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Abstract

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INFRARED ABSORPTION SPECTRA AND THE STRUCTURE OF THIOUREA DIOXIDE

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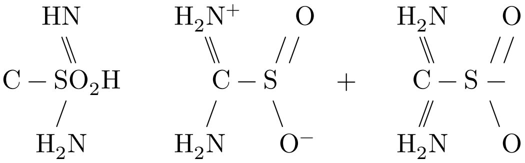
Barnett (¹), who synthesized thiourea dioxide $(NH_2)_2CSO_2$ by oxidizing thiourea with hydrogen peroxide, proposed for it the formula of formamidinesulfinic acid (I) on the basis of data on its composition and properties in solutions.



$$\begin{array}{c} HN \\ \backslash\!\backslash \\ C - SO_2H \\ / \\ H_2N \end{array} \qquad \begin{array}{ccc} H_2N^+ & & O \\ \backslash\!\backslash & & // \\ & C - S & \\ / & & \backslash \\ H_2N & & O^- \end{array} \quad + \quad \begin{array}{ccc} H_2N & & O \\ \backslash\!\backslash & & // \\ & C - S - & \\ // & & \backslash \\ H_2N & & O \end{array}$$

(I) (II) (III)

Hardcastle, to whose private communication the authors of the X-ray structural study of thiourea dioxide (²) refer, proposed formula II. In paper (²) the crystalline and molecular structure of thiourea dioxide was studied. It was found that all eight atoms of the $(H_2N)_2CS$ group lie almost in one plane, while the CSO_2 group forms a pyramid with the sulfur atom at the apex. One of the features of the structure, according to (²), is the presence of a weak CS bond (its length is 1.851 ± 0.016 Å, i.e., greater than the length of a single CS bond (~ 1.81 Å)), which explains the relative ease of rupture of this bond. The NH_2 and SO_2 groups of neighboring molecules are linked by hydrogen bonds. The lengths of both SO bonds (1.490 ± 0.008 Å) somewhat exceed the lengths of double bonds $S = O$ (~ 1.44 Å), but are considerably less than the lengths of single bonds $S - O$ (~ 1.82 Å). For the lengths of both CN bonds the same value is given, 1.310 ± 0.008 Å, almost equal to the lengths of CN bonds in thiourea (1.33 ± 0.01 Å (³)). Thus, the results of the X-ray structural study (²) seem to indicate that in thiourea dioxide in the crystalline state there is no double bond $C = N$ and no amidino grouping. Schematically, this can evidently be represented by formula III, in which the $C = N$ and $S = O$ bonds are intermediate between single and double bonds.

Since certain information on the state of bonds can sometimes be provided by the study of vibrational spectra, we investigated the IR absorption spectra of thiourea dioxide (undeuterated and deuterated) in the crystalline state.

Fig. 1. IR absorption spectra of thiourea dioxide and deuterated thiourea dioxide

Figure 1: Fig. 1. IR absorption spectra of thiourea dioxide and deuterated thiourea dioxide

Thiourea dioxide was synthesized, according to (^{1}), by oxidizing thiourea with hydrogen peroxide in the cold; the needle-shaped crystals that separated from the solution were filtered off, washed with alcohol, and dried in a vacuum desiccator over sulfuric acid. Deuterated thiourea dioxide was obtained by repeated (up to 13 times) recrystallization from heavy water (D_2O) at room temperature.

The spectra ($\sim$ 400-4000 cm^{-1}) were recorded on double-beam spectrophotometers IKS-14 and UR-10. Mulling techniques with Vaseline and fluorinated oils and pressing with potassium bromide were used. The absorption of the Vaseline oil was compensated as far as possible. The presence of ν(NH) bands in the region $\sim$ 3000-3300 cm^{-1} in the spectrum of deuterated

···of the investigated sample indicates that the latter contained an impurity of undeuterated or partially deuterated thiourea dioxide; however, in the other regions of the spectrum of the deuterated sample the intensity of the absorption bands of undeuterated dioxide is insignificant.

It was noted above that the results of the structural investigation (2) indicate that the bond between the $(NH_2)_2C$ group and the SO_2 group in the thiourea dioxide molecule is weak. The spectra obtained (Fig. 1) are consistent with these conclusions. Indeed, if the $(NH_2)_2C$ and SO_2 groups are connected by a weak bond, then deuteration should have practically no effect on the vibrational frequencies of the SO_2 group. The experiment showed that

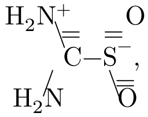
Fig. 1. IR absorption spectra of thiourea dioxide $(NH_2)_2CSO_2$ (**A**) and deuterated thiourea dioxide $(ND_2)_2CSO_2$ (**B**). The region 400—2000 cm^{-1} is in vaseline oil; 2000—4000 cm^{-1} and the separate section $\sim$ 1300—1500 cm^{-1} are in fluorinated oil. Absorption of vaseline oil is marked with an asterisk.

the vibrational frequencies of the SO_2 group practically did not change upon deuteration of thiourea dioxide. By analogy with the spectra of other compounds containing SO bonds, it may be expected that the bands of the stretching vibrations of the SO_2 group will be located in the spectra of thiourea dioxide in the region $\sim$ 900—1200 cm^{-1}. Comparison of the spectra of undeuterated and deuterated thiourea dioxide (Fig. 1) shows that the triplet in the region $\sim$ 1000—1100 cm^{-1} is not shifted upon deuteration and, consequently, belongs to the stretching vibrations of the SO_2 group. The band with a maximum at 503 cm^{-1}, which is shifted only slightly upon deuteration to 498 cm^{-1} (this shift is almost within the limits of experimental error), may be assigned to the deformation vibrations of this group. The low strength of the bond between the $(NH_2)_2C$ and SO_2 groups and the practical invariance of the vibrational frequencies of the SO_2 group upon deuteration indicate that the kinematic interaction of the two groups is small. Therefore, to a fairly good approximation, the vibrations of the $(NH_2)_2C$ and SO_2 groups may be considered separately. In this approximation the SO_2 group is a triatomic entity with C_{2v} symmetry and has three vibrational frequencies $\nu_1(A_1)$, $\nu_2(A_1)$, and $\nu_3(B_1)$, corresponding respectively to symmetric stretching, deformation, and antisymmetric stretching vibrations. To $\nu_2(A_1)$,

can be assigned the frequency 503 cm^{-1} (498 cm^{-1} in the spectrum of the deuterated dioxide). The assignment of the frequencies of the stretching vibrations of the SO_2 group is somewhat more complicated, since three frequencies were found instead of two. We assigned the highest frequency, 1060 cm^{-1} (1061 cm^{-1} for the deuterated dioxide), to the antisymmetric stretching vibration, and the doublet 1002 and 1027 cm^{-1} (1003 and 1026 cm^{-1} in the spectrum of the deuterated dioxide) to the symmetric stretching vibration. Apparently, the appearance in the spectrum of three, rather than two, frequencies of stretching vibrations of the SO_2 group is due to the influence of the crystalline state on the vibrations of the thiourea dioxide molecule. From the frequencies found, $\nu_1(A_1)$, $\nu_2(A_1)$, and $\nu_3(B_1)$, an approximate value of the force constant of the SO bonds was calculated from the equations for a nonlinear symmetric triatomic molecule given in (4). In doing so, for $\nu_1(A_1)$ the value 1015 cm^{-1} was adopted, the average of the two components found, 1027 and 1002 cm^{-1}. The calculated constants are equal (in mdyn/Å): $k_{SO} = 6.61$ and $k_{SO,SO} = 0.33$, where k_{SO} and $k_{SO,SO}$ are, respectively, the force constant of the SO bonds and the interaction coefficient of these bonds. The values obtained for the constants are, of course, approximate; what is important is not their absolute values but their order of magnitude. The magnitude of the force constant of the SO bonds in thiourea dioxide is smaller than the values of the force constants of double S=O bonds ($\sim$ 10–12 mdyn/Å (5)), but exceeds the values of the force constants of single S–O bonds ($\sim$ 2.7–4.3 mdyn/Å (5-7)). Consequently, in complete agreement with the structural data, the bonds in thiourea dioxide are intermediate between single and double.

The remaining bands in the investigated region of the spectrum are evidently due mainly to absorption by the $(NH_2)_2C$ group. In the spectrum of thiourea dioxide, an intense band is found with a maximum at 1696 cm^{-1}, shifting on deuteration to 1651 cm^{-1}. Such a small shift indicates that this band is not due to deformation vibrations of the NH_2 groups. Nor can it be assigned to vibrations with predominant participation of single C–N bonds, since the corresponding frequencies should be considerably lower. The only possibility remains–to assign this band to a vibration with predominant participation of the double C=N bond. Absorption bands assigned to stretching vibrations (predominantly) of double C=N bonds in the spectra of amidine derivatives lie in the region $\sim$ 1590–1690 cm^{-1} (8-10). The order of the shift of the band under discussion in the spectrum of thiourea dioxide upon deuteration ($\sim$ 45 cm^{-1}) is the same as for the frequencies of stretching vibrations (predominantly) of double C=N bonds of amidine groupings.

Thus, it must be concluded that in the thiourea dioxide molecule in the crystalline state there is a double C=N bond. It follows from this that the second CN bond must be single, i.e., contrary to the structural data (2), the CN bonds in the thiourea dioxide molecule are not identical; the equilibrium lengths of these bonds must also be different. Taking into account that, apparently, two hydrogen atoms are bonded to each nitrogen atom (2), one can conclude that the thiourea dioxide molecule has the structure



close to that proposed by Hardcastle (see above, formula II). The $-SO_2^-$ group, both SO bonds of which are equalized, bears a negative charge. The positive charge is concentrated on the NH_2^+ group, whose nitrogen atom is connected by a double bond to the carbon atom. Thus an acidic amidine grouping is present in the molecule.

Table 1 gives the vibrational frequencies found and their assignment. The complex asymmetric band in the region ~ 2900–3300 cm^{-1} (with principal maxima at ~ 3058 and ~ 3258 cm^{-1}), which shifts upon

Table 1

Wave numbers of the maxima of absorption bands, in cm^{-1}, found in the spectra of thiourea dioxide, and their assignment

Compound	ν_{as}(SO)	ν_s(SO)	$\delta(SO_2)$	$\nu(C=N)$	ν(NH)	ν(ND)	Other frequencies
$(NH_2)_2CSO_2$	1060	10271002	503	1696	$\sim$ 3258$\sim$ 3053$\sim$ 2790	–	1438 (superposed on the broad band $\sim$ 1350 – 1600) $\delta(NH_2)$, 1213, 1126, 743 $\delta(NH_2)$, 689, 621 $\delta(NH_2)$

Compound	ν_{as}(SO)	ν_s(SO)	$\delta(SO_2)$	$\nu(C=N)$	ν(NH)	ν(ND)	Other frequencies
$(ND_2)_2CSO_2$	1061	10261003	498	1651	–	$\sim$ 2448 $\sim$ 2260	$\sim$ 3225 ν(NH), $\sim$ 3145 ν(NH), $\sim$ 3070 ν(NH), 1758, 1695 $\nu(C=N)$ of undeuterated dioxide, 1545, 1502, 1412, 1318, 941, 895, 844 $\delta(ND_2)$, 786, 706 $\delta(ND_2)$, 693, 594 $\delta(ND_2)$, 553 $\delta(ND_2)$, $\sim$ 400

* C–24.2%.

deuteration in the region $\sim$ 2200–2600 cm^{-1} (with principal maxima at $\sim$ 2260 and $\sim$ 2448 cm^{-1}) are, beyond any doubt, assigned to stretching vibrations of the NH_2 groups perturbed by hydrogen bonds. The remaining bands, which shift substantially upon deuteration, are evidently assigned to deformation vibrations involving NH bonds (predominantly or partially).

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