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A method for the determination of the degree of association of organolithium compounds in liquid ammonia

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Abstract

A method for carrying out cryoscopy in liquid ammonia is presented. The degrees of association of some organolithium compounds in liquid ammonia have been determined.

Introduction

Liquid ammonia ($NH_3(l)$) is a convenient solvent for a variety of organic syntheses [1,2]. Its low acidity ($pK_a \approx 34$) permits the generation of a broad spectrum of organoalkali compounds and their reactions with a number of electrophilic reagents.

Reactions of organoalkali compounds with alkyl halides and epoxides (β-hydroxy alkylations) generally proceed much faster in $NH_3(l)$ than in the usual solvents such as diethyl ether and tetrahydrofuran (THF) [1,2]. For this reason use of ammonia as a solvent may have special advantages if the reactions of organoalkali compounds with alkyl halides or epoxides proceed sluggishly in the organic solvents. This is the case, for example, with lithium acetylides, $RC{\equiv}CLi$ [1,2], thioacetal-*S*-oxides $\{RC(Li)(SOC_2H_5)(SC_2H_5)\}$ [3], enolates derived from aldehydes and ketones [3], and cyclopentadienyllithium (CpLi) [3]. For an understanding of the observed differences in reactivity, knowledge about the structure of the alkali metal compounds in the various solvents is required. It is known that organolithium compounds can exist in a variety of structural forms, monomeric, dimeric, tetrameric, and hexameric structures have been commonly found in the solid state [4]. Recently X-ray structures of a dodecameric [5] and the first trimeric [6] carbon-lithium-bonded organolithium compound have been determined.

Information about the structure of organolithium compounds in solution can be obtained by NMR spectroscopy [7–9], cryoscopy [10,11] ebulliometry [12,13] and osmometry [14]. The available reports on NMR spectroscopy [16] and cryoscopy [15] in $NH_3(l)$ do not provide data concerning the structures of organolithium

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compounds in this solvent. Since the use of ebulliometry and osmometry is experimentally not very attractive, we have developed a method for carrying out cryoscopy in NH_3(l) which allows the determination of the degrees of association of some organolithium compounds.

Method

The design of the apparatus for our cryoscopic measurements (Fig. 1a) was based on previously described equipment [10,17–19]. It consists of an evacuable Schlenk-like vessel (4) in which the measuring probe (2) for collecting the ammonia and the ammonia solution (6) of the organometallic compound can be placed. The measuring probe can be fitted with a Pt-100 resistor mounted in a stainless steel tube (5). With the aid of the Pt-100 resistor, temperature measurements are performed on a Systemteknik S2541 thermolyzer. An X-Y-plotter is connected to the thermolyzer to give cooling curves. During the measurements, the ammonia solution is homogenized by stirring with a Teflon magnetic stirring bar (7). Dry NH_3(l) is obtained by distillation from sodium amide ($NaNH_2$). For this operation the condenser depicted in Fig. 1b is connected to a 1 l round-bottomed flask containing ca. 300 ml of NH_3(l) and ca. 0.2 mol of sodium amide prepared in situ (3). The spiral is cooled with a dry ice/acetone mixture (9) to −70 °C. This spiral can be connected to the measuring probe (2) via a ground glass joint (10). A plug of dry glass wool (8) placed in the glass tube of the condensor serves to trap particles of $NaNH_2$ which may be swept along with the ammonia vapors. The distillation rate can be increased

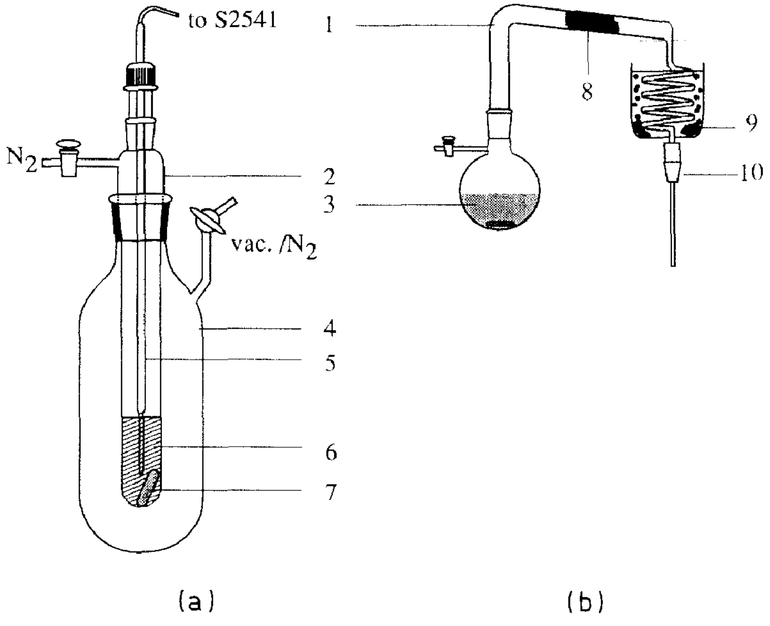


Fig. 1. Apparatus used for cryoscopical measurements (a) and destillation of liquid ammonia (b). (1) condenser used for NH_3(l) destillation; (2) measuring probe; (3) in situ prepared sodium amide in NH_3(l); (4) isolation vessel to regulate the cooling rate for the measuring probe; (5) Pt-100 resistor; (6) ammonia solution; (7) PTFE (Teflon) coated magnetic stirring bar; (8) dry glass wool; (9) dry ice/acetone mixture; (10) ground glass joint for connection to the measuring probe.

by blowing hot air around the round-bottomed flask containing the $NH_3(l)/NaNH_2$ mixture.

The various operations to be carried out in succession are as follows. After the Teflon stirring bar has been placed in the measuring probe (2), the lithium compound is introduced under Schlenk conditions. The amount of this compound is such as to give a concentration of 60 to 160 mmolal in the ca. 25 g of $NH_3(l)$ which will be condensed in the vessel. Concentrations above 200 mmolal give a deviation from the linear correlation with the freezing point [10]. Subsequently the measuring probe (2) is placed in the isolation vessel (4), which has previously been evacuated and flushed with nitrogen (thus preventing precipitation of ice on the inside, and allowing the ammonia solution (6) to be observed during the measurements). This system is connected to the previously evacuated and nitrogen flushed condenser (1) via a ground glass joint (10). The isolation vessel (4) and the condenser spiral are cooled with a dry ice/acetone mixture of ca. $-70\,^\circ C$. Subsequently the distillation can be started by connecting the round bottom flask, containing the $NaNH_2/NH_3$ mixture (3), to the condenser. After ca. 25 g of $NH_3(l)$ has been collected, the isolation vessel (4) is evacuated (0.1 mmHg) and the condenser is replaced by a cap. The cocks of vessel (2) and (4) can be subsequently closed, since the ammonia solution (6) at ca. $-70\,^\circ C$ is isolated by the vacuum in vessel (4). The condensate on the outside of the apparatus is removed by blowing with hot air and subsequently the amount of obtained $NH_3(l)$ can be determined by simple weighing. Finally the Pt-100 resistor (5) is mounted on the measuring probe and the stirred solution is slowly cooled to its freezing point by placing the system in a liquid nitrogen bath. A constant stirring rate for all the experiments is essential for the reproducibility of freezing points. The cooling rate of the ammonia solution (6) should be low when the freezing point is reached. This can be achieved by reducing the nitrogen pressure in the isolation vessel. Evacuation of vessel (4) to 0.1 mmHg guarantees a cooling rate of ca. $0.01\,^\circ C\ s^{-1}$, which is low enough. The freezing point of mercury ($-38.865\,^\circ C$, [20]) was used as a reference for all temperature measurements. The freezing point of dry $NH_3(l)$, obtained by distillation as described above, was found to be $-77.66\,^\circ C$. This value corresponds well with those reported in the literature (viz. $-77.74\,^\circ C$ [21] and $-77.75\,^\circ C$ [22,23]), and was reproducible.

Results and discussion

The calibration curve (Fig. 2) for the determination of the cryoscopical constant was derived from measurements with ammonia solutions of compounds that are assumed to be monomeric in $NH_3(l)$, namely *N*-methylpyrrole, pyridine, quinoline, and anisole. The resulting curve is linear (correlation coefficient 0.998) within the chosen concentration range. The least-squares method gives a cryoscopic constant (E_k) of $1.44(4) \pm 0.09\,^\circ C\ mol^{-1}\ kg^{-1}$. The value reported in 1925 [15] was $1.32\,^\circ C\ mol^{-1}\ kg^{-1}$. The difference probably originates from a small systematic error (equipment, method of measurement).

Cryoscopic measurements were carried out with the five lithium compounds mentioned below. They have a good solubility in $NH_3(l)$ at very low temperature, and are not subject to ammonolysis since their basicities are much lower than that of lithium amide.

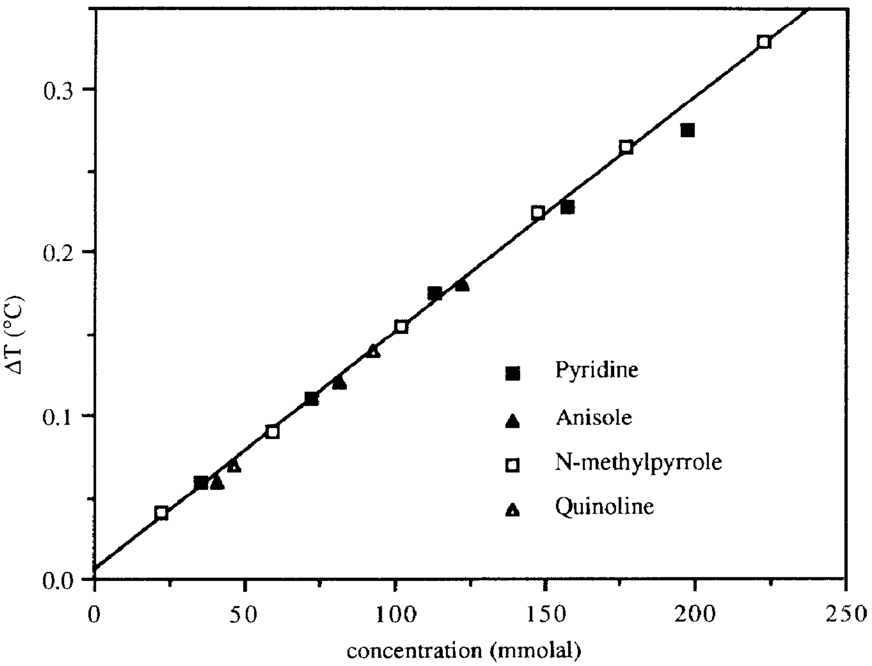


Fig. 2. Calibration curve for the determination of the cryoscopical constant of NH_3(l).

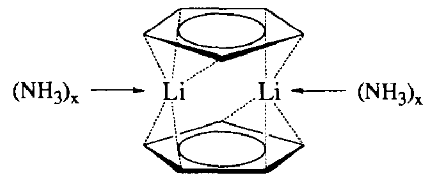
Some examples: {concentration (mmolal)}

PhC≡CLi (**1**) Found: $n = 1.56 \pm 0.14$ {150.0}. If **1** is assumed to be present in a monomer–dimer equilibrium, 56% may be present as a dimer and 44% as a monomer. Cryoscopy [10] and NMR [7] showed **1** to be mainly present as a dimer in THF. In the solid state **1** is a dimer [24], or a polymer consisting of tetrameric units [25].

PhOLi (**2**) Found: $n = 2.21 \pm 0.20$ {153.0}. NMR and vapor pressure elevation studies [26] indicate that **2** is a tetramer in pyridine and in dioxolane at room temperature. For steric reasons di-*ortho*-substituted lithium phenolates have lower degrees of association. Cryoscopy studies showed that lithium-2,6-di-t-butyl-4-cresol (solvated by THF) and lithiated 2,6-dimethylphenol are mainly dimeric in benzene and dioxane, respectively [11]. In the solid state lithium-2,6-di-t-butyl phenol solvated by THF is a dimer [27].

PhSLi (**3**) Found: $n = 1.32 \pm 0.12$ {153.8}. No structural data for this class of compounds are available in the literature.

C_5H_5Li (**4**) Found: $n = 1.40 \pm 0.13$ {153.3}. As far as we are aware there have been no report of the crystal structure of either unsolvated or solvated cyclopentadienyllithium (CpLi, "the simplest metallocene"), but NMR studies [28] in several polar solvents suggest the presence of contact-ion pairs. The cyclopentadienyl (Cp) ligand can bind to a metal in various ways: η^1, η^2, η^3, and η^5 Cp-metal complexes have been observed. Ab initio calculations on monomeric unsolvated CpLi show the preference for η^5-bonding of the Cp ligand towards lithium [29]. X-ray studies on trimethylsilyl-substituted CpLi derivatives [9,30] confirm this favoured η^5-bonding. These structures are monomeric in the solid state and in benzene when amine ligands are present.



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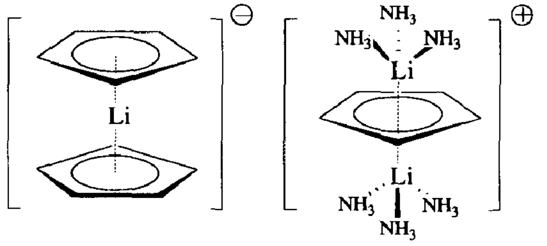

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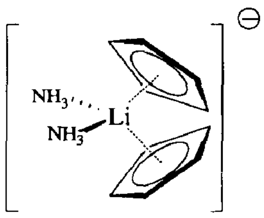

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The degree of association determined for cyclopentadienyllithium (**4**) in NH_3(l) suggests the presence of dimeric or higher aggregates. This gives rise to the question of the structure of these aggregates. The Cp-anion may bridge two lithium atoms in a η^2-η^3 fashion resulting in a dimer **5** in which the lithium atoms additionally can be solvated by NH_3-ligands. However, since η^5 bonding for the Cp-anion is preferred over η^2 and η^3 bonding [9,29,30], other possible aggregates are the triple ions (**6**). Recently a similar structure as proposed for the cation in **6** has been found: a methyl-cyclopentadienyl group bridges two lithium atoms which are additionally solvated by TMEDA (a chelating diamine) [31]. The cation in **6** may be replaced by a ammonia-solvated lithium cation. NMR and/or conductivity studies have to be done to distinguish between structures **5** and **6**. The sandwich triple anion in **6** may be distorted and solvated by two additional NH_3-ligands (**7**).

$H_2C{=}C(OLi)Ph$ (**8**) Found: $n = 2.18 \pm 0.20$ {70.8}. As far as we could ascertain, surprisingly, no structural data are available for **8** in solution or in the solid state. X-ray studies [32,33] led to the conclusion that lithium enolates solvated by THF are tetramers in the solid state. NMR studies in THF revealed that the simplest lithium enolate, viz. that of acetaldehyde, is a tetramer [34], and the lithium enolate of isobutyrophenone is involved in a tetramer-dimer equilibrium [8]. Cryoscopy on the lithium enolate of cyclopentanone in THF [10] revealed a degree of association of 2.70.

From our preliminary results the conclusion may be drawn that the degrees of association in NH_3(l) are lower than those in aprotic polar solvents such as diethyl ether, THF, dioxolane etc. This is consistent with high level ab initio calculations on the solvation energies of lithium first-row compounds, which appear to remain remarkably constant over a range of lithium compounds. The energy of solvation of lithium by water is calculated to be ca. -18.0 ± 1.2 kcal mol^{-1}, and that for solvation by ammonia is calculated to be -21.5 ± 1.3 kcal mol^{-1} [35]. In view of this and the smaller size of an NH_3 molecule relative to that of an ether molecule, NH_3 is expected to be a better Lewis base.

Experimental Section

Synthesis of organolithium compounds

All syntheses were carried out under nitrogen by Schlenk-tube techniques. The solvents used were distilled from sodium/benzophenone prior to use. Reagents were dried with an appropriate drying-reagent and, in case of liquids, distilled under nitrogen.

Organolithium compounds used in further measurements were checked for purity by ^1H and ^{13}C NMR spectroscopy with a Bruker AC200 (^1H: 200 MHz) spectrometer.

Phenylethynyllithium (1). A solution of n-BuLi (38.4 mmol) in 24 ml of hexane was added at room temperature to a mixture of 4.0 ml of phenylacetylene (excess) and 30 ml of hexane. A white precipitate of **1** formed immediately. After a further 30 min the white suspension was centrifuged and the precipitate was washed with hexane, than twice with pentane, and kept for 3 h (50 ° C) at 10^{-2} Torr.

Lithium-phenolate (2). n-BuLi (80.0 mmol) in 50 ml of hexane was added at room temperature to a mixture of phenol (7.5 g; 80.0 mmol) in 15 ml of hexane. A white precipitate of **2** formed immediately, and was washed twice with hexane and twice with pentane, and kept for 3 h (50 ° C) at 10^{-2} Torr.

Lithium-thiophenolate (3). n-BuLi (54.4 mmol) in 34 ml of hexane was added at room temperature to a mixture of diphenyldisulfide (11.9 g; 55 mmol) in 30 ml of hexane. A white precipitate of **3** formed immediately and was washed twice with hexane, twice with pentane, and then kept for 3 h (50 ° C) at 10^{-2} Torr.

Cyclopentadienyllithium (4). Cyclopentadiene was distilled from dicyclopentadiene over iron powder at 140–150 ° C. The monomer was collected at -70 ° C, dried with n-BuLi and redistilled ($T < 45$ ° C).

n-BuLi (80.0 mmol) in 50 ml of hexane was added at -35 ° C to 11.0 g of cyclopentadiene (167.0 mmol). A white precipitate of **4** was formed immediately. The mixture was warmed to room-temperature, the precipitate was washed twice with hexane then three times with pentane, and kept for 3 h (70 ° C) at 10^{-2} Torr.

Lithium-acetophenonenolate (8). n-BuLi (28.0 mmol) in 17.5 ml of hexane was added at room temperature to a mixture of trimethylsilylacetophenonenolate (5.4 g; 27.3 mmol) and 50 ml of diethyl ether. The mixture was stirred for 90 min and the solvents were removed in vacuo and 30 ml of pentane were added to the dry residue. A white precipitate of **8** was formed. The mixture was stirred for an additional 15 min and the precipitate then washed with benzene and twice with pentane, and kept for 3 h (25 ° C) at 10^{-2} Torr.

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