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## Abstract

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# MANIFESTATION OF A HYDROGEN BOND OF THE TYPE OH···O=C IN THE INFRARED ABSORPTION BAND OF THE CARBONYL GROUP OF KETONES

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The study of manifestations of the hydrogen bond in the bands of proton-acceptor groups can provide substantial information on the distortion of the electron shell of the acceptor molecule upon bond formation. The aim of the present work is to attempt to establish a correspondence between the spectroscopic manifestations of the hydrogen bond OH···O=C in the stretching-vibration band of the carbonyl group, on the one hand, and the characteristics of the molecules participating in the bond, on the other.

The degree of deshielding of the proton of the XH group by the electron cloud of the molecule (1) and the magnitude of the atomic dipole of the lone electron pair of atom V (2) are molecular characteristics determining the effectiveness of an interaction of the type XH···V. Proceeding from the fact that in molecules of the same type the change in these quantities occurs owing to the inductive effect of atoms or substituent groups, one may use data on the relative magnitude of the inductive effect of various radicals (3) in order to arrange these molecules in a series of increasing proton-donor or electron-donor ability. For hydroxyl-containing molecules, the degree of electronic deshielding of the proton of the OH group also determines the acidic properties of the molecules; therefore, the value of the dissociation constant of the corresponding acid in a suitable solvent may serve as its measure.

For ketones, however, a quantitative characteristic of electron-donor ability may apparently be the magnitude of their first ionization potential, which determines the energy required to detach an electron of the lone pair of the oxygen atom (4). The change in this quantity in the series of our objects correlates well with the data (3).

In the present work the following objects were investigated: hydroxyl-containing substances (in order of increasing proton-donor ability) $CH_3OH$, $C_6H_5OH$, $CH_2ClCOOH$, $CCl_3COOH$, $CF_3COOH$, and ketones (in order of increasing electron-donor ability; in parentheses is the value of the ionization potential in electron volts according to data of F. I. Vilesov (5)): 1,3-dichloroacetone

Fig. 1. Absorption spectra of solutions in $CCl_4$ of equimolar mixtures of cyclohexanone with trichloroacetic acid at concentrations of each component: 1—0.194 mol/l, 2—0.0155 mol/l

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(10.12), chloroacetone (9.90), acetone (9.71), cyclohexanone (9.14), camphor (8.76), pivalone (2,2,4,4-tetramethyl-3-pentanone) (8.65). Mixtures of acids with ketones and solutions of these mixtures in $CCl_4$ were studied. The work was carried out on an IKS-6 spectrometer with NaCl prisms and an OAP-1 receiver; the calculated spectral slit width was 3.2-4.6 $cm^{-1}$. Cuvettes of constant thickness made of fluorite, measured interferometrically, and demountable cuvettes with a ring and insert were used. The accuracy of frequency measurement was 1-3 $cm^{-1}$, depending on the band width.

Since the frequency and intensity of the carbonyl-group band depend strongly on the dielectric properties of the solvent as the medium (according to data, for example, of ($^6$), in various solvents the value of $\nu_{C=O}$ changes ···

in the interval 12 $cm^{-1}$), since it was desirable to reduce this influence to a minimum in order to be able to record only changes due to hydrogen bonding. This was achieved by diluting the binary acid—ketone system with an inert solvent ($CCl_4$), whose dielectric properties mainly determined the influence of the medium. Therefore it may be considered that this effect was always the same.

In all the cases we studied, in the spectra of systems containing ketone and acid molecules, over a certain concentration range, two bands are observed in the region of 1700 $cm^{-1}$. One of them coincides in frequency with the $\nu_{C=O}$ band of the ketone dissolved in $CCl_4$, while the other is shifted to lower frequencies. When the concentration of the solution is changed, the intensity is redistributed between these bands; therefore the first of them has been assigned to monomeric ketone molecules, and the second to molecules participating in an $OH \ldots O = C$ hydrogen bond. We compared the magnitude of the displacement of the $\nu_{C=O}$ band with the proton-donor and electron-donor characteristics of the molecules forming the complex.

**Fig. 1.** Absorption spectra of solutions in $CCl_4$ of equimolar mixtures of cyclohexanone with trichloroacetic acid at concentrations of each component: **1** —0.194 mol/l, **2** —0.0155 mol/l.

The possibility of using halogen-substituted carboxylic acids as proton donors, despite their strong dimerization, is determined by the difference in the electronic structure of the carbonyl group of an aliphatic ketone and of these acids. As a result of the considerable negative inductive effect of the halogen atoms, the magnitude of the atomic dipoles of the free electron pairs of oxygen in the acid molecule should be smaller than in the ketone molecule, and it may be expected that, in an equimolar mixture of ketone and acid, the energetically more favorable association of the mixed type will predominate (work with solutions containing an excess of acid is complicated by the acids' own absorption in the $\nu_{C=O}$ region).

Indeed, in the spectra of equimolar mixtures of ketones with trichloro- and trifluoroacetic acid, in the region of carbonyl vibrations two bands are observed which are absent from the spectra of solutions in $CCl_4$ of the two components taken separately. Upon dilution of the mixtures with carbon tetrachloride, the intensity of these bands decreases and new bands appear, characteristic of ketone and acid dissolved in $CCl_4$. This is illustrated in Fig. 1, which shows the absorption curves of solutions of a mixture of $CCl_3COOH$ with $(CH_2)_5CO$ in $CCl_4$. It is seen that, as the concentration of the solution decreases, the intensity of the bands (marked by arrows) increases: $\nu_{C=O}$ of cyclohexanone at 1717 $cm^{-1}$, and of the acid at 1751 $cm^{-1}$ (dimers) and 1787 $cm^{-1}$ (monomers). The band at 1691 $cm^{-1}$ belongs to the carbonyl group of cyclohexanone participating in a hydrogen bond with trichloroacetic acid; the band at 1764 $cm^{-1}$ belongs to the C=O group of the acid molecule whose hydroxyl group is bound to a ketone molecule. It can be seen that in this system, at concentrations that are not too low, bonding between different molecules takes place preferentially. The spectra of systems containing a ketone and trifluoroacetic acid look similar; however, in the spectrum of a mixture of monochloroacetic acid with cyclohexanone, the intensity of the bands corresponding to association of the mixed type is comparable with the intensity of the bands of the free ketone and acid dimers and rapidly decreases upon dilution of the mixture in $CCl_4$. A more complicated picture was observed in the spectra of mixtures of chloroacetone and dichloroacetone with $CF_3COOH$. In these ketones, in the $\nu_{C=O}$ region there are several bands belonging to rotational isomers, and both the positions and the relative intensities of these bands depend strongly on external conditions, in particular on the type of solvent ($^7$). The formation of a hydrogen bond leads to the appearance of new bands, and

in interpreting them it is necessary to take into account a possible shift of the equilibrium between rotational isomers. Fig. 2 shows the absorption curves of solutions of a mixture of chloroacetone with $CF_3COOH$. The bands at 1724 and 1752 $cm^{-1}$ belong to the gauche and cis forms of chloroacetone; the broad band centered at 1709 $cm^{-1}$ belongs to the carbonyl group of chloroacetone participating in a hydrogen bond. If this latter band belongs to bound molecules in the gauche form (a shift relative to the monomer of 15 $cm^{-1}$), then near 1737 $cm^{-1}$ one could expect the appearance of a band corresponding to molecules in the cis form participating in a hydrogen bond. In this region no distinct maximum is observed, apparently because of the considerable width and degree of overlap of the bands with neighboring bands, and the presence of absorption in the region of 1737 $cm^{-1}$ can be judged only tentatively, from the somewhat raised background.

Fig. 2. Absorption spectra of solutions in $CCl_4$ of equimolar mixtures of chloroacetone with trifluoroacetic acid at the concentration of each component: 1 —2.15 mol/l, 2 —0.028 mol/l

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If the 1709 $cm^{-1}$ band belonged to bound molecules in the cis form (a shift relative to the monomer of 43 $cm^{-1}$), then, because of the absence at 1681 $cm^{-1}$ of a shifted band of the gauche form, one would have to assume that there is no possibility for the formation of a hydrogen bond in molecules in the gauche form, whereas for steric reasons the opposite assumption is more reasonable (if the interpretation of Bellamy and Williams ($^7$) is correct). It is therefore natural to take the shift of the $\nu_{C=O}$ band of chloroacetone in the mixture with $CF_3COOH$ as equal to 15 $cm^{-1}$. For 1,3-dichloroacetone the shift of the $\nu_{C=O}$ band caused by the hydrogen bond OH···O=C with $CF_3COOH$ does not exceed 6 $cm^{-1}$.

**Table 1**

| Cyclohexanone —acid system | Cyclohexanone —acid system | $CF_3COOH$ —ketone system | $CF_3COOH$— ketone system | $CF_3COOH$— ketone system |
|---|---|---|---|---|
| acid | shift of the $\nu_{C=O}$ band of the ketone relative to the solution in $CCl_4$, $cm^{-1}$ | ketone | shift of the $\nu_{C=O}$ band of the ketone relative to the solution in $CCl_4$, $cm^{-1}$ | relative shift |
| $CH_3OH$ | 12 | $(CH_2Cl)_2CO$ | 6≤ | $3.5 \cdot 10^3 \leq$ |
| $C_6H_5OH$ | 15 | $CH_2ClCOCH_3$ | 15 | $8.7 \cdot 10^3$ |
| $CH_2ClCOOH$ | 19 | $CH_3COCH_3$ | 25 | $14.5 \cdot 10^3$ |
| $CCl_3COOH$ | 26 | $(CH_2)_5CO$ | 29 | $16.9 \cdot 10^3$ |
| $CF_3COOH$ | 29 | Camphor | 33 | $18.9 \cdot 10^3$ |
|  |  | Pivalone | 21.5 | $12.7 \cdot 10^3$ |

A summary of the results obtained is given in Table 1. In cases where the associated band had structure, the shift was measured from the center of the complex band. It is seen that the shift of the $\nu_{C=O}$ band of the ketone increases not only with increasing proton-donor ability of the acids in the series cyclohexanone—

acid, but also with increasing electron-donor ability of the ketones in the series trifluoroacetic acid—ketone.

Pivalone falls outside the general regularity. It must be assumed that the reason for this is the specificity of the geometrical structure of this molecule, in which the carbonyl group is strongly shielded by methyl radicals. The considerable chemical inertness of pivalone, which does not give certain reactions typical of ketones ([8]), is apparently due to the same cause. The formation of a strong hydrogen bond requires a small O···HO distance, which can be realized only in the absence of steric hindrance. Probably, for the hydrogen bond

between the molecules of pivalone and trifluoroacetic acid this requirement is not fulfilled. In the spectrum of the pivalone—phenol—$CCl_4$ system, which was recorded for comparison, the observed shift of the $\nu_{C=O}$ band of pivalone, 15.5 $cm^{-1}$, does not differ from the shift observed in the spectra of mixtures of cyclohexanone and dipropyl ketone with phenol in $CCl_4$. This makes it possible to assume that, for the hydrogen bond between phenol and pivalone molecules, steric hindrances are less significant because of the larger equilibrium distance O…HO in this case.

In conclusion it should be noted that formation of a hydrogen bond causes a noticeable increase in the integral absorption coefficient of the $\nu_{C=O}$ band (up to 200%).

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## CITED LITERATURE

1. V. M. Chulanovskii, *Izv. AN SSSR, Ser. Fiz.*, **22**, No. 9, 1103 (1958).
2. W. G. Schneider, *J. Chem. Phys.*, **23**, No. 1, 26 (1955).
3. H. K. Ingold, *Mechanism of Reactions and Structure of Organic Compounds*, IL, 1959, p. 60.
4. D. Cook, *J. Am. Chem. Soc.*, **80**, No. 1, 49 (1958).
5. F. I. Vilesov, DAN, **138**, No. 6 (1960).
6. L. B. Archibald, A. D. E. Pullin, *Spectrochim. Acta*, **12**, No. 1, 34 (1958).

7. L. J. Bellamy, R. L. Williams, *J. Chem. Soc.*, 1957, 4294.

8. *Dictionary of Organic Compounds*, **3**, IL, 1949, p. 506.

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