A. P. SIMONOV, D. N. SHIGORIN, T. V. TALALAEVA

and Corresponding Member of the Academy of Sciences of the USSR K. A. KOCHESHKOV

1961

SovietRxiv

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Abstract

Full Text

PHYSICAL CHEMISTRY

A. P. SIMONOV, D. N. SHIGORIN, T. V. TALALAEVA
and Corresponding Member of the Academy of Sciences of the USSR K. A. KOCHESHKOV

INFRARED ABSORPTION SPECTRA OF CERTAIN COMPOUNDS R–O–Li

In work (^{1}) it was shown that the compounds R–O–Li are strongly associated through the formation of intermolecular O–Li . . . O bonds. To the vibrations of the associated O–Li groups in the infrared spectra studied in (^{1}) of lithium alcoholates with normal aliphatic radicals and tert-C_4H_9OLi were assigned bands with frequencies in the region 400–600 cm^{-1}.

In the present work the i.r. absorption spectra of three lithium alcoholates with branched aliphatic radicals were studied: iso-C_3H_7OLi,

Fig. 1. Spectra of sublimed crystalline samples:
1–iso-C_4H_9OLi, 2–$(C_2H_5)_2 \cdot CHOLi$

Fig. 2. Spectra of isotopically substituted derivatives of lithium methoxide (paste in Vaseline oil):
1–CH_3OLi^6, 2–CD_3OLi,
3–CH_3OLi

iso-C_4H_9OLi and $(C_2H_5)_2CHOLi$; and also of two isotopically substituted molecules CH_3OLi^6 and CD_3OLi. The first three compounds are crystalline substances, readily soluble in ordinary organic solvents and subliming without decomposition (including also tert-C_4H_9OLi(^{1})) in a vacuum of the order of $5 \cdot 10^{-2}$ mm Hg and at temperatures of +100–150°C. The indicated lithium alcoholates also proved to be strongly associated in solutions. V. A. Dubovitskii and O. V. Nogina measured their molecular weights by the cryoscopic method. The association factor for all these compounds is equal to 5 in cyclohexane and benzene solutions with concentrations of the order of 1 mole % and to 3 in solutions with concentrations ~ 0.5 mole %. This apparently indicates that association of the compounds studied occurs according to one pat-

Table 1*

iso-C_3H_7OLi, crystalline, deposited	*iso*-C_3H_7OLi, crystalline (paste in vaseline oil)	*iso*-C_3H_7OLi, solution in cyclohexane 0.3 N, 100 μ	*iso*-C_4H_9OLi, crystalline, deposited	*iso*-C_4H_9OLi, crystalline (paste in vaseline oil)	*iso*-C_4H_9OLi, solution in hexane 1.05 N, 100 μ	$(C_2H_5)_2CHOLi$, crystalline, deposited	$(C_2H_5)_2CHOLi$, crystalline (paste in vaseline oil)	$(C_2H_5)_2CHOLi$, solution in cyclohexane 0.24 N, 100 μ	Band assignment
1455 (s) 1367 (s)	1455 (s) 1370 (s)	1365 (m)	1455 (m) 1387 (m)	1453 (m) 1387 (m)	1450 (m) 1385 (m)	1468 (s) 1370 (s)	1450 (s) 1370 (s)	1365 (m)	Deform. vibr. C—H
1350 (v.s.) 1327 (m)	1350 (s) 1330 (w. sh)	1353 (m) 1330 (w)	1357 (m) 1330 (v.w)	1355 (m) 1330 (w)	1360 (m)	1303 (w)	1300 (w)		
1150 (v.s.) 1123 (v.s.)	1155 (s) 1123 (m)	1155 (s) 1120 (m)	1133 (s) 1090 (v.s.)	1133 (s) 1087 (v.s.)	1130 (s) 1090 (v.s.)	1182 (m) 1145 (s) 1115 (m)	1140 (v.s.) 1113 (s)	1137 (s) 1110 (m)	Valence vibr. C—O
1060 (w)	1055 (w)					1067 (m. sh) 1050 (m) 1027 (m) 987 (s)	1067 (m. sh) 1047 (m) 1025 (s) 985 (s)	1066 (w) 1048 (w) 1025 (m) 985 (m)	Deform. vibr. >C—O—Li
975 (v.s.)	975 (s)	975 (s)	1020 (m)	1017 (m)	1020 (m)				
			955 (w) 943 (m)	953 (m) 940 (m)	955 (w) 940 (m)	945 (w)	948 (m)	947 (w)	Valence vibr. C—C
			903 (m)	900 (m)	903 (m)	915 (m) 906 (w. sh) 853 (m)	915 (m) 905 (m) 853 (w)	915 (w)	
820 (s)	820 (m)	820 (m)	820 (m)	820 (m)	820 (m)	783 (m) 750 (m)	785 (v.w) 747 (w)		

iso-C_3H_7OLi, crystalline, deposited	*iso*-C_3H_7OLi, crystalline (paste in vaseline oil)	*iso*-C_3H_7OLi, solution in cyclohexane 0.3 N, 100 μ	*iso*-C_4H_9OLi, crystalline, deposited	*iso*-C_4H_9OLi, crystalline (paste in vaseline oil)	*iso*-C_4H_9OLi, solution in hexane 1.05 N, 100 μ	$(C_2H_5)_2CHOLi$, crystalline, deposited	$(C_2H_5)_2CHOLi$, crystalline (paste in vaseline oil)	$(C_2H_5)_2CHOLi$, solution in cyclohexane 0.24 N, 100 μ	Band assignment
575 (s, br)	575 (s, br)	585 (m. br)	585 (v.s. br)	580 (v.s. br)	600 (s, br)	570 (s, br)	600 (s. br) 560 (s. br)	590 (m. br)	Vibr. assoc. groupsO—Li
525 (s. br)	520 (s. br)	540 (m. br)	545 (s. br)		550 (s. br)	530 (s. br)	490 (m. br)	500 (m. br)	
470 (s. br)	470 (v.s. br)	490 (m)	460 (s. br)	465 (s. br)	470 (s. br)	420 (s. br)	425 (m. br)		Deform. vibr.C—C—C

* v.s. —very strong, s —strong, m —medium, w —weak, v.w. —very weak, sh —shoulder, br —broad. Bands in the 500-600 cm^{-1} region are broad and poorly resolved; their centers are given in the table.

the end. The pentamers probably have a tetrahedral structure, while the trimers are six-membered rings.

The IR spectra were recorded on a Hilger H-800 double-beam spectrometer in the spectral region from 5 to 25 μ. The spectra of sublimed samples were recorded using a special cell, in which the substance was deposited in vacuo as a thin layer on a potassium bromide plate and, during recording of the spectrum, was kept in vacuo. All operations with the samples were carried out in an atmosphere of dry argon. The frequencies of the absorption bands (with the exception of very weak ones) are given in Table 1.

From Table 1 it is evident that the spectra of sublimed samples, crystalline samples recorded as a paste in Vaseline oil, and solutions do not differ substantially from one another (this also applies to the spectrum of sublimed tert.-C_4H_9OLi). In the spectra of the compounds studied, in the region 400-600 cm^{-1}, as also in the lithium alcoholates studied in (1), there are intense, broad, diffuse bands (Fig. 1), which apparently should be assigned to vibrations of associated O—Li groups. In order to check the correctness of this assignment, we obtained spectra of two isotopically substituted derivatives of the simplest molecule, lithium methylate CH_3OLi^6 and CD_3OLi (Table 2). From Table 2 it is evident that the band with frequency 537 cm^{-1} in CH_3OLi, assigned to vibration of associated O—Li groups (1), upon replacement of the Li^7 atom by the isotope Li^6 is shifted toward higher frequencies by approximately 25 cm^{-1}, and that replacement of H atoms by D in the methyl group has little effect on the position of this band (Fig. 2). These data confirm, to a certain extent, the correctness of the assignment made earlier.

Thus, the lithium alcoholates studied are strongly associated, with formation of intermolecular O—Li . . . O bonds; complex vibrations of associated O—Li groups, apparently, appear in the region 400-600 cm^{-1} and, possibly, in an even more distant infrared region of the spectrum.

Table 2

CH_3OLi	CH_3OLi^6	CD_3OLi	Assignment of frequencies
2923 (m)2842 (s)2792 (s)	2942 (m)2858 (s)2803 (s)		Stretching vibrationsC—H
		2260 (m)2170 (s)2122 (s)2092 (s)	Stretching vibrationsC—D
2080 (w)	2062 (m)		$2\nu_{C—O}$
1435 (s)1368 (s)1160 (m)	~1455 (m)~1370 (w)1168 (m)		Deformation vibrationsC—H—OCH_3
		1145 (s)	Deformation vibrations C—D (?)
		1040 (w)1005 (s)	—OCD_3 (?)Stretching vibrations C—O
1060 (v.s.)	1065 (v.s.)	907 (m)	Deformation vibrations C—D
537 (s)	560 (s)	530 (s)	Vibrations of associated groupsO—Li
428 (s)	~430 (v.s.)		Deformation vibrations CH_3(“rocking”)

Physicochemical Institute
named after L. Ya. Karpov

Received
13 VII 1961

CITED LITERATURE

1. A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, K. A. Kocheshkov, DAN, **136**, 634 (1961).

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