NMR spectra of a hydrocarbon-soluble organosodium compound and its lithium analogs

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^{1}H, ^{23}Na, and ^{7}Li NMR spectra of 2-ethylhexylsodium, 2-ethylhexyllithium, and isobutyllithium obtained in the reaction of the corresponding alkyl chlorides and metals have been recorded. The ^{1}H NMR signal for the protons of the CH_2Na group is shifted upfield compared with that for the protons of the CH_2Li group (doublets at δ −0.88 and δ −0.83, respectively). The composition of the products of reaction of 2-ethylhexyl chloride with sodium depends on the form of the metal reagent employed. The use of sodium balls with diameter up to 2 mm results in the formation of products containing ionic chlorine (30—50 % with respect to Na); the reaction with the dispersion proceeds faster and the reaction product is chlorine-free. The ^{23}Na NMR spectra of these substances are also different, which is explained by the formation of 2-ethylhexylsodium complexes with NaCl in the former case.

Key words: sodium alkyls; lithium alkyls; NMR; synthesis.

Until recently, the major part of the research in the field of organo derivatives of alkaline metals was carried out on organolithium compounds because of their ease of preparation and good solubility in hydrocarbons. The multinuclear NMR technique[1,2] proved to be particularly fruitful.

The application of spectral methods to the study of organosodium compounds[3] turned out to be limited, because nonsolvated, hydrocarbon-soluble organosodium compounds were unknown. Recently, a brief communication reported that, unlike alkylsodium derivatives with the linear structure, an *iso*-compound, 2-ethylhexylsodium (**1**), is hydrocarbon-soluble.[4] This made it possible to investigate the properties of alkylsodium derivatives by modern physicochemical methods and to compare the results obtained with the available vast information on the structure of organolithium compounds. The use of compound **1** as initiator of anionic polymerization provided a unique opportunity for studying the above-mentioned processes in the hydrocarbon medium without adding electron donors.[5]

The ^{1}H NMR spectra of compound **1** obtained in the reaction of 2-ethylhexyl chloride (**2**) with a sodium dispersion, as well as those of the lithium analogs, 2-ethylhexyllithium (**3**) and isobutyllithium (**4**) (Table 1), contain doublets at δ −0.8 to −0.9, assigned to the CH_2M group (alkyllithium derivatives are known to have signals in this region[6]). These signals disappear upon addition of D_2O, which corroborates their assignment to the groups containing the alkaline metal. The signals for the CH and CH_2 groups also appear in the spectra at δ 1.3—1.5, and those for the CH_3 groups at δ 0.9—1.0. The ratio of integrated intensities for the CH_3 and CH_2M groups corresponds to the above structure. The spectra of **1** and **3** have no doublet signals at δ 3.37, which belong to the CH_2Cl group, *i.e.*, the products obtained do not contain the unchanged **2**. However, a signal with δ 3.4 is observed in the spectrum of **4**, which points to the fact that the reaction of isobutyl chloride (**4**) with lithium did not go to completion. Analogous phenomena were observed[7] for other alkyllithium derivatives that can form equilibrium systems with alkyl halides.

Solutions of **1** in heptane are thermally unstable. After storage at room temperature for several weeks or

Table 1. NMR spectral data for several alkylmetal derivatives

Compound	^{1}H NMR (C_6D_{12})			^{7}Li NMR (heptane)	^{23}Na NMR (heptane)
	Group	δ	$^3J_{H,H}$/Hz	δ	
1	CH_2Na	−0.88	5.8	—	27
3	CH_2Li	−0.83	6.2	2.83	—
Bu^{n}Li	CH_2Li	−0.85*	—	1.64**	—
4	CH_2Li	−0.84	6.6	—	—

* See Ref. 6. ** See Ref. 9.

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Table 2. Content of ionic chlorine in the reaction products

Sodium form	Concentration of **1** /mol L^{-1}	Cl/Na
Dispersion	0.196	0.003
Sodium balls, purified by melting	0.065	0.51
Pieces of unpurified sodium	0.0905	0.35

upon heating to 70 °C, a dark-red color atop the solution and precipitation were observed. In this case, the signal for the protons of the CH_2Na group disappears, while the signals for the olefin and allyl protons appear at δ 5 and 1.9, respectively. It seems that the thermal decomposition of compound **1** results in the formation of sodium hydride and an olefin.

If sodium balls purified by melting were used in the synthesis of **1** instead of the sodium dispersion, the reaction proceeded more slowly and the fraction of the Wurtz-type reaction product increased. In addition, the product obtained contained much ionic chlorine, which was measured using the Volhard technique from the samples treated with water (Table 2). The solutions were previously separated from the precipitate. The lithium alkyls synthesized from alkyl chlorides[1,8] are known to often contain lithium chloride. The results of our study show that NaCl can also be retained in the solution due to complexation with **1**. The product obtained in the reaction with the sodium dispersion is almost free of ionic chlorine (see Table 2).

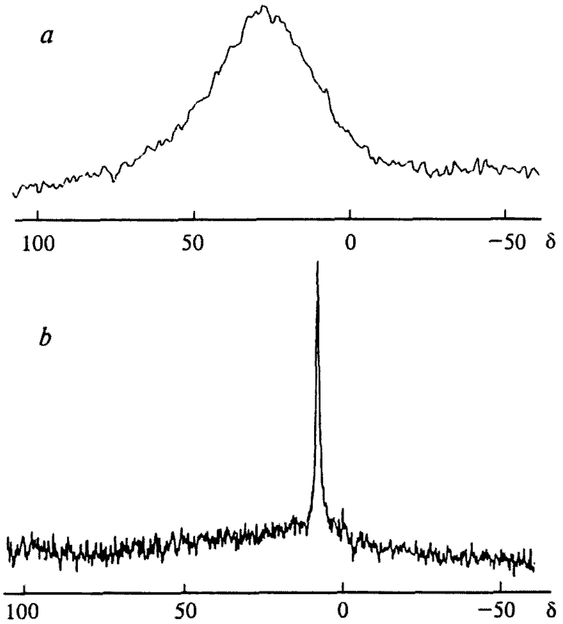

Fig. 1. The ^{23}Na NMR spectra of 2-ethylhexylsodium (**1**) obtained from finely dispersed sodium (*a*) and its complex with NaCl, synthesized from the sodium balls (*b*).

The ^{23}Na NMR spectra of the products obtained by different methods are shown in Fig. 1. A broad signal with maximum at δ 27 is observed in the spectrum of compound **1** synthesized using the sodium dispersion, while a narrow signal at δ 8.1 is recorded in the spectrum of the product obtained using sodium balls. The change in the spectrum shape might also be due to complexation with NaCl.

If small pieces of unpurified sodium were used in the synthesis, the product also contained (along with NaCl) (see Table 2) small amounts of sodium alkoxides in different degrees of association, which gave a multiplet at δ 3.7 in the ^{1}H NMR spectrum; the signal disappeared upon treating the product with D_2O.

The ^{7}Li NMR spectrum of compound **3**, like the spectra of other lithium alkyls,[9] is a narrow singlet (see Table 1).

Thus, the data available indicate a similarity in the structure of the sodium and lithium alkyls. The upfield shift of the signals for the protons of the CH_2Na group upfield compared with those of CH_2Li may be due to the higher electron density on the carbon atom of the CH_2Na group. A similar increase in the electron density in the aromatic ring on going from lithium to sodium and potassium was observed[10] for benzyl derivatives of alkaline metals.

Experimental

The dosage of the starting chemicals, the synthesis of metal alkyls, sampling during the synthesis, and NMR spectra measurements were carried out in a all-glass apparatus in high vacuum (10^{-3}—10^{-4} Torr) using the conventional technique of fragile thin partitions[11] employed for the work with alkaline-metal compounds. Heptane and deuteriocyclohexane were purified by standard procedures and then dried by butyllithium. Alkyl chlorides were treated with Al_2O_3 and recondensed in a vacuum unit.

NMR spectra were recorded on a Bruker-200-SY spectrometer. The ^{1}H NMR spectra were recorded in deuteriocyclohexane at 200.13 MHz. The chemical shifts were referenced to $SiMe_4$ (the chemical shift of the solvent residual protons is 1.44 ppm). The ^{7}Li and ^{23}Na NMR spectra were measured in heptane at 77.775 and 52.938 MHz, respectively (external standards, 10 % aqueous solutions of LiCl and NaCl).

The consumption of **2** during the synthesis was monitored by GLC on a Tsvet-1 chromathograph using a 1-m column with polymethylphenylsiloxane on Celite.

Reaction of 2-ethylhexylchloride (2) with sodium dispersion. A solution of **2** in heptane was added to a suspension of finely dispersed sodium in heptane at ~20 °C (Na : **2** = 2 : 1) and shaken in an ampule. A commercial dispersion in paraffin containing 30 % of sodium (particle size 10—25 μm) was used; it was repeatedly washed with heptane with heating to 40—50 °C *in vacuo*. According to GLC data, the reaction mixture was free of the initial alkyl chloride after 20 min. The product obtained was centrifuged in sealed ampules to separate the precipitate, and the yield was determined from alkalinity (using titration with HCl) and Gilman reaction with ethyl bromide. The yield of **1** is 60 %.

Reaction of 2 with small pieces of unpurified sodium. A solution of **2** in heptane was stirred for 6 h at ~20 °C with sodium pieces in a flat-bottomed flask with a magnetic bar sealed in glass. A tenfold excess of sodium with respect to **2** was used in the reaction. The yield of the active sodium is 30—60 %.

Reaction of 2 with sodium balls. In order to purify sodium from the oxidation products it was melted *in vacuo* and passed through a narrow constriction into a flat-bottomed flask. Decane dried with a sodium wire was added therein. The mixture was heated to the temperature above the melting point of sodium and stirred with a magnetic bar soldered in glass. The obtained sodium balls with diameter up to 2 mm were used in the reaction with **2** as described above. The yield of the active sodium is 30—60 %.

Synthesis of 2-ethylhexyllithium (3) and isobutyllithium (4). The corresponding alkyl chlorides were mixed with lithium pieces in heptane at ~20 °C using the technique employed in the reaction with sodium pieces. The yield of compound **3** is 90 %, and that of **4** is 30 %. The content of ionic chlorine in **3** did not exceed 6 %.

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