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Abstract

Full Text

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INFRARED SPECTRA OF ORGANOLITHIUM COMPOUNDS. INTERMOLECULAR LITHIUM BOND

The present work is devoted to a study of the infrared absorption spectra of organolithium compounds of the type Alk—Li and Ar—Li. For this purpose we investigated the spectra of methyl-, ethyl-, butyl-, dodecyl-, phenyl-, *p*- and *o*-tolyl-, and α-naphthyllithium, which were prepared and isolated by the methods described in papers (^{1,2}).

In the spectrum of methyllithium vapor (Fig. 1), in accordance with the theory of vibrations of molecules of this type, six fundamental frequencies are observed, the band with frequency 1052 cm^{-1} being assigned to the stretching vibration of the group $\overset{-\delta}{\mathrm{C}}—\overset{+\delta}{\mathrm{Li}}$. The validity of this assignment is consistent with an analysis of the spectra of ethyl-

Fig. 1. IR spectra of methyllithium in crystals (*a*) and vapor (*b*). NaCl and LiF prisms

butyl- and dodecyllithium. Thus, for this series of compounds the frequency of the stretching vibration of the C—Li group, equal to $\sim$ 1050 cm^{-1}, is characteristic. Changes in the intensity and position of this band in the spectra of crystals and solutions of organolithium compounds also support the accepted assignment. Thus, in the spectrum of powders of methyl- and ethyllithium in vaseline oil, in addition to the band with frequency 1056 cm^{-1}, a new intense band with frequency about 880 cm^{-1} is observed, which is absent from the spectrum of the vapor. In the spectrum of concentrated solutions of ethyllithium in benzene, the intensity of the new broad band with maxima at $\sim$ 925 cm^{-1} and 880 cm^{-1} is considerably greater than the intensity of the band of the free C—Li group. The change in the intensities of the bands at $\sim$ 1050 cm^{-1} and those lying in

Fig. 2. IR spectra of ethyllithium solutions in benzene at different concentrations. a –0.9 N solution, b –0.4 N solution, c –0.23 N solution. NaCl prism, d = 0.3 mm

Figure 2: Fig. 2. IR spectra of ethyllithium solutions in benzene at different concentrations. a –0.9 N solution, b –0.4 N solution, c –0.23 N solution. NaCl prism, d = 0.3 mm

the interval 915—880 cm^{-1} is interrelated. A relative increase or decrease in the intensity of the band at ~ 1050 cm^{-1} is always accompanied by a decrease or increase in the intensities of the bands lying in the region 915—880 cm^{-1}. These facts give clear confirmation of the correctness of assigning the 1050 cm^{-1} band to the stretching vibrations of the C–Li group.

The change in the frequency of the stretching vibration of the C–Li group on passing from the vapor state to the solid state and to solutions is evidently connected with the fact that the C–Li groups in crystals and solutions participate in some kind of intermolecular interactions, which leads to a shift of the C–Li band toward longer wavelengths.

Thus, the spectra unambiguously show that molecules of organolithium compounds in crystals and in solutions are associated with the formation of complexes. This conclusion is in complete agreement with the work of a number of authors ([3–6]), who present cryoscopic and ebullioscopic data confirming the association of these compounds. Naturally, on going from the solid state to solutions in nonpolar solvents, the character of the association must change substantially.

If the existence of chains is possible in crystals, then in solutions in nonpolar solvents it is more favorable to form associates with a decrease in the overall dipole interaction; this can be realized by the formation of various rings, as well as by changes in the character and length of the chain. Thus, in the spectra of freshly prepared solutions of ethyllithium in benzene, toluene, and *m*-xylene, most of the molecules are associated with predominance of one of the types of associates (926 cm^{-1}). Upon dilution, the relative intensity of the 926 cm^{-1} band decreases sharply, while the bands near 875 cm^{-1}, 1050 cm^{-1}, and 1100 cm^{-1} increase (Fig. 2).

Fig. 2. IR spectra of ethyllithium solutions in benzene at different concentrations. *a* –0.9 N solution, *b* –0.4 N solution, *c* –0.23 N solution. NaCl prism, *d* = 0.3 mm.

Upon heating a solution of ethyllithium in benzene to 70°, and also upon keeping it in a nitrogen atmosphere in the light, an analogous change in the intensities of the indicated bands is observed. It is possible that different types of associates actually exist in solution, which under the specified conditions transform into one another. Such a conclusion can be reconciled with cryoscopic data, which for benzene solutions of ethyllithium give association factors equal to six (4,7,8) and two (6). It may be assumed that the 875 cm^{-1} band belongs to the C—Li group in dimers, and the band with frequency 926 cm^{-1} to hexamers.

Investigation of the spectra of ethyllithium solutions in hexane, cyclohexane, and cyclohexene (the ethyllithium was recrystallized from these same solvents) shows that the fraction of molecules not participating in association is greater than the fraction of associated molecules, and that the character of the association in these solvents is different from that in aromatic hydrocarbons. Thus, in the spectra of ethyllithium in hexane and cyclohexane, the bands of free C—Li groups near 1050 cm^{-1} and 1100 cm^{-1} are very intense, while the bands at 926 cm^{-1} and 877 cm^{-1} appear only at high concentrations and their intensities fall upon dilution of the solution (Fig. 3). The character and degree of association of R—Li molecules in a given solvent must depend strongly on the length of the hydrocarbon chain. With increasing chain length, the probability of formation of cyclic associates should decrease, and the possibility of formation of linear complexes should increase. Methyllithium is an exception: in it the methyl group hinders the formation of cyclic associates in solutions, which, apparently, can explain the insolubility of CH_3Li in hexane and benzene. Obviously, changes in the character and degree of association of R—Li molecules as a function of the nature of the compound, the solvent, the concentration, and the temperature must strongly affect the dipole-

at the present moment. Therefore it could be assumed that the dipole moment of ethyllithium, measured in dilute solutions of hexane, should approach the dipole moment of a free molecule. Measurements carried out by V. N. Vasil' eva together with us did in fact show that in dilute solutions of ethyllithium in hexane $\mu \approx 1.1$ D; whereas the dipole moment of ethyllithium in benzene is equal to 0.77 D and does not change upon dilution. The different behavior of ethyllithium in aliphatic and aromatic hydrocarbons can be explained by the fact that the energy of the dispersion interaction between the cyclic associates and the benzene molecules is greater than with hexane molecules, owing to the greater polarizability of the molecules of the former solvent. The lower solubility of ethyllithium in hexane is apparently connected with this.

Our data indicate that benzene does not participate directly in the association of ethyllithium.

On the basis of all the experimental data we arrived at the conclusion that an association of organolithium compounds exists by means of an intermolecular lithium bond. Let us consider all possible cases of formation of this bond.

$$^{-\delta}-\mathrm{C}-{}^{+\delta}\mathrm{Li}\cdots{}^{-\delta}\mathrm{C}-{}^{+\delta}\mathrm{Li}\cdots;$$

$$^{-\delta}-\mathrm{C}-{}^{+\delta}\mathrm{Li}\cdots{}^{+\delta}\mathrm{H}-{}^{-\delta}\mathrm{C}-;$$

$$^{-\delta}-\mathrm{C}-{}^{+\delta}\mathrm{Li}\cdots{}^{+\delta}\mathrm{Li}-{}^{-\delta}\mathrm{C}-$$

Fig. 3. Infrared spectra of solutions of ethyllithium in hexane at different concentrations.

Figure 3: Fig. 3. Infrared spectra of solutions of ethyllithium in hexane at different concentrations.

Fig. 3. I.r. spectra of solutions of ethyllithium in hexane at different concentrations.
a—0.6 *N* solution, *b*—0.4 *N* solution, *v*—0.27 *N* solution. NaCl prism, $d = 0.1$ mm

Of the three possible cases, the first type of interaction is the most probable, because the groups

$$^{-\delta}\mathrm{C} - {}^{+\delta}\mathrm{Li}$$

possess dipole moments whose oppositely charged ends face one another. In the second and third cases the dipoles face one another with like-charged ends, and therefore these cases of interaction are less probable. If a lithium bond of the group $\mathrm{C} - \mathrm{Li}$ with a hydrogen atom, $\mathrm{C} - \mathrm{Li} \cdots \mathrm{H} - \mathrm{C}$, were realized, this interaction would be more favorable with hydrogens of methyl groups, and not only of molecules of organolithium compounds, but also of the solvent. In the presence of the interaction $\mathrm{C} - \mathrm{Li} \cdots \mathrm{H} - \mathrm{C}$, changes in the bands of the CH_3 group should be observed in the spectrum, and there would be no dependence of the intensities of the bands of the $\mathrm{C} - \mathrm{Li} \cdots$ groups on the concentration of the solvent. Experiment shows the opposite. Thus, there remains the sole possibility of explaining the association of organolithium compounds by means of a lithium bond involving the groups

$$^{-\delta} - \mathrm{CH}_2 - {}^{+\delta}\mathrm{Li} \quad \text{and} \quad {}^{-\delta}\mathrm{C} - {}^{+\delta}\mathrm{Li}.$$

An important condition ensuring the formation of a lithium bond between the groups

$$^{-\delta} - \mathrm{CH}_2 - {}^{+\delta}\mathrm{Li} \cdots {}^{-\delta}\mathrm{CH}_2 - {}^{+\delta}\mathrm{Li}$$

is the presence of dipole moments. However, direct interaction between the lithium and carbon atoms of two molecules

$$^{-\delta}\mathrm{C} - {}^{+\delta}\mathrm{Li} \cdots {}^{-\delta}\mathrm{C} - {}^{+\delta}\mathrm{Li}$$

is hindered by shielding by two hydrogen atoms bonded to carbon. Apparently, the lithium bond is also realized with some participation of the hydrogen atoms of the methylene group. This supposition is in agreement with the fact that bands with frequencies in the region 2750–2870 cm^{-1} are found in the spectrum of ethyllithium; these may be assigned to the groups $-H_2C-Li\cdots$ participating in the association. The indicated frequencies are not observed in the spectrum of ethyllithium vapor. Thus,

basis of the study of the infrared spectra of organolithium compounds we have discovered and investigated the phenomenon of the formation of an intermolecular lithium bond

$$\cdots\overset{-\delta}{CH_2}-\overset{+\delta}{Li}\cdots\overset{-\delta}{CH_2}-\overset{+\delta}{Li}\cdots \quad \text{and} \quad -\overset{-\delta_1}{C}-\overset{+\delta_1}{Li}\cdots\overset{-\delta_1}{C}-\overset{+\delta_1}{Li}\cdots$$

A special feature of this bond is that the carbon atom participating in its formation does not have an "unshared" electron pair. Nevertheless, this bond is sufficiently strong (the relative shift reaches 17%).

The explanation of these facts should apparently be sought in the special nature of the lithium atom: its small radius, considerably lower ionization potential, and greater possibility of using the *p*-orbital as compared with the hydrogen atom.

Apparently, the nature of the forces responsible for the association of molecules of organolithium compounds by means of the lithium bond does not differ in principle from the forces arising in the case of the formation of hydrogen bonds in the molecules B_2H_6 and R_2AlH (9). The formation of the lithium bond in the systems: $\overset{-\delta}{CH_2}-\overset{+\delta}{Li}\cdots\overset{-\delta}{CH_2}-\overset{+\delta}{Li}$ may be understood from the standpoint of the formation of molecular orbitals with the participation of the valence electrons of the CH_2-Li groups, as well as of the dipole interaction between them.

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