Production, Detection, and Characterization of Transient Hexavalent Technetium in Aqueous Alkaline Media by Pulse Radiolysis and Very Fast Scan Cyclic Voltammetry

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Summary In aqueous alkaline media technetium(VI) is a viable chemical species, with a lifetime of the order of milliseconds, which is potentially useful in the preparation of technetium radiopharmaceuticals.

The isotope of choice for diagnostic nuclear medicine procedures is ^{99m}Tc, generated as $^{99m}TcO_4^-$ from ^{99}Mo generators.[1,2] Conversion of this pertechnetate ion into radiopharmaceuticals is based upon the reduction of heptavalent technetium to lower oxidation states in aqueous media.[1,2] The logical first step in the reduction of TcO_4^- by a one-equivalent reductant is the generation of technetium(VI). Despite extensive studies[3,4] technetium(VI) has not yet been electrochemically detected owing to the rapid chemical and electrochemical reactions of this species in aqueous media. Depending on conditions, the first polarographic wave for the reduction of aqueous TcO_4^- can involve a net two-, three-, or four-equivalent reduction;[3,4] in the presence of gelatine the primary electrode process is purported to be a one-equivalent reduction.[5]

We have employed two very rapid experimental techniques to produce, detect, and characterize metastable technetium(VI) in aqueous alkaline media, thus demonstrating that hexavalent technetium is a viable chemical species capable of functioning as an important intermediate in radiopharmaceutical preparations.

When 10—100 μM solutions of $^{99}TcO_4^-$ in 0·10 M NaOH are irradiated with a beam of electrons under conditions designed to yield e_{aq}^-,[6] the optical density due to e_{aq}^- disappears according to a rate law first-order in $[e_{aq}^-]$ and first-order in $[TcO_4^-]$; k_2(25 °C) = $(2{\cdot}48 \pm 0{\cdot}05) \times 10^{10}$ l mol^{-1} s^{-1}. Concomitant with the disappearance of e_{aq}^- is the appearance of a new species, presumed to be TcO_4^{2-}. This is illustrated in Figure 1 which shows a streak camera spectrum[7,8] representing the difference between the spectrum of the initial TcO_4^- solution and that of the solution 100 μs after the electron pulse. The negative peak at *ca.* 290 nm results from loss of TcO_4^- (absorption maximum at 287 nm) while the positive peaks represent the spectrum of TcO_4^{2-}. This spectrum remains unchanged for 1 ms, the maximum amount of time it can be monitored by the instrumentation available. The diffuse reflectance spectrum reported[9] for solid $[Me_4N]_2TcO_4$ (prepared in acetonitrile) is not inconsistent with Figure 1, both spectra being characterized by maximum transmittance at *ca.* 400 nm which gives rise to the reported[10] violet colour of $[Me_4N]_2TcO_4$. From Figure 1 we estimate that ϵ (500—600 nm) = *ca.* 250 l mol^{-1} cm^{-1}; the spectrum recently reported[11] for pulse radiolysis-generated Tc^{VI} in neutral aqueous solution does not exhibit such strong absorption in the 500—600 nm region.

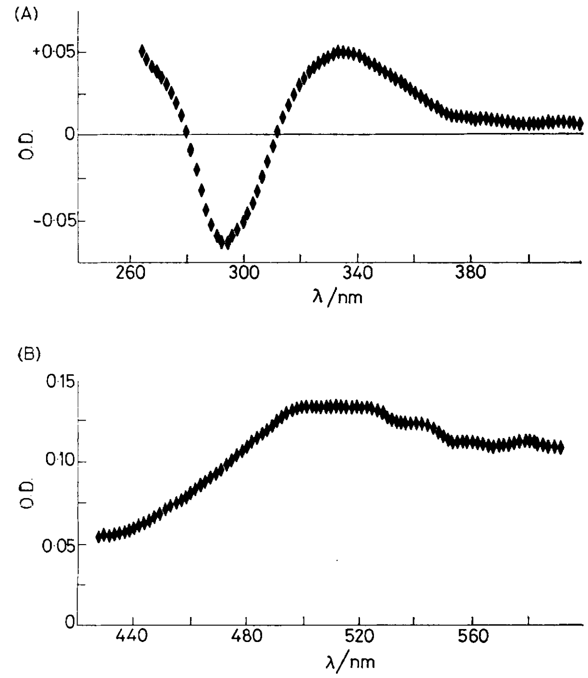

FIGURE 1. Streak-camera spectra resulting from reaction of e_{aq}^- with TcO_4^-. Conditions: 25 °C; $[OH^-]$ = 0·10 M; $[Bu^tOH]$ = 0·10 M; helium saturated solution; 5·00 cm pathlength; 100 μs after electron pulse; (A) 240—420 nm, $[TcO_4^-] = 5 \times 10^{-5}$ M; (B) 420—600 nm, $[TcO_4^-] = 5 \times 10^{-3}$ M.

When a 1·7 mM solution of $^{99}TcO_4^-$ in 0·12 M NaOH is subjected to very fast scan cyclic voltammetry on a hanging mercury drop electrode, the resulting voltammograms are very dependent on scan rate. Curve (A) of Figure 2 shows that at 1·0 V s^{-1} reduction of TcO_4^- begins at *ca.* −0·8 V (*vs.* S.C.E.), but by the time the scan reverses all reduced pertechnetate has undergone chemical reaction and no electrochemical re-oxidation occurs. Curve (B) shows that

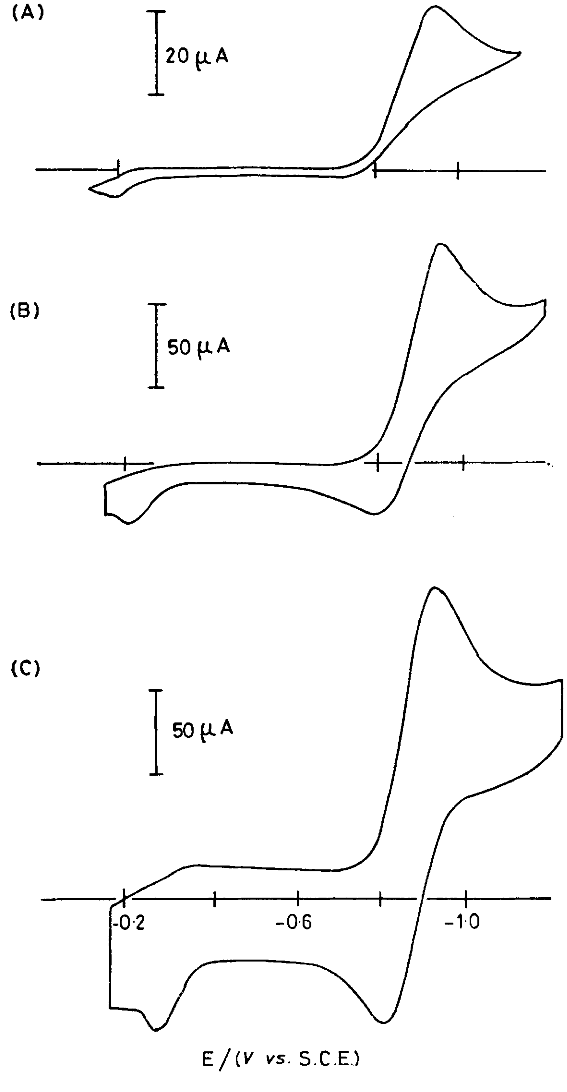

FIGURE 2. Cyclic voltammograms resulting from reduction of TcO_4^-. Conditions: 25 °C; $[OH^-]$ = 0·12 M; $[TcO_4^-] = 1{\cdot}7 \times 10^{-3}$ M; nitrogen saturated solution; hanging mercury drop electrode, surface area = $9{\cdot}4 \times 10^{-3}$ cm^2. Curves (A), (B), and (C) result from scan rates of 1, 20, and 100 V s^{-1}, respectively.

at 20 V s^{-1} electrochemical re-oxidation is beginning to compete with chemical reaction, while curve (C) shows that at 100 V s^{-1} electrochemical re-oxidation is essentially complete. Thus the electrogenerated technetium(VI) product, again presumed to be TcO_4^{2-}, is stable over a 10 ms time period, but undergoes detectable chemical reaction within 50 ms. Preliminary analysis of curve (C) within the Randles–Sevck equation,[12] using a literature value[13] for the diffusion coefficient of TcO_4^-, shows that n, the number of electrons transferred, is 1·0 as expected for production of TcO_4^{2-}. Also from curve (C), $E^{\circ\prime}$ for the TcO_4^{2-}/TcO_4^- couple is estimated to be −0·61 V (*vs.* N.H.E.).

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