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ASSOCIATION AND COMPLEXING OF ISOPROPYLLITHIUM AND SECONDARY BUTYLLITHIUM

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Summary

The first data on the heat of mutual transition of organometallic associates differing by association degree is obtained. For the process 3 $(i\text{-}C_3H_7Li)_4 \rightleftharpoons 2\ (i\text{-}C_3H_7Li)_6$ the value $-\Delta H$ is found to be equal to 4.9 ± 1.2 kcal/mol. The complexes of $i\text{-}C_3H_7Li$ with THF and trimethylamine are investigated.

Association of organolithium compounds has been studied by various methods [1] including UV spectroscopy and PMR [2]. Lewis and Brown have shown by the cryoscopic method [3] that the average degree of association (n) of isopropyllithium (i-PrLi) is 4 in dilute solutions and increases with concentration. The increase in n shows that apart from tetramers (T) other associates of a more complex structure are also present, probably hexamers (H). In this work infrared spectroscopy was used to investigate the association of i-PrLi over a wide range

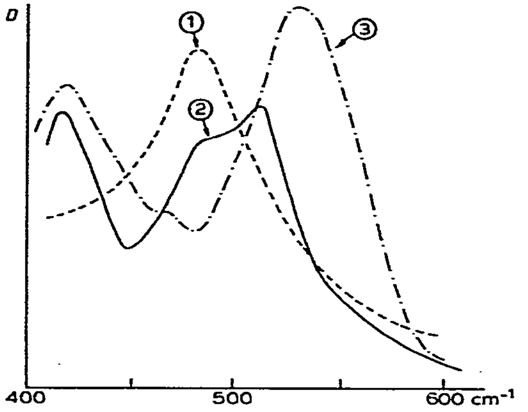

Fig. 1. IR spectra of i-PrLi in isooctane. (1) i-PrLi-7 (1.2 M, 4°C); (2) i-PrLi-7 (1.2 M, —54°C, same thickness of windows); (3) i-PrLi-6 (0.12 M, —30°C).

of temperatures (+20 to —100°C) and some thermodynamic parameters of the $(i\text{-PrLi})_4 \rightleftharpoons (i\text{-PrLi})_6$ equilibrium were established.

Spectra of 1,2 *M* *i*-PrLi in isooctane (2,2,4-trimethylpentane) are shown in Fig. 1. The 480 and 508 cm^{-1} bands (—54°C) are assigned to the C—Li stretching vibrations (ν(C—Li)) since when ^{7}Li is replaced by ^{6}Li, they shift by 50 cm^{-1} to high frequencies (Fig. 1). When the temperature is lowered, the intensities of the bands shift towards higher frequencies. The 480 cm^{-1} band is evidently due to the *i*-PrLi tetramer. As to the high frequency band at 508 cm^{-1}, its assignment to the *i*-PrLi hexamer is quite plausible since organolithium compounds, such as butyllithium (BuLi) [3] show a trend to hexamer structures.

The infrared spectra of *i*-PrLi at low temperatures exhibit a second ν(C—Li) band at 417 cm^{-1}; presumably it is also due to the *i*-PrLi hexamer. The corresponding band of the tetramer is below 400 cm^{-1} in the case of ^{7}Li and shifts to 428 cm^{-1} when it is replaced by ^{6}Li.

At the *i*-PrLi concentration of 0.24 *M* two types of associates are also observed, but the percentage of the hexamer species is not high. The enthalpy of the (T) $\rightleftharpoons$ (H) transition is calculated from the equation:

$$3\,\text{T} \overset{K}{\rightleftharpoons} 2\,\text{H}$$

Assuming that extinctions of the bands at 480 and 508 cm^{-1} are equal, we obtain

$$K = \frac{D_{508}^2}{D_{480}^3},$$

where D is integral optical density of the spectral curve. The value of $-\Delta H$ is (4.9 ± 1.2) kcal/mol. The equilibrium constant at —47°C is 3.4 l/mol.

The infrared spectra of the complexes *i*-PrLi: THF (tetrahydrofuran) = 1 and *i*-PrLi: TMA (trimethylamine) = 1 exhibit single ν(C—Li) bands at 470 and 465 cm^{-1} respectively. The analyses of intensities of the ν_{as}(C—O) bands of free THF (1073 cm^{-1}) and THF bound in complex (1050 cm^{-1}) and the bands of free TMA (1039 cm^{-1}) and TMA bound in the complex (1019 cm^{-1}) shows that at —30°C approximately one half of the electron donor becomes a part of the complex. Thus, the bands at 470 and 465 cm^{-1} are due to ν(C—Li) of the *i*-PrLi tetramer solvated by two donor molecules. It should be noted that n-BuLi, at —30°C, forms with TMA a complex of the same stoichiometry [4]. However, in the n-BuLi—THF system complexes in a 1 : 1 ratio are formed [5].

At the equimolar ratio of the components the *i*-PrLi complexes are relatively stable. In contrast, when the donor, such as THF, is in excess, the components begin to react with each other even at —30°C; the reaction products absorb at 552 cm^{-1}.

The infrared spectra of s-BuLi (^{7}Li) and s-BuLi (^{6}Li) in isooctane show two ν(C—Li) bands at 518 and 530 cm^{-1}. In benzene solution the bands shift to 512 and 524 cm^{-1}, respectively. This indicates that a certain interaction between BuLi and benzene occurs. The UV spectra also exhibit changes on passing from cyclohexane to benzene [6]. When the temperature changes from +20 to —100°C, no new bands assigned to ν(C—Li) appear and the observed bands are assigned to vibrations of the BuLi tetramer [6].

i-PrLi and BuLi were synthesired in all-sealed systems in pentane [7], then the solvent was replaced with isooctane, heptane or benzene. The complexes of *i*-PrLi with THF and TMA were prepared in special all-sealed systems previously evacuated to 10^{-5}—10^{-6} mmHg [7].

Infrared spectra were obtained under conditions described previously [4]. The absorption bands were separated into components with the aid of a BESM-6 computer under assumption of dispersion contours.

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