure of ethyl ether over the solution[10] as a function of its content of the electron-donor solvent. The curves for the above relations have an inflection or break on attainment of a 1 : 2 molar ratio of the electron-donor additive to the lithium alkyl. The subsequent form of the curves showed that, after further increase of the concentration of the ether or amine in solution, the state of the lithium alkyl did not alter significantly. Eastham and Gibson's conclusion[10,15] concerning the dimeric structure of n-butyl- and isobutyl-lithium in ethyl ether and in tetrahydrofuran cannot be regarded as unambiguous. Their results provide evidence only concerning the ratio of the number of moles of the ether (amine) and the lithium alkyl in the solvate complexes.

More reliable information about the degree of association of lithium alkyls in ethereal solutions (at room temperature) was obtained recently by West and Waack[38] by an isopiestic method. The degree of association of methyl- and phenyl-lithium in tetrahydrofuran at 75°C proved to be respectively 4 and 2, benzyl-lithium was not associated under these conditions, and in ethyl ether methyl- and n-butyl-lithium are tetrameric. Furthermore, Brown's[12] and Eastham's[10,15] conclusions are inconsistent with the data of Waack and coworkers[38,39] on the kinetics of the reactions of lithium alkyls with 1 : 1-diphenylethylene and triphenylmethane in ethyl ether and tetrahydrofuran at room temperature. The order of these reactions with respect to methyl- and n-butyl-lithium is close to 3.

Thus not only in hydrocarbon but also in ethereal solutions lithium alkyls are associated, which is evidence of considerable stability of their association complexes. The information about the true state of lithium alkyls under different conditions requires further revision.

II. KINETICS OF REACTIONS OF LITHIUM ALKYLS IN HYDROCARBON SOLUTIONS

The interpretation of data on the kinetics of reactions of lithium alkyls in solutions is far from simple. Any kinetic mechanism must take into account the association of the lithium alkyl. Until recently it was believed that in all cases only the monomer of the lithium alkyl, in equilibrium with association complexes, is reactive. This equilibrium is represented in Scheme 1, where the equation for the rate of reaction of RLi with a substrate S under the conditions of such equilibrium[4] is also included.

Scheme 1

$$(RLi)_n \overset{K_e}{\rightleftarrows} n\,RLi\,,$$

$$K_e = \frac{[RLi]^n}{\left(\frac{[RLi]_0}{n}\right)},$$

$$RLi + S \rightarrow \text{reaction product}\,,$$

$$V = k_1\,[S]\,[RLi] = k_1 K_e^{1/n}\left(\frac{[RLi]_0}{n}\right)^{1/n}[S] = k_{overall}[S]\,[RLi]_0^{1/n}.$$

Here and henceforth V represents the rate of reaction and the subscript 0 denotes the initial concentration.

Apart from the widely adopted mechanism in Scheme 1, Brown[4] postulates three further possible reaction mechanisms in which the lithium alkyl reacts as the association complex.

Scheme 2

$$(RLi)_6 \overset{K_e}{\rightleftarrows} (RLi)_4 + (RLi)_2\,,$$

$$K_e = \frac{[(RLi)]_4\,[(RLi)_2]}{[(RLi)_6]}\,,$$

$$(RLi)_2 + S \rightarrow \text{reaction product} + RLi\,,$$

$$V = k\,[(RLi)_2]\,[S] = k\,K_e^{1/2}\,[(RLi)_6]^{1/2}\,[S] = k_{overall}[RLi]_0^{1/2}\,.$$

Scheme 3

$$(RLi)_6 + S \overset{K_e}{\rightleftarrows} (RLi)_6S\,,$$

$$K_e = \frac{[(RLi)_6 \cdot S]}{[(RLi)_6][S]} = \frac{[c]}{([S]_0 - [c])\,([H]_0 - [c])},$$

where $[c] = [(RLi)_6.S]$ and $[H]_0$ is the initial concentration of the hexamers:

$$[c] \approx \frac{K_e \cdot [S]_0 \cdot [H]_0}{1 + K_e \cdot ([H_0] + [S]_0)}$$

If K_e is small, then $[c] \simeq K_e\,[S]_0\,[H]_0$ and $V = k[c] = kK_e[S]_0[H]_0$.

If $[S]_0 \gg [H]_0$ and $K_e[S]_0 \gg 1$, then $[c] \simeq [H]_0$ and $V = k[H]_0$.

If $[H]_0 \gg [S]_0$ and $K_e[H]_0 \gg 1$, then $[c] \simeq [S]_0$ and $V = k[S]_0$.

Scheme 4

$$(RLi)_6 \rightarrow (R_5Li_6)^+ + R^-\,.$$

$$R^- + S \rightarrow \text{reaction product}\,.$$

In Schemes 1–4 the possible reaction pathways by a heterolytic mechanism are postulated. It should be noted that in a hydrocarbon medium lithium alkyls may react also by a homolytic mechanism, for example, with alkyl halides[40].

According to Brown[4], Scheme 4 should be excluded from consideration as in this case the interaction of the substrate with RLi requires an unduly high activation energy.

Scheme 1 shows that the order of the reaction with respect to lithium alkyl is equal to the reciprocal of its degree of association. In many studies on the kinetics and the initiation of polymerisation by n-butyl-lithium[41] and also on its reactions with 1,1-diphenylethylene[42] and fluorene[43] the order with respect to lithium alkyl proves to be 1/6, which is satisfactorily consistent with data on the degree of association of n-butyl-lithium in hydrocarbons[35]. The principal association complex of t-butyl-lithium in hydrocarbon solutions in the tetramer[44] and, in agreement with this, the reaction order with respect to this lithium alkyl in reactions with fluorene and 1,1-diphenylethylene is close to 1/4.[45]

However, in many cases the agreement of the results with the above mechanism is poor. For example, Ziegler and coworkers[46] already established that the reactions of ethyl-, n-propyl-, and n-butyl-lithium with 1,1-diphenylethylene in a hydrocarbon is of first order with respect to each reactant. West and Glaze[47] arrived at a similar conclusion for the reaction of ethyl-lithium with benzyl chloride in benzene. The data on the kinetics of the reaction of ethyl-lithium with 1,1-diphenylethylene obtained by Brown[4] are inconsistent either with the results of Ziegler[46] or those of Evans and George[42], since the reaction order with respect to ethyl-lithium proved to be variable in the range 0.7–0.95. In reactions involving the metallation of fluorene with ethyl-lithium and the addition of the latter to 1,1-diphenylethylene in benzene solutions, a low order (1/9) with respect to ethyl-lithium was observed[48], although it is known that its degree of association in benzene is 6.[12,49]

Data inconsistent with Scheme 1 are also found in the literature on anionic polymerisation. Thus Hsieh[50] showed that the rate of initiation of the polymerisation of styrene, butadiene, and isoprene is directly proportional to the concentration of the lithium alkyl in hydrocarbon solutions. Worsfold and coworkers[51,52] observed a variable reaction order (0.5–1) with respect to n-butyl-lithium in the polymerisation of the same monomers in cyclohexane. Finally, we may point out the discrepancy between the results of O'Driscoll et al.[53] and Worsfold and Bywater[41] for the degree of association of n-butyl-lithium and benzene if the latter is estimated from the order of the initiation reaction in the polymerisation of styrene. At styrene concentrations in excess of 0.5 M the order is 1/3,[53] while at concentrations less than 0.03 M it is 1/6.[41] Brown[4,36] expressed doubts concerning the universality of the kinetic mechanism in Scheme 1, mainly in its principal postulate that only the monomeric form of the lithium alkyl participates in the reaction. The concentration of the monomer RLi in a hydrocarbon solution must be extremely low. At best, only the dimer of the lithium alkyl, formed by reaction (4), can be present in appreciable amounts. If, on the other hand, the monomer RLi is nevertheless the active species, the reaction rate is limited by the stage involving the dissociation of the dimer into the monomer:

$$(RLi)_2 \rightarrow 2\,RLi\cdot \qquad (6)$$

According to Brown's estimate[36], a reaction with participation of the monomer RLi is possible when the heat of dissociation of the dimer does not exceed 20 kcal mole^{-1}. He suggests that the enthalpy of association of $(RLi)_2$ is not less than the value established by Morton[54] for the dimer of polyisoprenyl-lithium (37 kcal mole^{-1}). In addition, Brown refers to data[55] on the heat of dissociation of the dimer of trialkylaluminium, which is 20.2 kcal mole^{-1}, and notes that the heat of dissociation of $(RLi)_2$ must be appreciably higher, since, in contrast to trialkylaluminium, lithium alkyls are associated in ethereal solutions[2].

Without rejecting the possibility of reactions with participation of lithium alkyl by Scheme 2, Brown believes Scheme 3 to be more likely. He showed previously[12] that

the hexamer of a lithium alkyl is capable of forming complexes with Lewis bases. Brown assumed that such complexes are naturally formed also with less basic nucleophiles: alkyl halides, olefine, and other compounds. The apparent order of the reaction with respect to RLi and the substance reacting with it depends on their relative contents in the solution and on the equilibrium constant K_e for the formation of the complex of the lithium alkyl and the substrate. Studies on polymerisation initiated by lithium alkyls have been carried out over a wide range of relative concentrations of RLi and olefins. Therefore Brown believes that the above examples of discrepancies between different data on the order of the polymerisation initiation reaction are not surprising.

Brown's critical comments concerning Scheme 1 were objected to by certain workers[56,57], who pointed out the errors in Brown's calculation based on Morton's incorrect data for the heat of association of polyisoprenyl-lithium and its degree of association, which is actually four[34,51] and not two[54]. Furthermore, it was pointed out[56,57] that Scheme 1 is as a rule inapplicable in those cases where the solvent is not an aromatic but an aliphatic hydrocarbon.

In contrast to aliphatic hydrocarbons, aromatic hydrocarbons are apparently capable of solvating lithium alkyls, albeit only to a slight extent, by virtue of the formation of π-complexes[34,53]. This is shown by the comparison of both polymerisation rates in these and other solvents[34,50,57] and the ultraviolet spectra of solutions of s-butyl-lithium in benzene and in cyclohexane[57]. The variable reaction order with respect to the lithium alkyl and the S-shape of the kinetic curve for the initiation stage observed in aliphatic hydrocarbons[51,52,57] have been explained by the autocatalysis of the reaction as a result of the formation of cross-association complexes of the lithium alkyl and the product of its addition to the monomer[56,57].

These considerations[56,57] refer to the initiation stage and the polymerisation under the influence of lithium alkyls. The problem of the applicability of Scheme 1 to various reactions of associated organolithium compounds in hydrocarbon media still remains open.

III. EFFECT OF ELECTRON-DONOR SOLVENTS ON THE KINETICS OF REACTIONS OF LITHIUM ALKYLS

1. General Postulates

The powerful effects of electron-donor solvents on the reactivity of lithium alkyls was noted a long time ago. Ziegler[46] already pointed out the much higher rate of addition of n-butyl-lithium and other lithium alkyls to the double bond of 1,1-diphenylethylene in ethyl ether compared with the benzene solution. In tetrahydrofuran the reaction is almost instantaneous[58].

When even small amounts of ether or an amine are added to the hydrocarbon solvent, the initiation stage of the polymerisation of styrene or diene hydrocarbons by the lithium alkyl is also greatly accelerated[51,59-62] and to a much greater extent than the chain propagation stage[51,54,62,63]. The effect of ethers and amines on the kinetics of the initiation stage of the polymerisation by lithium alkyls has not as yet been investigated adequately in a quantitative sense because of the high rates of this stage in the presence of electron-donor additives[58,60-62].

There are literature data concerning the activating effect of electron-donor solvents also on other reactions of lithium alkyls, for example the metallation of hydrocarbons by them or their interaction with alkyl and aryl halides. According to Gilman's data[64,65], metallation by lithium alkyls is facilitated on passing from solutions in hydrocarbons to solutions in ethyl ether and in particular to solutions in tetrahydrofuran, which has been confirmed by Waack[66]. The nucleophilic activity of lithium alkyls increases even more under the influence of bistertiary amines[67]. The complex of n-butyl-lithium with *NNN'N'*-tetramethylethylenediamine readily metallates toluene and benzene even at a moderate temperature.

The reactions of organolithium compounds with alkyl and aryl halides are usually considered from the standpoint of organic synthesis. The number of kinetic studies which provide information about the effect of electron-donor solvents on reactions of this type is small. Ziegler[68] noted that the half-life of the reaction between n-butyl-lithium and n-butyl bromide decreased by a factor of 20 when it was carried out in ethyl ether instead of benzene. The rates of this reaction differ by more than 4 powers of 10 between n-hexane and its mixture with 1,2-dimethoxyethane for an equimolar content of the ether and the lithium alkyl[21]. In ethyl ether n-butyl-lithium reacts with 1-bromo-octane almost 800 times faster than in n-hexane[22].

The solvent can change not only the rate of reaction or its order with respect to the lithium alkyl[39,42,43,58] but the actual reaction path. The change in reaction order under the influence of the solvent is readily understood, since the state of the lithium alkyl in solution depends on the solvent. It is also known that, depending on the type of reactants and the reaction conditions, in particular the solvent, the organolithium compound reacts with alkyl and aryl halides[15,40,69] either by a heterolytic mechanism—the Wurtz reaction [reaction (7)] and the exchange of alkyl radicals [reaction (8)] are of this type—or by a homolytic mechanism [reaction (9)]:

$$R'Li + R''X \rightarrow R'R'' + LiX, \quad (7)$$

$$R'Li + R''X \rightarrow R'X + R''Li, \quad (8)$$

$$R'Li + R''X \rightarrow R'^{\cdot} + Li^+ + R''^{\cdot} + X^- \quad (9)$$

The postulate that the reaction path can change is well illustrated, for example, by the data of Hoeg and Lusk[70], who investigated the reaction of n-butyl-lithium with n-benzyl chloride in several solvents. In ethyl ether and in n-hexane these reactants interact with formation of dibenzyl (I) and *p*-pentylbenzene (II):

$$C_6H_5CH_2Cl \xrightarrow[Et_2O(hexane)]{n\text{-}C_4H_9Li} [C_6H_5CH_2Li] \begin{cases} \xrightarrow{+C_6H_5CH_2Cl} C_6H_5CH_2CH_2C_6H_5 \ (I) \\ \xrightarrow{+n\text{-}C_4H_9Li} C_6H_5C_5H_{11} \ (II) \end{cases} \quad (10)$$

When the same reaction was carried out in tetrahydrofuran at room temperature, *trans*-stilbene was obtained in a yield of about 20% in addition to compounds (I) and (II). If the reaction follows the second pathway, then α-chlorodibenzyl (IV) and the carbanion of benzyl chloride (III) are formed as intermediates:

$$C_6H_5CH_2Cl \xrightarrow[THF]{+n\text{-}C_4H_9Li} \underset{(III)}{[C_6H_5\bar{C}HCl\overset{+}{Li}]} \xrightarrow{+C_6H_5CH_2Cl} \rightarrow \underset{(IV)}{C_6H_5CHClCH_2C_6H_5} \xrightarrow{+n\text{-}C_4H_9Li} C_6H_5CH{=}CHC_6H_5 + C_6H_5\overset{C_4H_9}{\overset{|}{C}}HCH_2C_6H_5 \quad (11)$$

An additional example is provided by data[71] on the change in the mechanism of the initiation by n-butyl-lithium of the polymerisation of methyl acrylate and methyl methacrylate when n-hexane is replaced by tetrahydrofuran.

The above findings by no means exhaust the literature data on the effect of solvents on the reactivity of lithium alkyls (see, for example, Bilevich and Okhlobystin[72]).

2. The Causes and the Principal Relations Governing the Effect of Electron-donor Solvents on the Kinetics of Reactions of Lithium Alkyls

The acceleration of the reactions of lithium alkyls in electron-donor solvents compared with hydrocarbon solvents must be attributed to the effect of two main factors: the increase of the polarity of the C–Li bond as a result of the specific solvation of lithium and the decrease of the degree of association of the organolithium compound. One should then bear in mind the change of the polarity of the C–Li bond not only in the ground but also in the transition state[4,22,69].

Thus West[47] established the occurrence of a kinetic isotope effect for the reaction between ethyl-lithium and benzyl chloride ($k^6_{LiEt}/k^7_{LiEt} = 1.029$). This finding is evidence of a significant weakening of the C–Li bond in the transition state. Therefore one may expect the acceleration of reactions of this type following the additional polarisation of the C–Li bond, for example, as a result of the solvation of lithium by the molecules of an electron-donor agent.

The increased polarity of the C–Li bond in electron-donor solvents (or when these are added to hydrocarbons) is confirmed by measurements of the infrared spectra[4,6,24,25] electrical conductivity[73], and dielectric constants[10,11] of RLi solutions and also by measurements of their NMR spectra[4,15,26]. On the other hand, as we have seen, in the presence of an electron-donor solvent the degree of association of the lithium alkyl falls and consequently the number of its kinetically active species should increase[22].

The problem of the interrelation of these factors is not entirely clear, although in some studies[22,58,63] the lowering of the degree of association of the organolithium compound is regarded as the most important factor accelerating the reaction. Probably, in each specific case, this problem must be solved separately considering the specific features of the mechanism of the given reaction. In this connection it is appropriate to consider data[21,74] on the effect of tetrahydrofuran (THF) and other electron-donor substances on the kinetics of the reactions of n-butyl-lithium with n-butyl bromide and with triphenylmethane.

The dependence of the rate constant for the first reaction on the content in n-hexane of ethers with 1 and 2 oxygen atoms is shown in Figs. 1*a* and 1*b* and has been explained[21,22] by the active participation in the reaction of the solvates of the association complexes of n-butyl-lithium, the composition and the reactivity of which are determined by the solvation properties of the electron-donor compounds.

The rate of this reaction changes most markedly with increasing ether content when small amounts of it are added to n-hexane: in the region of small molar ratios of the ether and the lithium alkyl (r), ranging from zero to 0.5 for ethyl ether or THF and in the region $r < 1$ for 1,2-diethoxy- and 1,2-dimethoxy-ethane.

Fig. 1 shows that the rate of reaction between n-butyl-lithium and n-butyl bromide continues to increase when ether with one oxygen atom is added also in the region with $r > 0.5$, although more slowly than for $r < 0.5$. The reasons for this increase are discussed in a recent brief communication by Screttas and Eastham[75]. They believe that the effects of the electron-donor solvent on the rate of reaction with participation of the lithium alkyl in the region of r less and greater than 0.5 are fundamentally different. In the region where $r < 0.5$ the ether (or amine) takes part in the solvation of the lithium alkyl and causes the breakdown of its association complexes into dimers [Eqn. (1)].

On the other hand, the increase in the rate of reaction with the concentration of the ether or amine in solution for $r > 0.5$ is attributed[75] to a kinetic, and not thermodynamic, effect of the electron-donor solvent, which facilitates charge transfer from the lithium alkyl to the substrate S, for example:

$$(BuLi)_2.THF + solvent + S \rightarrow [(BuLi)_2.THF]^+_{solvent} + S^- \qquad (12)$$

To describe the kinetic effect of the excess THF or another ether (D) relative to its amount required for the formation of the solvate $(BuLi)_2.D$, the following equation was proposed[75]:

$$V = k([D] - 0.5\,[RLi])^{\alpha}\,[RLi]^{\beta}\,[S]^{\gamma}, \qquad (13)$$

where α, β, and γ are reaction orders with respect to the electron-donor additive, lithium alkyl, and the substrate. Screttas and Eastham[75] applied this equation to their own[22] and certain literature data in order to determine α. In particular they employed the data of Shatenshtein et al,[21] on the kinetics of the reaction of n-butyl-lithium with n-butyl bromide in the presence of added 1,2-dimethoxyethane for $r > 0.5$, although the type of dependence of the rate constants on the content of THF and 1,2-dimethoxyethane is different (cf. Figs. 1*a* and 1*b*). The value of α proved to be close to unity in all cases.

Screttas and Eastham[75] themselves emphasised that their concepts concerning the kinetic role of the electron-donor solvents are extremely hypothetical. Furthermore, Screttas and Eastham evidently continued to hold the view that lithium alkyls are dimerised in ethereal solution. Nevertheless, one should not disregard the possibility of the acceleration of reaction on addition of ether in the region with $r > 0.5$ due to the additional solvation of the association complexes of the lithium alkyl accompanied by the formation, albeit in a small amount, of new reactive complexes of the lithium alkyl with the Lewis base[20,58,74].

We shall now consider how the addition of THF to n-hexane affects the rate of metallation of triphenylmethane by n-butyl-lithium. Fig. 3 shows that, when the concentration of tetrahydrofuran (c_{THF}) is varied from zero to 90 vol.%, the rate constant k increases continuously and the order of the reaction determined from the plot $\lg k$ against $\lg c_{THF}$ (Fig. 4) is approximately 3/2. A detailed study of the region of low THF concentrations (< 2 vol.%) showed that the k–c_{THF} curve makes an intercept on the abscissa axis corresponding to $c_{THF} = 0.36$ vol.% or 0.04–0.05 M. According to the experimental conditions, it corresponds to a molar ratio of the ether and the lithium alkyl of 0.5. This finding can serve as additional confirmation of the hypothesis[21] of the formation of solvate complexes of tetrahydrofuran with n-butyl-lithium, with composition corresponding to the ratio 1 : 2. However, the formation of such primary solvates is probably still insufficient for any significant acceleration of the metallation reaction. Its rate begins to increase only in the presence of an excess of tetrahydrofuran relative to the amount required for the formation of the above solvates.

Waack et al.[58] observed similar behaviour in the study of the effect of small amounts of tetrahydrofuran added to benzene or hexane on the rate of addition of n-butyl-lithium to 1,1-diphenylethylene. Its dependence on the concentration of tetrahydrofuran is very complex. For given proportions of the ether and lithium alkyl, the rate of reaction is greater at higher concentrations of the lithium alkyl. On the other hand, an increase of the concentration of n-butyl-lithium at a constant concentration of the ether entails a decrease of the rate. Waack[58] explained this by

the fact that the lower solvates of n-butyl-lithium are inactive in the reaction.

There arises now the problem of the causes of this marked difference between the effect of tetrahydrofuran on the kinetics of the normal Wurtz reaction and the metallation reaction. The effect of this ether on the kinetics of the metallation of triphenylmethane can be understood, for example, by assuming that the monomeric form of butyl-lithium is active in the reaction, an increase in its content being favoured by the additional solvation of the dimer of the lithium alkyl:

$$(BuLi)_2 \cdot THF \overset{+3THF}{\rightleftharpoons} 2\,[(BuLi) \cdot 2THF]. \qquad (14)$$

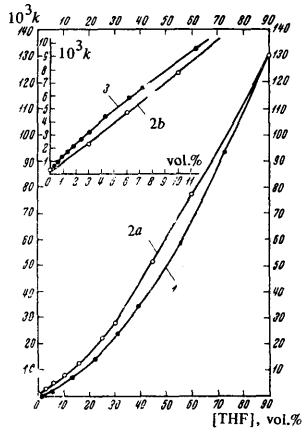


Figure 3. Dependence of the rate constant for the metallation of triphenylmethane with n-butyl-lithium on the content of tetrahydrofuran in n-hexane (*1*) or in ethyl ether (*2a* and *2b*) and on the content in the latter of 1,2-diethoxyethane (*3*).

One cannot exclude the possibility that phenomena involving the solvation of the transition state play a decisive role. Metallation and isotope exchange of hydrogen with bases belong to the same type of protophilic substitution of hydrogen and have similar mechanisms[76]. The transition state in processes of this type has the properties of a carbanion, as shown, in particular, by the determinations of the kinetic isotope effect (KIE) for these and other reactions[77-85].

The determination[74] of KIE (k_H/k_D) for the metallation of triphenylmethane by n-butyl-lithium in tetrahydrofuran, triethylamine, and ethyl ether and also in mixtures of the latter with 1,2-diethoxyethane yielded the same result: $k_H/k_D = 10$ at 25°C, although the rates of reaction in these solvates differed by factors up to 2500.

The relative rate constants (k_{rel}) for the reactions of n-butyl-lithium with n-butyl bromide (I) and triphenylmethane (II) are compared in Table 1. The rate constant for the reaction in the presence of added tetrahydrofuran was assumed to be unity in each case.

There is no correlation between k_{rel} and the polar properties of the solvent, i.e. the dielectric constants (DC) and dipole moments (μ). This is quite reasonable, since the effect of the above solvents on the kinetics of the reactions is due primarily to the specific solvation of the cation, which is of the donor–acceptor type. Furthermore, this hypothesis is not contradicted by the lack of correspondence between k_{rel} and the changes $\Delta\nu_{OD}$ (cm^{-1}) characterising the electron-donor properties of the additives based on the shift of the frequency of the OD bond in deuteriomethanol when the latter forms a hydrogen bond with the heteroatom of the electron donor[17]. The reason for the absence of a parallelism between k and $\Delta\nu_{OD}$ is that the specific solvation processes of alkali metal cations are very sensitive to steric factors[16,20,90,91].

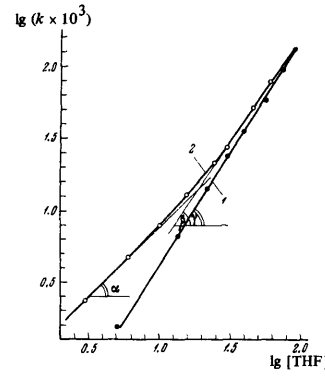


Figure 4. Determination of the reaction order of the metallation of triphenylmethane with n-butyl-lithium from the concentration of tetrahydrofuran in n-hexane (*1*) and in ethyl ether (*2*) (tan $\alpha = 1.0$; tan $\beta = 1.45$; tan $\gamma = 1.6$).

The sequence of the activating effects of the solvents on the reactions of n-butyl-lithium (Table 1) is in the main similar to that observed for other organic reactions of the anionic type[16,92,93]. The higher activity of added tetrahydrofuran and in particular 1,2-dimethoxyethane compared with ethyl ether and triethylamine has also been observed in measurements of the rates of the initiation[61] and chain propagation stages in anionic polymerisation[61,94-96] and also in the analysis of the structure of polydienes and the composition of copolymers[19,61,97-99].

The relative solvating capacity of solvents can also be assessed from the change in the electronic transition energy associated with the principal absorption band in the spectrum of a highly polar organic derivative of an alkali metal[100-102]. In this connection, we may note that the same sequence of solvent effects on the rate of the metallation reaction (Table 1) and on the bathochromic shift in the absorption spectrum of triphenylmethyl-lithium has been observed[74]. The absorption maxima in n-hexane, triethylamine, and ethyl ether are respectively in the region of 420, 430–435, and 435–440 nm. The addition of 11 vol.% of tetrahydrofuran to ethyl ether results in a bathochromic shift of 25 nm and the addition of 11 vol.% of 1,2-diethoxyethane leads to a shift of 55 nm (cf. also Ref. 103).

Attention must be drawn to the following features of the series of relative activities of solvents established for the reactions of lithium alkyls. According to Fig. 3 (curves *2b* and *3*), at low concentrations 1,2-diethoxyethane is more active than tetrahydrofuran but with increase in their content in ethyl ether the order of activity is reversed

(cf. curves *2a* and *3*), i.e. becomes of the type usually observed[16,93,94]. Probably the above concentration dependence is a consequence of different mechanisms of the solvation of the alkali metal by tetrahydrofuran and 1,2-diethoxyethane[16,90,91]. The differences in the solvation of the metal cation by these ethers, which determine their relative activities when the amounts added are small, are obliterated when the ether is used as the solvent. Then other factors, for example, steric considerations become of primary importance. The reversal of the sequence of these ethers is observed also when their effects on the equilibrium formation of diphenylsodium are compared[91] and the reaction itself is carried out in mixtures of either tetrahydrofuran or 1,2-diethoxyethane with n-heptane or when each ether is the solvent.

Relative rate constants for the reaction of n-butyl-lithium with n-butyl bromide (I) for [D]/[n-BuLi] = 1 and with triphenylmethane (II) at 25 °C

Electron-donor additive D	k_{rel} for reaction		DC(25°) (Ref.86 & 87)	$\Delta\nu$(OD), cm^{-1} (Refs.17 & 18)	μ, D (25°) (Refs.86,88,89)
	I[21]	II[74]			
Diethyl sulphide	0.018	—	5.72	—	—
Triethylamine	—	0.012*	2.42	289	0.77
Ethyl ether	0.6	0.067*	4.33	106	1.15
Tetrahydrofuran	1	1**	7.31	115	1.87
1,2-Diethoxyethane	26	1.25**	4.89	98	1.65
1,2-Dimethoxyethane	52	—	6.96	93	1.72

*90 vol.% of triethylamine or ethyl ether; 10 vol.% of n-hexane.
**5 vol.% of THF or 1,2-diethoxyethane; 85 vol.% of ethyl ether; 10 vol.% of n-hexane.

The study of reactions in mixtures of electron-donor solvents is of interest for the detection of the differences in their solvation properties, since it reveals competitive phenomena between the two solvents in specific solvation processes. Unusual data were obtained in measurements of the rate of anionic polymerisation in mixtures of tetrahydrofuran with 1,4-dioxan[104] and with 1,2-dimethoxyethane[99] and also in the study of the electronic absorption spectra of triphenylmethyl-lithium[74] and 1,1-diphenylhexyl-lithium[102] in mixtures of tetrahydrofuran with aliphatic ethers.

There are still few data on the kinetics of the reactions of lithium alkyls in mixtures of electron-donor solvents. Relations have been established[74] between the rates of metallation of triphenylmethane with n-butyl-lithium and the proportion of 1,2-diethoxyethane or tetrahydrofuran in ethyl ether (Fig. 3, curves *3* and *2a*). The fact that the order of the metallation reaction with respect to tetrahydrofuran changes from unity to 3/2 with increasing concentration of tetrahydrofuran in ethyl ether (Fig. 4), i.e. approaches the order in mixtures of tetrahydrofuran with n-hexane, which is approximately 3/2, may be attributed to competition between the two esters in the lithium solvation processes.

3. The Reactive Forms of Lithium Alkyls in Electron-donor Solvents

In considering the nature of the reactive forms of lithium alkyls in electron-donor solvents one must take into account not only the degree of association and the level and nature of the solvation of the organolithium compound but also the possibility of different states and different degrees of dissociation of the ion pair[16,90,91,105-107]. Bearing this in mind, Ebel[108] suggests the following mechanism for the change in the form of RM in solution and the nature of the bond C–M as a function of the solvent, the nature of the alkali metal M, and the alkyl group R:

$$\overbrace{(RM)_6 \rightleftarrows (RM)_4 \rightleftarrows (RM)_2}^{A} \rightleftarrows \overset{B}{RM} \rightleftarrows \overset{C}{R^-, M^+} \rightleftarrows \overset{D}{R^- \parallel M^+} \rightleftarrows \overset{E}{R^- + M^+}$$

where *A* are association complexes of RM, *B* is a molecule with a covalent bond C–M, *C* and *D* are ion pairs in contact and separated by the solvent, and *E* are free ions. The solvation of the association complexes and ions is not shown in the above mechanism.

As already mentioned, when discussing the kinetics of the reactions of lithium alkyls in the presence of an ether or amine, Scheme 1, (p. 842) is usually employed, i.e. only the monomeric form of the lithium alkyl (*B*) is regarded as reactive[39,58,66,109]. Brown[36] suggests that this is incorrect not only in hydrocarbon but also in electron-donor solvents. Until recently, Brown's hypothesis[4,36] of the possible active participation in the reaction of the association complexes of organolithium compounds was not supported by experimental data if one excludes the results of Eastham and Gibson[15,22] mentioned above (p. 842) (see also Refs. 93, 110, and 111). Brown's conclusions found more definite confirmation in the work of Waack[112], who investigated the kinetics of the metallation of triphenylmethane with phenyl-lithium and the rate of its addition to 1,10-diphenylethylene in tetrahydrofuran. The order of these reactions with respect to phenyl-lithium is 0.65 ± 0.03, i.e. the precision of the determination of the order shows with certainty that it is not unity or 0.5. Analysis of the possible reaction mechanisms and the corresponding reaction orders taking into account the dimeric state of phenyl-lithium in tetrahydrofuran led Waack et al.[112] to the conclusion that both the dimer and monomer of phenyl-lithium participate in the above reactions, the two species being in equilibrium:

$$\frac{1}{2}(PhLi)_2 \overset{K_e}{\rightleftarrows} PhLi\,. \qquad (15)$$

The rate of reaction is given by the equation

$$\frac{V}{[S]} = k_1 K_e \left(\frac{[PhLi]}{2}\right)^{1/2} + k_2 \left(\frac{[PhLi]}{2}\right), \qquad (16)$$

where k_1 and k_2 are respectively the rate constants for the reaction with participation of the monomer and dimer, K_e is the dissociation constant of the dimer, and [S] and [PhLi] are the concentrations of the reactants.

On the basis of these results, Waack[112] arrived at the general conclusion that, depending on the concentration of RLi and the rate constants for the reactions involving the monomer and the association complexes, the reaction order with respect to RLi may vary from 1 to $1/n$, where n is the degree of association of RLi in the given solvent.

The states *D* and *E* (in Ebel's scheme) of the C–M bond, including C–Li, have recently been considered in relation to the active centres of the growing polymeric chains in the study of the kinetics and mechanism of anionic polymerisation in electron-donor solvents. This has been demonstrated particularly clearly in the work of Szwarc and Schulz (see the appropriate reviews[113-115]).

We shall now consider the state of our knowledge concerning the participation of free carbanions in the reactions of lithium alkyls. The electrical conductivity of the hydrocarbon solutions of lithium alkyls is extremely low[63] and remains low even in the presence of electron-donor

additives[73]. Brown[4] admits the possibility that the reaction of RLi takes place partially by a mechanism involving free carbanions in a medium with a high solvating capacity (see Scheme 4, p. 842). However, several attempts[39,63,112] to explain the observed kinetics by the participation of free carbanions of lithium alkyls and even phenyl-lithium have been unsuccessful.

In considering the problem of the reactive forms of lithium alkyls in electron-donor solvents, one must bear in mind that the kinetic effect due to the solvents depends not only on the state of the organolithium compounds in the solutions but also on the mechanisms and other specific features of the reactions.

Summarising, we must emphasise that, although the principal causes of and the relations governing the effect of electron-donor solvents or the corresponding additives on the reactivity of lithium alkyls have been elucidated, some questions, connected with the current problem, still remain controversial.

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