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Central European Journal of **Chemistry**

50 years of superbases made from organolithium compounds and heavier alkali metal alkoxides

Review Article

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Abstract: A review of reactions of organolithium compounds (RLi) with alkali metal alkoxides is presented. On the one hand, simple lithium alkoxides form adducts with RLi the reactivity of which differs only slightly from that of RLi. On the other hand, after mixing heavier alkali metal alkoxides (R'OM, M = Na, K, Rb, Cs) with RLi, a new system is formed, which has reactivity that dramatically exceeds that of the parent RLi. A metal interchange, according to the equation RLi + R'OM = RM + R'OLi, occurs in this system, giving rise to a superbase. This reaction is frequently used for the preparation of heavier alkali metal organometallic compounds. Similar metal interchange takes place between R'OM and compounds such as lithium amides and lithium enolates of ketones or esters, thus demonstrating the general nature of this procedure. Superbases react easily with many types of organic compounds (substrates), resulting in the formation of a heavier alkali metal derivative of the substrate (metalation). The metalated substrate can react *in situ* with an electrophile to yield the substituted substrate, a procedure that is frequently used in synthetic and polymer chemistry. An improved mechanism of metal interchange and reaction of superbases with substrates is proposed.

Keywords: Superbases • Heavier alkali metal compounds • Lithium–heavier alkali metal interchange • Metalation
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1. Introduction

Classical superbases are made from organolithium compounds (RLi) and heavier alkali metal alkoxides (R'OM, M = Na, K, Rb, Cs). They are extremely strong bases, the reactivity of which greatly exceeds that of the parent RLi. Similar behavior is also exhibited by compounds, where lithium is bonded to nitrogen (in substituted amides) or to oxygen (in enolates of ketones or carboxylic acid esters). Superbases were discovered about fifty years ago, and since that time they have been widely used. In that time, several other names for superbases appeared, such as Complex bases, Lickor bases, Lochmann bases or Schlosser bases. The reaction of RLi with R'OM has become an important method for the preparation of heavier alkali metal compounds [1,2]. This up-to-date review of the

topic is concentrated on the organometallic chemistry of superbases. Some applications of superbases in organic and polymer chemistry are also mentioned, and references to relevant papers are given.

2. Reaction of RLi with lithium alkoxides

Lithium alkoxides and RLi form adducts [3]; one such adduct was isolated in crystalline form, and its structure was determined by X-ray diffraction [4]. The reactivity of these adducts does not differ substantially from that of RLi [5]. However, lithium alkoxides containing yet another heteroatom (oxygen, nitrogen) in their structure, such as lithium 2-methoxyethoxide or lithium 2-(dimethylamino) ethoxide, show quite different behavior. Adducts of RLi with these alkoxides exhibit reactivity similar to that of

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superbases. This effect can be explained by chelation of the RLi with both heteroatoms of the alkoxide and is potentiated by an entropy factor [6-9]. Reaction of these alkoxides can be understood as **true** "activation of organolithium compounds."

3. Reaction of RLi with heavier alkali metal alkoxides: discovery of superbases

Early reports of an alkoxide-promoting effect were observed in diene polymerization, using well-known Alfin catalysts [10]. The first mention of changed properties of organolithium compounds in the presence of heavier alkali metal alkoxides during diene polymerization appeared in the patent literature in 1963 [11]. Two related journal reports followed six years later [12,13].

A lithium–heavier alkali metal interchange in the reaction of RLi with heavier alkali metal alkoxides (R'OM, M = Na, K, Rb, Cs) was observed in 1964, giving rise to organic compounds of heavier alkali metals, RM [14-16]. The obtained reaction mixture (superbase) metalated smoothly, *e.g.* aromatic hydrocarbons. Both reactions were previously unknown (reviews [17,18]).

About three years later, Schlosser [19] described the increased reactivity of RLi in the presence of potassium *tert*-butoxide (*t*-BuOK). Further he investigated similar reactions with many organic substrates and contributed significantly to this topic (see chapter 5; reviews [20-23]).

4. Organometallic chemistry of superbases

The following chapters deal with reactions in which organometallic compounds appear as final products. The aim of these studies was primarily to learn more about the nature of superbases and to examine this reaction as a new method for the preparation of organic compounds of heavier alkali metals. Thus, the described experiments were performed in an inert atmosphere and under conditions that allowed isolation and analysis of the organometallic compounds. This approach made possible a more detailed insight into superbases properties.

4.1 Lithium–heavier alkali metal interchange: a key to superbases
4.1.1 Scope of the reaction
On mixing solutions of RLi and R'OM in aliphatic saturated hydrocarbons, a metal interchange takes place [14-16] (Reaction I):

$$RLi + R'OM \rightarrow RM + R'OLi$$

$$(M = Na, K, Rb, Cs; R = alkyl, aryl; R' = \textit{tert}\text{-alkyl}) \qquad (I)$$
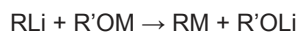
This reaction involves several partial steps as discussed below. Primarily alkyl (RCH_2Li) or aryllithium compounds are easily transformed into their heavier alkali metal analogues, RM; many of them have been prepared in a relatively pure state, *e.g.* CH_3Na [24,25], CH_3K [26], CH_3Rb, CH_3Cs [27], C_2H_5Na [28], C_6H_5Na, C_6H_5K [29], n-C_4H_9Na, n-$C_8H_{17}Na$, n-$C_{12}H_{25}Na$ [15], n-C_4H_9K, n-$C_6H_{13}K$, n-$C_{12}H_{25}K$ [16], R_2CK_2, R_2CRb_2, R_2Cs_2 [R = P(C_6H_5)$_2$=N-Si(CH_3)$_3$] [30], 2,6-Mes$_2C_6H_3$Na [Mes = mesityl] [31], $(CH_3)_3CCH_2CH$=$CHCH_2$Na [32], $(CH_3)_3SiCH_2M$ (M = Na, K, Rb, Cs) [33,39], R*Na, R*K, R*Rb, R*Cs (R* = CH[Si(CH_3)$_3$]$_2$ [34], C_4H_9Na [35], C_4H_9K [36], and other examples (see reviews [2,17,18,37,38]). Several isolated RM were analyzed by atomic absorption spectroscopy, which showed that the heavier alkali metal content was close to the calculated values, and the lithium content was mostly below 0.5%. In other cases, the structure of RM was determined by X-ray analysis. The formation of R'OLi was proven by IR spectroscopy [40]. Easy access to RM compounds stimulated investigation of their structure, particularly using X-ray diffraction methods [37].

Metal interchange also takes place in tetrahydrofuran (THF) solutions. The formation of heavier alkali metal organometallic compounds has been proven by various methods. An NMR investigation of a mixture of triphenylmethyllithium and cesium-3-ethyl-3-heptoxide in THF solution, supported by MNDO calculation, revealed the formation of discrete species of triphenylmethylcesium and lithium-3-ethyl-3-heptoxide [41]. In another case, triphenylmethylpotassium, -rubidium and -cesium were prepared from their lithium analogue and the corresponding *tert*-butoxides in THF. Their structures were confirmed by combined NMR and X-ray study [42]. Conversion of hex-5-en-1-yl-lithium to its sodium, potassium, rubidium and cesium analogues, after reaction with the corresponding 3-ethyl-3-heptoxides, was demonstrated through rearrangements induced by the metals used in each case [43].

Some branched organosodium compounds, *e.g.* 2-ethylhexylsodium, were found to be soluble in aliphatic hydrocarbons [44,45]. After mixing hydrocarbon solutions of 2-ethylhexyllithium with sodium or potassium alkoxides, no precipitate was observed; in the following reactions with substrates, heavier alkali metal derivatives of the substrate were isolated. Thus, it can be assumed that, in the reaction of 2-ethylhexyllithium with R'OM, a solution of the heavier

alkali metal compound in heptane has been formed [46]. This is advantageous for heterogeneous metalation of substrates that are insoluble in a hydrocarbon medium.

Metal interchange with secondary or tertiary alkyllithiums (R_2CHLi, R_3CLi) also takes place in hydrocarbons at room temperature, however, it is followed by rapid elimination of a heavier alkali metal hydride or methylide and alkene formation. The formed precipitates exhibit very high heavier alkali metal content (up to 90%) [15]. Similar formation of LiH enhanced by the presence of an alkoxide was described in the system of *tert*-butyllithium and lithium *tert*-butoxide [*t*-BuLi · *t*-BuOLi] [47] as opposed to the [BuLi · *t*-BuOLi] system [3].

A general procedure for the preparation of RM is as follows. The starting compounds are mostly used as 1 M solutions in aliphatic saturated hydrocarbons (or hydrocarbon-diethyl ether mixtures for less soluble and less reactive RLi [28,29]), at a molar ratio [R'OM]/[RLi] = 1.3. The mixture is stirred for one hour at room temperature (or at a lower temperature in the presence of diethyl ether). The formed precipitate is washed with the solvent to remove R'OLi. The alkoxides must be absolutely free of alcohols (for their preparation, see references [46,48]). Hydrocarbon-soluble, more branched R'OM (*e.g. tert*-pentoxides or (-)(R) menthoxides) appear much more favorable for the metal interchange in comparison with *tert*-butoxides [18]. Sodium trimethylsilanolate [17] or 2-methoxyethoxide [7] can also participate in metal interchange.
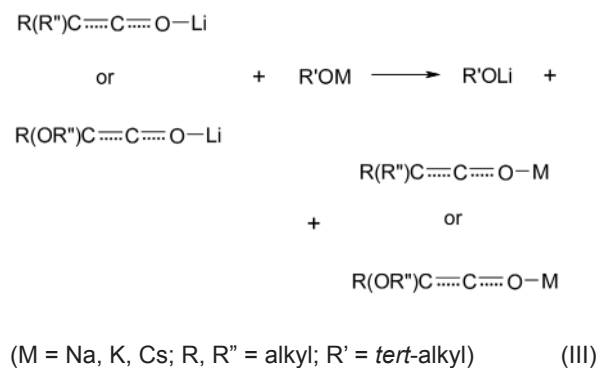
The lithium–heavier alkali metal exchange has also been observed [49] in compounds with a nitrogen–lithium bond such as lithium alkyl amides (Reaction II):

$$R_2N\text{-}Li + R'OM \rightarrow R_2N\text{-}M + R'OLi$$

(M = Na, K, Cs; R = alkyl; R' = *tert*-alkyl)   (II)
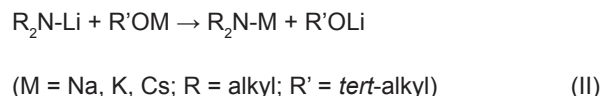
This interchange takes place readily with bulky lithium alkyl amides that are soluble in benzene, such as lithium diisopropylamide. Aliphatic hydrocarbons are not suitable as solvents. Several heavier alkali metal amides have been prepared in a relatively pure state, meaning that the contents of heavier alkali metal and nitrogen were close to the calculated values, and the lithium content was mostly below 0.5%. Also lithioindole [50] and other lithium amides [51,52] have been converted to their sodium derivatives using sodium *tert*-butoxide (*t*-BuONa). Lithium amides that are insoluble in benzene, *e.g.* lithium diethyl or dibutyl amide do not complete the reaction with sodium or potassium *tert*-butoxides and give rise to products with higher lithium

content [49]. Potassium diisopropylamide also has been prepared *in situ* by the reaction of *n*-butyllithium (BuLi) and *t*-BuOK with diisopropylamine, and it has been used in organic syntheses (*e.g.* references [53,54]).

In addition, the lithium–heavier alkali metal interchange also takes place with compounds having a special type of a lithium–oxygen bond, *i.e.*, with lithium enolates of ketones [55] and esters [56], according to Reaction III:

$$R(R'')C \cdots C \cdots O\text{-}Li$$

or   + R'OM $\longrightarrow$ R'OLi +

$$R(OR'')C \cdots C \cdots O\text{-}Li$$

$$R(R'')C \cdots C \cdots O\text{-}M$$

+   or

$$R(OR'')C \cdots C \cdots O\text{-}M$$

(M = Na, K, Cs; R, R" = alkyl; R' = *tert*-alkyl)   (III)

Some heavier alkali metal enolates have been isolated and analyzed. These reactions have been limited to branched lithio-ketones or lithio-esters (*e.g. tert*-butyl methyl ketone, esters of isobutyric acid) because a rapid autocondensation to an oxocarbonyl compound occurs with less sterically hindered carbonyl compounds Otherwise, heavier alkali metal enolates can be prepared more conveniently by the direct metalation of the parent carbonyl compound with heavier alkali metal hexamethyldisilazides, which are easily accessible.

The reaction of heavier alkali metal alkoxides with species as varied as organolithium compounds, lithium amides and lithium enolates demonstrates the general nature of this metal interchange.

4.1.2. Mechanism of the metal interchange

What is the driving force for this reaction? Precipitation of the reaction product that is insoluble in hydrocarbons is not the only reason for this interchange, as it also takes place well in THF solution as shown above. Therefore, some other effects must be involved.

It is well known that organic compounds or alkoxides of alkali metals form stable aggregates in solution, using electron deficient bonds [37,57-59]. The aggregation of organometallic compounds has to be at least partly disrupted during their reactions, and therefore, it cannot be omitted in their reaction mechanism. The de-aggregation of these compounds proceeds mostly stepwise, *e.g.* $[BuLi]_6 \rightleftarrows 1.5\,[BuLi]_4 \rightleftarrows 3\,[BuLi]_2 \rightleftarrows 6\,BuLi$, as follows from the kinetics of anionic polymerization
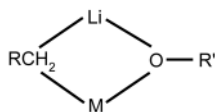
Scheme 1. Preferred structure of the RLi+R'OM adduct by computation.

[60] or NMR studies [59]. The direct de-aggregation $[BuLi]_6 \rightarrow 6\ BuLi$ appears to be energetically unfavorable [60]. In the presence of coordinating compounds, other equilibria may occur as well [61,62].

Mixed aggregates are also known. Examples include: [BuLi · t-BuOLi]$_4$ [3], which is tetrameric in benzene solution [63] or in the solid state [4], [(BuLi)$_x$ · (BuOLi)$_{4-x}$] [62], [t-BuLi · t-BuOLi]$_6$ [64] and other types [65,66]. The interaction of RLi with R'OLi was studied in detail by Brown [59,67,68]. Mixed dimetal aggregates have also been prepared, *e.g.* tetrameric lithium 4,6-dimethyl-2-(sodiomethyl)phenoxide [69], mixed *tert*-butoxides [(t-BuO)$_8$Li$_4$M$_4$] (M = Na, K, Rb, Cs) [70], the mixed aggregate [lithium-potassium pinacolone enolate · t-BuO]$_4$ [71] and others [72,73,74].

In the reaction of RLi and R'OM, it is a question whether the reactions involve monomeric or more aggregated species. There are indications that aggregates of RLi or R'OM are directly involved in some of the reactions (*e.g.* addition of R$_3$CLi onto ethene [75], the kinetic isotope effect [76] and the effect of the alkoxide structure on the reaction rates of superbases [62,77,78]; see also references [79] and [95]). Therefore, mechanisms of metal interchange with the participation of aggregated compounds should be considered as a tentative alternative below. The dimers seem to be suitable models for this reaction, although higher aggregates may react similarly [59,62,74,80].

After mixing RLi and R'OM solutions, coordination of R'OM onto RLi aggregates takes place. Aggregates of R'OM with their alternating oxygen and heavier alkali metal atoms may act like a multidentate donor. This reaction gives rise to a dimetal mixed aggregate (intermediate I) as demonstrated on dimers (Reaction IV), in which coordination bonds of lithium atoms are better saturated than those in the aggregate shown in Scheme 1. Such arrangement of the intermediate is in agreement with the hard and soft acids and bases (HSAB) concept [30,69,72,82,83], because the hard lithium atoms are bound to hard oxygen atoms and the softer heavier alkali metal atoms are linked to softer carbon atoms. Intermediate I should be considered as an adduct [BuLi · t-PeOM], as well as [BuM · t-PeOLi] (M = heavier alkali metal). The adduct [BuK · x t-PeOLi] has been isolated [81]. See also the structure of the tetrameric adduct [BuLi · t-BuOLi]$_4$ [5,69,74].

$$[RCH_2Li \cdot R'OM \longleftrightarrow RCH_2M \cdot R'OLi]_2$$
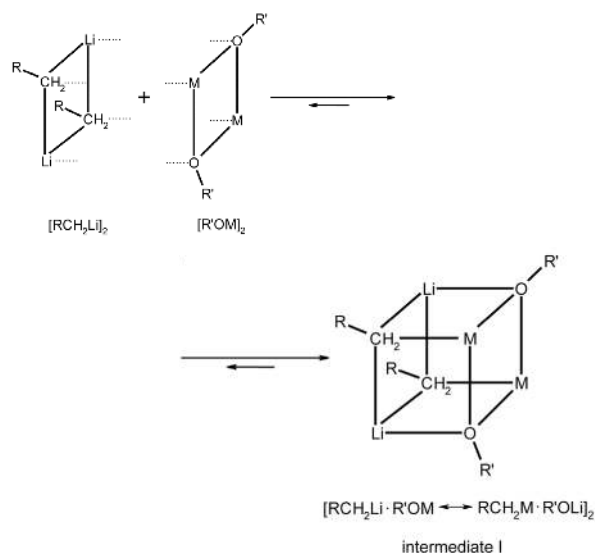
intermediate I

(R = alkyl, aryl; R' = *tert*-alkyl)   (IV)

In the next step, intermediate I splits into R'OLi and RM (Reaction V). The driving force for this reaction could be formation of R'OLi and its aggregation into very stable structures. This stability of lithium alkoxides follows from the HSAB principle [82,83]. The stability of lithium alkoxide aggregates is documented by t-BuOLi, which exists in its hexameric form even in the gas phase. It is also supported by the known superior strength of aggregation of lithium alkoxides in comparison with heavier alkali metal alkoxides as demonstrated by the minor influence of electron donating solvents on the aggregation degree of lithium alkoxides [57]. R'OLi appears as a common product in various metal interchanges (Reactions I–III).

$$[RCH_2M]_x + [R'OLi]_y$$

intermediate I
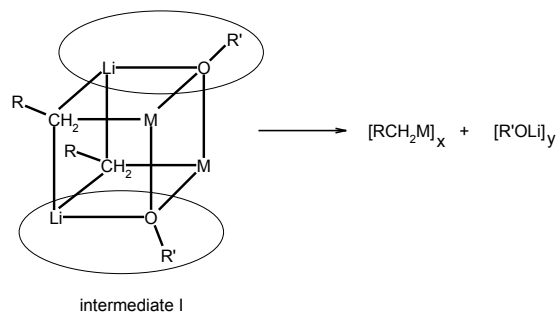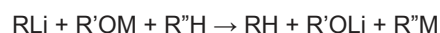
(R= alkyl, aryl; R' = *tert*-alkyl)   (V)

A computational investigation of mixed aggregates, which might be formed in the RLi + R'OM system, was published by Schleyer *et al.* [84]. Various structures of mixed aggregates were considered by these authors; the aggregate given in the Scheme 1 was found to be the most stable of the other investigated structures.

The structure of intermediate I in Reaction IV corresponds to a dimeric form of this aggregate which is closer to the structure it occurs in nature. In the above study, complete transmetalation (Reaction V) was found to be favorable only for M = Na; however, some effects, such as a higher aggregation degree of the involved compounds, were not evaluated. Another computation was performed on the model system [CH$_3$Li•CH$_3$OLi], which does not resemble experimentally relevant systems [85].

4.2 Reactions of superbases with substrates
4.2.1. Scope of the reaction

Superbases are very reactive reagents that react with various substrates and give rise to new organometallic compounds, e.g. in metalation of R"H (Reaction VI):

RLi + R'OM + R"H → RH + R'OLi + R"M

(M = Na, K, Rb, Cs; R = alkyl; R' = tert-alkyl,   (VI)
R" = alkyl, aryl; pK(R) – pK(R") > 2)

An essential feature of Reaction VI is that a heavier alkali metal derivative of the substrate is formed, as found, e.g. for C$_6$H$_5$K [16,18,86], C$_6$H$_5$CH$_2$K [16,18,46], C$_6$D$_5$CD$_2$K [87], C$_6$H$_5$C(CH$_3$)$_2$K [16,18], (C$_6$H$_5$)$_3$CNa [15], (C$_6$H$_5$)$_2$[(CH$_3$)$_3$Si]CNa, and (C$_6$H$_5$)$_2$[(CH$_3$)$_3$Si]CK [88]. This rule has been proven so far in all cases where R"M was isolated and/or analyzed. The heavier alkali metal content prevailed, and the lithium content was within limits [K]/[Li] = 2–30 (in hydrocarbon medium and after the precipitation of R"M).

Less reactive heavier alkali metal compounds also can be made by Reaction VI in THF solutions without formation of any precipitate. This was proven by NMR spectra [89,90], EPR spectra [91] and X–ray analysis of various isolated crystalline adducts of R"M with donors such as N,N,N',N",N"-pentamethyldiethylenetriamine (PMDTA) (e.g. C$_6$H$_5$CH$_2$K•PMDTA, C$_6$H$_5$CH$_2$Rb•PMDTA [92], or by synthesis of other compounds [93,94]). Further evidence of the metal interchange in solution was given by the polymerization of methyl methacrylate (MMA), initiated with a mixture of ethyl 2-lithioisobutyrate and t-BuONa. The microstructure of the formed poly(methyl methacrylate) corresponded to a growing polymer with a sodium counter-ion [95,96].

Various types of reactions of superbases with substrates exist. For their use in organic synthesis and polymer chemistry, see Chapter 5 and Chapter 6, respectively.

The preparation of specific organic compounds of heavier alkali metals by reaction of superbases with substrates is not as straightforward as the metal interchange itself. The first problem concerns the regioselectivity of substitution in substrates, which have multiple sites of similar reactivity towards a superbase, i.e., similar C–H acidity and/or steric hindrance. In such cases several different substitution products may arise depending on reaction conditions. Substrate molecules that either contain significantly more acidic sites (pK$_{RH}$ and pK$_{R'H}$ differs by at least two units) or sites close to a special functional group will be substituted preferentially at specific sites; for example, toluene is substituted predominantly in the methyl group and methoxybenzene is substituted in the position ortho to the methoxy group [complex proximity induced effect (CIPE)]. The structure and composition of the superbase can also influence the distribution of substituted products. For example, the presence of lithium alkoxides in superbases increases the extent of ring substitution in toluene metalation, while an excess of R'OM over RLi favors the side chain (methyl group) reaction [81].

Another problem in the preparation of specific organic compounds of heavier alkali metals by the above method arises from their contamination with lithium and alkoxide compounds (Table 1). The degree of lithium contamination essentially depends on the substrate structure and on reaction conditions. The less reactive substrates are usually more contaminated with lithium than the more reactive ones, e.g. [K]/[Li] = 2 for naphthalene, while [K]/[Li] = 25 for toluene. There are several methods for minimizing lithium contamination (see also Table 1): (i) the addition of a small amount of diethyl ether (under conditions preventing its cleavage), (ii) the use of the substrate in excess (e.g. benzene as a solvent) and (iii) the use of heavier alkali metal alkoxide in excess (e.g. [R'OM]/[RLi] = 1.3).

The metalation of toluene with the superbase prepared from 2-ethylhexyllithium (EtHexLi) and potassium tert-pentoxide (t-PeOK) was investigated with respect to the [t-PeOK]/[EtHexLi] ratio in the range of 0.3–1.3 and reaction time [46]. It was found that under all conditions used, neat benzylpotassium with a low lithium content was formed. The purity of benzylpotassium did not change even at concentration ratios [t-PeOK]/[EtHexLi] < 1, e.g. 0.3. In these cases, the amount of benzylpotassium produced corresponded exactly to the amount of the t-PeOK present. No further metalation of toluene took place although some unreacted RLi was still present. This means that **potassium alkoxide enters the reaction in a stoichiometric amount and does not act only as a catalyst**. At the same time, the reaction rate decreased considerably along with the lower concentration of t-PeOK, in agreement with the findings given below.

Table 1. Reaction of superbases with substrates R"H: R"H + RLi + *t*-PeOK = R"K + RH + *t*-PeOLi.

R"H	Reaction conditions[a]					Reaction products			
	RLi[b]	R"H/RLi	t-PeOK[c]/RLi	Et$_2$O[d]/RLi	Yield (%)	[K]/[Li]	R"H[e] (mol %)	t-PeOH[e] (mol %)
Toluene	EtHexLi	5	1	–	100	26	95	2
Toluene	EtHexLi	1	1	–	100	24	84	4
Toluene	EtHexLi	5	1.3	–	100	33	–	–
Benzene	EtHexLi	30	1	–	92	12	73	3
Benzene	EtHexLi	5	1	–	98	6	86	6
Benzene	EtHexLi	1	1	–	90	2.5	82	11
Benzene	EtHexLi	1	1.3	–	91	7	71	10
Benzene	EtHexLi	1	1	6	70	8	–	–
Cumene	BuLi	1	1.1	–	75	4	–	–
Cumene	BuLi	1	1.1	6	43	30	–	–
Naphthalene	BuLi	1	1.1	–	71	2	–	–
Naphthalene	BuLi	1	1.1	6	75	3	–	–
Naphthalene	BuLi	1	1.1	15	85	3.1	–	–

[a] *In heptane, room temperature, 1 h*
[b] *EtHexLi = 2-ethylhexyllithium, BuLi = n-butyllithium*
[c] *t-PeOK = potassium tert-pentoxide*
[d] *Et$_2$O = diethyl ether*
[e] *After hydrolysis*

In the case of toluene metalation with the [*t*-PeOK]/[EtHexLi] ratio higher than ca. 1.3, an adduct of benzylpotassium and *t*-PeOK was isolated [46], in contrast to preparation of butylpotassium (BuK) (reaction [1]), which does not form such adducts with excess *t*-PeOK [81].

The effect of lithium alkoxides in the reactions of superbases with substrates also has been examined [81]. Toluene has been metalated with the superbase made from BuLi and *t*-PeOK in the presence of lithium *tert*-pentoxide (*t*-PeOLi) with [*t*-PeOLi]/[BuLi] ratios ranging from 0–7, adjusted either by the addition of excess *t*-PeOLi or by careful washing of the BuK precipitate with heptane before toluene addition. The rate of toluene metalation by a superbase made from BuLi and one equivalent of *t*-PeOK (transformed to *t*-PeOLi before toluene addition according to Reaction V) was very close to the rate of metalation with neat BuK, where *t*-PeOLi has been completely washed out. Higher amount of *t*-PeOLi in relation to BuLi (7:1) caused a slight decrease of the metalation rate. Thus, **the presence of lithium alkoxides is not essential to achieve the very high reactivity of superbases** (see also [5]). The effect of *t*-PeOLi on the metalation rate is negligible in relation to the effect of *t*-PeOK [81].

By mixing BuLi, *t*-PeOK and *t*-PeOLi in molar ratios 1:1:3 in heptane, a clear solution was formed, from which a microcrystalline precipitate slowly separated.

The isolated precipitate with the [K]/[Li] ratio 0.7 readily metalated toluene to benzylpotassium; it was obviously an adduct of BuK and *t*-PeOLi. Thus, the solubility of BuK in heptane is increased *via* this adduct [81].

The general procedure for reactions of superbases with substrates in hydrocarbons is as follows. Most often, BuLi or 2-ethylhexyllithium are used as RLi. For the preparation of R"M by metalation, the ratio [RLi]/[R'OM]/[R"H] is usually 1:1.3:1 (a larger amount of substrate, if available, can be used). In the case in which the *in situ* reaction of the metalated substrate with an electrophile is intended, the amount of R'OM may be higher ([R'OM]/[RLi] = 2–3). Alkoxides R'OM that are more branched than *tert*-butoxides, *e.g. tert*-pentoxides, are preferred in both cases. Of cesium alkoxides, 3-ethyl-3-heptoxide is soluble in THF. The reaction mixture is stirred at room temperature for 1–3 h; in most cases, higher temperatures or prolonged stirring do not increase yields but lead to increased prevalence of side reactions [97-100].

Reactions of superbases were performed in aliphatic hydrocarbons, because isolation and analysis of the organometallic product was then possible. For other aims, especially in organic synthesis, the reaction of superbases with substrates may also be carried out in polar solvents such as THF or diethyl ether. To avoid a reaction of the superbase with the solvent, either low temperatures (below –50°C) have to be
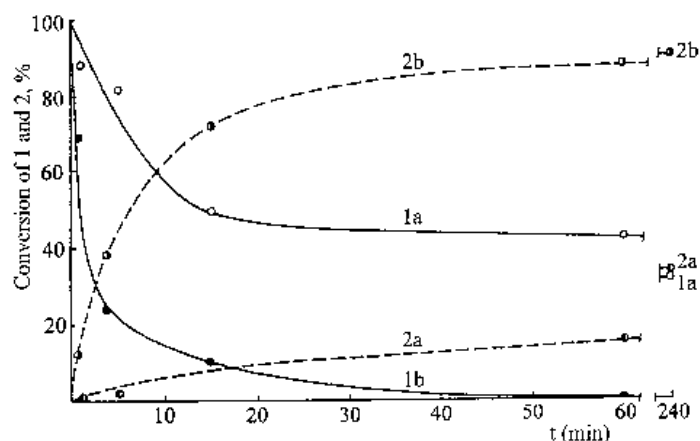
Figure 1. Metalation of ethylbenzene with various superbases. Reaction conditions: BuLi = 0.27 mol L^{-1}, heptane, 20°C, metalation quenched with methyl iodide; curves: 1a and 1b = ethylbenzene, 2a and 2b = cumene; curves a: [ethylbenzene]/[BuLi]/[*t*-BuOK] = 1:1:1; curves b: [ethylbenzene]/[BuLi]/[potassium 3-methyl-3-pentoxide] = 1:1:3.

used, or the product (metalated substrate) should be of lower basicity. Use of polar solvents can change the metalation parameters and product distribution. Schleyer *et al.* found that butylsodium (BuNa) [35] and BuK [36] dissolve in hexane in the presence of *N,N,N',N'*-tetramethylethylenediamine, forming very powerful metalation agents useful in organic synthesis (see, *e.g.* [37]).

4.2.2. Superbases of the second generation

The effect of structure and concentration of alkoxides R'OM was investigated in the reaction of *n*-octyl bromide with superbases prepared from BuLi and three different sodium alkoxides [(CH$_3$)$_3$CONa, (CH$_3$)$_2$(C$_2$H$_5$)CONa and CH$_3$(C$_2$H$_5$)$_2$CONa] at two concentration levels. The reaction rate increased significantly, more than a thousand times, with the increasing ratio [R'OM]/[RLi] = 1 to 3 and with branching of the alkoxide R'ONa [77,78]. At the same time, the yield of dodecane (the expected coupling product of BuNa and *n*-octyl bromide) increased two times.

Similar effects connected with the structure and concentration of alkoxides R'OM also have been found in metalations of aromatic hydrocarbons [101-103]. The rate of metalation of ethylbenzene by the superbases made from BuLi and the R'OK analogues listed above was estimated after quenching the reaction mixture with methyl iodide, which formed the expected product, cumene (Fig. 1).

The metalation rate and the yield of cumene were much higher using the superbase made from BuLi and an excess of the more highly branched alkoxide, in comparison with the superbase made from BuLi and one equivalent of *t*-BuOK [101]. A similar effect was also found in the double metalation of phenol [102], metalation of toluene [81,103] and the metalation of various polymers

[104,105]. Polymerization of MMA [95], styrene [106] and butadiene [107], initiated by organolithium compounds in the presence of R'OM, was also significantly influenced at higher concentration of alkoxides.

The examples given above show that superbases made from higher branched alkoxides R'OM (used in greater than equimolar amounts related to RLi) result in increased metalation rates and higher yields of the desired products, compared with superbases prepared from RLi and one equivalent of *t*-BuOM. Therefore, these superbases are designated as **superbases of the second generation** [18]. These more effective superbases are especially useful in metalations of substrates where *in situ* reaction of metalated substrates with electrophiles are intended.

4.2.3. Mechanism of the reaction of superbases with substrates

It has been reported several times [15,17,18,46] that reaction of superbases with substrates is complex. It is an oversimplification of the Reaction VI to consider that only RM and nothing else could be the active species. Instead, it is possible to consider that the formation of superbases is a dynamic process with partial reactions, involving aggregation and coordination equilibria, as well as the process of metal interchange. **Here, compounds with C–M bonds (M = heavier alkali metal) are formed adopting the mechanism described in chapter 4.1.2; they cause the high reactivity of superbases with substrates.** This conclusion follows from the fact that: (i) the final product of superbase reactions with substrates are heavier alkali metal derivatives of the substrate and (ii) in reactions of superbases with substrates, the heavier alkali metal alkoxides are really consumed in the reaction and do not act only as a catalyst (see chapter 4.2.1). The driving force for the metal exchange

is probably again a lithium alkoxide formation.

In principle, two procedures for mixing the superbase-forming reagents are feasible: (i) RLi and R'OM are mixed *prior* to addition of the substrate, and Reactions IV and V proceed. In this case, after the addition of the substrate, the heavier alkali metal compound or its derivative reacts as shown below (Reaction VII). This reaction may take place either heterogeneously on the surface of RM or in a very dilute solution of RM; its concentration may be increased *via* the adduct, *e.g.* [BuK•x *t*-PeOLi] .
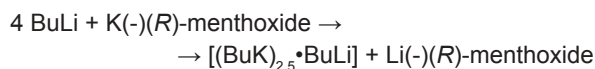
RM + R"H → RH + R"M
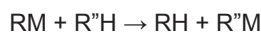
(R"H acidity > RH acidity)   (VII)
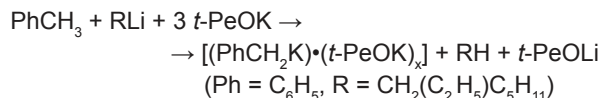
(ii) In another frequently used process, one component of a superbase is first mixed with the substrate and then the second component of the superbase is added. The conditions during this process are less easily defined, and partial reactions can proceed simultaneously. The intermediate I formed in the Reaction IV may: (i) split off R'OLi (Reaction V), in which case RM then reacts with the substrate *in statu nascendi* as shown in Reaction VII, or (ii) intermediate I or another similar compound coordinates to the substrate, forming a transition state that further reacts to give the final products (Reaction VIII).

intermediate I

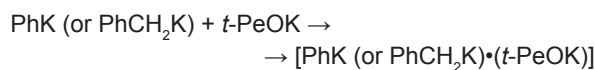transition state   (VIII)
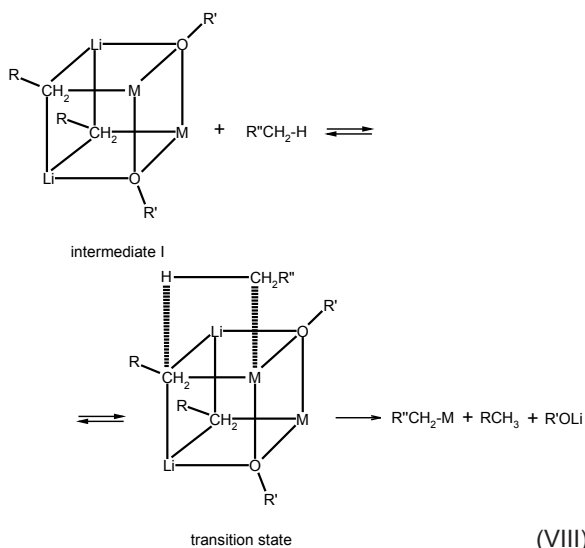
Which reaction pathway predominates will depend on relative reaction rates, *i.e.*, either (i) the overall rate resulting from the combined process described by Reactions V and VII, or else (ii) the rate of Reaction VIII. Reactions of substrates with superbases are controlled kinetically, and their progress is determined by the most

4 BuLi + K(-)(*R*)-menthoxide →
→ [(BuK)$_{2.5}$•BuLi] + Li(-)(*R*)-menthoxide

Scheme 2. [16]

PhCH$_3$ + RLi + 3 *t*-PeOK →
→ [(PhCH$_2$K)•(*t*-PeOK)$_x$] + RH + *t*-PeOLi
(Ph = C$_6$H$_5$, R = CH$_2$(C$_2$H$_5$)C$_5$H$_{11}$)

Scheme 3. [46]

PhK (or PhCH$_2$K) + *t*-PeOK →
→ [PhK (or PhCH$_2$K)•(*t*-PeOK)]

Scheme 4. [46,86]

favorable transition state (see, *e.g.* [80,108]). The ratio of these rates may vary from case to case, and it is difficult to specify a universal reaction pathway or a common active species in all superbases reactions. However, compounds with C–M bonds must be involved.

Substrates with a functional group that has a lone electron pair follow the CIPE mechanism (Reaction IX) [80,109]. The reaction pathway followed (either Reactions V and VII or VIII) depends again on specific conditions.

transition state   (IX)
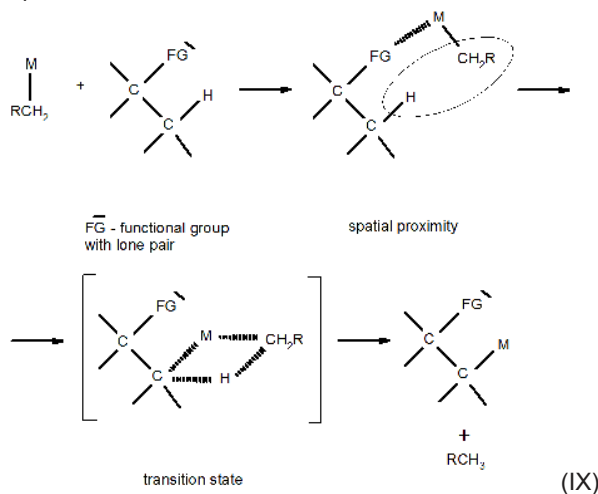
For reactions of organolithium compounds with substrates, another mechanism that involves the participation of radical anions has been suggested [59,110]. Generally, radical reactions with heavier alkali metal compounds are even more frequent (see reactions, *e.g.* [99,111]) and, therefore, they cannot be quite excluded also in superbase reactions. During spontaneous decomposition of 2-ethylhexylpotassium, unpaired electrons were detected by EPR [46, note 21]. Obviously, more effort is needed to understand these processes.

Schemes 2–4 show formation of various adducts of organopotassium compounds which were isolated, demonstrating the variety of possible interactions.

Which metal is bonded to the substrate after reaction with a superbase has been investigated also, although indirectly, *i.e.*, according to the structure of the final product obtained from *in situ* reaction of the metalated substrate with an electrophile. However, these results are inconclusive, indicating a high content of either the heavier alkali metal (*e.g.* [96,112,113]) or lithium (*e.g.* [114-116]) in the metalated substrate. The reaction sequence of RLi + R'OM + substrate + electrophile is quite complex, and therefore, it is difficult to provide a simple solution.

5. Application of superbases in organic synthesis

The use of superbases in synthetic organic chemistry is widespread. In most cases, it involves the reaction of a superbase with an organic substrate and *in situ* reaction of the metalated substrate with an electrophile. It covers many types of organic compounds as well as various types of reactions. Variations in superbase structure and choice of solvents make the control of selectivity in substrate substitution possible [22,117-119].

Many research teams have used superbases in this manner. Especially notable contributions to this field have been made by the Schlosser research group, as documented by many papers and reviews (*e.g.* [20-23]), and also by the groups of Schleyer, *e.g.* [36,98], Brandsma, *e.g.* [122,123] and more recently by Venturello *et al.*, *e.g.* [117,120,121].

6. Application of superbases in polymer chemistry

In polymer chemistry, superbases have been used as initiators of anionic polymerizations, for control over the microstructure of synthesized polymers or for the introduction of various substituents into polymer chains. Some examples are shown below.

Anionic polymerization of various vinyl monomers, initiated with a mixture of RLi and R'OM, has been investigated by researchers around the world. Only a few of the relevant papers are mentioned here, dealing with (i) dienes (Hsieh, Wofford [11-13]; Halasa *et al.* [113,124,125]; Arest-Yakubovich *et al.* [107,116,126,127]; Gordon III. *et al.* [128,129]), (ii) styrene [106], (iii) styrene-butadiene copolymers [13,116,130-132]), (iv) methyl methacrylate (Lochmann,

Vlček *et al.* [95,96,133,134]), (v) ethylene oxide [135] and other compounds.

By varying the structure, metal and concentration of the components of a superbase, pronounced changes in polymerization parameters (such as polymerization kinetics, monomer conversion and initiator efficiency or polymer stereoregularity) can be achieved. As a consequence, properties of the resulting polymers (such as molecular weights, molecular weight distribution and other physical properties) can also be influenced.

Some polymers may be used as substrates in reactions with superbases, enabling a multisite metalation or addition on multiple bonds in the polymer. The metalated polymers can then be converted to their derivatives by (i) reaction with an electrophile, yielding multisite functionalized polymers, (ii) reaction with the same or different monomer, capable of anionic polymerization and giving rise to grafted, branched, comb-like or block (co)polymers, or (iii) reaction with suitable functionalized polymers. A variety of polymeric structures are accessible *via* these reactions. Various homopolymers, such as polystyrene [104,136], chloro-terminated polyisobutylene [137], polybutadiene [138], poly(trimethylvinylsilane) [139], dendritic polyether [140], telechelic polyisobutylene [141] or poly(4-methylstyrene) [142], have been metalated in this way. These metalated polymers were functionalized with electrophiles such as carbon dioxide, deuterium oxide, trimethylsilyl chloride, aldehydes, alkyl halogenides and others.

Nonpolar statistical or block copolymers may be similarly substituted. If the difference in C–H acidities of two copolymer units A and B is sufficiently high [pK_A(A) – pK_A(B) > 2], then only more acidic units can be selectively metalated and substituted, *e.g.* in poly (styrene-block-4-methylstyrene) [142], hydrogenated poly(butadiene-block-isoprene) [143-145], hydrogenated poly(isoprene-block-styrene) [146] or poly(isobutylene-*co*-4-methylstyrene) [105].

7. Conclusion

The reactions of RLi and R'OM, particularly in the presence of a reactive substrate, are inherently complex. The reaction products are compounds substituted with a heavier alkali metal. The lithium–heavier alkali metal interchange must take place at some stage and is an integral part of these reactions. Thus, the term "transformation of organolithium compounds" seems to be more appropriate for these processes than the term used up to this point, "activation of organolithium compounds."

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