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Abstract

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INFRARED ABSORPTION SPECTRA OF THE ALKOXIDES OF BERYLLIUM, MAGNESIUM, AND ALKALINE-EARTH METALS

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The vibrational spectra of alkoxy compounds of the type $E(OR)_n$ have at present been studied in greatest detail for derivatives of nonmetallic elements—boron ([1,2]), carbon ([3]), silicon ([4]), phosphorus, arsenic ([3,5]), etc. These compounds are typical esters of inorganic acids, and the O—E bonds in them are to a considerable extent covalent. In metal alkoxides, the sharp increase in the ionicity of the O—Me bond (in comparison with the corresponding alcohols and esters) should apparently lead to a redistribution of electron density and to a change in the nature of the bonds within the alkoxyl group, i.e., should be substantially reflected in the positions of the frequencies in the infrared spectra. On the other hand, owing to the ionic character of the O—Me bond, the mechanical factor (associated with the change in the mass of atom E) in the case of alkoxides will play a smaller role than in esters. The data available in the literature on the infrared spectra of lithium ([6–8]) and sodium ([7,8]) alkoxides do not make it possible to outline any general regularities concerning the influence of the electronegativity of the metal on the character of the spectrum of the alkoxide. In the present work we attempted to reveal this relationship by studying the infrared spectra of the methylates and ethylates of the elements of the second main subgroup.

Experimental Part

The methylates and ethylates of Be, Mg, Ca, Sr, and Ba were obtained by interaction of the corresponding metals with absolute alcohols (in the synthesis of Be and Mg ethylates, iodine was used as catalyst) ([9,10]). Beryllium methylate was synthesized by an exchange reaction of ethylate with methyl alcohol (under prolonged boiling). Freshly prepared preparations were used, the analysis of which (for C, H, and metal) agreed well with the theoretical content*. Suspensions of the alkoxides in Vaseline oil (for recording in the region 1300-650 cm^{-1}) and in hexachlorobutadiene (regions 3100-2500 and 1600-1300 cm^{-1}) were prepared in dry

Table 1

Principal frequencies in the infrared spectra of CH_3OH and the

methylates of Be, Mg, Ca, Sr, and Ba

	$2\delta(E)CH_2$	$\nu(E)CH_3$	$\nu(A)CH_3$	$\delta(E)CH_3$	$\delta(A)CH_3$	ν C—O
CH_3OH gas (12)	–	2978	2845	1477	1455	1034
$Be(OCH_3)_2$	–	2939	2832	1471	1370	1104, 1046
$Mg(OCH_3)_2$	2937 (?)	2937, 2890	2816	1464	1405, 1384	1105, 1075–47
$Ca(OCH_3)_2$	2931	2864	2814	1474	1405	1161, 1060
$Sr(OCH_3)_2$	2922	2823	2780	1468	1400	1156, 1060
$Ba(OCH_3)_2$	2919	2788	2755	1471	1409	1161, 1070

* In view of the fact that $Be(OCH_3)_2$ is described here for the first time, we give the results of its complete chemical analysis:
Found, %: Be 12.82, 12.74; C 34.21, 34.40; H 8.89, 8.90
$Be(OCH_3)_2$. Calculated, %: Be 12.79; C 33.80; H 8.45.

chamber in an argon atmosphere. The measurements were carried out on a double-beam spectrometer of the IKS-14 type with LiF and NaCl prisms.

The IR absorption spectra are presented in Figs. 1 and 2; the values of the frequencies and their assignments, according to the data ([4,7,11,12]), are given in Tables 1 and 2.

Discussion of results

On examining the data in Tables 1 and 2, attention is first of all drawn to the fact that, in the series of alcoholates of Group II, the greatest change is undergone by the frequencies of the stretching vibrations of the C–H bonds (the CH_3 group in the case of the methylates and the CH_2 group in the case of the ethylates). At the same time, the frequencies of the deformation vibrations of the C–H bonds are practically not shifted. In the region of the stretching vibrations of the C–H bonds, the spectral pattern is complicated by the presence of overtones of the deformation vibrations of C–H: one overtone of the doubly degenerate deformation vibration in the case of the methylates and three bands for the ethylates.

Fig. 1. IR spectra of methylates of Be, Mg, Ca, Sr, and Ba

Let us now consider the position of the frequencies of the stretching vibrations of C–O. Taking into account the considerable ionic character of the Me–O bonds in the methylates of the alkaline-earth metals, it will not be a great error to assume

Table 2

The most important frequencies in the IR spectra of C_2H_5OH and ethylates of Be, Mg, Ca, Sr, and Ba

Compound	$\nu(E)$ CH_3	$2\delta_1$ CH	$\nu(A)$ CH_3	$\nu(B)$ CH_2	$\nu(A)$ CH_2	$2\delta_2$ CH	$2\delta_3$ CH	δ CH δ_1	δ CH δ_2	δ CH δ_3	ν C–O	ν C–C
C_2H_5OH liquid	2973	2926	–	–	–	–	–	1461	1377	1328	1086, 1059	881
C_2H_5OH crystal (13)	2974	2926	2875	–	–	2742	2712	1452	–	–	1095, 1049	879
$Be(OC_2H_5)_2$	2969	2922	?	2894	2869	2753	2727	1413	1382	1358	1124, 1075	921
$Mg(OC_2H_5)_2$	2964	2922	–	2850	2850	2720	2720 (?)	1447	1382	1319	1123, 1070	893; 877
$Ca(OC_2H_5)_2$	2957	2925	2856	2847	2813	2716	2608	1434	1382	1319	1108, 1058	882
$Sr(OC_2H_5)_2$	2952	2910	2856	2802	2760	2696	2590	1442	1383	1312	1115, 1057	881
$Ba(OC_2H_5)_2$	2951	2918	2857	2786	2744	2680	2576	1437	1380	1312	1117, 1058	882

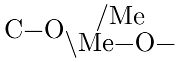
that the methoxyl groups (ions) retain a certain independence in the lattice. Then the metal atoms should not take a significant part in the vibrations of the O–C bond. Indeed, from the data in Tables 1 and 2 it is seen that a decrease in the mass of the cation in the series of methylates and ethylates Ba–Sr–Ca does not lead to a change in the frequencies of the C–O stretching vibrations. A certain increase in the C–O frequencies in the alcoholates as compared with the alcohols is due to the mass effect–in the vibration of the C–O bond in alcohol molecules the entire hydroxyl group participates. The considerable splitting of ν C–O in the IR spectrum of $Mg(OCH_3)_2$ is connected, in all probability, with the more covalent character of the Mg–O bond. In the case of the ethylates, such a change in the character of the bond on passing from the alkaline-earth metals to Be and Mg is manifested in a small increase in the values of ν

C–O. The phenomenon under consideration may be due, on the one hand, to a mechanical factor (interaction of vibrations of the C–O and Me–O bonds), acting only in the case of light metals. On the other hand, the very character of

Fig. 2. IR spectra of ethylates of Be, Mg, Ca, Sr, and Ba

Figure 1: Fig. 2. IR spectra of ethylates of Be, Mg, Ca, Sr, and Ba

the C—O bonds changes: as a result of the strong acceptor function exhibited by Mg and Be atoms, oxo bridges of the type



$$\mathrm{C{-}O}\begin{smallmatrix}/\mathrm{Me}\\ \backslash\mathrm{Me{-}O{-}}\end{smallmatrix}$$

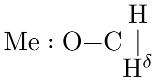
must exist, considerably stronger than in the case of alkaline-earth metals.

Fig. 2. IR spectra of ethylates of Be, Mg, Ca, Sr, and Ba

Unlike the frequencies of vibrations of C—O bonds, the stretching vibrations of C—H in the spectra of the methoxide ion lie considerably lower than in the nonionized molecule CH_3OH: for $Ba(OCH_3)_2$ the shifts of the doubly degenerate antisymmetric and symmetric vibrations are, respectively, 190 and 90 cm^{-1}. Owing to the high characteristic nature of ν C—H, this effect may be caused mainly by a decrease in the force constant of the bonds under consideration. To calculate the force constants of the C—H bonds in methyl alcohol and in the methylates, we used an approximate method (^{3}). From data on the frequencies of the totally symmetric stretching vibration of the CH_3 group, the following values of the force constants of the C—H bonds were found:

	CH_3OH	$Be(OCH_3)_2$	$Mg(OCH_3)_2$	$Ca(OCH_3)_2$	$Sr(OCH_3)_2$	$Be(OCH_3)_2$
$K \cdot 10^{-5}$, dyn/cm	4.51	4.47	4.42	4.42	4.31	4.23

An analogous lowering of the frequency ν CH in comparison with alcohols in the spectra of a series of sodium alcoholates was associated by Caubold (^{7}) with "anionic hyperconjugation." By this term he denoted conjugation of α-C—H bonds (σ-bonds) with an unshared pair of p-electrons at the oxygen atom, accompanied by transfer of negative charge from oxygen to hydrogen. The phenomenon under consideration can apparently also be explained with the aid of ideas about the inductive effect: the additional negative charge arising on the O atom (when the hydroxyl hydrogen is replaced by a metal) is induced on the hydrogen atoms at the α-carbon atom.



$$\mathrm{Me : O{-}C}\begin{smallmatrix}\mathrm{H}\\ |\\ \mathrm{H}^{\delta}\end{smallmatrix}$$

As a consequence of this, the C—H bond becomes less ionic or, in other words, the electronegativity of carbon with respect to hydrogen decreases. At the same

Fig. 3. Dependence of the positions of the frequencies of C—H stretching vibrations in the spectra of alcoholates on the ionization potentials of metals

Figure 2: Fig. 3. Dependence of the positions of the frequencies of C—H stretching vibrations in the spectra of alcoholates on the ionization potentials of metals

time, it is known that there is a direct dependence between the electronegativity of an element and the force constant of its bond with hydrogen (16). From what has been said it is clear that a decrease in the degree of ionicity of the O—E bond from Ba to H should lead to a gradual decrease in the induction effect and to an increase in the force constant of the α-C—H bonds. Figure 3 presents the dependence of the positions of the frequencies of C—H stretching vibrations on the ionization potentials of Group II metals.

Fig. 3. Dependence of the positions of the frequencies of C—H stretching vibrations in the spectra of alcoholates on the ionization potentials of metals

In favor of the assumption of an inductive mechanism for the decrease in the positive charge on hydrogen there is also the fact that the C—O bond length in molecules of alkali methylates, 1.40-1.42 Å (14, 15), and of methyl alcohol, 1.428 Å (17), is practically the same. The assumption of the presence of hyperconjugation is also contradicted by the fact that the frequencies of C—O stretching vibrations along the series Ba—Sr—Ca do not change, whereas ν CH undergo substantial shifts.

An increase in the force constants of the C—H bond with increasing electronegativity of the element was previously found by Reitz, using as an example the methyl esters of a series of inorganic acids (3); however, in the case of alcoholates of active metals, the effect considered here proved to be expressed much more sharply.

In conclusion, let us briefly discuss the positions of the frequencies of C—C stretching vibrations in the spectra of ethylates. As is seen from the data in Table 2, the indicated frequency is not shifted in the alcoholates in comparison with ethyl alcohol (the same is also true for alkali ethylates (6, 7)). An interesting exception is $Be(OC_2H_5)_2$, in whose spectrum ν C—C is shifted toward higher frequencies by 40 cm^{-1}. It is possible that this shift is due to purely mechanical factors. In any case, from an analysis of the spectra of other alcoholates and of C_2H_5OH it may be concluded that the frequency of stretching vibrations of the C—C bond adjacent to C—O, in the presence of α-hydrogen atoms, is much less sensitive to changes in the charge of the alkoxyl group (or the degree of ionicity of the O—E bond) than ν α-CH.

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CITED LITERATURE

1. K. Krishnan, Proc. Ind. Acad. Sci., **54 A**, 89 (1961).
2. L. Kahovec, Zs. phys. Chem., **40 B**, 135 (1938).
3. A. W. Reitz, R. Sabathy, Zs. phys. Chem., **41 B**, 152 (1938).
4. H. Kriegsmann, K. Licht, Zs. Elektrochem., **62**, 1163 (1958).
5. P. R. Shagidullin, T. E. Pavlova, Izv. AN SSSR, OKhN, 1963, 2117.
6. A. P. Simonov, D. N. Shigorin et al., DAN, **136**, 634 (1961).
7. F. H. Seubold, J. Org. Chem., **21**, 156 (1956).
8. Z. Kęcki, J. Witanowski, Roczn. Chem., **37**, 881 (1963).
9. N. Ya. Turova, A. V. Novoselova, Usp. khim., **34**, 385 (1965).
10. N. Ya. Turova, A. V. Novoselova, K. P. Semenenko, ZhNKh, **4**, 997 (1959).
11. L. Bellamy, *Infrared Spectra of Complex Molecules*, IL, 1963.
12. R. Mecke, Landolt-Börnstein, 1, T. 2, 1951, S. 345.
13. J. Wagner, Zs. phys. Chem., **40 B**, 439 (1938).
14. P. J. Wheatley, J. Chem. Soc., 1960, 4270; H. Dunken, J. Krauße, Zs. Chem., **1**, 27 (1961).
15. E. Weiss, Helv. chim. acta, **46**, 2051 (1963).
16. A. D. Walsh, Proc. Roy. Soc., **207 A**, 13 (1951).
17. Beilstein' s Handb. org. Chem., **1**, 1150 (1958).

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