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Abstract

Full Text

PHYSICAL CHEMISTRY

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CHANGES IN THE INTENSITIES OF INFRARED ABSORPTION BANDS OF THE C=O AND N–H GROUPS IN N-MONOSUBSTITUTED AMIDES UPON FORMATION OF A HYDROGEN BOND

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The formation of a hydrogen bond (H-bond) N–H···O=C is manifested in the infrared spectrum in a change in the frequency and intensity of the absorption bands associated with vibrations of the C=O and N–H groups. One of the reasons with which the observed changes are connected is the redistribution of electron density in these groups under the influence of interactions leading to the formation of an H-bond. The change in the intensity of the band ν_s(N—H) upon formation of an H-bond has been investigated in a number of works ([1]), whereas such data for the band ν_s(C = O) are insufficient.

In the present work the integrated absorption coefficients of both the ν_s(N—H) bands and the ν_s(C = O) bands have been studied in four N-monosubstituted amides: N-butylacetamide, N-ethylacetamide, N-ethylbenzamide, and N-methylmethacrylamide, in associated and nonassociated states. We recorded spectra of solutions of the indicated amides in carbon tetrachloride at various concentrations from 2 mol/l to $1 \cdot 10^{-3}$ mol/l. In concentrated solutions the molecules of these compounds are linked by an intermolecular H-bond N–H··· O=C. The spectra were recorded on a UR-10 spectrometer in the regions 1580 –1800 and 3200–3500 cm^{-1}. The rate of spectrum recording was 50 cm^{-1}/min, slit program 4. With the cell thicknesses used (from $1 \cdot 10^{-3}$ cm to 1 cm), absorption of the solvent at 1600 cm^{-1} did not exceed 60%. The substances used were additionally purified by distillation or recrystallization.

Fig. 1. Infrared spectra of N-methylmethacrylamide (solvent CCl_4, concentra-

Fig. 2. Dependence of the integral coefficient of the band $B\nu(\mathrm{C=O})$ on the relative content of free molecules in solution: *a*—N-butylacetamide; *b*—N-ethylacetamide; *v*—N-ethylbenzamide; *g*—N-methylmethacrylamide.

Figure 2: Fig. 2. Dependence of the integral coefficient of the band $B\nu(\mathrm{C=O})$ on the relative content of free molecules in solution: *a*—N-butylacetamide; *b*—N-ethylacetamide; *v*—N-ethylbenzamide; *g*—N-methylmethacrylamide.

tion 2 mol/l (1), 0.15 mol/l (2), 0.015 mol/l (3))

Figure 1 shows, as an example, the spectra of N-methylmethacrylamide at various concentrations. As is seen from the figure, at $C = 2$ mol/l practically all molecules are involved in an H-bond, which is characterized by a broad ν(N—H) band with frequency 3330 cm^{-1}. The bands 1660 and 1618 cm^{-1} are assigned respectively to $\nu_s(\mathrm{C=O})$ and $\nu_s(\mathrm{C=C})$ vibrations (the molecules are involved in an H-bond). At $C = 1.5 \cdot 10^{-2}$ mol/l only bands of non-

perturbed vibrations ν(N—H) with frequency 3475 cm^{-1}, $\nu_s(\mathrm{C=O})$—1672 cm^{-1} and $\nu_s(\mathrm{C=C})$—1626 cm^{-1}.

The integral absorption coefficients (B) of the bands ν_s(N—H) and $\nu_s(\mathrm{C=O})$ were determined by summing the absorption coefficients over the entire contour of the band. The band $\nu(\mathrm{C=O})$ was not resolved into bands belonging to free molecules and to molecules included in an H-bond. At the limiting concentration values such a resolution was not required, since single $\nu(\mathrm{C=O})$ bands were observed (corresponding, respectively, to a free and to a perturbed H-bond). For each concentration, from the band of free ν_s(N—H), the relative content of free molecules was determined,

$$\alpha = \frac{C_{\text{free}}}{C_{\text{bond}} + C_{\text{free}}}.$$

Figure 2 presents the dependence of the integral absorption coefficient $B\nu_s(\mathrm{C=O})$ on α. At $\alpha = 0$ the value of B refers to bound molecules, and at $\alpha = 1$ only to free ones. Table 1 gives the values of the integral coefficients $B\nu_s(\mathrm{C=O})$, as well as the corresponding values of $B\nu_s$(N—H). As can be seen from Table 1, the intensity of the ν_s(N—H) band for all N-monosubstituted amides only increases upon formation of an H-bond, as is usually observed ([1]). A different course of intensity was observed for the band $B\nu_s(\mathrm{C=O})$ (see Fig. 2). Thus, upon formation of an H-bond, the intensity of $\nu_s(\mathrm{C=O})$ in N-butylacetamide increases, in N-ethylacetamide and N-ethylbenzamide it practically does not change, and in N-methylmethacrylamide it decreases significantly.

Fig. 2. Dependence of the integral coefficient of the band $B\nu(\mathrm{C=O})$ on the relative content of free molecules in solution: *a*—N-butylacetamide; *b*—N-ethylacetamide; *v*—N-ethylbenzamide; *g*—N-methylmethacrylamide.

Let us consider one of the possible reasons leading to the difference in the character of the change in intensities of the ν(N—H) and ν(C = O) bands upon formation of an H-bond. As is known, the intensity of an IR band is proportional to the square of the change in the dipole moment of the oscillator $B \sim (\mu')^2$, where

$$\mu' = \left(\frac{\partial \mu}{\partial r}\right)_{r=r_0},$$

μ is the effective dipole moment of the bond, and r is the distance between atoms. Let us compare how the dipole moments of the C = O and N—H groups change upon formation of an H-bond. According to modern concepts ([2,3]), upon formation of an H-bond the principal role is played by electrostatic and donor-acceptor interactions. These interactions can, for our case, be described by the following three structures:

$$\begin{array}{rll} \mathrm{N:H} & :\mathrm{O=C} & \text{(I)} \\ \mathrm{N^-:H^+} & :\mathrm{O=C} & \text{(II)} \\ \mathrm{N:\cdot H} & {}^+\cdot\,\mathrm{O=C} & \text{(III)} \end{array}$$

Structure II describes electrostatic interactions leading to polarization of the C = O group, while structure III describes donor-acceptor interactions that lead to transfer of an electron from the C = O group to the N—H group. These interactions affect the dipole moments in different ways.

ments of the N–H and C=O groups. The dipole moment of the N–H group increases both in electrostatic (structure II) and in donor-acceptor interactions (structure III). On the other hand, the dipole moment of the C=O group may either increase (structure II) or decrease as a result of a decrease in the electron density on the C=O group (structure III). These differences in the change of the dipole moment of the N–H and C=O groups may be the cause of the experimentally observed difference in the change in–

Table 1

Frequencies and integral absorption coefficients of the bands ν(C = O) and ν(N – H) in N-monosubstituted amides, belonging to free and H-bonded molecules

Compound	$\nu(C=O)$, bonded molecules: ν, cm^{-1}	$\nu(C=O)$, bonded molecules: B, $l\cdot mol^{-1}\cdot cm^{-2}$	$\nu(C=O)$, free molecules: ν, cm^{-1}	$\nu(C=O)$, free molecules: B, $l\cdot mol^{-1}\cdot cm^{-2}$	$\Delta\nu$, cm^{-1}	ΔB, $l\cdot mol^{-1}\cdot cm^{-2}$	$\nu(N-H)$, bonded molecules: ν, cm^{-1}	$\nu(N-H)$, bonded molecules: B, $l\cdot mol^{-1}\cdot cm^{-2}$	$\nu(N-H)$, free molecules: ν, cm^{-1}	$\nu(N-H)$, free molecules: B, $l\cdot mol^{-1}\cdot cm^{-2}$	$\Delta\nu$, cm^{-1}	ΔB, $l\cdot mol^{-1}\cdot cm^{-2}$
N-butylacetamide	1650	$3.9\cdot 10^4$	1685	$2.3\cdot 10^4$	35	$+0.9\cdot 10^4$	3290	$2.3\cdot 10^4$	3460	$2.1\cdot 10^3$	170	$+2.1\cdot 10^4$
N-ethylacetamide	1655	$2.3\cdot 10^4$	1686	$2.2\cdot 10^4$	31	$+0.1\cdot 10^4$	3300	$2.3\cdot 10^4$	3460	$2.0\cdot 10^3$	160	$+2.1\cdot 10^4$
N-ethylbenzamide	1643	$2.5\cdot 10^4$	1674	$2.5\cdot 10^4$	31	0	3320	$2.7\cdot 10^4$	3465	$2.3\cdot 10^3$	145	$+2.5\cdot 10^4$
N-methylmethacrylamide	1660	$1.1\cdot 10^4$	1672	$2.3\cdot 10^4$	12	$-1.2\cdot 10^4$	3330	$7.0\cdot 10^4$	3475	$3.0\cdot 10^3$	145	$+6.7\cdot 10^4$

–intensity of the bands $\nu_s(N-H)$ and $\nu_s(C=O)$ upon formation of the H-bond. These qualitative considerations do not take into account a whole series of factors that play a large role in the spectroscopic manifestation of the H-bond ([1], [4]). A more complete interpretation can probably be obtained with further development of the predissociation theory ([4]), in which the principal propositions of the modern theory of the H-bond will be taken into account.

The contribution of structures I, II, III to $N-H\ldots O=C$ should be determined by the general distribution of electron density in the molecules forming the H-bond. The increase observed by us in the intensity of $\nu(C=O)$ upon formation of an H-bond in N-butylacetamide may be associated with the predominance of structure II, whereas the decrease in the intensity of this band in N-methylmethacrylamide may be associated with a large contribution from structure III. The increase in the contribution of donor–acceptor interactions upon formation of the H-bond by N-methylmethacrylamide can be explained by the influence of conjugation on the electron density of the C=O group of this molecule. According to work ([5]), conjugation in $C=C-C=O$ increases the electron-donor properties and lowers the ionization potential of the carbonyl group. It may be assumed that the increase in the electron-donor ability of the C=O group in N-methylmethacrylamide leads to an increase in the contribution of structure III to the $N-H\ldots O=C$ interaction, which is manifested in the decrease in the intensity of $\nu_s(C=O)$ upon formation of the H-bond.

Dilution of N-methylmethacrylamide in CCl_4 is also accompanied by a shift of the frequency ν_s(C=C) from 1618 to 1626 cm^{-1} (Fig. 1). This indicates a decrease in the electron density in the C=C group upon formation of an H-bond, in the case of conjugation C=C–C=O.

In conclusion, we note that, upon formation of an H-bond in N-methylmethacrylamide,

the greatest increase in the integral absorption coefficient of ν(N—H) is observed in comparison with the other cases (see Table 1), which may also be associated with the relatively large contribution of structure III in N—H ... O=C interactions.

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REFERENCES

1. G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, San Francisco, 1960.
2. N. D. Sokolov, *UFN*, **62**, 205 (1955).
3. C. A. Coulson, *Valence*, Oxford, 1958.
4. M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov, *Molecular Vibrations*, 2, Moscow, 1949.
5. F. I. Vilesov, *DAN*, **132**, 1332 (1960).

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