Pulse Radiolysis Studies of Electron Transfer in Aqueous Disulphide Solutions

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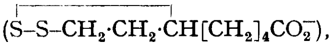
Summary Electron transfer to oxidised lipoate, from the electron adduct of thymine, the carboxylate radical-ion $\dot{C}O_2^-$ and the ethanol and propan-2-ol radicals has been observed directly by pulse radiolysis.

THE pulse radiolysis technique provides a convenient method for the generation of a variety of free radicals in solution. Often, by the choice of suitable systems, the subsequent reactions of these radicals with particular solutes can be studied in isolation.

The apparatus and method of solution preparation have been described.[1,2] Solutions (pH 7) were exposed to a minimum of light. Analysing light of wavelength < 350 nm was removed by filters. Lipoate,



$(S{-}S{-}CH_2{\cdot}CH_2{\cdot}CH[CH_2]_4CO_2^-)$,

contained less than 1% of the reduced analogue. A 0·2 μs electron pulse dose *ca.* 500 rad was used.

On pulse radiolysis of deaerated solutions of lipoate (2×10^{-3} M) containing 2-methylpropan-2-ol (1 M), a transient absorption (λ_{max} 410 nm), was observed. The absorption was similar to that observed on pulse radiolysis of deaerated solutions of cystamine, oxidised glutathione, and lysozyme[3-5] and is assigned, similarly, to the corresponding radical anion with the odd electron located on the sulphur bridge. At lower lipoate concentrations, the solvated electron (e_{aq}^-) absorption was apparent immediately after the radiation pulse. At 600 nm this decayed exponentially and first order in lipoate concentration, attributable principally to:

$$H_2O \rightsquigarrow e_{aq}^- + OH \qquad (1)$$

$$OH + (CH_3)_3COH \rightarrow \dot{C}H_2(CH_3)_2COH + H_2O \qquad (2)$$

and

$$e_{aq}^- + \text{lipoate} \rightarrow \text{lipoate}\dot{}^{-}\ (3)\ (k_3 = 1{\cdot}5 \times 10^{10}\ \text{M}^{-1}\,\text{s}^{-1}).$$

The resulting absorption assigned to lipoate$\dot{}^-$ decayed slowly over hundreds of μs. However, when oxygen was present ([O_2] *ca.* $2{\cdot}5 \times 10^{-4}$ M), it decayed rapidly and exponentially, corresponding to:

$$\text{lipoate}\dot{}^{-} + O_2 \rightarrow \text{lipoate} + O_2^-\ (4)\ (k_4 = 0{\cdot}9 \times 10^{9}\ \text{M}^{-1}\,\text{s}^{-1}).$$

On radiolysis of solutions containing 2-methylpropan-2-ol (1 M), thymine (10^{-2} M), and lipoate (2—8×10^{-4} M), the lipoate$\dot{}^-$ absorption was again observed. The rate of the absorption formation was exponential and first order in lipoate concentration in agreement with:

$$e_{aq}^- + \text{thymine} \rightarrow \text{thymine}\dot{}^{-}\ (5)\ (k_5 = 1{\cdot}8 \times 10^{10}\ \text{M}^{-1}\text{s}^{-1}).^{6}$$

and $$\text{thymine}\dot{}^{-} + \text{lipoate} \rightarrow \text{thymine} + \text{lipoate}\dot{}^{-}\ (6)\ (k_6 = 2{\cdot}8 \times 10^{8}\ \text{M}^{-1}\,\text{s}^{-1}).$$

Similarly, on radiolysis of solutions containing lipoate (2—8×10^{-4} M) and also containing either (a) propan-2-ol and acetone (1 M), or, (b) nitrous oxide (*ca.* 2×10^{-2} M) and ethanol or formate (10^{-1} M), the exponential formation of the lipoate$\dot{}^-$ absorption was observed, in accord with the reactions:

$$\text{(a)}\quad OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH \qquad (7)$$

$$e_{aq}^- + (CH_3)_2CO \rightarrow (CH_3)_2CO\dot{}^{-} \qquad (8)$$

$$(CH_3)_2CO\dot{}^{-} + H_2O \rightleftharpoons (CH_3)_2\dot{C}OH + OH^- \qquad (9)$$

$$(CH_3)_2\dot{C}OH + \text{lipoate} \rightarrow \text{lipoate}\dot{}^{-} + (CH_3)_2CO + H^+ \qquad (10)$$

$$(k_{10} = 1{\cdot}8 \times 10^{8}\ \text{M}^{-1}\,\text{s}^{-1})$$

and,

(b) $$e_{aq}^- + N_2O \rightarrow N_2 + OH + OH^- \qquad (11)$$

$$OH + HCO_2^- \rightarrow \dot{C}O_2^- + H_2O \qquad (12)$$

$$\dot{C}O_2^- + \text{lipoate} \rightarrow \text{lipoate}\overset{-}{\cdot} + CO_2 \qquad (13)$$

$$(k_{13} = 5{\cdot}5 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1})$$

or, $$OH + C_2H_5OH \rightarrow \dot{C}_2H_4OH + H_2O \qquad (14)$$

$$\dot{C}_2H_4OH + \text{lipoate} \rightarrow \text{lipoate}\overset{-}{\cdot} + C_2H_4O + H^+ \qquad (15)$$

$$(k_{15} = 1{\cdot}0 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}).$$

Direct observations of electron transfer from the isopropyl alcohol and carboxylate radicals to other solutes have been reported previously.[7-9] Initial experiments show that electron transfer from $\dot{C}O_2^-$ to one or more of the disulphide bridges in lysozyme also occurs.[10] Likewise, it has been suggested that some apparent anomalies on radiolysis of aqueous solution of thymine, formate, cysteine, and cystine might be explained by the occurrence of the reaction of $\dot{C}O_2^-$ with the disulphide.[11] Direct observation of this reaction by pulse radiolysis is limited, however, by the rapid dissociative decay of the corresponding radical anion $RSSR^-$ formed from cystine:

$$RSSR^- \rightleftharpoons RS\cdot + RS^-$$

$$RS\cdot + RS\cdot \rightarrow RSSR$$

The electron adduct of cystamine also decays rapidly.[3] It appears that the cyclic configuration present in lipoate and lysozyme hinders dissociation and enables the radical anion to be observed directly, even when formed relatively slowly by electron transfer reactions.

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