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IR SPECTRA OF SOME O-ACYL DERIVATIVES OF HYDROXAMIC ACIDS

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The hydroxamic acids and their various derivatives are convenient compounds for studying questions relating the amide—imidol (hydroxam—hydroxim) tautomerism [1-5], as well as for studying acid—base interactions due to competing groups [6, 7].

The aim of the present studies was to examine the effect of different radicals and substituents, situated at the distal ends of molecules of the N,O-diacyl derivative of hydroxylamine, on the behavior of the individual functional groups in the molecule. It was also of interest to examine the character of the hydrogen bond, which can form in these compounds.

TABLE 1. Characteristic Vibrational Frequencies of the Carbonyl and Imino Groups in O-Acyl Derivatives of Hydroxamic Acids

Compound	Formula	$\nu_{C=O}$ (I)*	$\nu_{C=O}$ (II)†	ν_{NH}
		cm^{-1}		
I	C_6H_5-CONHOH	1645		3300
II	C_6H_5-CONHOK	1620		3250
III	C_4H_9-CONHOCO-C_6H_5	1655	1773	3200
IV	C_4H_9-CONHOCO-C_6H_4-NO_2-*n*	1700	1770	3125
V	C_5H_{11}-CONHOCO-C_6H_5	1665	1775	3230
VI	C_5H_{11}-CONHOCO-C_6H_4-NO_2-*n*	1690	1790	3230
VII	$C_{17}H_{35}$-CONHOCO-C_6H_5	1675	1775	3240
VIII	$C_{17}H_{35}$-CONHOCO-C_6H_4-NO_2-*n*	1668	1780	3250
IX	C_6H_5-CONHOCO-C_6H_5	1655	1770	3195
X	*n*-O_2N-C_6H_4-CONHOCO-C_6H_5	1675	1780	3190
XI	C_6H_5-CONHOCO-C_6H_4-NO_2-*n*	1670	1780	3150
XII	*n*-O_2N-C_6H_4-CONHOCO-C_6H_4-NO_2-*n*	1685	1780	3130
XIII	*n*-CH_3O-C_6H_4-CONHOCO-C_6H_5	1655	1770	3340
XIV	C_6H_5-CONHOCO-C_6H_4-OCH_3-*n*	1650	1775	3335
XV	*n*-CH_3O-C_6H_4-CONHOCO-C_6H_4-OCH_3-*n*	1710	1755	3280
XVI	*n*-O_2N-C_6H_4-CONHOCO-C_6H_4-OCH_3-*n*	1700	1760	3300
XVII	*n*-CH_3O-C_6H_4-CONHOCO-C_6H_4-NO_2-*n*	1650	1770	3335
XVIII	*m*-Cl-C_6H_4-CONHOCO-C_6H_5	1645	1768	3185
XIX	*m*-Cl-C_6H_4-CONHOCO-C_6H_4-NO_2-*n*	1675	1775	3200
XX	C_6H_5-CH_2CONHOCO-C_6H_5	1665	1770	3155
XXI	C_6H_5-CH_2CONHOCO-C_6H_4-NO_2-*n*	1675	1790	3200
XXII	C_6H_5-CONHOCO-C_4H_3O-α ‡	1670	1780	3230
XXIII	α-C_4H_3O-CONHOCO-C_6H_5	1663	1770	3140

*Carbonyl group belongs to the amide grouping R—CONH—.
†Carbonyl group belongs to the ester grouping —OCO—R.
‡C_4H_3O is α-furyl.

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TABLE 2. Comparative Data for the Characteristic Vibrational Frequencies of the Carbonyl and NH Groups in the Solid Phase (KBr) and in a Solvent (CCl_4)

Compound*	Solvent	$\nu_{C=O}$(I)	$\nu_{C=O}$(II)	ν_{NH}
		cm^{-2}		
VII	In tablet with KBr	1675	1775	3240
	In CCl_4	1735	1773	~3550
IX	In tablet with KBr	1655	1770	3195
	In CCl_4	1730	1765	3347
XXIII	In tablet with KBr	1663	1770	3140
	In CCl_4	1713	1770	3360

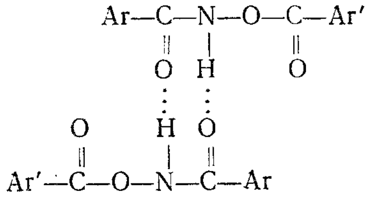
*See Table 1.

In order to clarify these questions, the IR spectra of some O-acyl derivatives of hydroxamic acids in KBr tablets and, in somes cases, in CCl_4 were studied (see Tables 1 and 2).

All the studied compounds had absorption maxima in the 1645-1710- and 1750-1790-cm^{-1} regions characteristic of carbonyl group (amide and ester) stretching vibrations, as well as in the 3125-3335- and 1240-1295-cm^{-1} regions characteristic of NH- and CN-group stretching vibrations, respectively (Fig. 1). Data derived from a study of the IR spectra of a systematic series of this class of compounds does not exist in the literature, with the exception of one or two reports [8, 9].

Results of the studies showed that both in the solid phase (KBr Tablets) and in CCl_4 solution all the studied substances existed in the hydroxamic form, which was confirmed by the absence in the spectrogram of characteristic frequencies for the C=N bond and the OH-group and conversely by the presence of absorption bands for the —CONH-,—OCOR-, and NH-groups (1645-1700, 1750-1790, and 3125-3330, 1490-1540 cm^{-1}, respectively). Assignment of the absorption maximum in the 1760-1790-cm^{-1} region to the vibrations of the carbonyl group present in the ester grouping is confirmed by the fact that a corresponding absorption is absent for benzhydroxamic acid. It should also be noted that in the majority of cases the high-frequency carbonyl band is of lower intensity than the low-frequency band, which has also been observed for the spectra of phthalimides and other compounds [10].

Comparison of the absorption frequencies of the carbonyl groups [amide (I) and ester (II)] and of the amino group in the solid phase and in CCl_4 (see Table 2) showed that while $\nu_{C=O}$ (I) and ν_{NH} on passing from the solution to the solid state shift to lower frequencies [by 50-80 cm^{-1} for the C=O (I) group and by 150-300 cm^{-1} for the NH group], $\nu_{C=O}$ (II) remains practically unchanged. From this it can be assumed that in the solid phase an intermolecular hydrogen bond is present which is formed between the C=O (I) group of one molecule and the amino group of another, i.e., molecules of O-acyl derivatives of hydroxamic acids are present in the solid phase, in all probability, as dimers:



Study of the IR spectra of benzhydroxamic acid in KBr revealed an absorption band for the C=O group with a frequency of 1645 cm^{-1}; for the NH and OH groups the absorption frequencies were 3300 and 3070 cm^{-1}, respectively. In CCl_4 the absorption band for the C=O group appeared with a frequency of 1670 cm^{-1}. The low intensity of the absorption in the region of the NH- and OH-group frequencies did not permit a rigorous assignment of these frequencies to be made (benzhydroxamic acid and its O-acyl derivatives are scarcely soluble in CCl_4; the saturated solutions were examined). The lower values of the C=O group frequencies in the solid state compared with solution can also be explained by the development of the intermolecular association. When $\nu_{C=O}$ of benzhydroxamic acid is compared with $\nu_{C=O}$ of its

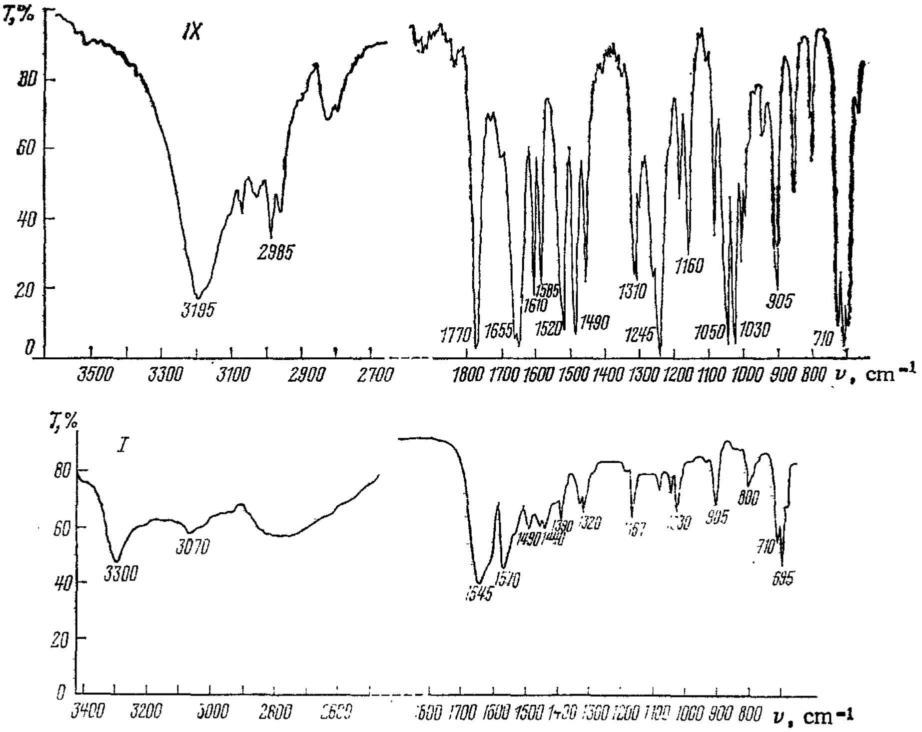


Fig. 1. IR spectra of dibenzhydroxamic (IX) and benzhydroxamic (I) acids in KBr plates.

potassium salt the latter is found to be lower by 25 cm^{-1}, which is due to the formation of the anionic structure.

It was of interest to trace the effect of various substituents, situated at the para position of the benzene nucleus, on the vibrational frequency of the carbonyl groups in molecules of an N,O-diacyl derivative of hydroxylamine.

It was expected that when substituents of differing electronic character were introduced into these compounds in direct proximity to the C=O (I) or C=O (II) groups a corresponding change in the vibrational frequency of these groups would occur. It is known that with increase in the electron density on the oxygen atom of a carbonyl groups its dynamic coefficient and, consequently, the vibrational frequency are reduced; on the contrary, the opposite effect was observed. Thus, introduction of electronegative substituents into the vicinity of the carbonyl shifted the electron cloud of the carbonyl group to the center of the bond and led to a reduction in the polarity and an increase in the frequency. As for the effect of electropositive substituents, in this case the reverse action has been observed [11]. As seen from Table 1, a nitro group, present in the para position of the benzene ring, in the majority of cases leads to an increase in $\nu_{C=O}$ (compare V with VI; VII with VIII; IX with X, XI, XII; XIV with XVI; XVIII with XIX, etc,). However, this change in vibrational frequency does not always occur to the same extent for both carbonyls. Thus, whereas for $\nu_{C=O}$ (I) the change is essentially regular, for $\nu_{C=O}$ (II) the dependence sometimes breaks down. Introduction of a nitro group into series with C=O (II) leads to a marked change in $\nu_{C=O}$ (I) also.

A methoxyl group introduced into the para position of the benzene ring does not cause a change in the vibrations of the carbonyl groups (compare IX with XIII and XIV). However, when two methoxyl groups are introduced, in addition to the expected decrease in $\nu_{C=O}$ (II), an anomalous change in $\nu_{C=O}$ (I) is also observed, associated with an increase. At the same time, the combined effect of a nitro and a methoxyl group changes the dynamic coefficient of the carbonyl groups and, as would be expected, a corresponding decrease or increase of $\nu_{C=O}$ (I) and ν_{C-O} (II) occurs.

It should be noted that increase in the number of carbon atoms in the aliphatic radical present in series with C=O (I) leads to an increase of $\nu_{C=O}$ by 10 cm^{-1}. A similar increase in frequency of the C=O- group vibration (I) is observed when the benzhydroxamic acid is benzoylated.

As regards the frequencies of the NH-group vibrations, the latter appear as broad absorption bands, which, assuming the presence of a hydrogen bond, in the solid phase must be intermolecular in character, and in solution, intramolecular, since when the concentration is varied the value of ν_{NH} remains practically unchanged. A complete correspondence between ν_{NH} and the character of the substituent was noted. Substitution of phenyl by 2-furyl in the given compounds led to an increase in the vibrational frequencies of the carbonyl groups, which does not agree with the conclusions based on the electron-donor character of the furyl radical displayed in the α,β-unsaturated ketones of the furan series [12].

The O-acyl derivatives of hydroxamic acids were prepared by reacting the potassium salt of the appropriate hydroxamic acid with the chlorides of benzoic, para-nitrobenzoic, para-methoxybenzoic, and furancarboxylic acids in dioxane solution with the application of heat [13].

Measurement of the IR spectra of the O-acyl derivatives of the hydroxamic acids was carried out on a UR-20 instrument in the 700-4000-cm^{-1} region, using potassium bromide tablets at concentrations of 1 mg substance in 100 mg, and in carbon tetrachloride solution at a concentration of $3 \cdot 10^{-3}$ mole/liter.

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COMPENSATION OF SPECTRAL DENSITIES DURING THE MEASUREMENT OF CHARACTERISTICS OF A SCATTERING MEDIUM

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Spectral measurements of various characteristics of scattering media are carried out by using the ratio between the values of luminous fluxes, both incident and reflected — refracted and scattered, which in most cases are not comparable and differ in their energy characteristics by several orders of magnitude. During the measurement of scattering indices of seawater [1-3], the measured fluxes differ particularly strongly from each other. Measurement of attenuation, scattering, and transmission indices in the sea led to the traditional approach which consists in using a large collection of graduated, stepped attenuators to compare the fluxes studied. In most cases, the apparatus contains an electrical light source, whose fluxes are used by experimenters to isolate various spectral intervals for measuring different characteristics of the medium. In thermophysical measurements, the concept of the radiation flux is interpreted through its parameters, i.e., the temperature and the spectral

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