Sodium Dihydrido-bis(2-methoxyethoxo)aluminate (SDMA): Structure and Behaviour in Solutions

Stanislav Heřmánek*, Otmar Kříž, Jiří Fusek, Bohuslav Čáseký, and Zbyněk Černý
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 25068 Rež near Prague, Czechoslovakia

Z. Naturforsch. 40b, 582–584 (1985); received October 10, 1984/January 1, 1985

Alkoxohydridoaluminates, Equilibria in Solvents, Sodium Dihydrid-bis(2-methoxyethoxo)aluminates

SDMA, according to $^{27}$Al NMR almost uniform in benzene, is increasingly disproportionated in the presence of donors in the following order: $C_6H_6 < BuO < EtO < anisole < dioxane < THF < monoglyme < diglyme to the NaAIH$_{2-}(OCH_2CH_2OCH_3)$ compounds; the structure in solutions is represented by an open-chain oligomer with four-coordinated Na and Al atoms and with Na$^+$ autocomplexed by two bidentate $-OCH_2CH_2OCH_3$ ligands belonging to two neighbouring Al Atoms.

Sodium dihydrido-bis(2-methoxyethoxo)aluminate (SDMA), a medium member of the NaAlH$_{x-}(OCH_2CH_2OCH_3)$ family ($1: x = 0, 2: x = 1, 3: x = 2, 4: x = 3, 5: x = 4$), prepared directly from Na, Al and 2-methoxyethanol and delivered as 70% toluene solution under the SYNHYDRIDE trade name (Synthezia Kolfn, Czechoslovakia) or VITRIDE (Hexcel, San Francisco, USA) is an important reducing agent for C=O, C=N or C=N groups and an excellent catalyst for some polymerizations [1]. The outstanding stability of SDMA not only in ethers but also in aromatic hydrocarbons (benzene, toluene) changed this compound into one of the most safe and appropriate aluminium hydrides for the laboratory and, especially, industrial applications. In spite of the more than 15 years use of SDMA and more than 300 papers dealing with it [1], information on its structure and behaviour in solutions — especially important for the result of reduction — is sparse and contradictory. Solvent-free SDMA forms a honey-like compound unsuitable for the single crystal X-ray diffraction study and, therefore, it was studied mostly in solutions. From the IR spectra it was deduced [2] that SMDA disproportionates in solutions ($C_6H_6, EtO, THF$), and that the Al atoms are intramolecularly complexed with methoxy oxygens under the formation of five- or six-coordinated Al atom. On the contrary, from the $^{27}$Al NMR results it was concluded that SDMA does not disproportionate in THF, as it shows only one $^{27}$Al NMR signal at $\delta = 67$ ($W_{1/2} = 200$ Hz) [3].

We now report results of a comprehensive $^{27}$Al NMR study which enabled to solve this long term problem. The $^{27}$Al NMR spectra measured in aromatic hydrocarbons (benzene, toluene) have revealed SDMA as an almost uniform compound, exhibiting on wide, symmetrical, unsplitted signal at $\delta = 101.5 \pm 0.3$ and in some samples showed only imperceptible signals of 2 or 5. The line width ($W_{1/2}$) of the signal decreases with lowering concentration (1700 35%, 1200 7%, 900 1.4%), increasing temperature (Hz°C: 1200; 23, 550/70) and $^1H$ decoupling (by 180 Hz at 23°C but only by ca. 10 Hz at 70°C) (Fig. 1 a–d). The simultaneous use of all factors together with an apodization narrows the signal to 310 Hz (Fig. 1 e) without lowering the symmetry...
of the signal. The practical absence of the well distinguishable signal of the stable tetraalkoxoaluminate 5 in benzene ($\delta = 69.2$ ppm, $W_{1/2}$ of 0.4 mol solution: 290 Hz at 25 °C and 117 Hz at 70 °C) as well as of further signals documents the distinct stability of SDMA in aromatic hydrocarbons over a wide range of temperatures (20–110 °C).

In solvents of donor character the stability of SDMA decreases in the order: $C_6H_6 < Bu_2O < Et_2O < anisole < THF < monoglyme < diglyme, as follows from the growing amount of the 1–5 disproportionation products (Fig. 2). Distinct but somewhat lower measure of disproportionation has been also observed after the addition of the above solvents to the benzene solution of SDMA. The signal at $\delta = 67$ assigned [3] to SDMA in THF appertains in reality to the narrow signal of 5.

The hypothesis that SDMA is stabilized in benzene by an intramolecular autocomplexation of the Na$^+$ cation with two bidentate $-OCH_2CH_2OCH_3$ ligands [1] has been confirmed by the results of both the addition of 18-crown-6-ether to the benzene solution of SDMA and the addition of two equivalents of 2-methoxyethanol to the benzene solution of Bu$_4$N$^+$AlH$_4^-$. In both cases, bonds between the cation and the Al-anion are suppressed and a homogeneous mixture of products of disproportionation results. The stabilization by the autocomplexation with Na$^+$ also explains why only ethers able to compete with the donating power of the $-OCH_2CH_2OCH_3$ ligands break the Na—O—Al bridges to such an extent that a distinct disproportionation occurs and a significant quintet of AIH$_4^-$ appears.

The high stability of SDMA in benzene can be understood by assuming structure 3a in which all four oxygen atoms present in 3 are used for the saturation of coordination sites of Na$^+$ and where the greatest number of strong O-bridges between Na and Al exists. The formation of a maximum of these strong bridges in a given system is also, very likely, the thermodynamic driving force for the redistribution of symmetrical 1 and 5 in favour of unsymmetrical 3 [4]. It is an analogy of redistribution in AlR$_3$—AlX$_3$ systems (X = H, Cl, OR) to the less symmetrical R$_2$Al—X—AlR$_2$ products [5].

The dominance of oligomer 3a over monomer 3b found by the earlier molecular weight measurements [6, 7] is in accord with significant steric strains in 3b, in which the planar four membered Na$^+$ violates mutually a perpendicular arrangement of two five-membered rings having a common tetrahedral sodium atom.

The four-coordination of the Al atom in 3 is in agreement with the chemical shift $\delta^{(27)Al} = 101.5$ (benzene) which falls into the region of other signals of tetrahedral aluminium in benzene ($\delta$: 1 100 ± 1; 5 69.0, AlCl$_3$-dimer 98.2, etc.). Intermediates with five-coordinated Al atoms (non-observable due to a small amount in the $^{27}Al$ NMR spectra but probably visible in the IR spectra [2]), necessary for the alkoxo- and hydride intermolecular exchange processes are, very likely, also present in SDMA solutions. It follows from our $^{27}Al$ NMR study of the 3/5 system in which changes in $\delta$ and $W_{1/2}$ of the Al signals are proof of a fast exchange of hydrogens and of the
alkoxy groups. The intermolecular exchange of H atoms is probably also a cause of a significant loss of the $^1$H-coupling on heating (Fig. 1d).

Our study has shown that SDMA in benzene is a complicated system in which an exchange of ligands proceeds but in which at any given time compound 3a strongly prevails. A similar system and, consequently, similar behaviour can be expected in pure ethers of a low donacity (Et$_2$O, Bu$_2$O, anisole) or in their mixtures with aromatic solvents. In the presence of ethers of a high donacity (THF, monoglyme, diglyme), however, a fast disproportionation to the single 1—5 compounds prevails. In such systems the proportion of 1 is high and in the case that 1 is consumed in a reaction, its content is continuously restored to the account of 2—4 so that the whole system approaches the behaviour of NaAlH$_4$ till the consumption of the hydridic content.

[8] 54.2 MHz $^{27}$Al NMR spectra were recorded on a Varian XL-200 spectrometer, using solutions sealed under nitrogen in 10 mm tubes including a sealed capillary with aqueous Al(H$_2$O)$_6^{3+}$ as the standard.
[9] The assignment of individual signals to the appropriate compounds 1—5 is based on our findings that signals of AlH$_4^-$ occur at 95—105 ppm, of AlH$_2$OR$^-$ at 115—125 ppm, of AlH$_3$(OR)$^-$ at 100—115 ppm, of AlH(OR)$_2$ at 75—90 ppm and of Al(OR)$_4$ at 50—75 ppm according to R, cation or solvent.