Pulse-radiolytic Investigation of the Reduction of Titanium(III) Ions in Aqueous Solutions

By **Olga I. Mićić** * and **Milica T. Nenadović**, Boris Kidrič Institute of Nuclear Sciences, Vinča, 11001 Beograd, P.O. Box 522, Yugoslavia

The absorption spectrum and decay kinetics of intermediates formed by the reaction of titanium(III) ions with H atoms, hydrated electrons, and carboxyl radicals have been studied in aqueous solution using the pulse-radiolysis technique. The product of the reaction with H atoms in acid solution is a Ti^{3+}–H hydride intermediate which decomposes by a first-order process with a half-life of *ca.* 3 s. Titanium(II) is formed by reaction with hydrated electrons and $^{\cdot}CO_2H$ radicals. The absorption spectrum of titanium(II) and the kinetics of its reactions are reported and discussed. The formation of molecular hydrogen by reaction of Ti^{2+} with water is suppressed by the other solutes in the solutions. Titanium(III) reacts with $^{\cdot}CO_2H$, $^{\cdot}CH_2CO_2H$, and $^{\cdot}CH(CO_2H)_2$ radicals to give titanium–radical complexes.

THE oxidation of titanium(III) by aliphatic radicals and H atoms has been studied by Behar and co-workers.[1,2] They conclude that molecular hydrogen is formed according to reactions (1) and (2). They did not observe

$$Ti^{3+} + H \longrightarrow Ti^{3+}\text{–}H;\ k_1 = 4.2 \times 10^7\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ \text{(ref. 1)} \quad (1)$$

$$Ti^{3+}\text{–}H + H^+ \longrightarrow Ti^{4+} + H_2 \quad (2)$$

hydride intermediates Ti^{3+}–H although there is evidence of the formation of similar species in analogous reactions of Fe^{2+} and Cr^{2+} cations.[3-6] Less information is available about the possibility of reducing Ti^{3+} by radical reaction to lower oxidation states. The pulse radiolytic study of the reduction of Ti^{3+} by the CO_2H radical in acid aqueous solutions [7] is the sole example we have found in the literature.

In the present study we obtained direct evidence for intermediates in the reactions of Ti^{3+} with hydrated electrons and carboxyl radicals. Our results clearly indicate that these intermediates are Ti^{2+} in both cases and that its properties are in many respects different to those of the Ti^{3+}–H complex. In addition, some steady-state γ-radiolysis studies were carried out in order to characterize the properties of the intermediate species and to establish the mechanism of the primary processes in the reduction of titanium(III) in aqueous solutions. These experiments are also expected to give more information about the reactions in which molecular hydrogen is produced.

EXPERIMENTAL

Materials.—Titanium(III) sulphate solutions were prepared by dissolving titanium metal (B.D.H) in 4 mol dm^{-3} H_2SO_4 under an argon atmosphere at 60 °C in a preparation vessel. The titanium(III) solutions were transferred to all-glass syringes (100 cm^3) by applying argon pressure and then diluted. The pH of the solutions was adjusted with Na[OH]. Solutions were prepared from analytical grade chemicals (E. Merck or B.D.H.). Triply distilled water was used throughout.

Procedure.—The concentration of titanium(III) was determined spectrophotometrically. An excess of iron(III) sulphate was added after irradiation, and the decrease in absorbance of Fe^{3+} was taken as a measure of the change in Ti^{3+} concentration. The molar absorption coefficient of Fe^{3+} was measured at 304 nm for each solution at high solute concentration. Molecular hydrogen and carbon dioxide were determined by gas chromatography,[8] and formaldehyde by spectrophotometry using phenylhydrazine as a reagent.[9] The formation of chlorine in solutions of $Ti_2[SO_4]_3$ containing KCl was controlled by use of *o*-toluidine.[10] The rate constant for the reaction of the hydrogen atom with Ti^{4+} ions was determined in $TiCl_4$ solutions containing 2 mol dm^{-3} H_2SO_4, and the concentration of Ti^{4+} was checked by the hydrogen-peroxide method.[11] The pH of the solution was determined in an argon atmosphere. The accuracy of the measurements was ±0.01 pH unit.

For pulse radiolysis a Febetron 707 (Field Emission Corp.) electron accelerator with pulse duration of 20 ns was used, the operating conditions being similar to those described previously.[12] The total light path through the cell was 5.1 cm. The absorbed doses were in the range 0.5—9 krad per pulse,† measured by using a potassium hexacyanoferrate(III) dosimeter [13] and taking ε_{420} $[Fe(CN)_6{}^{3-}]$ as 1 000 dm^{-3} mol^{-1} cm^{-1} and $G[Fe(CN)_6{}^{3-}] = 5.6$.

Steady-state irradiations were performed with a ^{60}Co γ-source. The total absorbed doses were in the range 5—50 krad and the dose rate was 10 krad min^{-1}. The measurements were made at 20 ± 1 °C.

RESULTS AND DISCUSSION

Titanium(III) *Hydride Complex.*—Titanium(III) ions react with OH radicals, H atoms, and hydrated electrons which form in the radiolysis of water. Under the strongly acidic conditions used in the present study, hydrated electrons are rapidly converted into H atoms [equation (3)], therefore only H and OH radicals were

$$e^-(aq) + H^+ \longrightarrow H + H_2O \quad (3)$$

considered as primary species in the radiolysis of the acidic solutions. The ion $[Ti(OH_2)_6]^{3+}$ has an acid dissociation constant of *ca.* 2×10^{-3} dm^3 mol^{-1} at 25 °C (ref. 14) and to avoid precipitation of titanium(III) it is necessary to work at pH < 3. We chose to work in solutions containing 0.3 mol dm^{-3} H_2SO_4. The solutions at pH 2.5 were only used for studying the reaction with hydrated electrons.

The relatively large rate constant for the OH radical

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† Throughout this paper: 1 rad = 10^{-2} kg^{-1}.

reaction compared with the rate constant for reaction (1) made feasible the investigation of Ti^{3+}–H. Pulse radiolysis of concentrated and diluted solutions of Ti^{3+} allowed us to distinguish between the products of reactions (1) and those of (4). In dilute solutions the oxidation of Ti^{3+} occurs as in (4) and there is little or no

$$Ti^{3+} + OH \longrightarrow Ti^{4+} + [OH]^-;\ k_4 = 3 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 15)} \quad (4)$$

reduction by H atoms due to competition of reaction (1) with (5). For absorbed doses higher than 8 krad per

$$H + H \longrightarrow H_2;\ k_5 = 1 \times 10^{10}—1.5 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 16)} \quad (5)$$

pulse and titanium concentrations less than 5×10^{-4} mol dm^{-3}, reaction (1) can be neglected. Under these conditions the increase of absorption in the u.v. region [Figures 1 and 2(*a*), lower curves] was attributed to the product of reaction (4). The spectra of Ti^{4+} given in Figures 1 and 2 were registered 30 μs after the pulse. In the 250—350 nm region absorbances decreased during the first 10 μs and then remained constant. The change of the spectra with time is connected with the build-up (from the free Ti^{4+} ion formed during irradiation) of different Ti^{4+} aqua-ions in the solution containing the sulphate ion.[17] The pH of the solution also affected the shape of the spectra, probably due to aggregation at lower hydrogen-ion concentrations.

In concentrated Ti^{3+} solutions (5×10^{-2} mol dm^{-3}) (Figure 1) reactions (1) and (4) are dominant and reaction (5) takes place to a smaller extent. After correction for the contribution from Ti^{4+}, the spectrum of long-lived Ti^{3+}–H was obtained and is given by the full line of Figure 1. From the known rate constants for reactions (1) and (5), the concentration of Ti^{3+}–H, under the experimental conditions, is 1.9×10^{-5} mol dm^{-3}. The decay of Ti^{3+}–H, observed in the region 300—370 nm, followed first-order kinetics with a half-life of *ca.* 2 s, which does not change with the wavelength or Ti^{3+} concentration in the range of interest. The low rate of decomposition indicates that the metal–hydride bond in Ti^{3+}–H is more covalent than ionic. This rate is much lower than that for corresponding hydride intermediates of Fe^{2+} and Cr^{2+} ions for which $k_2 = 1 \times 10^4—1.8 \times 10^4$ dm^3 mol^{-1} s^{-1} (refs. 3 and 6).

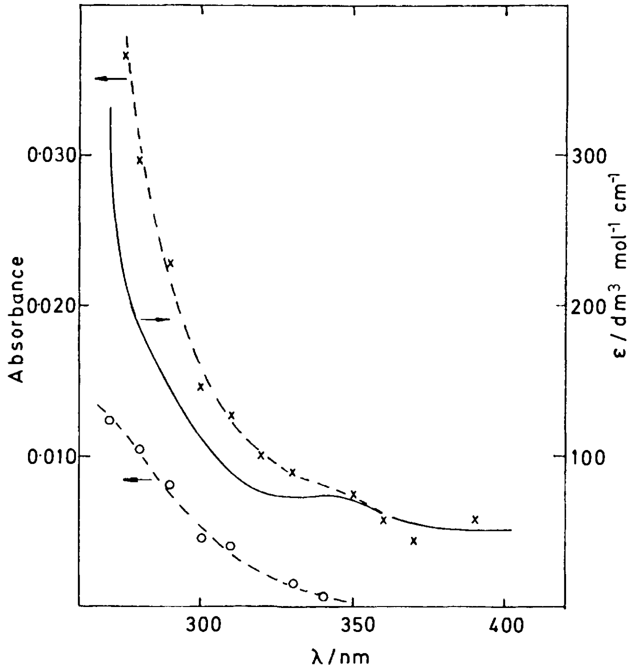

FIGURE 1 Absorption spectra of intermediates formed in argon-saturated aqueous titanium(III) sulphate solutions. Absorbed dose 6.2 krad per pulse. (○), 5×10^{-4} mol dm^{-3} Ti^{3+} and 3×10^{-1} mol dm^{-3} H_2SO_4, the absorption being measured 30 μs after the pulse; (×), 5×10^{-2} mol dm^{-3} Ti^{3+} and 3×10^{-1} mol dm^{-3} H_2SO_4, the absorption being measured after 2 μs. Both spectra include corrections for Ti^{3+} absorption. The full line represents the spectrum of the Ti^{3+}–H intermediate

Rate constants and product yields for deaerated Ti^{3+} solutions in the presence of different solutes

Reaction	Rate constant (dm^3 mol^{-1} s^{-1})	$[Ti^{3+}]$/ mol dm^{-3}	Additive (*c*/mol dm^{-3})	pH	*G*(product) [a]
$Ti^{3+} + H$	$4.2 \geqslant 10^7$ [b]	2×10^{-2}	H_2SO_4 (0.3)	0.5	$G(H_2) = 3.4$, $G(Ti^{4+}) = 6.9$
$Ti^{3+} + e^-(aq)$	k_9/k_3 — 0.51 [c]	3.2×10^{-2}	$Na_2[SO_4]$ (0.2)	2.4	$G(H_2) = 1.7$, $G(Ti^{4+}) = 6.9$
		3.2×10^{-2} [d]	NaCl (0.7)	2.3	$G(H_2) = 1.4$
		5×10^{-3}—3×10^{-2}	EtOH (2) $Na_2[SO_4]$ (0.2)	2.3—2.5	$2.8 > G(H_2) > 1.7$
		3×10^{-2}	$Na_2[SO_4]$ (0.2) Allyl alcohol (7×10^{-3})	2.5	$G(H_2) = 0.55$
$Ti^{3+} + CO_2H$	$(4 \pm 1) \times 10^6$ [e]	2×10^{-3}	H_2SO_4 (0.3) HCO_2H (2)	0.5	$G(H_2) = 3.2$, $G(CO_2) = 6.1$, $G(Ti^{4+}) = 3.4$, $G(HCHO) = 0.9$
		1×10^{-3}	HCO_2H (2)	2.5	$G(H_2) = 1.8$, $G(CO_2) = 2.0$
$Ti^{3+} + CH_2CO_2$	$(4 \pm 1) \times 10^6$ [e]	2×10^{-3}	H_2SO_4 (0.3) $MeCO_2H$ (2)	0.5	$G(H_2) = 2.8$, $G(CO_2) = 6.6$, $G(Ti^{4+}) = 5.1$ [f]
$Ti^{3+} + CH(CO_2H)_2$	8×10^6 [f]	2×10^{-3}	H_2SO_4 (0.3) Malonic acid (2)	0.5	$G(H_2) = 1.7$, $G(CO_2) = 1.0$, $G(Ti^{4+}) = 7.5$ [f]
$Ti^{3+} + [Cl_2]^-$	4×10^8 [g]	2×10^{-3}	KCl (0.5)	0.5	$G(Cl_2) \leqslant 0.5$, $G(Ti^{4+}) = 6.9$

[a] Obtained by steady-state γ-radiolysis, with a 20-krad dose at 10 krad min^{-1}. [b] From ref. 1. [c] At ionic strength $I = 0.84$ mol dm^{-3}. [d] Prepared with $TiCl_3$. [e] Calculated by a method of successive approximations (M. S. Matheson and L. M. Dorfman, ' Pulse Radiolysis,' M.I.T. Press, Cambridge, Massachusetts, 1969, p. 55) taking into account the competition with carboxyl-radical recombination. [f] From ref. 2. [g] From ref. 7.

In γ-irradiated solutions of Ti^{3+} (5×10^{-2} mol dm^{-3}) containing H_2SO_4 (0.3 mol dm^{-3}) the values $G(H_2) = 3.4$ and $G(Ti^{4+}) = 6.9$ were obtained with 20 krad at a dose rate of 10 krad min^{-1} (Table). These yields decreased with increasing absorbed dose so that $G(H_2) = 2$ and $G(Ti^{4+}) = 4.8$ for a dose of 100 krad. Titanium(IV) is accumulated with dose so that reaction (6) can compete with (1). In this work the rate constant for reaction (6)

$$H + Ti^{4+} \longrightarrow Ti^{3+} + H^+ \qquad (6)$$

was determined by measuring the yield of molecular hydrogen in the presence of ethanol (0.1 mol dm^{-3}) for various concentrations of Ti^{4+} ion (5×10^{-3}—2×10^{-1} mol dm^{-3}) in H_2SO_4 solutions (2 mol dm^{-3}). Under these conditions, reaction (6) competes with (7). From

$$H + C_2H_5OH \longrightarrow H_2 + C_2H_4OH; \quad k_7 = 2.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 15)} \qquad (7)$$

these results $k_6 = 5.95 \times 10^7$ dm^3 mol^{-1} s^{-1} was obtained. The existence of reaction (6) can only partially explain the large decrease of $G(H_2)$ and $G(Ti^{4+})$ with dose. It is probable that other products accumulated in the irradiated solutions also react with H atoms or the Ti^{3+}–H intermediate.

Reaction with the Hydrated Electron.—The absorption spectra of intermediates formed by the pulse radiolysis of an argon-saturated solution at pH 2.5 are given in Figure 2(*a*). The spectrum remains constant from 5 μs to several seconds in the region 320—600 nm. These spectra differ greatly from the spectrum at pH 0.5. It can also be seen that $G(H_2)$ is much lower than at pH 0.5 (Table). There are several possible explanations for such behaviour. According to one the intermediate formed in the reaction with H atoms cannot be the same as in acid solutions, since at pH 2.5 a mixture of $[Ti(OH_2)_6]^{3+}$, $[Ti(OH_2)_5(OH)]^{2+}$, and $[Ti(OH_2)_4(OH)]^{2+}$ ions is present in solution.[14,18] Addition of allyl alcohol (to scavenge H atoms without formation of H_2) decreases $G(H_2)$ (Table). On the other hand, the presence of a high concentration of ethanol [reaction (8)] at constant concentrations of Ti^{3+} and H^+ ions does not increase $G(H_2)$ even though ethanol scavenging of H atoms should produce H_2. This shows that the observed decrease in $G(H_2)$ at pH 2.5 is not the result of H reactions with different titanium(III) aqua-ions. As shown in the Table, only the ratio $[Ti^{3+}] : [H^+]$ affects $G(H_2)$. At higher pH, hydrated electrons can reduce Ti^{3+} ions: if reaction (8) is fast

$$e^-(aq) + Ti^{3+} \longrightarrow Ti^{2+} \qquad (8)$$

enough to compete with (3). In that case the absorption spectrum in Figure 2(*a*) can be attributed to Ti^{2+} or to Ti^{2+} and Ti^{3+}–H intermediates. We determined the rate constant for reaction (8) (Table) by steady-state kinetics; the value is in agreement with that of $<8 \times 10^9$ dm^3 mol^{-1} s^{-1} given by Buxton and Sellers.[19] Determination of the yields of molecular hydrogen in solutions containing ethanol (Table) provides a basis for the determination of k_8/k_3, since H atoms formed in reaction (3) react with ethanol yielding H_2. In the presence of 0.2 mol dm^{-3} $Na_2[SO_4]$, $k_8/k_3 = 0.51$, whence $G(Ti^{2+}) = 2.35$ and $G(Ti^{3+}\text{–}H) = 0.85$ under our experimental conditions [Figure 2(*a*)].

It should be pointed out that Ti^{2+} ions do not produce H_2 by reaction with water or H^+ ions. $G(H_2)$ is much lower than the corresponding G values for Ti^{2+} reduces the solutes (Ti^{4+}, $[SO_4]^{2-}$, H_2O_2, *etc.*) before reacting with water. Even at pH 2.5 where $[SO_4]^{2-}$ is replaced with Cl^- there is no difference in $G(H_2)$ (Table).

We conclude that the transient having the broad spectrum reaching into the visible region [Figure 2(*a*)] is Ti^{2+}.

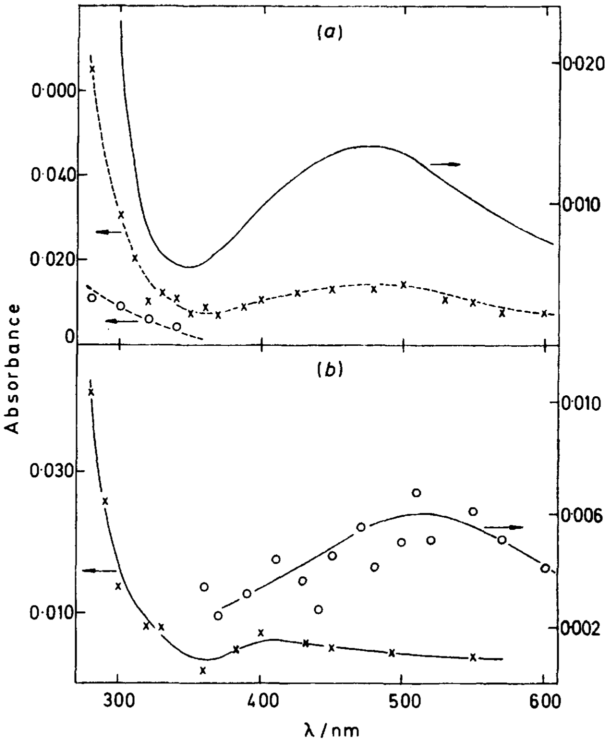

FIGURE 2 Absorption spectra of intermediates formed in argon-saturated aqueous titanium(III) solutions. Absorbed dose 6.2 krad per pulse. (*a*) pH 2.5; (○), 5×10^{-4} mol dm^{-3} Ti^{3+} and 0.2 mol dm^{-3} $Na_2[SO_4]$; (×), 2.5×10^{-2} mol dm^{-3} Ti^{3+} and 0.2 mol dm^{-3} $Na_2[SO_4]$. The full line represents the spectrum of Ti^{2+} ions after correction for the absorption of Ti^{4+} and Ti^{3+}–H. (*b*) 2×10^{-3} mol dm^{-3} Ti^{3+}, 3×10^{-1} mol dm^{-3} H_2SO_4, and 2 mol dm^{-3} HCO_2H; (×), 0.1 ms after the pulse; (○), 0.3 s after the pulse

Reactions with CO_2H *Radicals.*—In formic acid solutions H and OH radicals are converted into CO_2H radicals which behave as a strong reducing agent. We have observed transients formed by the reaction of Ti^{3+} with CO_2H radicals. Buxton and co-workers[7,19] assumed that Ti^{2+} is produced by that reaction immediately, without formation of the Ti^{3+}–CO_2H intermediate. They recorded a transient absorption spectrum with $t_{\frac{1}{2}} = 1.8$ ms. We found that in the reaction with CO_2H two intermediates are formed [Figure 2(*b*)]. The initial intermediate decays with a $t_{\frac{1}{2}} \sim 2$ ms; the second one has a lifetime of several seconds. The second radical has a broad spectrum, similar to that of Ti^{2+} formed by the reaction of Ti^{3+} with e^-(aq). The initial intermediate is most probably a complex formed by reaction (9).

$$Ti^{3+} + CO_2H \longrightarrow Ti^{3+}\text{-}CO_2H \qquad (9)$$

We have found Ti^{4+}, CO_2, and formaldehyde (Table) as stable products of the reaction between Ti^{3+} and CO_2H. The formation of Ti^{4+} is consistent with the mechanism of reduction of CO_2H. However, CO_2 is also produced, even in significant yield, and could be expected only from oxidation of CO_2H radicals. In seeking an explanation for the conflicting evidence of the formation of Ti^{4+} and CO_2 we assumed that reactions (9) and (10) take place as well as that Ti^{2+}, formed by

$$Ti^{3+}\text{-}CO_2H \longrightarrow CO_2 + Ti^{2+} + H^+ \qquad (10)$$

oxidation of CO_2H, may undergo two-electron oxidation to form Ti^{4+} by reaction with formic acid. The formation of formaldehyde shows that Ti^{2+} ions reduce formic acid. However, the yield of formaldehyde is much lower than that of Ti^{4+} probably due to formation of some other products in the process of oxidation of Ti^{2+} to Ti^{4+}.

It can be seen that H_2 is not produced by the reaction of Ti^{3+} with CO_2H (Table). Similar behaviour was observed in the reaction of Ti^{3+} with hydrated electrons at pH 2.5. The reduction of water to molecular hydrogen by Ti^{2+} seems to be a very slow process which can easily be suppressed by the presence of other solutes in aqueous solutions.

Reactions with some Carboxyalkyl Radicals.—Experiments in which formic acid was replaced by acetic or malonic acid gave weak long-lived transient absorption probably indicating formation of $Ti^{3+}\text{-}RCO_2H$ complexes. The species $^{\bullet}CH_2CO_2H$ and $^{\bullet}CH(CO_2H)_2$ which resemble alkyl radicals are most likely added to Ti^{3+}. It is known that Ti^{3+} is oxidized to Ti^{4+} by reaction with aliphatic radicals, and it has been suggested [2,5] that this mechanism involves the formation of a complex of Ti^{4+} and carbanions. Titanium(IV) is formed in significant yields (Table) from reactions with $^{\bullet}CH_2CO_2H$ and $^{\bullet}CH(CO_2H)_2$ radicals. As in the presence of HCO_2H, we have found formation of CO_2. However, in malonic acid solutions $G(CO_2) = 1.0$ is much lower than $G[^{\bullet}CH(CO_2H)_2]$. The formation of CO_2 indicates that the mechanism of oxidation of Ti^{3+} with $^{\bullet}CHCO_2H$ and $^{\bullet}CH(CO_2H)_2$ is rather complex and that besides reaction (12) another decomposition path of $Ti^{3+}\text{-}RCO_2H$ exists. However, since the transient absorption in acetic and malonic acid solutions containing Ti^{3+} is very weak, the procedure used in this study does not permit an unequivocal identification of the intermediates and observation of their kinetics.

$$Ti^{3+} + R \longrightarrow Ti^{3+}\text{-}R \qquad (11)$$

$$Ti^{3+}\text{-}R + H^+ \longrightarrow RH + Ti^{4+} \qquad (12)$$

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