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SPECTRAL STUDY OF 3-HYDROXYPYRIDINE AND 8-HYDROXYQUINOLINE IN GASEOUS PHASE

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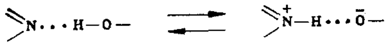
The IR spectral data of 3-hydroxypyridine and 8-hydroxyquinoline in the condensed state show that the two compounds are present in ionic form, while in the gaseous-phase state they are present in a neutral form. In 8-hydroxyquinoline in the gaseous-phase, a weaker intramolecular hydrogen bond is retained than in the CCl_4 solution.

Much attention is being paid at present to the study of compounds in the gaseous phase by physical methods [1, 2]. Both physical and chemical properties of the compounds are being studied, and by comparison with the data for the condensed state (solution, crystal), we can evaluate the influence of different types of intermolecular interactions on the electron density distribution in the molecule, its structure, conformational features, reactivity, etc.

The present article is a continuation of previously reported studies on the structural features of 9,10-anthraquinone derivatives in the gaseous phase and condensed states by the IR spectroscopy [3, 4], and is directed to the study of 3-hydroxypyridine (I) and 8-hydroxyquinoline (II). The structure of compounds I and II in the condensed state (solution, crystal) has until now been studied in a fair detail [5, 6]. However, the presence of strong intermolecular (for I) and intramolecular (for II) hydrogen bonds made it difficult to determine the positions of the proton:



A B

The available data on the structure of 8-hydroxyquinoline in the crystalline state and in solutions in protonic solvents are interpreted as corresponding to the Zwitterionic form B [5]. In the present work, results are given for the study of the structure of compounds I and II in the gaseous phase, in which the intermolecular dissociates decompose and the individual free molecules can be studied. The results obtained are shown in Table 1 and Figs. 1 and 2.

In the IR spectrum of the crystalline compound I, a very broad absorption band is observed with anomalously low frequency and with maxima at about 2500 and 1850 cm^{-1}. The spectrum of the crystalline O-deuterated derivative I is characterized by the appearance of additional bands at 2140, 1439, and 1042 cm^{-1}, so that the absorption bands of compound (I) in the 3000-1800 cm^{-1} region can be assigned to the OH (or HN^+) vibrations. All the frequency shifts during the isotopic substitution are close to theoretical: 2920/2410 = 1.33; 1880/1440 = 1.30; 1380/1042 = 1.32. On transition into a gaseous phase, the spectra of compound I and the O-deutrated derivative of I differ substantially in the absence of absorption bands

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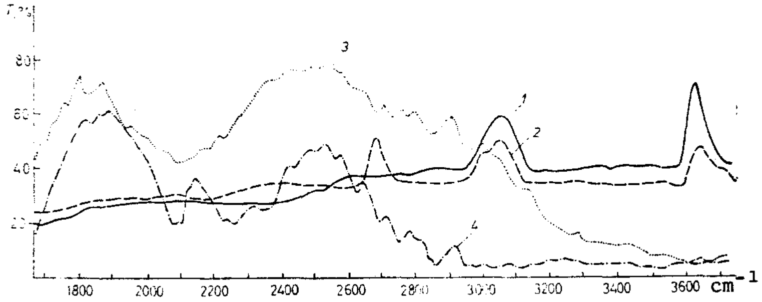

Fig. 1

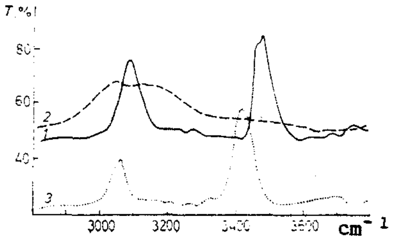

Fig. 2

Fig. 1. IR absorption spectra of 3-hydroxypyridine (I) and its O-deuterated derivative in the gaseous phase at 200°C (1 and 2) and in crystalline state (3 and 4).

Fig. 2. IR absorption spectra of 3-hydroxyquinoline in the gaseous phase at 200°C (1) and in the condensed state [2) KBr tablet; 3) solution in CCl_4].

TABLE 1. IR Spectra of Compounds I and II in Gaseous Phase*

Compound	T, °C	IR spectrum, cm^{-1}		$A \cdot 10^4$ liter·mole^{-1}·cm^{-2}
		ν_{OH}	$\Delta\nu_{1/2}$	
I	200	3658 3648	36,0	0,49±0,01
	250	3647	37,0	0.48±0,01
	300	3647	39,0	0,48±0,01
II	150	3450 3480	24.4	0,69±0,01
	200	3462	27,4	0.69±0.01
	250	3461	31,5	0,72±0,01
	300	3462	35.4	0,71±0,01
	350	3462	39,6	0,83±0,01
III [7]	130—150 250	3655	37,0	0,43±0,04

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*$\Delta\nu_{1/2}$) halfwidth of the ν_{OH} band; A) integral intensity of the ν_{OH} band.

in the 1700-3000 cm^{-1} region. The bands appearing at 3648, 3658 cm^{-1}, characteristic for the IR spectra of the gaseous phase, were assigned to the stretching vibrations of the free OH group, as confirmed by their shift to 2700 cm^{-1} during isotopic substitution (ratio 3653/2700 = 1.35). The position and intensity of ν_{OH} (Table 1) are close to the IR spectrum of phenol (III) [7] in the gaseous phase. In the spectrum of the gaseous-phase of compound I, the absorption bands at 1345 and 1210 cm^{-1}, as in the case of phenol vapors, are also sensitive to the isotopic substitution (they disappear during deuteration) and can be assigned to deformational vibrations of the OH group. It is interesting to note that in the IR spectrum of the gaseous-phase of 2-hydroxyanthraquinone, the absorption band of the stretching vibrations of the OH group also lies at 3656 cm^{-1} [3]. Thus in the gaseous phase under the conditions with the absence of intermolecular intractions, compound 1 has a neutral structure, similar to the structure of phenol, while in the crystalline state a zwitterionic form is characteristic for this compound.

Analysis of the experimental data for compound II (Table 1, Fig. 2) shows that the most prominent difference in the IR spectrum of the gaseous-phase from the IR spectrum of the crystal, consists in considerable increase in the frequency of the stretching vibrations of ν_{OH} (or ν_{NH^+}). The spectrum of the crystalline form is characterized by a broad diffusion band at about 3100 cm^{-1}, while in the gaseous phase and in solution, narrow bands with maxima at 3462 and 3415 cm^{-1}, respectively, are observed. From the data in [5], the absorption band at 3415 cm^{-1} was assigned to ν_{OH}, perturbed by an intramolecular hydrogen bond. It can be assumed that the 3462 cm^{-1} band in the spectrum of the gaseous phase is of the same nature as in the spectrum of a solutions, i.e., it corresponds to the vibrations of the OH group; the decrease in the ν_{OH} frequency in the spectrum of a solution and increase in its intensity in the spectrum of the gaseous phase, compared with the corresponding parameters for compounds I and II (Table 1), is caused by the presence of an intramolecular hydrogen bond. The increase in the ν_{OH} frequency in the spectrum of the gaseous phase of compound II by ∿47 cm^{-1} relative to the spectrum of the solution can be regarded as the result of weakening of the —OH...N hydrogen bond in the intramolecular ring, possibly due to small changes in the bond lengths of the aromatic system and of the intramolecular ring [1].

Thus, in the absence of intermolecular interaction, compounds I and II in the gaseous phase have a neutral structure. On transition into the gaseous state and in the temperature range of 150-350°C, compound II retains the —OH...N intramolecular hydrogen bond.

EXPERIMENTAL

The IR spectra were recorded in the 1000-3800 cm^{-1} region on a UR-20 spectrophotometer. The gaseous phase spectra were obtained using a 13-cm long thermostatted gas cuvette with windows from silicon single crystals 0.5-0.6 mm thick, in the temperature range of 150-350°C. The technique of obtaining the spectra of the compounds in the gaseous phase and the measurement of intensities are described in [8].

3-Hydroxypyridine was recrystallized twice from benzene and dried over KOH under vacuum at 78°C, mp 128°C. The O-deuterated derivative of I was obtained by refluxing hydroxypyridine for 6 h in two portions of D_2O, and was dried over KOH under vacuum at 78°C. 8-Hydroxyquinoline was purified by double crystallization from ethanol and sublimation in vacuo, mp 75.4°C.

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