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Abstract

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PROTON MAGNETIC RESONANCE IN SELENOUREA

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Selenourea is one of the compounds of the type $EC(NH_2)_2$, where E denotes the elements O, S, Se. A schematic view of the selenourea molecule is given in Fig. 1. Urea $OC(NH_2)_2$ ([1], [2]) and thiourea $SC(NH_2)_2$ ([3], [4]) have already been studied by the nuclear magnetic resonance method. In these studies the presence of reorientation (internal rotation) of urea molecules above 300° K and of thiourea molecules above 220° K was found.

We have studied, by the proton magnetic resonance method, a polycrystalline sample of selenourea in the temperature range from 77° K to room temperature. In doing so, we obtained the dependence of the second moment of the proton-resonance absorption line on temperature, presented in Fig. 2.

The value of the second moment at low temperatures, equal to 18.2 oersted, makes it possible to determine the distance between protons in the NH_2 groups. It may be assumed that the N–H distance in such compounds, as follows from numerous determinations ([5], [6]), is about 1 Å; therefore the contribution from the interaction of a proton with the nearest nitrogen to the second moment, calculated by the Van Vleck formula ([7]), is 2 oersted. The contribution of the protons of neighboring NH_2 groups is more difficult to calculate, since the crystal structure of selenourea is unknown. It may be supposed, however, that it is close to the structure of thiourea. Under this assumption, the contribution of the protons of neighboring groups to the second moment is 0.15 oersted. The remaining 15.85 oersted are due to the proton-proton interaction within the NH_2 group. According to the Van Vleck formula this corresponds to a distance between the protons in the NH_2 groups equal to 1.75 Å, which is close to the analogous distance in urea ([8]) and thiourea ([6]).

The decrease of the second moment from 18.2 to 6.9 oersted as the temperature changes from 130 to 180° K may be caused either by rotation (reorientation) of the NH_2 groups about the C–N bond, or by rotation of the whole molecule about its Se=C axis. As is known ([9]), upon reorientation of groups of atoms the decrease of the second moment is determined by the factor

Fig. 1. Schematic view of the selenourea molecule

Figure 1: Fig. 1. Schematic view of the selenourea molecule

$$k = \frac{1}{4}(3\cos^2\theta - 1)^2, \tag{1}$$

where θ is the angle between the direction of the proton-proton vector and the axis of reorientation. It is easy to see that a decrease of the second moment from 18.2 to 6.9 oersted corresponds to an angle $\theta = 30°$. Such an angle is realized only if the selenourea molecule rotates about the Se=C axis (see Fig. 1), whereas rotation of the NH_2 group about the C–N bond does not satisfy this condition (the angle between the C–N reorientation axis and the p–p vector is 90°). It should be noted that the decrease of the second moment from 18.2 to 6.9 oersted could also be explained by rocking of the NH_2 groups about the C–N bond through an angle of $\$\pm 40°.However, asDasshowed(\hat{}\{10\}\$)$, the probability of such large amplitudes of oscillation is negligibly small, and therefore this possibility should be rejected as unrealistic.

The dependence of the second moment on temperature makes it possible to calculate the height of the potential barrier that hinders the rotation of the molecules $SeC(NH_2)_2$. As Gutowsky and Pake showed ([11]), the temperature dependence of the second moment is determined by the expression

$$S_2(T) = S_2^{\mathrm{l}} + (S_2^{\mathrm{h}} - S_2^{\mathrm{l}})\,\frac{\pi}{2}\,\mathrm{arc\,tg}\left(\frac{\gamma S_2^{1/2}(T)}{2\pi\nu_k}\right), \tag{2}$$

where S_2^{l}, S_2^{h}, and $S_2(T)$ are the second moments, respectively, at low temperatures, high temperatures, and at temperature T; ν_k is the correlation frequency of reorientation, which can be represented in the form ([10,11])

$$\nu_k = \nu_0 \exp\left(-\frac{V_0}{kT}\right) = \frac{1}{2\pi}\left(\frac{2V_0}{I}\right)^{1/2} \exp\left(-\frac{V_0}{kT}\right); \tag{3}$$

where V_0 is the so-called torsional frequency of rotation of a molecule with moment of inertia I over a barrier of height V_0; k is Boltzmann' s constant; T is the absolute temperature.

The moment of inertia of the selenourea molecule for its rotation about the Se = C axis was calculated on the assumption that the C—N and N—H distances are analogous to the corresponding distances in urea and thiourea, and is $I = 70.5 \cdot 10^{-40}$ g · cm^2.

Fig. 1. Schematic view of the selenourea molecule

Fig. 2. Temperature dependence of the second moment of the proton-resonance absorption line in a polycrystal of $SeC(NH_2)_2$

Figure 2: Fig. 2. Temperature dependence of the second moment of the proton-resonance absorption line in a polycrystal of $SeC(NH_2)_2$

With the aid of formula (2), from experimental data on the temperature dependence of the second moment one can determine the dependence of the correlation frequency ν_k on temperature. Comparing it with the dependence calculated by formula (3), one can, for a known moment of inertia, determine the height of the potential barrier V_0. Figure 3 gives the theoretical dependences $\nu_k(T)$, calculated by formula (3), for different values of V_0, and the experimental values calculated by formula (2). As can be seen from the figure, the experimental values agree well with the theoretical dependence for

$$V_0 = (6.0 \pm 0.4) \text{ kcal/mole}.$$

Fig. 2. Temperature dependence of the second moment of the proton-resonance absorption line in a polycrystal of $SeC(NH_2)_2$

Thus, it may be regarded as established that, in selenourea crystals, reorientation (rotation) of the $SeC(NH_2)_2$ molecules takes place around the Se = C axis at temperatures above 130° K. It should be noted, however, that such "rotation" is not continuous. The torsional frequency of rotation of a selenourea molecule having energy greater than V_0, as is seen from formula (3), is of the order $\nu_0 \approx 10^{12}$ Hz. The reorientation process itself apparently consists of very rapid turns of the molecules, repeated rather frequently, through an angle of 180°, and more rarely through 360° or more. The correlation frequency ν_k in fact represents the result of averaging these turns over all the molecules participating in the motion, on the assumption that their rotation occurs uniformly with frequency ν_k.

The correlation frequency determined from the experimental data for a temperature of 150° K is of the order of 10^4 Hz, and for room temperature about 10^{10} Hz. Thus, even at room temperature the lifetime of a molecule in the state of "rest" is approximately 100 times greater than the time spent by the molecule in rotation, while at a temperature of 150° K the ratio of these times is 10^8.

Of great interest is the nature of the potential barrier limiting the rotation of selenourea molecules. Although in the general case the nature of such barriers is unclear, in this particular case one may assume that the barriers limiting the rotation of the molecules $SeC(NH_2)_2$ are intermolecular hydrogen bonds $NH \cdots Se$. This, in particular, is confirmed by the fact that the barriers to rotation of thiourea and urea molecules, calculated according to ([2], [3]), are respectively 9 and 12.7 kcal/mole. At the same time it is known ([8]) that the hydrogen bond $NH \cdots S$ in thiourea is weaker than the bond $NH \cdots O$ in urea. From our point

Fig. 3. Temperature dependence of the correlation frequency of reorientation of $SeC(NH_2)_2$ molecules

Figure 3: Fig. 3. Temperature dependence of the correlation frequency of reorientation of $SeC(NH_2)_2$ molecules

of view this is understandable, since strong hydrogen bonds NH ··· E should correspond to high potential barriers limiting the rotation of $EC(NH_2)_2$ molecules. Thus, the value we have obtained for the barrier height for rotation of selenourea molecules, $V_0 = 6$ kcal/mole, indicates that the hydrogen bonds NH ··· Se are still weaker than the bonds NH ··· S and NH ··· O in thiourea and urea.

Fig. 3. Temperature dependence of the correlation frequency of reorientation of $SeC(NH_2)_2$ molecules

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