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Abstract

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STUDY OF THE STRUCTURE OF COMPLEXES OF ALIPHATIC ORGANOLITHIUM COMPOUNDS

It is known that organolithium compounds are associated; the nature of these associates has not yet been definitively clarified, but it is evidently connected with the interaction of the groups CH_2—Li, leading to the formation of multicenter electron orbitals. The capacity of organolithium compounds for association is apparently decisive in the behavior of this class of compounds in numerous reactions.

With the aim of further investigating the structure of this class of compounds, we studied the IR spectra of aliphatic molecules R—Li. Their molecular weights were determined by the ebullioscopic method. In order to be able to assign the bands in the IR spectra accurately to definite vibrations and to clarify the participation of individual groups and atoms in the association, the IR spectra of isotopically substituted ethyllithium molecules were measured

$$(C_2H_5Li^7,\ C_2H_5Li^6,\ CH_3CD_2Li^7,\ CD_3CH_2Li^7,\ CD_3CD_2Li^7)$$

and of *n*-amyllithium (*n*-$C_5H_{11}Li^7$, *n*-$C_5H_{11}Li^6$) in the region from 4000 to 400 cm^{-1}. Ethyllithium derivatives were investigated in the vapor phase (beginning of distillation at $p \approx 8 \cdot 10^{-3}$ mm Hg and $t = 90$–$98°$), in solutions (benzene, hexane, diethyl and dibutyl ethers), and in crystals (in vaseline oil and in benzene solution at $-70°$).

n-Butyllithium, *n*-amyllithium, and *n*-dodecyllithium were studied only in solutions (benzene, hexane, cyclohexane, diethyl ether).

The IR spectra were measured on a Hilger H-800 double-beam spectrometer with LiF, NaCl, and KBr prisms. Ebullioscopic measurements were carried out on the apparatus described by A. I. Shatenshtein et al. ([1]).

Because of the great sensitivity of organolithium compounds to oxygen and moisture, all operations for preparing the substances and assembling the cuvettes were carried out in an atmosphere of dry argon.

Table 1 gives the principal bands observed in the IR spectra of isotopically substituted ethyllithium molecules in the vapor phase and in benzene solutions. From these data it is evident that the spectra for one type of molecule in the vapor phase and in benzene solution differ little from one another, whereas isotopic substitutions sharply change the spectrum.

Thus, the intense band near 500-550 cm^{-1} is noticeably shifted, upon replacement of Li^7 by Li^6, toward shorter wavelengths, and in the opposite direction upon replacement of H by D in the α-CH_2 group. Approximate calculations for the valence vibration of the CH_2—Li group under the above-mentioned substitutions give an analogous change in the frequency of this vibration. This confirms the correctness of assigning the band near 500-550 cm^{-1} to the vibration of the CH_2—Li group in the complex ([2,3]). The frequency of this vibration, moreover, is somewhat increased on going from ethyllithium to longer-chain organolithium compounds and decreases when neutral solvents are replaced by donor ones (Table 2). This is apparently connected mainly with the different strength, geometry, and type of complexes, which are affected by the polarity of the bond, steric hindrance of the radicals, the donor properties of the solvents, etc. The degree of association in this case noticeably

Table 1

IR spectra of isotopically substituted ethyllithium molecules

$C_2H_5Li^7$ vapor	$C_2H_5Li^7$ solution in benzene	$C_2H_5Li^6$ vapor	$C_2H_5Li^6$ solution in benzene	$CH_3CD_2Li^7$ vapor	$CH_3CD_2Li^7$ solution in benzene	$CD_3CH_2Li^7$ vapor	$CD_3CH_2Li^7$ solution in benzene	$CD_3CD_2Li^7$ vapor	$CD_3CD_2Li^7$ solution in benzene
2952	2945	2955	2960	2950	2950				
2920		2930			2930				
2880	2870	2875	2870	2870	2873	2811			
2846	2832	2841	2840			2780	2790		
2785	2792	2795	2790			2760	2750		
2760	2755	2750	2755			2215			2215
						2164	2158		2170
				2138	2135				
				2092	2080				2100
				2040	2035	2040	2046		2040
				1468					
1443	—	1445	—	1443	—				
1382	—	1387	—	1367	—	1382	—		
				1155		1124	1126		
1098	1095	1097	1090			1063	1074		
							1059		

$C_2H_5Li^7$ vapor	$C_2H_5Li^7$ solution in benzene	$C_2H_5Li^6$ vapor	$C_2H_5Li^6$ solution in benzene	$CH_3CD_2Li^7$ vapor	$CH_3CD_2Li^7$ solution in benzene	$CD_3CH_2Li^7$ vapor	$CD_3CH_2Li^7$ solution in benzene	$CD_3CD_2Li^7$ vapor	$CD_3CD_2Li^7$ solution in benzene
1049	1050	1047	1050	1044		1040	1037		
				983	975				984
945	–	950				940			937
916	900	921	923	906	910				
881	877					885	885		854
				710	–	755	758		
						727	725		684
									653
532	530	550	550	510	512	532	529		513

Table 2

Vibrational frequencies of CH_2–Li groups in complexes

Compound	Vapor	Hexane	Benzene	Diethyl ether	Dibutyl ether	Cryst. (benzene) at −70°
$CH_3CH_2Li^7$	531	528	527	497	516	442
$CH_3CH_2Li^6$	550	550	550	–	530	460
$CD_3CH_2Li^7$	532	529	–	504	512	–
$CH_3CD_2Li^7$	512	514	512	479	–	435
$CD_3CD_2Li^7$	–	515	513	481	–	436
n-$C_4H_9Li^7$	–	555	558	525	–	565
n-$C_5H_{11}Li^7$	–	550	–	–	–	–
n-$C_5H_{11}Li^6$	–	570	–	–	–	–
n-$C_{12}H_{25}Li^7$	–	556	–	–	–	562
n-$C_{12}H_{25}Li^7$	–	–	–	–	–	517

has no effect on the position of the band of the CH_2–Li group. Thus, although the degree of association decreases as the radical becomes more complex (ethyllithium and *n*-dodecyllithium in benzene, Table 3), the position of the absorption band of the CH_2–Li group differs by 30 cm^{-1} in the hexameric

complexes of ethyllithium and *n*-butyllithium in benzene and nearly coincides for hexameric *n*-butyllithium and the tetrameric complex of *n*-dodecyllithium in benzene. The lowering of the CH_2—Li vibrational frequency in ether solutions is apparently connected with the formation of complex acceptor–donor complexes between the initial complexes of the organolithium compound and ether molecules. At the same time, preservation of the hexameric complex in ether makes *n*-butyllithium more stable in this solvent than ethyllithium, which lowers the degree of association in ether at low concentrations to 4.5–5.

Table 3

Association factors of organolithium compounds

	Benzene	Benzene	Cyclohexane	Cyclohexane	Diethyl ether	Diethyl ether
	conc., mole %	assoc. factor	conc., mole %	assoc. factor	conc., mole %	assoc. factor
Ethyllithium	0.2—0.92	5.9±0.5	—	—	0.13—1.63	4.6—5.9
n-*Butyllithium*	0.19—1.5	7±0.5	—	—	0.11—0.46	6.2±0.4
n-*Dodecyllithium*	0.083—0.42	3.7±0.25	0.065—0.36	3.65±0.25		

It was noted earlier that in the spectra of ethyllithium solutions there is an intense band near 920 cm^{-1}, the origin of which was unknown (Table 1). Investigation of the infrared spectra of isotopically substituted molecules showed that this band is shifted upon various substitutions of H by D, but is not changed when Li^7 is replaced by Li^6. An approximate calculation for the C—C stretching vibration in five isotopically substituted ethyllithium molecules gave values close to the experimental ones. This made it possible to assign the bands in the region 925—850 cm^{-1}, observed in the spectra of ethyllithium vapors and solutions, predominantly to the C—C stretching vibration.

In the region of the C—H and C—D stretching vibrations, along with absorption lying within the limits usual for aliphatic radicals, intense bands are observed that are shifted by 50—100 cm^{-1} toward longer wavelengths (Table 1). The use of isotopic substitution in individual groups of the ethyl radical made it possible to establish that the frequencies of the absorption bands of the CH_3 groups do not differ noticeably from their usual values. The shifted bands, however, belong to vibrations of the CH_2 groups located in the α-position to the lithium atom. Moreover, these lowered bands are also observed in the spectra of *n*-butyllithium, *n*-dodecyllithium, etc.

An approximate calculation shows that the distortion of the H—C—Li angles possible upon formation of complexes cannot explain such a strong lowering of

the frequency of the C–H stretching vibration in the α-CH_2 group. Apparently, this is connected with a change in the valence state of the α-carbon atom as a result of an increase in the negative charge on it due to the inductive effect of the neighboring electropositive lithium atom. According to Bent' s data ([4]), an increase in the negative charge on the α-C atom should lead to some lengthening and weakening of the C–H bond located in the α-position relative to Li, and consequently to a lowering of the frequency of the stretching vibration of these bonds.

The calculation shows that, in order to lower the frequency of the C–H stretching vibration by 50–100 cm^{-1}, the force constant of this bond must be decreased from $8 \cdot 10^6$ to $7 \div 7.5 \cdot 10^6$ cm^{-2}, which, in comparison with Linnett' s data ([5]), is entirely possible for such an electropositive element as lithium. On going from solution to the crystalline state (in the case of ethyllithium), there occurs a considerable lowering of the vibration frequency of the CH_2–Li groups (Table 2) and a decrease in the difference in the positions of the C–C vibration band upon various isotopic substitutions. Substances that do not pass under the experimental conditions (benzene solution at −70°) into the crystalline state change their spectrum only slightly (*n*-butyllithium, *n*-dodecyllithium).

It is characteristic that in the spectra of ethyllithium derivatives, on going from solution to the crystalline state, only the isotopic shift upon replacement of Li^7 by Li^6 remains almost constant $\left(\frac{\nu_{CH2-Li^6}}{\nu_{CH2-Li^7}}\right.$ in solutions 1.037; in crystals 1.040), whereas replacement of H by D leads to a larger change in it $\left(\frac{\nu_{CH2Li^7}}{\nu_{CD2-Li^7}}\right.$ in solutions 1.029, in crystals 1.016).

The strong shift of the vibrational bands of the CH_2—Li groups, observed on passing from one aggregate state to another, and also the noticeable decrease in the isotopic shift upon replacement of H by D, are apparently connected with a change in the structure of the complexes. The valence vibrations C—H (C—D) change only slightly in these transitions.

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