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Abstract

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Investigation of the Nature of Secondary Chemical Bonds

The phenomenon of delocalization of valence electrons that originally belonged to a given primary bond, accompanied by the appearance of multicenter molecular orbitals and the formation of new (secondary) chemical bonds, is observed in extensive classes of compounds. A large number of works have been devoted to this problem ([1], [2]). If primary (strong) chemical bonds are formed through direct interaction of the valence electrons of neighboring atoms, then secondary (less strong) bonds in many cases arise as a result of an additional interaction of these valence electrons, which manifests itself after their entry into the common system of chemical bonds of the molecule, when the energy states of the electrons change substantially. Thus, the emergence of secondary chemical bonds depends not only on the nature of the given atom that has entered the molecule, but also on the properties of the entire molecular system, and on the character of the distribution of electron density in the molecule. In order to study the nature of the indicated types of chemical bonds, we have studied in detail the infrared absorption spectra of organolithium compounds, as well as various acetylene derivatives. Analysis of the infrared spectra of the compounds R—Li and Ar—Li shows that the free C—Li group has a characteristic frequency of valence vibration of 1050-1100 cm^{-1}. On the basis of measurements of the dipole moments of dilute solutions of R—Li compounds in hexane, the electric moment of the C—Li bond was found; it proved to be equal to 1.1-1.2 D. The presence of vibrational frequencies and the comparatively small dipole moment of the C—Li bond make it possible to conclude that this bond has a covalent character in the studied classes of organolithium compounds. In the infrared spectra of crystalline organolithium compounds and of their solutions (in benzene, hexane, etc.), additional bands are found which are absent from the spectra of vapors and are shifted relative to the latter toward longer wavelengths (870 cm^{-1}, 926 cm^{-1}, 970 cm^{-1}). These bands characterize the valence vibrations of —C—Li···groups participating in the formation of complexes. The strong change in the frequencies of the valence vibrations of C—Li groups

$$(\Delta\nu = \nu_0 - \nu = 1050 - 870 = 180\ \text{cm}^{-1})$$

indicates their direct participation in the formation of complexes. With respect to complex formation, lithium may be placed in the same series with the elements Be, B, Al, etc. Molecules of organolithium compounds, analogously to compounds of Be, B, Al, etc., form complexes with one another by means of the lithium bond, which is a secondary chemical bond. Thus, to the known series of complexes of compounds of B, Be, Al may now be added complexes of organolithium compounds, for example:

[structural formulas of cyclic complexes involving Li, Be, B, and Al bonds]

Direct experimental proof of the common nature of the secondary chemical bonds responsible for the association of molecules of organometallic compounds of lithium, beryllium, boron, and aluminum is the existence of mixed complexes between these compounds of the type: $R{-}Li \cdot Be(R)_2$; $R{-}Li \cdot Al(R)_3$, etc. (6). The common nature of secondary chemical bonds in complexes of organometallic compounds of Li, Be, B, Al, etc., is due to the characteristic nature of these elements and their primary chemical bonds M–C. Common to all the elements is the presence of vacant, energetically low-lying *p*-orbitals and the possibility, with a small expenditure of energy, of changing the energy state of the valence electrons in the direction $s \to p$. Thus, the possibility is created for the formation of multicenter molecular electron orbitals, and in particular three-center ones, which occurs in the complexes of the compounds Li, Be, B, Al (12), etc., under consideration. Consequently, atoms of the indicated elements can participate in the formation of chemical bonds not only by using valence electrons, but also by providing vacant orbitals for electrons participating in the formation of primary bonds in other molecules. As a result of this, secondary chemical bonds arise between molecules. For example, in the case of a dimeric complex of an organolithium compound, each "bridging" carbon atom can form with two lithium atoms a three-center orbital (two electrons in the field of three nuclei). Such an orbital is energetically more stable than an ordinary C–Li bond, since the lithium atom can provide for bond formation not only one valence electron, but is also capable of providing two orbitals. The common nature of primary and secondary chemical bonds in organometallic compounds of Li, Be, Al, etc., is manifested in the similarity of their physicochemical properties (solubility in nonpolar solvents, small dipole moments, etc.). Therefore it is not surprising that organolithium compounds, as well as organoaluminum compounds, having atoms and primary and secondary chemical bonds analogous in their nature, are catalysts in the polymerization reaction of ethylene and its derivatives. From all that has been said it is clear that the physicochemical properties and reactivity of organolithium, organoaluminum, etc., compounds should be explained from the standpoint of the covalent character of the bonds (C–Li, C–Al, etc.) and their pronounced ability to form secondary chemical bonds with one another and with other molecules. Therefore it may be considered that one of the main elements of the mechanism of initiation of the polymerization reaction of ethylene and its derivatives with the participation of R–Li or $Al(R)_3$ is the formation of a complex between a monomer molecule and a molecule of the organometallic compound (of type (I))

$$>\mathrm{C}{=}\mathrm{C}<\cdots\underset{p}{\overset{\mathrm{M}}{\vdots}}-\mathrm{C} \qquad \text{(I)}$$

(p-vacant orbital of the metal Li, Al, etc.). In this complex a secondary chemical bond arises as the result of formation of a three-center orbital (two π-electrons in the field of three nuclei). The formation of the indicated complex, apparently, in some cases may initiate the chain process of polymerization. Compounds of the $TiCl_4$ type are also capable of activating the double bond and destroying secondary chemical bonds between Me—C groups, which promotes the formation of the main complex (I). With the aid of EPR, the authors and V. I. Smirnova showed that, in the interaction of $TiCl_4$ with R—Li, radicals arise. It is known that some polymerization processes are initiated by R—Li compounds in the absence of $TiCl_4$. The strength of complex (I) will depend on the character of the π-bond, steric factors, and other features of the structure of the monomer molecule, as well as on the nature of the primary chemical bond Me—C and the characteristics of the vacant orbital, -

constituted by the metal (Me). Direct experimental proof of the possibility of formation of complex I is the appearance of colored complexes of ethyllithium with styrene, α- and β-methylstyrene, and other unsaturated compounds, which leads to the appearance in the IR spectrum of an intense new C=C band shifted to the long-wavelength side (~1580 cm^{-1}) and disappearing with the disappearance of the color. The associates of lithium acetylides studied by us (^{7}) and of the acetylene molecules themselves and their derivatives (^{8}) may be assigned to the same type of complexes. Another interesting property of the lithium atom in C—Li groups is its ability, analogously to atoms of B, Be, Al, to form secondary bonds by acceptor-donor interaction (with participation of unshared electron pairs of donor atoms), thereby forming stable complexes R—Li···X (where X = O<, N<, etc.). Our study of the IR spectra of ethyllithium and butyllithium in hexane solution with additions of various ethers and tertiary amines, as well as Ar—Li dissolved in ethers, shows the presence of complexes of the indicated type differing in strength. On the basis of the results obtained, it may be predicted that the catalytic activity of organolithium compounds can be regulated by various additives (ether, amine, halide, etc.), which change the character of the R —Li···complexes or destroy them completely. The strength of complexes formed with participation of secondary chemical bonds depends on the characteristic features of the primary chemical bond (polarity, strength). The indicated features of the Me—C bond are determined to some extent by the mutual influence of groups in the molecule. Thus, for example, σ,π-conjugation of the bonds

$$\overset{+\delta}{\mathrm{Li}} \overset{\sigma}{-} \overset{-\delta}{\mathrm{C}} - \mathrm{C} \equiv \mathrm{C}-$$

in benzyllithium compounds (C_6H_5—CH_2Li), fluorenyllithium, etc., can appreciably change the polarity and strength of the C—Li bonds. The σ,π-conjugation under consideration causes changes in the electronic spectra of molecules and is the reason for the color of a number of organolithium compounds. In contrast to C—Li, C—Al, etc. groups, O—H, N—H, and other bonds cannot form secondary chemical bonds through three-center orbitals with participation of the electrons of the primary bond, since O, N, or H atoms have no vacant low-energy orbitals. Therefore, for O—H, N—H, etc. groups in systems without π-electrons, participation in the formation of secondary chemical bonds of the acceptor-donor type is characteristic, through the use of unshared electron pairs of the donor atom A—H···B. At the same time, O—Li, Al—O, etc. groups can form secondary chemical bonds both of the acceptor-donor type and with the aid of three-center orbitals involving the electrons of the primary bond. However, from the standpoint of maximum delocalization of valence electrons, for R—O—Li the formation of secondary chemical bonds through three-center orbitals is the most energetically favorable; this provides the key to explaining the characteristic properties of R —O—Li compounds manifested in vibrational and electronic spectra, as well as in the electrical properties of molecules.

Especially effectively, O—Li, O—Al, etc. groups participate in the formation of secondary intramolecular metal-element bonds in molecules with π-electrons of the acetylacetonate type (inner-complex compounds). In this case O—H, N—H, etc. bonds behave analogously to O—Li, O—Al···and other groups: they form intramolecular secondary chemical (hydrogen) bonds which, in their nature, differ little from metal-element secondary bonds ([3,9]). In the systems considered, the energy of secondary intramolecular hydrogen or metal-element bonds is determined by the equation: $E = E_\mathrm{d} + E_\mathrm{a} + E_\pi$ (E_d and E_a are the energies of dipole and acceptor-donor interaction). The term E_π determines the energy of interaction of the O—H, O—Li, O—Al, etc. group with the π-electrons of the system and has the greatest value ([3,6,1]).

In systems such as acetylacetonates and similar compounds, quasi-aromatic rings with π-electron interaction are formed as a result of the sharing of six electrons of the system (four π-electrons of the C=C and C=O bonds and two electrons of the primary —O bond).

The study of the IR spectra of intracomplex compounds of metals (Al, Cr, Fe, Cu, Mg, etc.), carried out by one of us ([9]), showed that in these substances an almost complete equalization of the corresponding bonds in the rings is observed. These results are in agreement with X-ray structural data ([13]). The principal factors determining the formation of a ring with π-electron interaction and equalized bonds are: first, deformation of the electron cloud of the —O group in a direction perpendicular to the bond ($\sigma \to \pi$), which is promoted by the strong σ, π-conjugation —O—C=C—; second, the presence of free p- or d-orbitals at the metal atoms, used by the π-electrons of double bonds (C=O, etc.). With such an interpretation, it is also assumed that the changed p-orbital of the hydrogen atom is used by the π-electrons of the system, although with lower efficiency than in the case of metal atoms (Li, Al, etc.). The study of the electronic spectra of a number of systems shows that, in the excited state, the efficiency of utilization of the p^*-orbital of the hydrogen atom by the π-electrons of the system increases considerably (10). In the systems under investigation, the π-electrons of the C=O groups, using the free orbital of the atom (H, Li, Al, etc.), form a distinctive molecular three-center orbital, which also causes redistribution of the π-electron density in the system. Similarly, secondary bonds of π-electrons also arise in simpler systems

$$\mathrm{C = O + Al}$$

called π-complexes (11).

Thus, in intracomplex systems the atoms H, Li, Al, etc. participate in the formation of chemical bonds not only by using valence electrons, but also by providing free orbitals. Thus, the atoms of hydrogen and lithium use one valence electron each and additionally provide one orbital each, while the aluminum atom gives three valence electrons ($3s\,3p^2$) for bond formation and provides altogether six orbitals ($3s\,3p^3\,3d^2$), which corresponds to six equivalent Al—O bonds. If all that has been said is summarized, one may conclude that there exist various types of secondary chemical bonds which exert a strong influence on the physicochemical properties and reactivity of compounds.

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1. D. N. Shigorin, *ZhFKh*, **25**, 737 (1951); *ZhFKh*, **32**, 1739 (1958); *Probl. fiz. khim.*, issue 1, 171 (1958).
2. Ya. K. Syrkin, *Usp. khim.*, **28**, 903 (1959).
3. A. N. Rodionov, D. N. Shigorin et al., *Izv. AN SSSR, OKhN*, 1958, 120; *DAN*, **123**, 113 (1958); *Izv. AN SSSR, ser. fiz.*, **9**, 1110 (1958).
4. K. A. Kocheshkov, *Probl. fiz. khim.*, issue 1, 156 (1958).
5. D. N. Shigorin, *Acta Spectrochimica*, London, 1959, p. 226.
6. G. Wittig, F. Bickelhaupt, *Ber.*, **91**, 865 (1958).
7. A. N. Rodionov, G. V. Kazennikova et al., *DAN*, **129**, 121 (1959).
8. D. N. Shigorin, M. M. Shemyakin, N. N. Kolosov, *Izv. AN SSSR, OKhN*, 1958, 1133.

9. D. N. Shigorin, *ZhFKh*, **27**, 554 (1953); *Izv. AN SSSR, ser. fiz.*, **17**, 596 (1953).
10. D. N. Shigorin, N. A. Shcheglova, N. S. Dokunikhin, *DAN*, **133**, No. 2 (1960).
11. V. N. Filimonov, A. N. Terenin, *DAN*, **109**, 799 (1956).
12. E. G. Hoffmann, G. Schomburg, *Zs. Elektrochem.*, **61**, 1101 (1957).
13. L. M. Shkol' nikova, E. A. Shugam, *Kristallografiya*, **5**, 1 (1960); E. A. Shugam, *DAN*, **81**, 853 (1951).

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