

Pulse Radiolysis of Penicillamine in Aqueous Solution: the Thiyl Radical and the Disulphide Radical Anion

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Summary The $RS\cdot$ radical and the $RSSR^-$ radical anion of penicillamine have λ_{max} 330 nm, ϵ_{330} $1.22 \times 10^5 M^{-1} cm^{-1}$ and λ_{max} 450 nm, ϵ_{450} $7.5 \times 10^5 M^{-1} cm^{-1}$, respectively, and K_1 for the equilibrium, $RS\cdot + RS^- \rightleftharpoons RSSR^-$ is $2.5 \times 10^5 M^{-1}$ at pH 8.

ADAMS *et al.*¹ have shown that the thiyl radicals produced by pulse radiolysis of aqueous solutions of mercaptans combine with the sulphhydryl anion to give a radical anion complex.



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This complex has been observed with several compounds including cysteamine,¹ cysteine,² hydrogen sulphide,³ and several alkyl mercaptans.⁴ The same transient was produced from disulphides by addition of solvated electrons,¹



In the absence of RS^- the radical anion decays rapidly by the reverse of reaction 1. In both cases the thiyl radicals eventually combine to give disulphide.



Adams *et al.* noted a small difference between the spectrum of RSSR^- generated by reaction 1 and that produced by reaction 2 and suggested that the difference, higher absorption at about 300 nm, was due to the $\text{RS}\cdot$ radical. We have been investigating the transients produced by pulse radiolysis of penicillamine, $\text{HO}_2\text{C}\cdot\text{CH}(\text{NH}_2)\cdot\text{C}(\text{CH}_3)_2\text{SH}$, in aqueous solution and have observed both the $\text{RS}\cdot$ radical and the RSSR^- radical anion directly.

Solutions were buffered with phosphate (8 mM) and were irradiated with 0.04–1 μs pulses of 35 Mev electrons. Spectra were measured with a split light-beam system. Aqueous potassium thiocyanate solution saturated with nitrous oxide was used for dosimetry,⁵ G_e 4.22×10^4 .

The RSSR^- radical anion was produced from the disulphide by reaction 2. An argon-saturated solution of penicillamine disulphide (5 mM, pH 6.0), containing *t*-butyl alcohol (0.5 M) to remove $\cdot\text{OH}$ radicals, was used. The decay of the RSSR^- transient gives a good first-order plot with $k_{-1} = 1.5 \times 10^6 \text{ s}^{-1}$. The extinction coefficient was determined by using short pulses (40 ns) and extrapolating the first-order plot to mid-pulse to obtain the initial concentration, and by assuming $G(\text{RSSR}^-) = G(e_{aq}^-) = 2.7$. The spectrum of RSSR^- is shown in Figure 1,

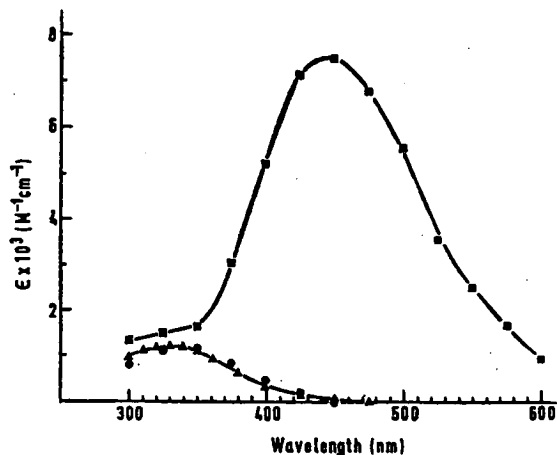
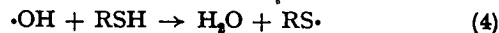


FIGURE 1. Absorption spectra of the RSSR^- radical anion from penicillamine disulphide (■), the $\text{RS}\cdot$ radical from penicillamine (▲), and the transient remaining after decay of the radical anion (●).

λ_{max} 450 nm, ϵ_{450} $7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. These values are similar to those reported by Adams *et al.*⁶ for cysteamine, λ_{max} 410 nm, ϵ_{410} $8.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, and by Henglein and co-workers⁴ for mercaptoethanol, λ_{max} 420 nm, ϵ_{420} $8.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

A 2.5 mM solution of penicillamine at pH 5 and saturated with nitrous oxide was pulse-irradiated and the spectrum obtained is shown in Figure 1. At pH 5 the mercapto-group is un-ionised so that the $\text{RS}\cdot$ radical produced by



should not be converted into RSSR^- ; the spectrum confirms this in that absorption at 450 nm is very low. We attribute this spectrum with λ_{max} at 330 nm to $\text{RS}\cdot$. By assuming $G(\text{RS}\cdot) = G(\cdot\text{OH}) = 5.95$,⁵ we determined ϵ_{330} $1.22 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $k_3 = 2.6 \pm 0.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value of ϵ is much higher than that reported recently by Jayson *et al.*⁷ for the $\text{RS}\cdot$ radical from mercaptoethanol, λ_{max} ca. 350 nm, ϵ_{max} $0.13 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The RSSR^- produced from the disulphide of penicillamine decays to a more stable transient which has the spectrum shown in Figure 1. This spectrum matches very closely that assigned to $\text{RS}\cdot$, as expected if RSSR^- decays by the reverse of reaction 1.

When penicillamine was irradiated in solutions with pH in the range 7–9, the resulting spectra had contributions from both $\text{RS}\cdot$ and RSSR^- . The ratio of these species should be given by the equilibrium expression:

$$K_1 = \frac{[\text{RSSR}^-]}{[\text{RS}\cdot][\text{RS}^-]}$$

The fraction of penicillamine in the form RS^- was determined as a function of pH by the method of Benesch and Benesch.⁸ $[\text{RSSR}^-]$ was calculated from the maximum absorption at 450 nm and $[\text{RS}\cdot]$ from the stoichiometric relationship $G(\cdot\text{OH}) = G(\text{RS}\cdot + \text{RSSR}^-)$. From these quantities the equilibrium constant K_1 was determined to be $2.5 \pm 0.1 \times 10^3 \text{ M}^{-1}$ at pH 8.0, independent of concentration over the range studied, 1 to 10 mM. The expected absorption spectra for solutions of penicillamine were calculated from K_1 and the spectra of $\text{RS}\cdot$ and RSSR^- . The calculated curves for several concentrations of penicillamine are shown in Figure 2, together with the experi-

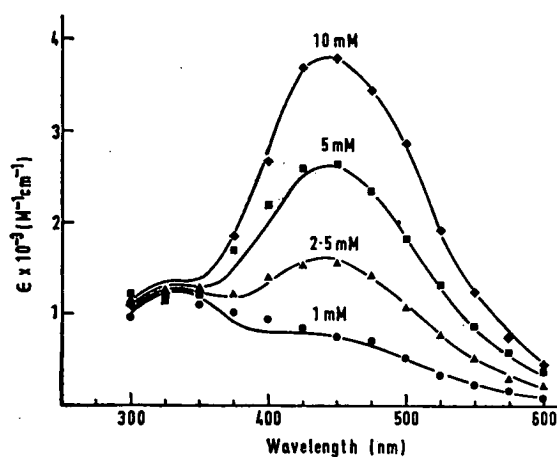


FIGURE 2. Absorption spectra of pulse-irradiated penicillamine solutions at pH 8.0. Solid lines are calculated curves; points were measured experimentally.

mental points obtained by pulse irradiation of the appropriate solutions. The agreement between the two lends

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support to the values obtained for K_1 and the extinction coefficients. During these experiments it was observed that the absorption at 450 nm reached a maximum shortly after the pulse whereas the absorption at 330 nm was highest at the end of the pulse. This is consistent with RS-

radicals being formed during the pulse, then reacting to give the RSSR- radical anion.

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