Pulse Radiolysis Studies of Electron Transfer Reactions in Aerobic Solution

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Summary The reaction of oxygen with the free-radical intermediates of the nicotinamide adenine dinucleotide and the *p*-benzoquinone–hydroquinone oxidation–reduction couples have been studied by pulse radiolysis.

ELECTRON-TRANSFER from O_2^- has previously been observed on pulse radiolysis of the strong oxidant tetranitromethane.[1] However, in biological systems the rapid reaction of O_2^- with other solutes has been considered unlikely. The present studies in model multi-solute systems suggest that, on radiolysis of some quinone-containing biological systems, reactions of O_2^- may occur.

The apparatus and the method of solution preparation have been described.[2,3] Transient absorption spectra observed after 1 μsec on pulse radiolysis of neutral de-aerated aqueous solutions containing an excess of 2-methylpropan-2-ol or of propan-2-ol and acetone can be attributed principally to reactions of the solvated electron, e_{aq}^-, or alcohol radical, $(CH_3)_2\dot{C}OH$, respectively.[4-6]

On pulse radiolysis of de-aerated solutions of NAD$^+$ (2×10^{-3} M) and 2-methylpropan-2-ol (1 M), a transient absorption (λ_{max} 400 nm) was observed. The absorption was similar to that observed previously in nitrous oxide–formate solutions of NAD$^+$ and is assigned similarly[7] to the neutral radical NAD·. The absorption decayed slowly over hundreds of μsec. In aerated solution ([O_2] *ca.* $2{\cdot}5 \times 10^{-4}$ M), however, the absorption decayed rapidly and exponentially. This is attributed to the reaction:

$$\text{NAD}\cdot + O_2 \rightarrow \text{NAD}^+ + O_2^- \text{ (1) } (k_1 = 1{\cdot}9 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}).$$

The value for k_1 agrees with a reported approximate value of 10^9 M^{-1}sec^{-1}.[8]

On pulse radiolysis of solutions of benzoquinone ($1{\cdot}45 \times 10^{-4}$ M) containing 2-methylpropan-2-ol (1 M) and saturated with nitrogen or oxygen ([O_2] *ca.* $1{\cdot}3 \times 10^{-3}$ M) a strong transient absorption (λ_{max} 430 nm) was observed. The absorption closely resembled that observed on pulse radiolysis of solutions containing benzoquinone and hydroquinone[9] and assigned to the semiquinone radical-anion $C_6H_4O_2^-$. In nitrogen-saturated solutions, the absorption appeared rapidly, in agreement with

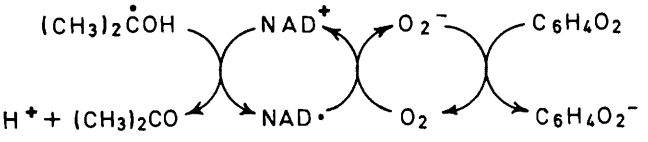
$$e_{aq}^- + C_6H_4O_2 \rightarrow C_6H_4O_2^- \text{ (2) } (k_2 = 1{\cdot}25 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}.[10])$$

In oxygen-saturated solutions, however, the absorption appeared more slowly. The rate of appearance was exponential and first-order in benzoquinone concentration, in accordance with

$$e_{aq}^- + O_2 \rightarrow O_2^- \text{ (3) } (k_3 = 1{\cdot}88 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}.[11])$$

and $$O_2^- + C_6H_4O_2 \rightarrow O_2 + C_6H_4O_2^- \text{ (4) } (k_4 = 9{\cdot}6 \times 10^8 \text{ M}^{-1}\text{sec}^{-1})$$

On pulse radiolysis of a solution containing acetone (1 M), propan-2-ol (1 M), NAD$^+$ (2×10^{-2} M), oxygen (*ca.* $2{\cdot}5 \times 10^{-4}$ M), and benzoquinone (2×10^{-5} M) an absorption similar to that of NAD· was observed immediately after the radiation pulse. This decayed rapidly, but after 10 μsec, was followed by a slowly forming absorption which, after 200 μsec, resembled that of the semiquinone radical-anion. These spectral changes are attributed tentatively to the reaction sequence



When concentration differences are considered, measured absolute rate constants for the individual reactions are in agreement with this scheme.

$$(CH_3)_2\dot{C}OH + O_2 \rightarrow \text{products (5) } (k_5 = 4{\cdot}2 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}.[6])$$

$$(CH_3)_2\dot{C}OH + \text{NAD}^+ \rightarrow (CH_3)_2CO + \text{NAD}\cdot + H^+ \text{ (6) } (k_6 = 1{\cdot}0 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}.)$$

$$\text{NAD}\cdot + C_6H_4O_2 \rightarrow \text{NAD}^+ + C_6H_4O_2^- \text{ (7) } (k_7 = 3{\cdot}6 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}.)$$

and $$(CH_3)_2\dot{C}OH + C_6H_4O_2 \rightarrow (CH_3)_2CO + C_6H_4O_2^- + H^+ \text{ (8) } (k_8 = 4{\cdot}1 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}).$$

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