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Abstract

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ON THE QUESTION OF THE STRUCTURE OF BENZHYDROXAMIC ACIDS AND SOME OF THEIR DERIVATIVES

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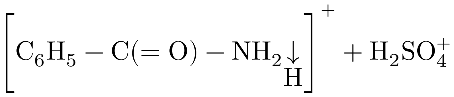
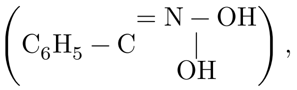
In order to study the structural features of benzhydroxamic acids and of the α- and β-forms of tribenzhydroxylamine in the liquid phase, we carried out an investigation of the absorption spectra in the ultraviolet region of solutions of benzamide, mono- and dibenzhydroxamic acids, and the α- and β-forms of tribenzhydroxylamine in various solvents. The electronic spectra of solutions of the indicated compounds were studied by the method of quantitative ultraviolet spectrography according to Henri (^{1}) on an ISP-22 spectrograph. The spectrum of benzamide in ethanol is characteristic of aromatic amides with one carbonyl group (Fig. 1, 1).

The action of concentrated (96%) sulfuric acid on benzamide causes the appearance of a second absorption band and an increase in the intensity of the absorption maximum (see Fig. 3, 1). This can be explained by the formation of a salt through addition of a proton of sulfuric acid to the noncovalent electron pair of the nitrogen atom of benzamide:



$$\left[C_6H_5-C(=O)-NH_2\underset{H}{\downarrow}\right]^+ + H_2SO_4^+$$

In the spectrum of a solution of monobenzhydroxamic acid in ethanol, a typical phenolic absorption band is observed (Fig. 1, 2). No data have been obtained indicating the existence of molecules of monobenzhydroxamic acid having the structure of hydroxamic acid



$$\left(C_6H_5-C\begin{array}{l}=N-OH\\ \quad|\\ \quad OH\end{array}\right),$$

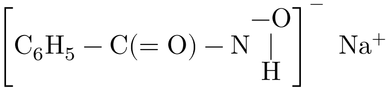
Apparently, in alcoholic solution monobenzhydroxamic acid, as in the crystalline state, exists only in the form of molecules of hydroxamic acid having the structure

Fig. 1 and Fig. 2 absorption spectra

Figure 1: Fig. 1 and Fig. 2 absorption spectra

$$C_6H_5-C(=O)-NH-OH$$

([3]). The shift of the absorption maximum of a solution of monobenzhydroxamic acid in sodium alcoholate into the long-wavelength region (by 40 Å) (Fig. 2, 1) and the 3.2-fold increase in intensity indicate salt formation at the hydroxyl group of monobenzhydroxamic acid:

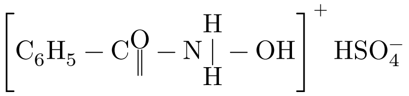


$$\left[C_6H_5-C(=O)-N\overset{-O}{\underset{H}{|}}\right]^{-} Na^{+}$$

An analogous optical effect occurs during salt formation in phenols ([2]).

Under the influence of sulfuric acid, the absorption curve of monobenzhydroxamic acid undergoes a change similar to the curve of benzamide. The appea-

there appears a second absorption band in the middle ultraviolet with a maximum at $\lambda = 2760$ Å and $\varepsilon = 5000$ (Figs. 3, 2). The identical nature of the change in the spectra of monobenzhydroxamic acid and benzamide under the influence of sulfuric acid indicates identical changes in the electronic structures of these compounds. Apparently, such a change in the spectrum in this case is also associated with the formation of a complex salt:



$$\left[C_6H_5-C\overset{O}{\|}-N\overset{H}{\underset{H}{|}}-OH\right]^{+} HSO_4^{-}$$

Dibenzhydroxamic acid in ethanol gives an electronic spectrum analogous to the spectrum of monobenzhydroxamic acid. The difference consists only in a shift of the maximum of the absorption band toward the ultraviolet by 60 Å and a decrease in its intensity by a factor of two (Figs. 1, 2, 3). The similarity

Fig. 1

Fig. 2

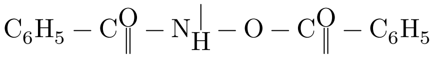
Fig. 1. Absorption spectra of solutions in alcohol ($2\cdot10^{-2}$—$2\cdot10^{-4}$ mol.): 1 —benzamide in alcohol, 2 —monobenzhydroxamic acid, 3 —dibenzhydroxamic acid, 4 —α-form of tribenzhydroxylamine, 5 —β-form of tribenzhydroxylamine

Fig. 2. Absorption spectra of solutions in sodium alcoholate ($2\cdot10^{-2}$—$2\cdot10^{-4}$ mol.): 1 —monobenzhydroxamic acid, 2 —dibenzhydroxamic acid, 3 —α-form of tribenzhydroxylamine, 4 —β-form of tribenzhydroxylamine

Fig. 3. Absorption spectra of solutions in 96% sulfuric acid ($2 \cdot 10^{-2}$—$2 \cdot 10^{-4}$ mol.): 1—benzamide, 2—monobenzhydroxamic acid, 3—dibenzhydroxamic acid, 4—α-form of tribenzhydroxylamine, 5—β-form of tribenzhydroxylamine.

Figure 2: Fig. 3. Absorption spectra of solutions in 96% sulfuric acid ($2 \cdot 10^{-2}$—$2 \cdot 10^{-4}$ mol.): 1—benzamide, 2—monobenzhydroxamic acid, 3—dibenzhydroxamic acid, 4—α-form of tribenzhydroxylamine, 5—β-form of tribenzhydroxylamine.

of the type of absorption in dibenzhydroxamic and monobenzhydroxamic acids indicates the similarity of the chemical structure of the molecules of these substances. Therefore, dibenzhydroxamic acid (like monobenzhydroxamic acid) may be assigned a hydroxamic structure and dibenzhydroxamic acid may be regarded as the benzoic ester of monobenzhydroxamic acid:



$$C_6H_5 - \overset{O}{\underset{\|}{C}} - \underset{H}{\overset{|}{N}} - O - \overset{O}{\underset{\|}{C}} - C_6H_5$$

A certain shift of the absorption maximum toward the ultraviolet and a decrease in intensity occur as a consequence of the absence in dibenzhydroxamic acid of the hydroxyl group and the presence of ether oxygen. Under the action of sodium alcoholate, the absorption band of dibenzhydroxamic acid is sharply displaced toward longer wavelengths (by 650 Å), whereas the absorption maximum, on the contrary, is shifted toward the ultraviolet (by 100 Å) and increases in intensity by a factor of 1.5 (Fig. 2, 2). This optical effect can be explained by the fact that, under the influence of sodium alcoholate, salt formation occurs not at the hydroxyl group, as was the case with monobenzhydroxamic acid, but at the NH group, through replacement of the H atom by sodium:

$$\left[C_6H_5{-}C(=O){-}\ddot{N}{-}O{-}C(=O){-}C_6H_5\right]^- \ Na^+$$

The absorption spectrum of a solution of dibenzhydroxamic acid in concentrated sulfuric acid (Fig. 3, 3) makes it possible to assume salt formation at the NH group through addition of a proton of sulfuric acid to the unshared electron pair of the nitrogen atom:

$$[C_6H_5{-}C(=O){-}N(H)_2{-}O{-}C(=O){-}C_6H_5]^+ \ HSO_4^{\,-}$$

Fig. 3. Absorption spectra of solutions in 96% sulfuric acid ($2 \cdot 10^{-2}$—$2 \cdot 10^{-4}$ mol.): **1**—benzamide, **2**—monobenzhydroxamic acid, **3**—dibenzhydroxamic acid, **4**—α-form of tribenzhydroxylamine, **5**—β-form of tribenzhydroxylamine.

The α- and β-forms of tribenzhydroxylamine in ethanol and in sodium alcoholate solution have substantially different spectra. This reliably indicates a difference in the electronic structures of these substances and confirms our conclusions that the α- and β-forms of tribenzhydroxylamine are not polymorphic modifications of one and the same substance, but isomeric substances possessing different chemical structures (⁀3).

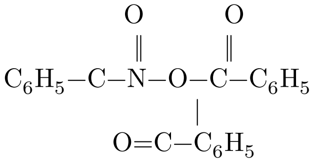
The absorption curve of a solution of the α-form of tribenzhydroxylamine in ethanol resembles in its configuration the curve of an alcoholic solution of benzamide. As in benzamide, the curve of the α-form of tribenzhydroxylamine consists of a single absorption band with a diffuse maximum, but differs by a high absorption intensity (20-fold) (Fig. 1, 4). The similarity of the spectra of benzamide and the α-form, most likely, can be explained by the fact that the α-form should be regarded as substituted benzamide, in which two H atoms in the NH_2 group are replaced by a benzoyl radical

$$C_6H_5{-}C(=O){-}$$

and an ether grouping

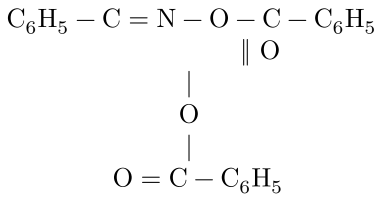
$$-O{-}C(=O){-}C_6H_5,$$

and the α-form of tribenzhydroxylamine as having a hydroxamic structure:



$$\begin{array}{c} \quad\; O \qquad\quad O \\ \quad\;\, \| \qquad\quad\;\, \| \\ C_6H_5{-}C{-}N{-}O{-}C{-}C_6H_5 \\ \qquad | \\ \qquad O{=}C{-}C_6H_5 \end{array}$$

Thus, it is legitimate to consider that the spectrum of the α-form of tribenzhydroxylamine develops from the spectrum of benzamide and attains high intensity of absorption due to the effect of interaction of the noncovalent pair of nitrogen electrons with the π-electrons of two carbonyl groups and with the noncovalent electrons of the ether grouping. This conclusion is in good agreement with the conclusions drawn in the investigation of the infrared absorption spectra of the α-form of tribenzhydroxylamine (3). The absorption curves of the β-form of tribenzhydroxylamine in alcohol and of the sodium alcoholate have no similarity either to any of the spectra of benzhydroxamic acids and differ sharply from the spectrum of benzamide, which indicates a special electronic structure of the β-form. The high intensity of the absorption maxima in the curves of the β-form, as compared with the absorption curves of the α-form of tribenzhydroxylamine, indicates a more excited electronic state of this form. This assumption agrees with the conclusions drawn in the investigation of the absorption spectra in the infrared region, namely that the β-form has a double bond $C = N$, i.e., has the structure of a derivative of hydroximic acid (^{3}):



$$\begin{array}{c} \mathrm{C_6H_5 - C = N - O - C - C_6H_5} \\ \qquad\qquad\quad \| \; \mathrm{O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{O = C - C_6H_5} \end{array}$$

A somewhat different spectral picture is given by the absorption of solutions of the α- and β-forms of tribenzhydroxylamine in concentrated (96%) sulfuric acid. In the spectra of solutions of these forms in sulfuric acid, the differences between the curves disappear, and they have almost coincident absorption maxima (Figs. 3, 4, 5). The identity of the absorption curves of the α- and β-forms of tribenzhydroxylamine in this case can apparently be explained by the identical products that are formed upon cleavage of the α- and β-forms of tribenzhydroxylamine under the influence of sulfuric acid. Indeed, as we have established experimentally, under the action of concentrated sulfuric acid both forms of tribenzhydroxylamine are converted into dibenzhydroxamic and benzoic acids.

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