

A Study of the Ti(III)–H₂O₂–SCN[−] Reaction

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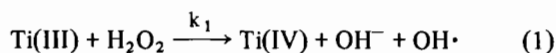
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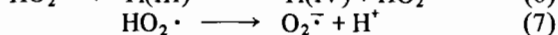
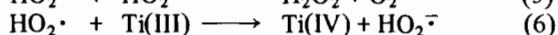
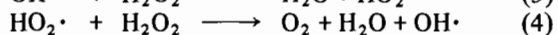
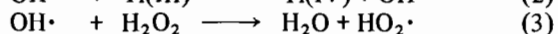
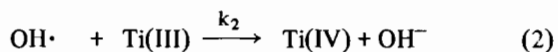
Both stop-flow and continuous flow methods have been used to study the reactions occurring when acidic solutions of Ti(III), H₂O₂ and SCN[−] were mixed. The progress of the reactions was followed through a strong absorption at 480 nm, characterizing the radical species (SCN)₂^{−•}. The kinetic data are shown to be consistent with the SCN[−] ion acting as an efficient scavenger for OH• radicals produced in the primary slow reaction between Ti(III) and H₂O₂.

Introduction

The generation of free radicals in aqueous solutions by means of the reactions of substrates, usually organic, with a dilute mixture of titanium(III) ions and hydrogen peroxide has become a routine method [1, 2]. For the purpose of e.s.r. studies of the radicals, continuous flow techniques normally are employed, but the stop-flow technique also has been used in investigating the kinetics of the primary processes involved in the method [3]. The initial step in the reaction sequence may be written [4, 5]

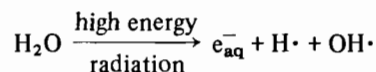


Thus the subsequent processes may be compared with reactions of the hydroxyl radical generated in aqueous solutions by pulse radiolysis. However, the further reactions have variously been proposed for the titanium(III)–hydrogen peroxide system:

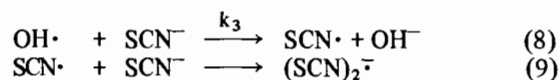


The extent to which each of these reactions is involved will depend on the relative concentrations of the initial reactants and the pH, but clearly the situation is potentially complex [6–8].

The pulse radiolysis technique involves a quite different primary process which may crudely be represented as



The yield of OH• radicals has been estimated by scavenging with SCN[−] ions, which give the strongly absorbing radical anion [9, 10] species (SCN)₂^{−•}, thus



In the present work we have studied the reaction between OH• and the thiocyanate ion with both stop-flow and continuous flow apparatus, generating the primary OH• radicals by the Ti(III)–H₂O₂ reaction.

Experimental

Analytical grade reagents were used throughout, and solutions were made up in nitrogen purged distilled water. Titanium(III) chloride and potassium thiocyanate (typically *ca.* 4 × 10^{−3} and 0.1 mol dm^{−3}, respectively) were mixed together in one of the solution reservoirs, and hydrogen peroxide (typically 1 × 10^{−3} mol dm^{−3}) was contained in the other reservoir. Both solutions were maintained at the same pH value (below one, typically 0.75) by the presence of H₂SO₄.

The detailed features of the stop-flow apparatus used have been described elsewhere [11]. The time taken for passage of a volume element of solution from the mixer to the exit of the 35 mm long optical cell was 6 ms, and the dead time for observation across the flow at the entrance to the cell was 2 ms. Adjustments were made to compensate for the varying spectral sensitivity of the equipment by resetting the zero and 100% transmission lines at each wavelength change. The volume of each solution required for one experiment was approx. 0.3 cm³,

but the total volume of solution required to fill the apparatus was 5 cm³. Measurements were made at room temperature, 20 °C.

The fast continuous flow measurements were made with equipment derived from a standard e.s.r. flow system. The solutions flowed from twin reservoirs of 5 dm³ capacity with gravity feed from a height of 1.5 m at a rate of 0.5–4 cm³ s⁻¹. The minimum "dead time" from the mixing chamber to the observation cell was approx. 20 ms. The cell itself was made of fused silica, with a rectangular part of approx. 2 × 2 mm cross-section and 10 mm length joined to the mixer by 2 mm diameter capillary tubing, of variable length. A Unicam SP8000 spectrophotometer was used for recording the absorption spectra of the mixed solutions in the flow cell.

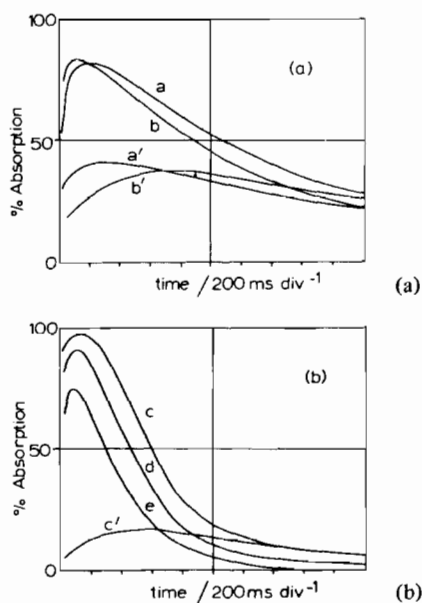


Fig. 1. Absorption-time profiles for the Ti(III)-H₂O₂-SCN⁻ reaction. Solution A: [Ti(III)] = 8.0 × 10⁻³ mol dm⁻³, [SCN⁻] = 0.10 mol dm⁻³. B: [H₂O₂] = 2.0 × 10⁻³ mol dm⁻³. a, a' 400 nm; b, b' 420 nm; c, c' 460 nm; d 540 nm; e 580 nm.

Results and Discussion

Figures 1 (a) and (b) show series of absorption-time profiles obtained by mixing solutions having the following compositions: A: [Ti³⁺] = 8.0 × 10⁻³ mol dm⁻³, [SCN⁻] = 0.10 mol dm⁻³. B: [H₂O₂] = 2.0 × 10⁻³ mol dm⁻³.

The curves designated a, b, c, d and e show the wavelength dependence of the absorption over the range 400–580 nm. The curves a', b' and c' show the equivalent results obtained in the range 400–480 nm when SCN⁻ was omitted from solution A. All the data shown are normalized to the same absorption

scale. These experiments showed two distinct absorption phenomena contributing to the overall profiles obtained from the mixed solutions A and B. The stronger absorption, peaking below 200 ms after mixing, maximized at approx. 480 nm, while the weaker component, peaking around 400–600 ms, gave its maximum absorption in the region 410–420 nm. The experiments showed that SCN⁻ was essential for the 480 nm absorption but made no contribution to that at 410–420 nm.

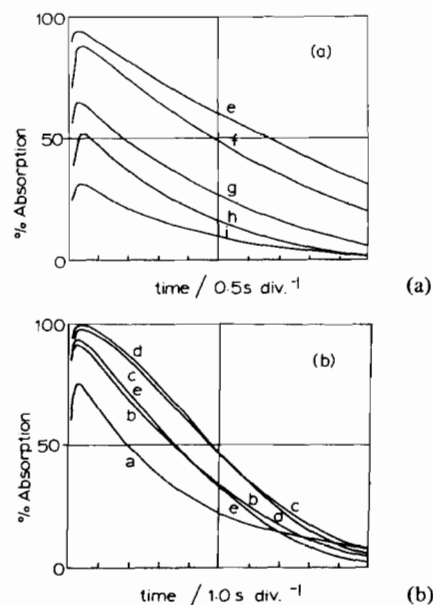


Fig. 2. Absorption-time profiles for the Ti(III)-H₂O₂-SCN⁻ reaction. Solution A: [Ti(III)] = 2.0 × 10⁻³ mol dm⁻³, [SCN⁻] = 0.10 mol dm⁻³. B: [H₂O₂] = 5.0 × 10⁻⁴ mol dm⁻³. a, 400 nm; b, 440 nm; c, 460 nm; d 480 nm; e, 500 nm; 520 nm; g, 540 nm; h, 560 nm; i, 580 nm.

Figures 2(a) and (b) show absorption-time profiles for the Ti(III)-H₂O₂-SCN⁻ reaction obtained from solutions containing the same SCN⁻ concentration as before, but with 4X lower Ti(III) and H₂O₂ concentrations. The reactions clearly were very much slower. Again it is apparent that the wavelength for maximum absorption of the transient species is approx. 480 nm, but that there is a much weaker contribution from the species absorbing at shorter wavelength. A plot of absorbance values at the maxima against wavelength gave the result shown in Figure 3. No corrections were made here for the residual absorption at low wavelength (see Figure 1), since this evidently is negligibly small when the Ti(III)-H₂O₂ concentrations are kept very low relative to SCN⁻. The peak absorption is seen to occur between 460 and 480 nm.

The absorption spectra derived from the stop-flow experiments were approximately reproduced by measurements with the fast continuous flow system, using the stop-flow results to determine the optimum

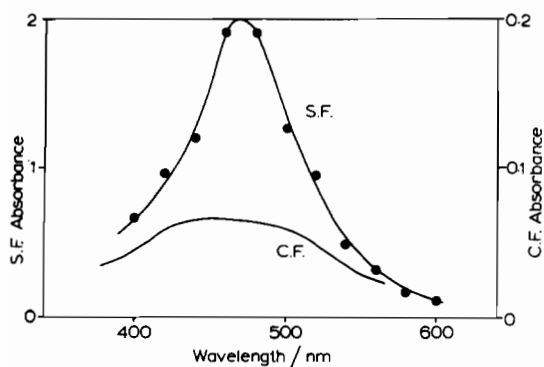


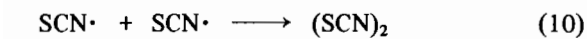
Fig. 3. Absorbance characteristics of the transient species in the Ti(III)-H₂O₂-SCN⁻ reaction. S. F. = Stop-flow, 35 mm path length; C. F. = Continuous-flow, 2 mm path length.

time after mixing at which to make the measurements. Due to the length (10 mm) of the slit-shaped radiation beam, a wide range of times after mixing (20–100 ms interval, depending on flow rate) were spanned by the continuous flow absorption measurements, resulting in some lack of register between the two sets of spectra. Figure 3 includes data from both types of measurement.

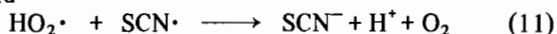
The absorbance characteristics shown in Figure 3 are consistent with the transient species being the (SCN)₂⁻ radical anion [9], formed by reactions (8) and (9). Under the acidic conditions used in these experiments, and with the excess Ti(III) used over the H₂O₂ concentration, reaction (2) may safely be taken as the principal competing reaction for OH· radical scavenging. However, the rate constant, *k*₂, for reaction (2) has been reported as 3 × 10⁹ mol⁻¹ dm³ s⁻¹, from which it may be concluded that essentially all the OH· radicals produced by the primary Ti(III)-H₂O₂ reaction will give rise to (SCN)₂⁻ radical anions with the set of experimental conditions used in this work.

The (SCN)₂⁻ radical anion concentrations may readily be determined from the reported value [3] of the molar absorption coefficient, ε(475 nm) = 7.6 × 10³ mol⁻¹ dm³ cm⁻¹. From the data represented in Figures 1 and 2, maximum radical concentrations of approx. 8 × 10⁻⁵ mol dm⁻³ were calculated.

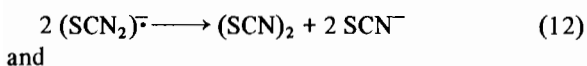
In acid solution in the absence of metal ions the decay of the (SCN)₂⁻ absorption has been attributed to the reactions [9]



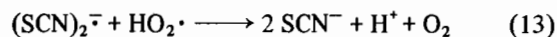
and



However, under the conditions used in our experiments (large excess of SCN⁻) these should perhaps be rewritten as



and



The curves shown in Figures 1 and 2 display a slower decay than would be expected for these fast reactions [9] and this slow decay may be attributed to the primary reaction which governs the rate of OH· radical production. The large excess of Ti(III) over H₂O₂ present in the solutions allows the reactions to be treated as pseudo first order and the expression

$$\frac{d[(\text{SCN})_2^-\cdot]}{dt} \cong \frac{d[\text{OH}\cdot]}{dt} = k_1 [\text{Ti(III)}] [\text{H}_2\text{O}_2] \\ \cong k_{\text{obs}} [\text{H}_2\text{O}_2],$$

where *k*_{obs} is the pseudo-first-order rate constant determined from the data shown in Figures 1 and 2, may be used to determine the rate constant *k*₁. Measurements were made at several wavelengths for both sets of data shown in Figures 1 and 2, the latter yielding a value of *k*₁ ≅ 5 × 10² mol⁻¹ dm³ s⁻¹. Typical pseudo-first-order plots of these data are shown in Figures 4 (a) and (b).

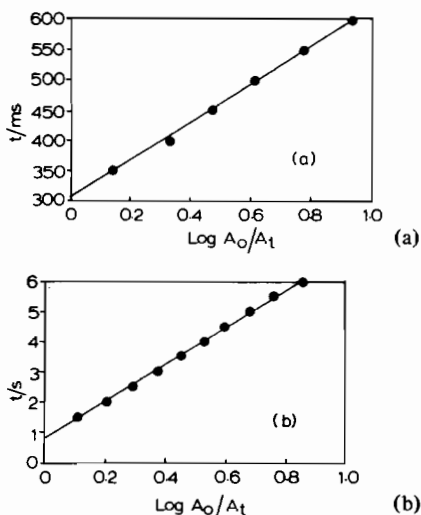


Fig. 4. Pseudo-first-order plots for the Ti(III)-H₂O₂-SCN⁻ reaction. (a) Solution A: [Ti(III)] = 8.0 × 10⁻³ mol dm⁻³, [SCN⁻] = 0.10 mol dm⁻³. B: [H₂O₂] = 2.0 × 10⁻³ mol dm⁻³. Measurements at 560 nm. (b) Solution A: [Ti(III)] = 2.0 × 10⁻³ mol dm⁻³, [SCN⁻] = 0.10 mol dm⁻³. B: [H₂O₂] = 5.0 × 10⁻⁴ mol dm⁻³. Measurements at 500 nm.

From the rate data shown in Figure 1 it is apparent that although [Ti(III)] > [H₂O₂] in these experiments some intermediate formation of a complex between Ti(IV) and H₂O₂ occurred. The 420 nm absorption band of this complex has been used in an earlier study of the Ti(III)-H₂O₂ reaction [13], and its rate constant for formation from Ti(IV) and H₂O₂ has been determined as 5.9 × 10² mol⁻¹ dm³ s⁻¹ in H₂SO₄ solution [14]. The mononuclear complex Ti(O₂)OH⁺ is believed to be the major

species [15] present below pH 1, giving a molar absorption coefficient of $690 \pm 20 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ [16]. The fact that this is only 9% of the corresponding value for the $(\text{SCN})_2^-$ species at its absorption maximum needs to be considered in estimating the extent of interference from this complex in the data presented in Figures 1–3. This is seen to be significant in Figure 1, but negligible at the lower concentration represented by the data in Figure 2 from which the reported k_1 value was determined.

It is possible that throughout this work the OH· radical should be considered as coordinated with Ti(IV), rather than free in solution [7]. However, our results yield no evidence on this point and under the conditions used (excess SCN^- and low Ti(IV) concentration) it is unlikely that a significant fraction of the OH· radicals would be coordinated [8]. Furthermore, the $(\text{SCN})_2^-$ radical anion is unlikely to be coordinated with either Ti(III) or Ti(IV) species in the presence of the large excess of SCN^- . Certainly the agreement of our absorption spectrum for the transient $(\text{SCN})_2^-$ species with that obtained from pulse radiolysis experiments indicates that the radical anion is free in solution.

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