small to be of any real value, and are estimated to be about 0.06 Å. The corresponding value for the angles is then 3°.

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Radiation-induced Organic Sulfur Radicals at 77°K

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The electron spin resonance (ESR) spectra induced when organic substances containing SH or SS groups are irradiated at room temperature or at low temperatures followed by annealing at 200°K or higher, are in part due to the formation of the organo-sulfur radical, $R-CX_2-S\cdot$[1-5]. In polycrystalline samples these sulfur radicals exhibit a resonance similar to that shown in Fig. 1 (upper curve).

Studies of irradiated molecular mixtures have yielded support for the hypothesis that the above sulfur radicals may be formed by intermolecular radical reac-
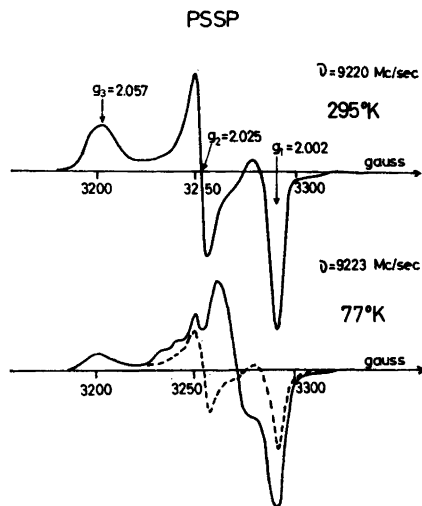

Fig. 1. First derivative ESR spectra of oxidized penicillamine irradiated at 295°K (upper curve) and at 77°K. PSSP was prepared by oxidation of PSH (Sigma Chem. Co.) with oxygen. The samples were freeze-dried from a solution of pH = 8.4 and irradiated in vacuum with 220 kV X-rays to a dose of 0.5 megarad. The spectra were recorded at 77°K with an X-band spectrometer. The dashed curve, which is the sulfur pattern, is identical with the upper spectrum. With the application of Kneubühl's [9] theory the three principal g-values can be calculated. The results given in this figure are in excellent agreement with those for other organo-sulfur radicals of the type $R-CX_2-S\cdot$.

tions.[6] Thus, in experiments where molecular mixtures containing a thiol or a disulfide and a macromolecule have been irradiated, at low temperatures and subsequently heat-treated, a transfer of radiation energy from the macromolecule to the sulfur-component with the formation of $R-CX_2-S\cdot$ radicals has been observed. On the other hand, Akasaka *et al.*[7] have recently suggested that the organo-sulfur radicals may be formed by an intramolecular transformation. From experiments on single crystals of cystine dihydrochloride, irradiated at 77°K, both Akasaka *et al.*[7] and Box and Freund [8] suggest that one of the radicals initially formed is a charged radical with an unpaired electron in the S—S bond, $(R-CH_2-S-S\dot{-}CH_2-R)^-$. Subsequent heat-treatment resulted in spectral changes and Akasaka *et al.*[7]

assumed that the primary sulfur radical splits into a semistable $RCH_2-S \cdot$* radical at dry ice temperature. Finally, at higher temperatures the organo-sulfur radicals discussed above were formed presumably by rotation of the CH_2-S group.

According to both the above mentioned hypotheses, the formation of the $R-CX_2-S \cdot$ radicals involved secondary processes which necessitate temperatures above approximately 170°K. In the present communication we would like to present some experiments on oxidized penicillamine, PSSP, (P = HOOC–$CH(NH_2)C(CH_3)_2-$) which indicate that the $R-CX_2-S \cdot$ radicals may be formed even at 77°K.

The lower spectrum in Fig. 1 shows the ESR pattern obtained when PSSP is irradiated at 77°K. It appears that the dashed curve, which is the spectrum of penicillamine irradiated at room temperature, fits nicely to the low field part of the spectrum, suggesting that $R-C(CH_3)_2-S \cdot$ radicals are present. According to this interpretation it can be calculated that approximately 50 % of the composite spectrum can be ascribed to $R-C(CH_3)_2-S \cdot$ radicals. In similar experiments with the thiol, PSH, the qualitative spectra indicate that, on the maximum, 15 % of the resonance at 77°K may be due to sulfur radicals. No other thiols and disulfides studied exhibit resonances which can be ascribed to this particular type of sulfur radicals when irradiated at 77°K.

When oxidized penicillamine was irradiated at 77°K and subsequently heat-treated the number of $R-C(CH_3)_2-S \cdot$ radicals remained constant to about 220°K, whereas upon further heat-treatment a significant formation of additional $R-C(CH_3)_2-S \cdot$ radicals takes place (Fig. 2). In recent experiments (to be published) on PSSP irradiated both as a free base and in the hydrochloride form it was found that the initial formation of sulfur radicals at 77°K was the same for the two forms. However, the second phase of the formation of $R-C(CH_3)_2-S \cdot$ radicals was different. Thus, in the case of the hydrochloride derivative the secondary reactions started at a temperature approximately 75° lower than for the free base.

The present results indicate that in the case of oxidized penicillamine at least two mechanisms are involved in the formation of the $R-CX_2-S \cdot$ radicals. The sulfur radicals which appear in the second phase after heat-treatments seem to be formed
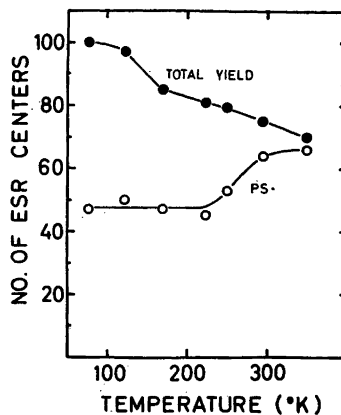
Fig. 2. Effect of heat-treatment on the number of radicals in PSSP. The yield of ESR centers was calculated by double integration of the first derivative spectra and comparison with reference samples. The number of sulfur radicals was obtained by decomposition of the spectra. The sample was irradiated at 77°K and subsequently heat-treated for 3 min at the temperatures indicated. The annealing temperature is given along the abcissa.

by the same mechanism as when other sulfur-containing substances are irradiated. On the other hand, the $R-CX_2-S \cdot$ radicals present at 77°K may be due to primary processes, or they may be formed by inter- and/or intramolecular processes which can take place even at 77°K. The presence of 4 methyl groups adjacent to the disulfide bond probably represents a sterical hindrance for intermolecular reactions. However, the methyl groups may weaken the disulfide bond and thus facilitate its rupture with the consequent formation of $R-CX_2-S \cdot$ radicals.

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A Method for the Resolution of Composite Radial Pair Distribution Functions

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The superposition of distances between different types of atom pairs in experimental pair radial distribution functions of vitreous systems, makes it difficult to interpret such functions. As the present note will show, it is possible to circumvent this difficulty in favourable cases.

In a system consisting of J different species of atoms, there are $(J + 1) \, J/2$ ways to combine atom species in different pairs. (For instance: $J = 2$ species of atoms, A and B, will give the three pairs A-A, A-B and B-B). An atomic center radial distribution curve from a composite system with J different kinds of atoms may therefore be considered composed of the $(J + 1) \, J/2$ individual distribution curves of each possible pair of atoms. These individual distribution curves may thus in principle be determined from $(J + 1) \, J/2$ independent and relevant measurements. (In some cases it may be found useful to treat a polyatomic system as two-atomic, lumping all but one type of atoms into a single category. Only three independent intensity curves are then needed.)

Independent measurements may be obtained when the relative scattering efficiency of the different species of atoms can be altered. This can be done by: 1) using different types of radiation, *e.g.* X-rays, neutrons, or electrons, 2) using one kind of radiation at different wavelengths,

taking advantage of the dispersion, 3) using isomorphic (or isotopic substitution with neutrons) of one species of atoms in the structure. To take advantage of this additional information, we shall derive the appropriate expression for the scattered intensity from an amorphous system as a function of the structure and the scattering efficiency of the different atomic species.

The atomic form factor (or scattering efficiency), f_j, of the j'th species of atoms under specified scattering conditions will be written as the complex quantity:

$$f_j = f_j{}^0 + \Delta f_j{}' + i\Delta f_j{}''$$

The number of atoms of species j is taken to be n_j so that the total number of atoms, N, in a system with J different kinds of species, is given by:

$$N = \sum_{j=1}^{J} n_j$$

The amplitude, A, of radiation scattered by this system is:

$$A = \sum_{j=1}^{J} \sum_{m=1}^{n_j} f_j \exp(2\pi i \mathbf{q} \mathbf{R}_{jm})$$

where $\mathbf{q}$ is the scattering vector and $\mathbf{R}_{lm}$ is a vector defining the position of the m'th atom of species j.

To obtain the intensity of the scattered radiation, we note that

$$AA^* = \sum_{j=1}^{J} \sum_{m=1}^{n_j} f_j \exp(2\pi i \mathbf{q} \mathbf{R}_{jm}) \sum_{k=1}^{J} \sum_{n=1}^{n_k} f_k{}^*$$
$$\exp(-2\pi i \mathbf{q} \mathbf{R}_{kn})$$
$$= \sum_{j=1}^{J} \sum_{k=1}^{J} \sum_{m=1}^{n_j} \sum_{n=1}^{n_h} f_j f_k{}^* \exp[2\pi i \mathbf{q}(\mathbf{R}_{jm} - \mathbf{R}_{kn})]$$

Introducing:

$$r = |\mathbf{R}_{jm} - \mathbf{R}_{kn}|$$

for the distance between atom jm and kn, and:

$$s/2\pi = |\mathbf{q}| = 2 \sin\theta/\lambda$$

for the length of the scattering vector, θ being the scattering angle and λ the wave length, and averaging over all directions in space (see, *e.g.*, Viervoll [1]), we obtain

$$I(s) = \overline{AA^*} = \sum_{j=1}^{J} \sum_{k=1}^{J} \sum_{m=1}^{n_j} \sum_{n=1}^{n_k} [(f_j{}^0 + \Delta f_j{}')$$
$$(f_k{}^0 + \Delta f_k{}') + \Delta f_j{}'' \, \Delta f_k{}''] \frac{\sin sr}{sr}$$

Let us for simplicity assume that the particular pair of any atom with itself ($r = 0$) is not counted in the above summation. The double summation over all atom