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Abstract

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STUDY OF THE STRUCTURE OF LITHIUM ALKOXIDES BY INFRARED ABSORPTION SPECTRA

the O–Li···O bond

The study of the structure of organolithium compounds by various methods (IR spectra, cryoscopy, dipole moments ([1–3])) has shown that these compounds are associated. Complexes of organolithium compounds are, by their nature, similar to the known complexes of B, Be, Al that arise as a result of the formation of three-center molecular orbitals involving electrons that form primary chemical bonds B–H, Be–C, Al–C, etc. ([4,5]). In contrast to the groups Li–C, Al–C, and the like, the groups Li–O, Al–O, and others can form secondary chemical bonds not only through the formation of multicenter electronic molecular orbitals, but also through acceptor-donor interaction, as a result of which complexes involving Li–O, Al–O groups and others should be stronger than those involving bonds of the first type.

The present work was undertaken with the aim of studying the structure of compounds R–O–Li and of experimentally verifying the considerations stated regarding their complex formation.

Of the lithium alkoxides we obtained, lithium tert-butoxide, tert-C_4H_9OLi, readily soluble in various organic solvents, was studied in the greatest detail. This compound was prepared by the action of metallic lithium on tert-butyl alcohol in diethyl ether, then isolated in crystalline form and purified by fourfold recrystallization from ether and hexane.

The preparation of compounds R–O–Li and the various operations with them were carried out in an argon atmosphere.

In order to study the properties of the O–Li bond, the specific electrical conductivity of tert-C_4H_9OLi was measured in a hexane solution with a concentration of $1.17\,N$ at room temperature; it proved to be less than $2 \cdot 10^{-7}\ \Omega^{-1}$. The dipole moment of lithium tert-butoxide in hexane solution at $+25^{\circ}$C, measured by V. N. Vasil' eva, is close to $0.74\,D$.

Finally, from data on molecular-weight measurements by the cryoscopic method,

kindly carried out by V. A. Dubovitskii and O. V. Nogina, it follows that tert-C_4H_9OLi, dissolved in cyclohexane, is associated at a solution concentration of 0.088 N, the association factor being equal to 5 (molecular weight calculated 80.06, found 396). The value of the dipole moment given above apparently refers to the complex, the formation of which is also possible in hexane solution.

Thus, the data obtained make it possible to conclude that the O–Li bond in tert-C_4H_9OLi is covalent in character and that association is present even in dilute solution. The IR spectra measured by us for tert-C_4H_9OLi in the crystalline state and in solutions (Table 1) confirm the conclusion stated above. The spectra were recorded on double-beam IR spectrometers IKS-14 and H-800 of the Hilger firm.

Table 1

Crystalline state(paste in Vaseline or fluorinated oil)	Solution in hexane1.17 N;50 μ layer	Solution in $CCl_4$0.4 N;50 μ layer	Frequency assignment ([6]-[8])
2945 (v.s.)2850 (s.) 1925 (w.)	~2950 (s.)~2850 (m.)	2950 (s.)2850 (m.)	Valence vibrations C–H
1470 (w.)1375 (m.)1353 (s.)	~1460 (w.)1378 (w.)1355 (m.)	1467 (m.)1378 (m.)1354 (s.)	Deformation vibrations of CH_3 groups
1209 (v.s.)	1212 (v.s.)	1210 (v.s.)	Valence vibrations >C–O
1013 (m.)	1012 (w.)	1009 (w.)	Deformation vibrations (“rocking”) of CH_3 groups
970 (v.s.)	971 (s.)	971 (s.)	>C–O–(Li)
883 (w.)	868 (v.w.)	880 (v.w.)	Deformation vibrations (“rocking”) of CH_2 groups
748 (m.)	746 (m.)	?	Valence vibrations C–C
578 (v.s.)507 (s.)	580 (s.)510 (m.)	579 (s.)510 (m.)	Vibrations of associated O–Li
462 (m.)~395 (s.)	463 (m.)~400 (m.)	461 (m.)400 (m.)	Deformation vibrations C–C–C

The IR spectra of solutions of tert.-C_4H_9OLi in hexane, CCl_4, cyclohexane, dioxane, diethylamine, and triethylamine do not differ substantially from the

spectrum of the crystalline sample. Raising the temperature, in the case of the solution in triethylamine, to +70-80° C likewise does not lead to any noticeable change in the spectrum. Such indifference of tert.-C_4H_9OLi toward active solvents and elevated temperatures indicates the great strength of its complexes.

A rough calculation carried out for CH_3OLi shows that the appearance of the frequency of the valence vibration of a free O—Li group should be expected in the region 1400-1700 cm^{-1}; however, the data of studies on the IR spectra of alcohols ([6-8]), as well as the spectra of tert.-C_4H_9ONa and tert.-C_4H_9OK obtained by us for comparison, do not allow any of the bands in the indicated region, or in any other region, to be assigned to vibrations of a free O—Li group. At the same time, the intense bands in the long-wavelength part of the spectrum with frequencies 580 cm^{-1} and 510 cm^{-1}, absent in the spectrum of tert.-C_4H_9OH and disappearing first upon decomposition of tert.-C_4H_9OLi in air, should apparently be assigned to complex vibrations of a chain with lithium bonds ("bridges") ···Li—O···Li—O···Li —in a complex having, possibly, a spatial structure (of the tetrahedral type) in the case of the pentamer.

Funk ([10]), who studied Raman spectra and IR spectra of Be and Li acetylacetonates, assigned, in the latter case, a band with frequency 510 cm^{-1} to the metal—ligand vibration. The nature of the bond in the O—Li···O bridge of the quasiaromatic ring of lithium acetylacetonate ([11]) differs little from the case considered by us, but, apparently, its strength is greater in the former case.

The existence of strong complexes of tert.-C_4H_9OLi can probably be explained by two causes: 1) the formation of three-center intermolecular electron orbitals by the lithium atom of one molecule supplying a free p-orbital for the electrons participating in the σ-bond O—Li of another molecule; as a result, this pair of valence electrons participates in the formation of two O—Li···O bonds (I a); 2) an acceptor-donor interaction through use of the unshared pair of p-electrons of the oxygen atom and the free p-orbital of lithium in another molecule,

additionally strengthens the intermolecular bond (I b). In the case under consideration, taking into account the overlapping three-center molecular orbitals and the participation in the formation of the intermolecular bond of the lone pair of *p*-electrons of the oxygen atom, one may apparently speak of a significant delocalization of the electrons with the formation of multicenter molecular orbitals. One may suppose that in crystals there exist peculiar polymeric chains consisting of some number of quasi-conjugated bonds O—Li ... O, of type (I)

$$\cdots \text{Li—O} \cdots \text{Li—O} \cdots \text{Li—O} \cdots \qquad (I)$$

or of some other formations with effective delocalization of electrons, which may lead to a decrease in the energy difference between the ground and excited electronic states of the system. A basis for such an assumption may be provided by the fact that luminescence has been observed in compounds of this class.

We have obtained the luminescence spectrum of crystalline and of hexane-dissolved tert-C_4H_9OLi (rather bright in the case of crystals and appreciably weaker emission in solutions) upon excitation with wavelength $\lambda = 365$ mμ at $T = 77°K$, which is a broad band with a maximum in the region of 430 mμ. In the case of the solution in hexane, the maximum of the fluorescence band is about 410 mμ. The absorption of light by the system, within the framework of our treatment, can be explained by the transition of an electron from the multicenter molecular orbital of the ground state to an excited multicenter orbital. Another possibility for excitation of the system consists in the transition of an electron of the lone pair of the oxygen atom to an excited multicenter orbital.

In addition to the compound described, we studied the IR spectra of a series of lithium alcoholates with normal aliphatic radicals: CH_3OLi, C_2H_5OLi, *n*-C_3H_7OLi, and *n*-C_4H_9OLi. These alcoholates are crystalline compounds, decomposing in air, very slightly soluble or not at all soluble in organic solvents (hexane, cyclohexane, benzene, toluene, pyridine, dioxane, diethylamine, triethylamine, etc.), in view of which we were unable to obtain sufficiently distinct spectra of solutions. The spectra of crystalline samples (paste in Vaseline or fluorinated oils) are given in Table 2 (frequencies in cm^{-1}).

Bearing in mind that tertiary lithium butylate is strongly associated, one may suppose that lithium alcoholates with unbranched aliphatic radicals are even more strongly associated, which explains their insolubility or very slight solubility (in the alcoholates with a longer hydrocarbon chain) in those solvents in which tert-C_4H_9OLi dissolves well. The existence of associates of ROLi compounds is in agreement with data on the ability of metal alkoxides to polymerize ([20]). The *n*-ROLi compounds also give luminescence spectra (in the present work we shall not examine this question in detail), which, possibly, serves as confirmation of the presence of association between molecules in crystals. From this point of view, taking into account data on the IR spectra of the corresponding alcohols, alcoholates of Ge, Al, etc. ([12,6,13–19]), spectra of the methylates and ethylates of Na and K obtained by us for comparison, and also the behavior of bands in the spectra under the action of air on R—O—Li (broadening of bands up to their disappearance), one may approximately assign the principal bands in the spectra and, in particular, assign to complex vibrations of associated O—Li groups in band complexes with frequencies: CH_3OLi 670 cm^{-1}, 537 cm^{-1}; C_2H_5OLi–675 cm^{-1}, 515 cm^{-1}, 457 cm^{-1} (?); *n*-C_3H_7OLi–576 cm^{-1}, 527 cm^{-1}, 498 cm^{-1}; *n*-C_4H_9OLi 565 cm^{-1}, 483 cm^{-1}.

Table 2

Crystalline CH_3OLi	Assignment of principal frequencies	Crystalline CH_3OLi	Assignment of principal frequencies
2923 (med.)	C–H stretching vibrations	1060 (v. s.)	C–O stretching vibration
2842 (s.)	C–H stretching vibrations	862 (w.)	?
2792 (s.)	C–H stretching vibrations	760 (w.)	?
2595 (w.)	?	670 (med.)	Associated Li–O vibrations
2080 (w.)	2-C–O stretching	585 (med. shoulder)	Associated Li–O vibrations
1570 (med.)	?	537 (s.)	Associated Li–O vibrations
1435 (s.)	Deformation vibrations of CH_3	428 (s.)	Deformation vibrations of CH_3 relative to C–O
1318 (s.)	Deformation vibrations of CH_3	410 (med. shoulder)	Deformation vibrations of CH_3 relative to C–O
1160 (med.)	$-OCH_3$		

C_2H_5OLi: 2957 (s.), 2917 (med. shoulder), 2848 (s.), 2808 (s.), 2713 (med.), 2606 (med.), 2123 (w.), 1794 (w.), 1490 (med. shoulder), 1455 (s., unresolved), 1435 (s.), 1378 (v. s.), 1363 (med. shoulder), 1155 (s.), 1107 (v. s.), 1058 (v. s.), 970 (w., shoulder), 885 (s.), 720 (broad), 675 (s.), 515 (s.), 457 (med. shoulder), 428 (med.), 405 (med.).

n-C_3H_7OLi: 2945 (s.), 2910 (med.), 2860 (med.), 2835 (med.), 2790 (s.), 2700 (med.), 2660 (w.), 2600 (v. s.), 2155 (w.), 1630 (med. broad), 1450 (med.), 1380 (s.), 1297 (broad), 1247 (w.), 1153 (med. shoulder), 1110 (s.), 1078 (v. s.), 1015 (med.), 976 (w.), 882 (s.), 576 (s.), 527 (s.), 498 (med.), 450 (med.), 395 (s.).

n-C_4H_9OLi: 2950 (v. s.), 2905 (v. s.), 2843 (s.), 2800 (s.), 2710 (med.), 2595 (w.), 1625 (broad), 1455 (s.), 1432 (s.), 1375 (s.), 1155 (med.), 1120 (med.), 1085 (v. s.), 1002 (med.), 970 (w.), 905 (w.), 882 (w.), 800 (w.), 730 (med.)?, 672 (w.), 565 (v. s.), 483 (s.), 435 (v. s.), 400 (s.).

However, a more exact assignment of the bands in the spectra and more definite

conclusions concerning lithium alcoholates with a normal aliphatic radical will become possible as a result of using data from the study of isotopically substituted compounds (D, Li^6), X-ray structural analysis of compounds (^{21}), and also calculations of the vibrations of the simplest free and associated molecules R–O–Li.

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