Reports of the Academy of Sciences of the USSR

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 156, No. 6

CHEMISTRY

I. M. GINZBURG, L. A. LOGINOVA

SPECTROSCOPIC MANIFESTATIONS AND THE ENERGY OF THE INTRAMOLECULAR HYDROGEN BOND IN THIOSALICYLIC ACID

(Presented by Academician A. N. Terenin, 26 II 1964)

At present it may be regarded as firmly established that the SH group of sulfhydryl molecules participates in the formation of H-bonds of the type SH ···Y, where Y may be a sulfur atom of the same molecules (self-association) or another atom with an unshared electron pair, belonging to some electron-donor molecule (mixed association). A number of works have shown that, on passing from pure aliphatic (1,2) and aromatic (3) mercaptans to solutions in inert solvents, the band of the stretching vibration of the SH group in the infrared spectra shifts to higher frequencies; moreover, within a certain concentration interval, bands of both free and associated sulfhydryl groups are observed. Still more considerable shifts of the SH band were observed in studies of stronger H-bonds between thiophenol and a series of electron-donor molecules (4–6). However, in all the works listed, only the region of the stretching vibration of the SH group was investigated, and there are no data relating to changes in the spectrum of the electron-donor molecule with atom Y. Meanwhile, it is precisely the changes in the vibrations of fixed electron-donor molecules caused by the formation of H-bonds SH ···Y and OH ···Y that can provide the most valuable information for comparing the relative proton-donor ability of OH and SH groups. A comparison of the energies of the indicated hydrogen bonds would also be very interesting; however, data on the energies of H-bonds of the type SH ···Y are completely absent from the literature.

In the present work, infrared spectra were obtained for solutions in CCl_4 of salicylic and thiosalicylic acids in the region of the stretching vibration of the carbonyl group (NaCl prism) and of the stretching vibration of the SH group (LiF prism). The spectra were recorded on a single-beam infrared spectrometer IKS-12, equipped with an optoacoustic receiver OAP-1 and an alternating-current amplifier. The spectra of thiosalicylic acid were obtained at five different temperatures (7–60°).

1. It is known (7,8) that in the salicylic acid molecule there is a strong intramolecular H-bond with the formation of a six-membered ring, which determines the chemical and biological properties of this compound. In the crystalline state and in not very dilute solutions, in addition, cyclic dimers characteristic of carboxylic acids are formed, so that both unshared

pairs of the oxygen atom of the carbonyl group take part in the formation of two H-bonds:

(Figure: structural formula of cyclic dimer of salicylic acid with intramolecular and intermolecular hydrogen bonds)

In accordance with such a structure, in the spectrum of salicylic acid in the region of carbonyl absorption, at concentrations of 0.01–0.005 mol/liter, we observed two bands, attributable to dimers (1662 cm^{-1}) and to monomers (1696 cm^{-1}) with an intramolecular hydrogen bond. The shift of the frequency of the carbonyl group associated with the monomer–dimer equilibrium is here 34 cm^{-1}, which is considerably smaller than, for example, for benzoic acid (45 cm^{-1}). This is due to the weakening, because of the presence of an intramolecular H bond, of the electron-donor properties of the unshared pair responsible for the formation of dimers. If the frequency of the free carbonyl group is taken to be equal to the frequency of the carbonyl group of the monomer n-CH_3O–C_6H_4COOH (1737 cm^{-1} [9]), then the shift caused by the formation only of an intramolecular H bond in salicylic acid is 41 cm^{-1}.

Fig. 1. Absorption spectra of solutions in CCl_4 of thiosalicylic acid at concentrations (in mol/l):
1 –0.015; 2 –0.002; 3 –0.0004.

In the carbonyl region in the spectrum of a solution of thiosalicylic acid (Fig. 1), at a concentration of 0.015 mol/liter, a band at 1687 cm^{-1} is observed, corresponding to dimers. When the concentration is decreased, bands appear at 1732 and 1718 cm^{-1}, the intensity of which increases with further dilution of the solution. The presence of these two bands of approximately equal intensity can be explained by the existence at room temperature of an equilibrium between two structures of monomeric molecules: with an intramolecular hydrogen bond (I) and without it (II)

$$\text{(I) thiosalicylic acid with intramolecular SH}\cdots\text{O=C H-bond} \rightleftharpoons \text{(II) thiosalicylic acid without this bond}$$

The absence of a doublet structure of the dimer band means that, as the concentration is increased, with the formation of dimers through the carboxyl groups, the intramolecular hydrogen bonds $SH \cdots O = C$ are broken, and the carbonyl oxygen (unlike in salicylic acid) participates only in the intermolecular H bond. The shift of the frequency of the carbonyl group caused by the formation of the intramolecular H bond $SH \cdots O = C$ is 14 cm^{-1}, while the shift due to the formation of dimers is 45 cm^{-1}, i.e., it coincides with the value $\Delta\nu_{C=O}$ of benzoic acid. The latter circumstance agrees with the conclusion that there is no intramolecular H bond of type I in dimers of thiosalicylic acid.

Table 1

Compound	Monomer, free $\Delta C = O$, cm^{-1}	Monomer with intramolecular H bond $\Delta C = O$, cm^{-1}	Dimer $\Delta C = O$, cm^{-1}	Monomer—intramolecular H bond $\Delta\nu_{C=O}$, cm^{-1}	Monomer—dimer $\Delta\nu_{C=O}$, cm^{-1}
C_6H_5COOH	1740		1695		45
o-HOC_6H_4COOH	1737(9)	1696	1662	41	75
o-HSC_6H_4COOH	1732	1718	1687	14	45

The results of the investigation of the carbonyl region are presented in Table 1, into which, for comparison, data for benzoic acid have been included.

The validity of the conclusions concerning the types of equilibria in a solution of thiosalicylic acid is confirmed by an investigation of the absorption spectra in the region—

of the stretching vibration of the SH group (Fig. 2). At a concentration of 0.015 mol/l, when almost all molecules are dimerized, the spectrum shows a band of free sulfhydryl groups at 2562 cm^{-1} with a shoulder at about 2530 cm^{-1}, apparently due to the H-bond SH ···O with the oxygen of the hydroxyl group of the dimers. Upon dilution and, consequently, with a decrease in the fraction of dimers, the intensity of the 2562 cm^{-1} band decreases, which means a decrease in the number of free sulfhydryl groups, since some of them become involved in an intramolecular H-bond with the liberated carbonyl groups. Taking the shift of the carbonyl band $\Delta\nu_C = 0$, caused by the formation of intramolecular H-bonds OH ···O = C and SH ···O = C in the compounds studied, as a measure of their strength, one may conclude that, all other conditions being equal, the sulfhydryl group has a lower ability to form an H-bond than the hydroxyl group.

(Figure: Fig. 2)

Fig. 2. Absorption spectra of solutions in CCl_4 of thiosalicylic acid with concentrations (in mol/l): 1 —0.015; 2 —0.003; 3 —0.00075

2. The temperature dependence of the intensities of the carbonyl bands of structures I and II makes it possible to calculate the energy of the intramolecular H-bond in thiosalicylic acid. The equilibrium constant for the mutual transition of structures I and II is equal to the ratio of their concentrations C_I/C_{II}. Expressing the concentration through the optical density D and the absorption coefficient ε, we obtain the equilibrium constant $K = \varepsilon_{II} D_I / \varepsilon_I D_{II}$. On the other hand, the equilibrium constant is equal to $K = A' \exp(-\Delta H/RT)$, where $-\Delta H$ is the energy of hydrogen-bond formation. Combining the two expressions, one may write

$$\frac{D_I}{D_{II}} = A\exp(-\Delta H/RT).$$

Assuming the temperature dependence of the absorption coefficients of both forms I and II to be the same, their ratio $\varepsilon_I/\varepsilon_{II}$ may be included in the pre-exponential factor A, which is independent of temperature. The H-bond energy is found from the graph of the dependence of $\ln D_I/D_{II}$ on $1/T$ (Fig. 3). To determine D_I and D_{II}, the bands were separated graphically.

(Figure: Fig. 3)

Fig. 3. Dependence of $\ln D_I/D_{II}$ on $1/T$ for a solution of thiosalicylic acid in CCl_4

The energy of the intramolecular H-bond in thiosalicylic acid SH ···O=C is 0.9 ± 0.3 kcal/mol. The magnitude of the error is connected chiefly with the choice of the line of complete transmission and with the graphical separation of the bands.

The energy of the intramolecular H-bond in salicylic acid, according to data[10,11], is about 5 kcal/mol.

Thus, direct measurement of the energy indicates substantially weaker proton-donor properties of the SH group in comparison with the OH group.

3. In connection with the results obtained, it is important to note that the direct dependence, widely observed for hydroxyl-containing compounds, between the ability of a molecule to act as a proton donor in an H-

the bond and with its strength as an acid (pK) is not fulfilled when proton-donor molecules are compared in which the X atoms of the XH bond are in different periods of the Mendeleev table. Thus, in the series of hydrohalic acids, whose strength increases from HF to HI, the energy of the H-bond formed by these acids with one and the same electron-donor molecule changes in the reverse order (12). An analogous effect is observed in the present work for SH and OH groups, of which the former, in analogous compounds, possesses stronger acidic properties (13), but, other conditions being equal, forms a less strong H-bond.

The experimentally observed inverse relation between the ability of proton-donor molecules to form an H-bond and their acidic properties, manifested in the ability to ionize with complete transfer of the proton to a base molecule, is apparently connected with the difference in the nature of these two phenomena. The concept of a hydrogen bond and of complete proton transfer as limiting cases of one and the same process, determined by a donor–acceptor mechanism, does not reflect these differences. It may be supposed that the interaction between an acid and a base begins with the formation of a hydrogen bond. However, the subsequent stages of this process, leading to proton transfer, will be determined by other characteristics of the reacting molecules.

The strength of the hydrogen bond RXH···YR′ for a given electron donor YR′ depends chiefly on the degree of protonization of the hydrogen atom, X—H (14). In the case of one and the same atom X, both the degree of protonization and the acidic properties of the molecules are determined by the influence of the radical R on the X—H bond and therefore vary in parallel. When proton-donor molecules with different X atoms are compared, differences in the electronic structure of these atoms must be taken into account. Thus, in compounds with an SH group the proton is more strongly screened by the electron cloud of the molecule than in analogous hydroxyl-containing compounds, which is connected with the greater spatial delocalization of the valence orbitals of the sulfur atom in comparison with the orbitals of oxygen. This same circumstance is the reason for the lower energy of the proton bond in the SH group as compared with OH.

Thus, replacement of the oxygen atom by sulfur in the X—H group causes, on the one hand, a decrease in the degree of protonization of the hydrogen atom, leading to weakening of the hydrogen bond with the electron donor YR′, and, on the other hand, loosening of the X—H bond, increasing its ability to ionize with complete transfer of the proton.

The difference in the nature of the H-bond and of the donor-acceptor interaction associated with charge transfer is also observed when electron-donor molecules are compared in which the atoms with an unshared pair are located in different periods of the system of elements (15).

The authors express their gratitude to Prof. V. M. Chulanovskii for useful advice and comments and to G. S. Denisov for discussion.

Leningrad
Chemical-Pharmaceutical Institute

Received
22 II 1964

CITED LITERATURE

1. R. Spurr, H. F. Byers, *J. Phys. Chem.*, **62**, 425 (1958).
2. M. O. Bulanin, G. S. Denisov, R. A. Pushkina, *Optics and Spectroscopy*, **6**, 754 (1959).
3. M. L. Josien, C. Castinel, P. Saumagne, *Bull. Soc. chim. France*, 1957, 648.
4. M. L. Josien, P. Dizabo, P. Saumagne, *Bull. Soc. chim. France*, 1957, 423.
5. A. Wagner, H. J. Becher, K. Kottenhahn, *Chem. Ber.*, **89**, 1708 (1956).

6. W. Gordy, S. Stanford, *J. Am. Chem. Soc.*, **62**, 497 (1940).
7. L. Pauling, *The Nature of the Chemical Bond*, 1947, p. 300.
8. C. J. W. Brooks, G. Eglinton, J. F. Morman, *J. Chem. Soc.*, 1961, 661.
9. M. St. C. Flett, *Trans. Farad. Soc.*, **44**, 767 (1948).
10. D. N. Shigorin et al., *DAN*, **108**, 672 (1956).
11. J. Hermans, S. J. Leach, H. A. Scheraga, *J. Am. Chem. Soc.*, **85**, 1390 (1963).
12. D. N. Shchepkin, Report at the VII European Congress on Molecular Spectroscopy, Budapest, 1963.
13. J. Mathieu, A. Allais, *Principles of Organic Synthesis*, IL, 1962, p. 586.
14. V. M. Chulanovskii, *Izv. AN SSSR, Ser. Fiz.*, **22**, 1103 (1958).
15. I. M. Ginzburg, *Optics and Spectroscopy*, **17**, No. 2 (1964).

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