Radiolysis of Neutral Aqueous Solutions of Cysteine in the Presence of Oxygen

By J. E. PACKER* and R. V. WINCHESTER

(*Chemistry Department, University of Auckland, Auckland, New Zealand*)

THE radiolysis of aqueous solutions of cysteine has received considerable attention, but there is little data on oxygenated neutral solutions, which are of interest from the viewpoints of biology and protective action. Some of our results are given in the Table.

In the absence of oxygen, reactions (1)—(5) account for several reported results.[1-3] In the presence of oxygen, we find G(-RSH) and G(H_2O_2) are greatly increased and that, with the cysteine concentration shown in the Table, the only sulphur-containing products formed in significant amounts are cystine and hydrogen sulphide. By measuring G(H_2S) at various oxygen concentrations we find

$$\text{RSH} + \cdot\text{OH} \rightarrow \text{RS}\cdot + H_2O \qquad (1)$$

$$\text{RSH} + e^-_{\text{aq}} \rightarrow \text{R}\cdot + \text{HS}^- \qquad (2)$$

$$\text{RSH} + \text{H}\cdot \begin{array}{l} \nearrow \ \text{RS}\cdot + H_2 \qquad (3a) \\ \searrow \ \text{R}\cdot + H_2S \qquad (3b) \end{array}$$

$$\text{R}\cdot + \text{RSH} \rightarrow \text{RH} + \text{RS}\cdot \qquad (4)$$

$$2\text{RS}\cdot \rightarrow \text{RS}\cdot\text{SR} \qquad (5)$$

$[O_2]$ mole/litre	Scavenger[a]	$G(-RSH)$[b] (c)	(d)	$G(H_2O_2)$ (c)	(d)
0	None	9·7	8·4	0·7	
$2·54 \times 10^{-4}$	None	29	37	6·4	9·4
$2·54 \times 10^{-4}$	Acetone	17	17	4·0	5·7
$2·54 \times 10^{-4}$	N_2O	29	39	3·1	6·0

[a] Sufficient to scavenge almost all e^-_{aq}; [b] RSH = cysteine; [c] [RSH] = 1×10^{-3} M; [d] [RSH] = 3×10^{-3} M.

a value of $(k_{e_{aq}^-} + RSH)/(k_{e_{aq}^-} + O_2)$ in good agreement with that found by other workers using different techniques.[2,3] We find that $G(-RSH)$ and $G(H_2O_2)$ increases with increasing cysteine concentration but is independent of oxygen concentration.

For pure cysteine hydrochloride solutions Packer found that $G(H_2O_2)$ was equal to $G_{H_2O_2} + G_{e^-_{aq}} + G_H$ and independent of oxygen concentration,[1] and suggested the following mechanism

$$e^-_{aq} \text{ or } H\cdot \rightarrow O_2^- \text{ or } HO_2 \qquad (6)$$

$$RSH + O_2^- \text{ or } HO_2\cdot \rightarrow RS\cdot + HO_2^- \text{ or } H_2O_2 \qquad (7)$$

To account for $G(-RSH)$ he postulated a short-chain reaction producing an intermediate peroxide which was reduced to cystine and water by cysteine.

$$RS\cdot + O_2 \rightarrow RSO_2\cdot \qquad (8)$$

$$RSO_2\cdot + RSH \rightarrow RSO_2H + RS\cdot \qquad (9)$$

$$RSO_2H + 3RSH \rightarrow 2RS{\cdot}SR + H_2O \qquad (10)$$

The higher values of $G(H_2O_2)$ now found at pH 7 suggest that hydrogen peroxide is produced by a route other than (6) and (7), and radiolytic yields in the presence of nitrous oxide in sufficient concentration to scavenge almost all the e^-_{aq} support this view. The yield of thiyl radicals, RS•, from water radiolysis products should be unaltered by the addition of nitrous oxide because reactions (6) and (7) would be replaced by reactions (11) and (1)

$$N_2O + e^-_{aq} \xrightarrow{H^+} N_2 + \cdot OH \qquad (11)$$

and consequently $G(-RSH)$ should not change. However $G(H_2O_2)$ should be lowered because its production *via* reactions (6) and (7) has been eliminated. The increase of both $G(-RSH)$ and $G(H_2O_2)$ with increasing cysteine concentration in the presence of nitrous oxide, is consistent with hydrogen peroxide being a product of a series of reactions initiated by thiyl radicals and oxygen. A possible step, producing hydrogen peroxide at this pH, is

$$RSO_2H + RSH \rightarrow RS{\cdot}SR + H_2O_2 \qquad (12)$$

Radiolytic yields in the presence of sufficient acetone to scavenge almost all the e^-_{aq} are also consistent with the above mechanisms as acetone will eliminate the formation of RS• by reactions (6) and (7) and thus decrease $G(-RSH)$ and $G(H_2O_2)$. However the reaction between e^-_{aq} and acetone in the presence of oxygen will provide another source of hydrogen peroxide, accounting for the values of $G(H_2O_2)$ in the presence of acetone being intermediate between the values found in the N_2O-free and N_2O systems.

We thank the United States Air Force Office of Scientific Research for financial support.

(*Received, May 6th,* 1968; *Com.* 551.)

---

[1] J. E. Packer, *J. Chem. Soc.*, 1963, 2320.

[2] D. A. Armstrong and V. G. Wilkening, *Canad. J. Chem.*, 1964, **42**, 2361; V. G. Wilkening, M. Lal, M. Arends, and D. A. Armstrong, *ibid.*, 1967, **45**, 1209; V. G. Wilkening, M. Lal, M. Arends, and D. A. Armstrong, *J. Phys. Chem.*, 1968, **72**, 185.

[3] A. El. Samahy, H. L. White, and C. N. Trumbore, *J. Amer. Chem. Soc.*, 1964, **86**, 3177.