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Interactions of alkoxides

XVII *. Properties of complex bases from organolithium compounds and various sodium alkoxides affected by the structure and concentration of the alkoxide

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Abstract

In reactions of a substrate with complex bases (CB) prepared from organolithium compounds and heavier alkalimetal alkoxides the reaction rates and relative product yields depend on the structure and concentration of the CB components. For the model reaction of CB with alkyl bromides, changes in the identity and concentration of the alkoxide reduced reaction half-times by as much as three orders of magnitude, and higher yields of the product of Wurtz coupling were obtained. Sodium 3-methyl-pentoxide-3 was found to be considerably more effective than sodium t-butoxide.

Introduction

When an organolithium compound (Z–Li) and a heavier alkali metal alkoxide (ROM, M = Na, K, Rb, Cs) are mixed a metal–metal exchange reaction occurs to give an organic compounds of the heavier alkali metal (Z–M) and lithium alkoxide. If a third component of suitable reactivity is present during this reaction or is added afterwards, it gives a compound with the heavier alkali metal. Thus R'M is formed from R'H provided $pK(Z-H) > pK(R'-H)$ [2–8]. In such reactions a stoichiometric amount of the heavier alkali metal alkoxide is consumed, and thus the alkoxide does not merely activate the organolithium compound [6]. However, the fact that the final product of the reaction between the complex base [Z–Li + ROM] (further only CB) and the third component is a heavier alkali metal derivative, R'M, does not necessarily mean that an intermediate Z–M species, such as butylpotassium, is the active species in this reaction [6,8]. The lithium–heavier alkali metal exchange can

* For communication XVI see ref. 1.

occur even with compounds containing an N-Li bond or with Li enolates of ketones and esters [8], and so is rather general. The reactions often give high yields of final products in high purity and are therefore useful for the preparation of organic derivatives of heavier alkali metals or of reactive intermediates for organic synthesis. The nature of CB and their reactions have also been studied by other authors, e.g. [9-12].

The pronounced effect of the concentration of the heavier alkali metal alkoxide in the CB on their properties has been described previously [1,13]. The effect of the structure of the alkoxides was the subject of the present investigation made on a model reaction with alkyl bromides (cf. ref. 14).

Experimental

All operations involving organometallic compounds were carried out under purified argon. Sodium t-pentoxide and sodium 3-methyl-pentoxide-3 were prepared by reaction of an excess of sodium with the appropriate alcohol in a mixture of

Table 1

Rates of reaction ^a of complex bases derived from organolithium compounds (Z-Li) and various sodium alkoxides (RONa) with alkyl bromides (R'Br), and the yield of coupling product (dodecane)

RONa Type	x^b mol. l ⁻¹	Reaction half-time ($t_{1/2}$) (min)	Acceleration of reaction by change in		Total reaction acceleration $F(T)^e$	Yield of dodecane (mol%) ^f
			alkoxide structure $F(S)^c$	alkoxide concentration $F(C)^d$		
<i>C₄H₉Li (0.246 mol · l⁻¹) + C₈H₁₇Br</i>						
I	0.246	1	>1000	1	1	35
II	0.246	1	74	>13	>13	47
III	0.246	1	40	>25	>25	55
I	0.74	3	16	1	>60	75
II	0.74	3	8	2	>125	81
III	0.74	3	0.8	20	>1250	53 ^g
<i>C₄H₉CH(C₂H₅)CH₂Li (0.246 mol · l⁻¹) + C₈H₁₇Br</i>						
I	0.246	1	40	1	1	-
III	0.246	1	11	3.5	3.5	-
I	0.74	3	29	1	1.4	-
III	0.74	3	1	29	40	-
<i>C₄H₉CH(C₂H₅)CH₂Li (0.26 mol · l⁻¹) + C₄H₉Br</i>						
I	0.26	1	23	1	1	-
II	0.26	1	9	2.5	2.5	-
III	0.26	1	10	2.3	2.3	-
I	0.78	3	20	1	1.2	-
II	0.78	3	3	6.7	7.7	-
III	0.78	3	0.8	25.5	29	-

^a Reaction conditions: [Z-Li]/[R'Br] = 1, heptane, -30 °C. RONa: (CH₃)₃CONa (I), (CH₃)₂(C₂H₅)CONa (II), (CH₃)(C₂H₅)₂CONa (III). ^b $x = [RONa]/[Z-Li]$. ^c $F(S) = t_{1/2}$ (alkoxide I)/ $t_{1/2}$ (alkoxide i). ^d $F(C) = t_{1/2}$ ($x=1$)/ $t_{1/2}$ ($x=3$). ^e Total reaction acceleration $F(T) = t_{1/2}$ (alkoxide I)/ $t_{1/2}$ (alkoxide i, $x=1$ or 3). ^f Yield of dodecane based on R'Br consumed. ^g Another product was so formed; under other conditions this was formed only in trace amounts.

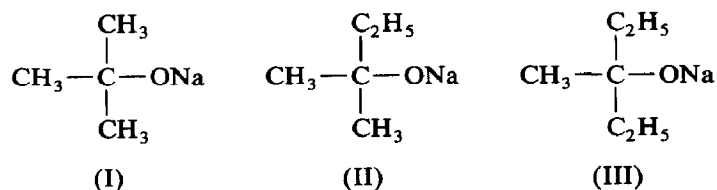
heptane and THF (2/1 by volume); they were isolated by crystallization at -70°C and vacuum-dried at 60°C . 2-Ethylhexyllithium (EtHexLi) was prepared as described in ref. 6. Heptane was dried with lithium aluminium hydride.

Reaction procedure

The organolithium compound Z-Li 0.002 mol was mixed with sodium alkoxide and heptane in the ratio given in Table 1, care being taken that the temperature of the mixture did not exceed -30°C [15*]. The mixture was then stirred at the chosen temperature for 15 min, during which a variable amount of precipitate was formed depending on the composition of the mixture. Subsequently 0.002 mol of alkyl bromide was added, after an appropriate time, the mixture in separate ampoules was hydrolyzed and the amount of bromide ion formed was determined mercurimetrically [16]. Conversion curves were constructed (Fig. 1), and the reaction half-time was determined graphically. The amounts of octyl bromide and dodecane in the organic layer of the reaction mixture were determined by GLC, as described in ref. 1.

Results and discussion

The results shown in Table 1 and Fig. 1 indicate that the structure and concentration of the sodium alkoxide in the CB greatly affect the rate of the reaction of CB with organic halides. The rate of the reaction depended on the alkoxide in the CB in the sequence sodium t-butoxide (I) < sodium t-pentoxide (II) < sodium 3-methyl-pentoxide-3 (III). This dependence applied for CB species with the molar



ratio $x = [\text{RONa}]/[\text{Z-Li}]$ equal of either 1 or 3. In keeping with results described in ref. 1, the CB species with the higher alkoxide content reacted more rapidly than those containing an equimolar amount of the same alkoxide. The two effects, i.e. the change into reactivity of the CB with the alkoxide structure and with its increased concentration, were to some extent additive, so that the overall effect could be maximized by a suitable combination of the effects. For example, the CB derived from butyllithium and alkoxide III, with $x = 3$, reacted with octyl bromide > 1250 times as rapidly as that made from alkoxide I with $x = 1$. Use of various combinations of reactants gave a wide range of rates, but in some cases the total acceleration factors that could be achieved reached the extent of few tens only.

The mechanism of the reactions of CB with a third component is probably rather complex, involving a number of separate reactions and both aggregation and solubility equilibria. The organic derivatives of alkali metals involved are present in

* Reference numbers with asterisks indicate notes in the list of references.

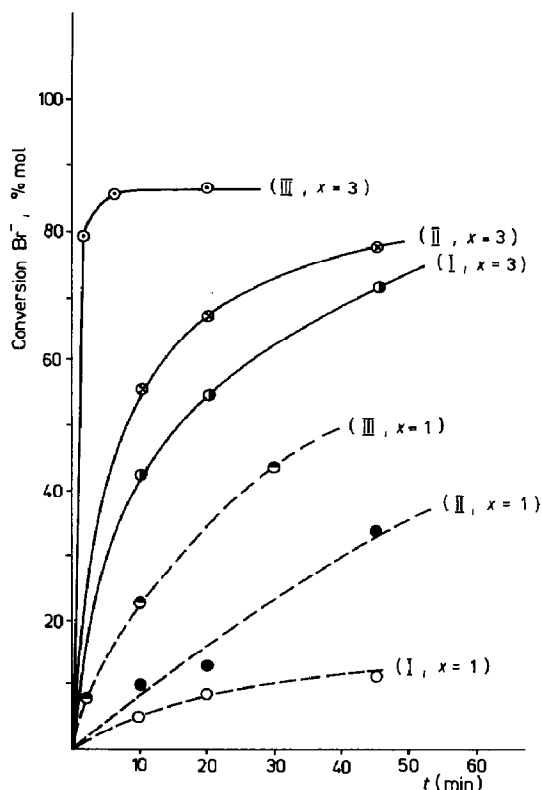


Fig. 1. Rate of generation of bromide ion Br^- in the reactions of complex bases from butyllithium and sodium alkoxides (RONa) I, II or III, with octyl bromide. RONa: $(\text{CH}_3)_3\text{CONa}$ (I), $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{CONa}$ (II), $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{CONa}$ (III). Reaction conditions: $[\text{C}_4\text{H}_9\text{Li}]$ 0.246 mol/l, $[\text{RONa}]/[\text{C}_4\text{H}_9\text{Li}] = x$, $[\text{C}_4\text{H}_9\text{Li}]/[\text{R}^+\text{Br}] = 1$, heptane, -30°C .

the form of supermolecular aggregates, and their reactions are usually accompanied by separation of a poorly soluble species, so that a heterogeneous system is produced. Under these conditions the effects of alkoxide structure and concentration on the reaction rate of CB may be very diverse: either a new more reactive supermolecular aggregate with an increased RONa content may be formed (compare similar aggregates in the system butyllithium–lithium butoxide [16], or the adduct of phenylpotassium with potassium t-pentoxide [7]), or there may be a physical effect, such as a change in the degree of aggregation and/or solubility of the participating compounds.

The effect of alkoxide structure on the properties of the CB species evidently is connected with the extent of alkoxide substitution in the vicinity of the $(\text{C})\text{O}-\text{Na}$ bond. It is well known that supermolecular aggregates of alkoxides are formed by participation of these bonds, and that the degree of alkoxide aggregation decreases with increasing substitution in their neighbourhood [17,18]. Interaction of alkoxides with other compounds competes with alkoxide autoaggregation, and so interactions are expected to be stronger with more highly substituted alkoxides, which are more weakly autoaggregated. The structure and effects of alkoxides I to III are in accord with this view.

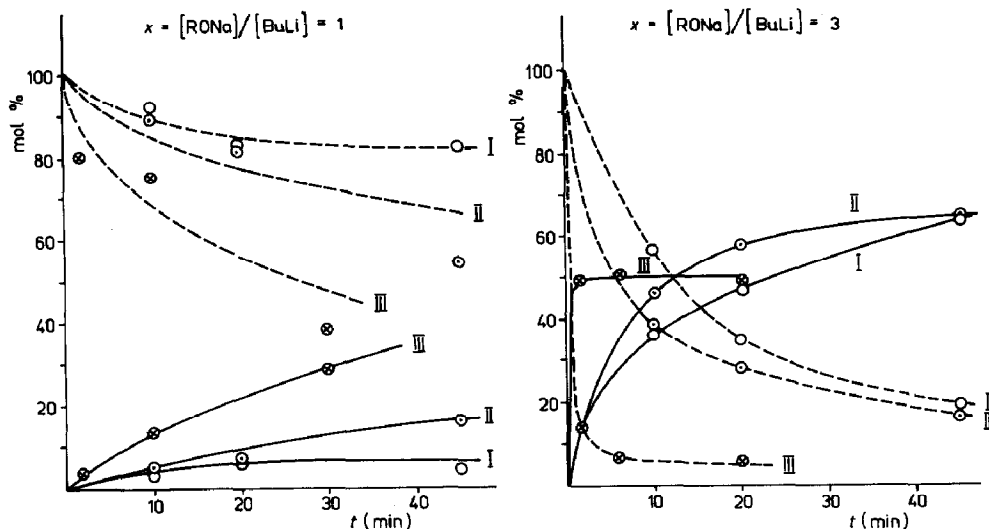


Fig. 2. Variation with time of the extent of conversion of octyl bromide and generation of dodecane in reactions with the complex bases derived from butyllithium and sodium alkoxides (RONa) I, II or III. For conditions and notes see Fig. 1. Curves: octyl bromide - - - -, dodecane ———.

The effects of structure and concentration of heavier alkali metal alkoxides on the reactivity of the CB depend also on the structure of the organolithium compound $Z\text{-Li}$, and it was less pronounced for EtHexLi than for BuLi . Thus a change in the concentration of alkoxide I only marginally affected the reactivity of the CB from EtHexLi , in contrast to the marked effect observed for the CB from BuLi . Similarly the CB from BuLi and an equimolar amount of alkoxide I was very much less reactive than the system containing EtHexLi (see the half-time ratio $t_{1/2}(\text{BuLi})/t_{1/2}(\text{EtHexLi}) = F(Z\text{-Li}) > 25$); with alkoxide III this difference was considerably smaller ($F(Z\text{-Li}) = 3.6$). With the CB containing three moles of alkoxide, the effect of the structure of the $Z\text{-Li}$ was much less pronounced. One of the reasons for the different behaviour of EtHexLi could be that 2-ethylhexylsodium [6] is more soluble in heptane than butylsodium; the same is true for the intermediary adducts of EtHexLi with alkoxides, which formed less precipitate. It thus appears that in the case of compounds containing an 2-ethylhexyl group, the alkoxides have smaller effects on the solubility and/or the degree of aggregation of intermediates, and so are also less effective in changing the reactivity of the CB. It should be noted that the kinetic measurements were carried out at -30°C where the stability of the intermediate adducts $[Z\text{-Li}\cdot\text{ROM}]$ is considerably higher [15 *], and so their participation more probable.

The relative amounts of separate products in reactions of the CB species with organic halogenides were also dependent on the structure and concentration of the heavier alkali metal alkoxide. The results in Table 1 and Fig. 2 indicate that in reactions of octyl bromide with a CB containing in addition to BuLi various amounts of alkoxides I, II or III, show that the yield of dodecane (the product of coupling) increased with increase in the degree of substitution of the alkoxide and with its concentration. This applied for both an equimolar and a three-molar ratio of alkoxide to organolithium compound. The low yield of dodecane in the reaction

of CB with alkoxide III and $x = 3$, shown in Table 1, is associated with an increase in the amount of another product, which was not investigated in detail. Under other conditions, only trace amounts of this product were formed.

Further modifications of the CB species and studies of their reactions with various third components are being investigated.

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