566. *Nuclear Resonance Spectra of Sulphoperamidic Acid.*

By R. E. RICHARDS and R. W. YORKE.

Line shapes and second moments have been measured for the hydrogen resonance spectra of sulphoperamidic acid crystals at 20° K, 90° K, and at room temperature. High-resolution hydrogen resonance spectra have also been obtained for a solution of this substance in dimethylformamide. It is shown that this substance both in the crystalline state and in solution in dimethylformamide exists as the zwitterion $H_3N^+O\cdot SO_3^-$. In the crystalline state the H–H distance is 1·72 Å with an upper limit of 1·75 Å. If ∠HNH is assumed to be tetrahedral this leads to an N–H distance of 1·06 Å with an upper limit of 1·07 Å.

SULPHOPERAMIDIC ACID can be represented in two possible ways, one of which is a zwitterion

$$\text{(I)}\quad NH_2\cdot O\cdot SO_3H \qquad\qquad H_3N^+O\cdot SO_3^-\quad \text{(II)}$$

Sommer *et al.*[1] favoured structure (I), regarding the acid as the amide of Caro's acid $HO\cdot O\cdot SO_3H$ on account of its strong oxidizing properties. Wannagat and Pfeiffenschneider [2] tried unsuccessfully to liberate Caro's acid by hydrolysis and by gentle oxidation of the NH_2 group with derivatives of nitrous acid. The decomposition of sulphoperamidic acid in ether suspension with diazomethane solution at —20° to +20°C did not proceed as expected; instead of $NH_2\cdot O\cdot SO_3\cdot CH_3$, a compound with three methyl groups all attached to the nitrogen atom was produced. Thus under mild conditions the total sulphur could be detected as sulphate. The methylated acid gave an identical *X*-ray pattern with that of the compound obtained by the union of trimethylamine oxide and sulphur trioxide which probably has the formula $(CH_3)_3N^+O\cdot SO_3^-$. This corresponds with the compound $C_5H_5N\cdot O\cdot SO_3$ prepared by Baumgarten and Erbe [3] from pyridine *N*-oxide and sulphur trioxide. Sulphoperamidic acid, which can be prepared from hydroxylamine and sulphur trioxide, was not therefore interpreted as the amide of Caro's acid but as the sulphur trioxide adduct to the amine oxide formula (NH_3O) of hydroxylamine. This formula was first discussed by Baumgarten and Erbe in 1938 but they finally favoured structure (I).

Further confirmation of the zwitterion formula has therefore been attempted, by

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[1] Sommer, Schulz, and Nassau, *Z. anorg. Chem.*, 1925, **147**, 142.
[2] Wannagat and Pfeiffenschneider, *Naturwiss.*, 1956, **43**, 178.
[3] Baumgarten and Erbe, *Ber.*, 1938, **71**, 2603.

locating the positions of the hydrogen atoms from the hydrogen magnetic resonance spectra.

EXPERIMENTAL

The acid was prepared by Sommer, Schulz, and Nassau's method.[1] Pure dry ether, methanol, and chloroform were prepared by the usual methods. 30 ml. of chlorosulphuric acid were allowed to flow slowly from a dry pipette on to 13 g. of hydroxylamine sulphate. A vigorous reaction took place and when the mixture was warmed to about 100° the acid was precipitated. Heating was continued for 5 min. until the toughness of the thin paste stopped increasing. The mixture was allowed to cool in a desiccator and was then added slowly to ice-cold dry ether. The acid was made into a paste by stirring the suspension so that it could be filtered off rapidly under suction. It was washed with dry ether several times and dried in a desiccator over phosphoric oxide.

A fairly pure product is obtained directly, but to obtain a purer form, the whole mixture was dissolved with prolonged stirring in about 60 ml. of dry, ice-cold methyl alcohol, care being taken to avoid a rise in temperature. The solution was filtered and allowed to drop into 120 ml. of dry chloroform, from which stirring precipitated the pure acid as fine crystals. These were filtered off and dried in a vacuum-desiccator in which they were stored until required. The sulphoperamidic acid was found to be 98·2% pure by dropping a known weight into an excess of acidified 10% potassium iodide solution. Iodine was liberated and this was titrated against 0·1N-sodium thiosulphate solution.

The acid for the broad-line nuclear resonance experiments was transferred directly from the desiccator to a dry box and was rammed with a glass rod into a thin-walled hard-glass tube. It was then cooled in liquid oxygen and quickly sealed off.

The high-resolution nuclear resonance experiments were obtained on a saturated solution in dimethylformamide.

The hydrogen resonance spectra were obtained on the broad-line apparatus[4] at room temperature, 90° K with use of liquid oxygen as a coolant, and 20° K with use of liquid hydrogen as a coolant. The spectra on the high-resolution apparatus[5] were obtained at 27° C.

RESULTS

The Solid.—At room temperature the nuclear resonance spectrum was very easily saturated, so the radio-frequency voltage on the coil was reduced to about 4 mv. At liquid-oxygen temperatures the sample was less easily saturated but at liquid-hydrogen temperatures a low radio-frequency voltage was required.

FIG. 1. *Derivative curve of hydrogen resonance of sulphoperamidic acid at* 90° K.

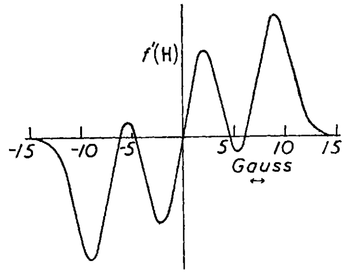
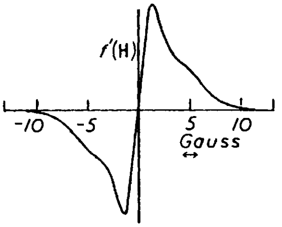


FIG. 2. *Derivative curve of hydrogen resonance of sulphoperamidic acid at* 20°.



Twelve good recordings were obtained at 90° K and their mean second moment, each having been corrected for modulation broadening and for field inhomogeneity, was 28·6 gauss^2 with a standard deviation of 0·75 gauss^2. Seven of the traces were chosen whose second moment did not deviate from the mean by more than 0·5 gauss^2. A curve was then plotted by using the mean values of each of the ordinates on the seven curves (Fig. 1). The value of the modulation used is shown by the small double-headed arrow. Fig. 3 shows the absorption curve obtained by integration of the derivative curve.

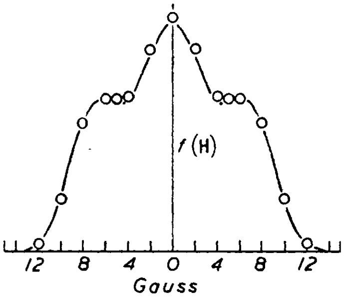
[4] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261.

[5] Leane, Richards, and Schaefer, *J. Sci. Instr.*, 1959, **36**, 230.

Eight recordings at 20° K gave a mean corrected second moment of 28·4 gauss^2 with a standard deviation of 1·0 gauss^2.

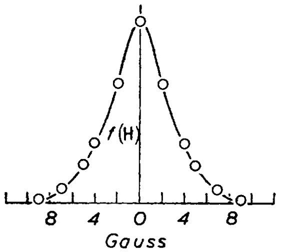
At room temperature the mean corrected second moment for seven derivative curves was 7·3 gauss^2 with a standard deviation of 2·1 gauss^2. The averaged derivative curve is shown in Fig. 2 and the corresponding absorption curve in Fig. 4.

FIG. 3. *Absorption curve of hydrogen resonance of sulphoperamidic acid at* 90° K.



Circles are theoretical points for an equilateral triangle of protons for which $\alpha = 3{\cdot}96$ gauss and $\beta^2 = 3{\cdot}74$ gauss^2.

FIG. 4. *Absorption curve of hydrogen resonance of sulphoperamidic acid at room temperature.*



Circles are theoretical points for an equilateral triangle of protons for which $\alpha = 3{\cdot}96$ gauss and $\beta^2 = 1{\cdot}27$ gauss^2 rotating about the C_3 axis.

The Solution.—The solution in dimethylformamide gave only a single broadened peak apart from the normal dimethylformamide spectrum. This peak was shifted to lower applied fields by 71 c./sec. (2·37 p.p.m.) from the single low-field proton resonance peak of the dimethylformamide.

DISCUSSION

If the acid has structure (I) then the crystal would approximate to a collection of protons in pairs, together with some relatively distant and isolated protons. In this case the absorption curve for a single proton would be superimposed upon that for a proton pair. Thus the single proton would add a central peak to the doublet of the proton-pair absorption curve and the resultant curve might have three maxima, although it is difficult to predict accurately the relative intensities of the central and outer ones. If the triplet curve does actually arise in this way then the separation of the outer maxima would correspond to the separation for a proton pair in a polycrystalline solid. This is about $2{\cdot}5\mu/x^3$ where x is the interproton distance in the pair. Since the separation of the outer maxima was 12·5 gauss an approximate value for x would be 1·12 Å. If the $\angle$HNH is assumed to be 120° as in urea, the N–H distance would then be 0·65 Å. This value is very much lower than any other corresponding value which has been found, and this in itself is evidence against structure (I). Further, if this very small N–H distance did occur, the second moment expected for structure (I) would be very much larger than observed.

Alternatively, if structure (I) is assumed to have the interproton distance of the pair equal to that found in urea (1·79 Å) and the third proton is 2·4 Å away (the sum of the van der Waals radii), the intramolecular second moment for this configuration would be 10·9 gauss^2. The intermolecular second moment in this compound could hardly be greater than 5 gauss^2, giving a total second moment of 16 gauss^2. This is very much less than the observed value. The shape and second moment of the absorption curve are therefore not consistent with structure (I).

If the substance has structure (II) and is a zwitterion then the protons would occur in groups of three at the corners of an equilateral triangle. Andrew and Bersohn [6] have

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[6] Andrew and Bersohn, *J. Chem. Phys.*, 1950, **18**, 159.

calculated the theoretical line shape for this configuration and the actual line shape may be obtained by applying a Gaussian broadening function (β^2) by using the method described by Pake.[7] This takes into account the additional broadening due to the protons of neighbouring molecules, the nitrogen nuclei, the effect of finite magnitude of field modulation and the magnetic-field inhomogeneities. The theoretical points calculated for $\alpha = 3{\cdot}96$ gauss and $\beta^2 = 3{\cdot}74$ gauss^2 are shown in Fig. 3 superimposed on the observed absorption curve at 90° K. Now $\alpha = 3\mu/2d^3$, where d is the length of the side of the equilateral triangle, and in this way a value of $1{\cdot}75 \pm 0{\cdot}01$ Å is obtained for the interproton distance. The value of β^2 was chosen to give the best fit with the experimental curve and the sensitivity of this method is shown in previous work by Freeman and Richards [8] on potassium amide and Richards and Yorke [9] on nitroguanidine.

The measurements at 20°K showed that there was no difference within experimental error in the second moment from that at 90°K and this indicated that there is no molecular motion at 90° K. This is supported by the close agreement between the theoretical and experimental absorption curves. This close agreement also provides very strong evidence that sulphoperamidic acid has structure (II) and not structure (I).

The interproton distance of 1·75 Å derived above should be corrected for librational, stretching, and bending motions of the nuclei. Ibers and Stevenson [10] have carried out a thorough quantitative analysis of these corrections and they estimate that the liberational correction (about 2%) for the ammonium ion in various salts is about five times as important as corrections due to stretching and bending motions of the bonds. The accurate corrections require a knowledge of the frequencies of the various librational modes of the molecule in the crystal and these are not available for sulphoperamidic acid or even for glycine which is a roughly comparable example. The librational motion causes the second moment to be slightly smaller than the rigid-lattice value, so that the uncorrected N–H distance is too large. The above value may therefore be regarded as an upper limit on the distance. Kromhout and Moulton [11] made an approximate correction for librational motion in the NH_3 group in glycine from the fact that the barrier height against rotation was about 4 kcal./mole. If this correction is assumed for sulphoperamidic acid the interproton distance would be about 1·72 Å. If $\angle$HNH is assumed to be tetrahedral, a value of $1{\cdot}07 \pm 0{\cdot}015$ Å is obtained for the uncorrected N–H bond distance and 1·05—1·06 Å for the corrected distance. In glycine the corresponding distances were 1·07 and 1·06 Å. These distances are quite appreciably longer than the value (1·03 Å) found for the N–H distance in ammonium chloride.[10,12]

At room temperature the shape and width of the line were quite different from those at 90° K and 20° K. Since the second moment of $7{\cdot}3 \pm 2{\cdot}1$ gauss^2 was reduced to approximately a quarter of the rigid lattice value, the NH_3 group is probably undergoing rotational reorientation at a frequency greater than about 100 kc./sec. about an axis perpendicular to the plane of the protons. The shape and second moment of the derivative curve closely resemble those obtained from acetonitrile at 90° K by Gutowsky and Pake.[13] In this case the methyl group was rotating about an axis normal to the plane of the protons. Fig. 4 shows the experimental absorption curve together with the calculated points for a rotating NH_3 group, $\alpha = 3{\cdot}96$ gauss and $\beta^2 = 1{\cdot}27$ gauss^2 being used. The agreement between theory and experiment is very close and confirms that the motion occurring in this substance at room temperature is rotational reorientation about the C_3 axis.

High-resolution Experiment.—Since sulphoperamidic acid gave only a single hydrogen resonance line in solution in dimethylformamide it probably also exists in a zwitterion

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[7] Pake, *J. Chem. Phys.*, 1948, **16**, 327.

[8] Freeman and Richards, *Trans. Faraday Soc.*, 1956, **52**, 802.

[9] Richards and Yorke, *Trans. Faraday Soc.*, 1958, **54**, 321.

[10] Ibers and Stevenson, *J. Chem. Phys.*, 1958, **28**, 929.

[11] Kromhout and Moulton, *J. Chem. Phys.*, 1955, **23**, 1673.

[12] Gutowsky, Pake, and Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.

[13] Gutowsky and Pake, *J. Chem. Phys.*, 1950, **18**, 162.

form in this solvent. Structure (I) would have been expected to give rise to two peaks of relative intensities 2 : 1. Takeda and Jardetzky[14] have studied glycine and other amino-acids in acidic media. The NH_3 peak of glycine only appeared at high acid concentrations, since exchange took place in other solutions, but it appeared as a singlet. The broadening is not due to exchange of intermediate frequency with the solvent, but to quadrupole interaction with the nitrogen nuclei.[15] The position of the NH_3 peak of glycine was given by Takeda and Jardetzky as 964 c./sec. on a frequency scale on which the position of the aromatic protons in toluene was 1000 c./sec. and that of the methyl protons was 1197 c./sec. On this scale the centre of the triplets observed[16] in acid solution for the NH_4^+ ion occurred at 970 c./sec. and the methylammonium ion resonance[15] at 953 c./sec. The sulphoperamidic acid peak would occur at 904 c./sec. on this scale. It is therefore shifted to lower applied fields than the NH_3^+ peak for the other molecules. This would be expected since the NH_3^+ group in sulphoperamidic acid is adjacent to an oxygen atom unlike the other compounds and this would cause a further decrease in the diamagnetic shielding of the protons. It is possible, however, that changes in the bulk diamagnetic shielding, associated with changes in the solvation pattern, may also contribute to this lowering.

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PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, February 27th,* 1959.]

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[14] Takeda and Jardetzky, *J. Chem. Phys.*, 1957, **26**, 1346.
[15] Roberts, *J. Amer. Chem. Soc.*, 1956, **178**, 4495.
[16] Ogg, *Discuss. Faraday Soc.*, 1954, **17**, 215.