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Abstract

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Study of the Structure of Complexes of Organolithium Compounds with Simple Ethers by the Method of Infrared Spectra

Our earlier investigations showed that organolithium compounds are covalent and form complexes ([1]). On the basis of our own and literature data we came to the conclusion that the nature of these complexes is evidently close to that in compounds of boron, beryllium, and aluminum, and is due to the collectivization of the valence electrons of the C—Me bonds with the formation of multicenter orbitals involving the vacant *p*-orbitals of the metal atom. If lithium, with respect to complex formation, can indeed be placed in the same series as Be, B, and Al, then it should be expected that other types of complexes, studied for compounds of Be, B, and Al, should also occur in the case of organolithium compounds. Thus, it is known that compounds of Be, B, and Al can form complexes of the acceptor-donor type through filling of the vacant *p*-orbitals of the metal atom by an unshared electron pair belonging to the donor molecule ([2,3,4]). As investigations have shown, the strength of such complexes depends on the donor strength of the partner and decreases in the series:

$$\text{tert.-amine} > \text{tert.-phosphine} > \text{ether} > \text{sulfide.}$$

Organolithium compounds also form complexes with ethers and amines ([5,6,8]), but there have been no detailed studies of these complexes. It is known only that the stability of ether solutions of organolithium compounds depends to a large extent on the structure of both the ether and the organolithium compound, and increases in the series ([7]):

$$(n\text{-}C_{12}H_{25})_2O < (C_2H_5)_2O < (C_3H_7)_2O < (n\text{-}C_4H_9)_2O < (n\text{-}C_6H_{13})_2O.$$

At the same time, the question of the interaction of organometallic (and, in particular, organolithium) compounds with ethers, amines, etc., is not only of theoretical interest, since small additions of such donor molecules lead to a sharp change in the reactivity of organometallic compounds, which is evidently connected with a change in the character and strength of the complexes. Clarification of this question could, to some extent, make it possible to control the course and rate of the reaction.

The aim of the present work was to elucidate, with the aid of infrared absorption spectra, the influence of simple ethers on the structure and character of complexes of organolithium compounds. The spectra were measured on an H-800 double-beam infrared spectrometer with a NaCl prism in the region from 2000 to 650 cm^{-1}, in a 100 μ cell.

All the substances investigated were either dissolved in ethers or obtained directly in them; moreover, in the latter case the presence of a large amount of LiBr did not lead to noticeable changes in the spectral region studied. Some organolithium compounds were also investigated in benzene solutions with gradual addition of ethers.

The spectra obtained were compared with the data of our earlier works ([1]), on the basis of which the absorption bands were assigned to vibrations of the C—Li···O groups.

On considering the data obtained (Table 1), it is seen that in the spectra of freshly prepared solutions of almost all the organolithium compounds studied—

Fig. 1. A —IR spectra of phenyllithium solutions in ethers: 1 —in diethyl ether (0.75 N), 2 —in dipropyl ether (1.16 N), 3 —in dibutyl ether (0.67 N). **B** —IR spectra of aromatic organolithium compounds in dibutyl ether: 1—phenyllithium (0.67 N); 2 —*o*-tolyllithium (0.91 N), 3—*p*-tolyllithium (0.8 N). NaCl prism; $d = 100\mu$

Table 1

Frequencies of C—Li vibrations in cm^{-1}

No.	Compounds	$(C_2H_5)_2O$	$(n\text{-}C_3H_7)_2O$	$(iso\text{-}C_3H_7)_2O$	$(n\text{-}C_4H_9)_2O$	$(iso\text{-}C_5H_{11})_2O$
1	Methyllithium	900(4); 1008(7)	890(2); 975(2)	—	900(3); 1045(5)	—
2	Ethyllithium	895(6); 994(2)	885(4);	—	893(6)	893(6); 1053(3)
3	*n*-Butyllithium	900(6); 965(7); 1000(7)	—	—	—	—
4	Phenyllithium	903(5); 979(6); 1002(7)	975 (2)	963(4)	1068(5)	1065(5)
5	*o*-Tolyllithium	905(4); 965(2); 1000(6)	980(4)	970(6)	1060(6)	1054(4); 1073(4)

No.	Compounds	$(C_2H_5)_2O$	$(n\text{-}C_3H_7)_2O$	$(iso\text{-}C_3H_7)_2O$	$(n\text{-}C_4H_9)_2O$	$(iso\text{-}C_5H_{11})_2O$
6	*m*-Tolyllithium	898(3); 998(4)	905(4); 920(4); 1000(4)	–	1067(5)	1065(4)
7	*p*-Tolyllithium	900(3); 995(6)	973(4)	–	1072(4)	1063(4)
8	*p*-Cl-phenyllithium	–	–	968(7)	1063(4)	–
9	*p*-Br-phenyllithium	–	–	963(7)	1067(6)	–
10	Mesityllithium	–	–	–	1080(5)	–
11	Fluorenyllithium	900(3); 975(8); 998(5)	–	973(5)	1073(3)	1065(3)

···compounds in one and the same ether, a similar picture is observed (Fig. 1A). Replacement of one ether by another, however, sharply affects the positions of the bands that we have assigned to the C–Li···O groups (Fig. 1B).

Analysis of the spectra shows that, as the hydrocarbon radicals in the ethers become more complex, the bands of the C–Li···O groups shift toward shorter wavelengths.

Fig. 2. A –IR spectra of solutions of methyllithium in diethyl ether (0.78 N): 1 –fresh solution, 2 –solution aged under argon for 7 days. B –IR spectra of solutions of methyllithium in dibutyl ether: 1 –dissolved at 20°, 2 –dissolved at 120°. NaCl prism; $d = 100\ \mu$.

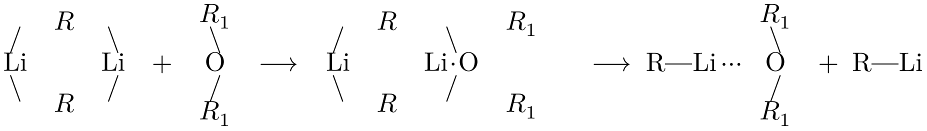
Thus, if in the spectra of all the organolithium compounds studied in diethyl ether the most shifted bands are observed at about 900 cm^{-1}, then in dipropyl and diisopropyl ethers they occur at 970 cm^{-1}, while in dibutyl and diisoamyl ethers there is only one intense band at about 1050–1090 cm^{-1}, which we already assign to a free or weakly bound C–Li group. This is evidently a consequence of steric hindrance to the approach of molecules to distances sufficiently short for complex formation. In this case, owing to the equal donor strength of the aliphatic ethers, the final result in all cases should be complexes of similar strength (as in the etherates of organoaluminum compounds (^{4})), but their formation proceeds the more slowly, the more complex the structure of the ethers and of the molecules of the organolithium compound.

Thus, whereas for the most active organolithium compound–ethyllithium–a complex absorbing at about 900 cm^{-1} is formed almost immediately in all ethers, for more complex and less active molecules this process proceeds with time. Indeed, on standing, a solution of *o*-tolyllithium

in dibutyl ether under argon over the course of several days there occurs a weakening of the intensities of the bands of free and weakly bound C–Li groups

(1040-1060 cm^{-1}) and a strengthening of the band near 900 cm^{-1}. The same is observed in the case of methyllithium and *n*-butyllithium in diethyl ether (Fig. 2A). The process of formation of a strong complex can be accelerated by raising the temperature of the solution, as is seen from Fig. 2B.

Thus, when organolithium compounds are dissolved in ethers, at first, apparently, deformation and dissociation of the primary complexes occur owing to acceptor-donor and dipole interaction with the ether; then, gradually (depending on the structure of the radicals of both components), new complexes are formed between the molecules of the ether and the organolithium compound according to the acceptor-donor type.



At the same time, as the strength of the new complexes increases, the polarity of the C—Li bond is enhanced, which should be manifested in a change in the reactivity of the organolithium compound and in the stability of the latter in solution. This, probably, is the reason for the high activity of ethyllithium in many reactions carried out in ethereal solutions, and for its low stability in this medium.

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Note: Figure translations are in progress. See original paper for figures.