Photochemical Generation of Sn(III) in Hydrochloric Acid Solutions

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In the flash photolysis of Sn(II) in a deaerated hydrochloric acid solution, Sn(III) was produced. Sn(III) has an absorption maximum at 280 nm in a 1 mol dm^{-3} hydrochloric acid solution. In the flash photolysis of a deaerated Sn(IV) solution, intermediates of Sn(III) and Cl_2^- were produced. Transient absorption spectra of intermediates generated by the flashed Sn(IV) solutions were measured under various concentrations of dissolved oxygen. Since Sn(III) reacts with oxygen very rapidly, only Cl_2^- was confirmed in the oxygen-saturated Sn(IV) solution. In the flash photolysis of Sn(IV) solutions containing Sn(II), the yield of Sn(III) increased with an increase of the added Sn(II), due to the generation of Sn(III) by the reaction of Cl_2^- with Sn(II). It was found that only Sn(III) was produced in the irradiation of 5.0×10^{-4} mol dm^{-3} Sn(IV) solution containing Sn(II) at concentrations of more than ca. 7×10^{-5} mol dm^{-3}. The reaction rate constant for the reaction of Sn(II) with Cl_2^- was estimated to be 8.9×10^{8} mol^{-1} dm^3 s^{-1}. The mechanisms for the photochemical generation of Sn(III) are discussed.

Flash photolysis and pulse radiolysis have proved to be very useful in the generation and characterization of metal ions in unusual valency states. The species formed include the metal ions known to be formed as intermediates in thermal reactions. However, they are poorly characterized beause of their instability and difficulty to form novel valency states in other ways. Though the chemical properties and behavior of these species have been investigated, much still remains to be studied.[1,2]

The stable oxidation states of non-transition elements usually differ by two units in their mononuclear compounds. Most oxidation–reduction reactions of such elements involve either a two-equivalent change with the direct formation of a stable oxidation state or successive one-equivalent steps. In the latter case, an unstable intermediate oxidation state of non-transition metal is produced, which may show some of the characteristics of a free radical. In Sn(II)–Sn(IV) redox chemistry, unstable Sn(III) is assumed to be an intermediate.[3–6] Only a few studies of the intermediate oxidation state, Sn(III), have been carried out briefly regarding radiation chemistry.[7–9] In a previous paper, we reported on the photochemical generation of Sn(III) from tin ions in deaerated aqueous hydrochloric acid solutions.[10] In the present paper we give more details regarding Sn(III) generated upon the irradiation of tin ions in hydrochloric acid solutions.

Experimental

Sn(II) solutions used for flash photolysis were obtained by adding $SnCl_2$ to a deaerated solution of hydrochloric acid. The deaerations were carried out by bubbling with oxygen-free nitrogen obtained through a tube containing heated cupper metal pieces. All preparations of Sn(II) solutions should be carried out with adequate safety precautions. Mixed gases were prepared by mixing pure oxygen and nitrogen. The oxygen content in the mixture was determined gas chromatographically. Sn(IV) solutions containing dissolved oxygen at the desired concentration were obtained by bubbling with the mixed gas. Sn(IV) solutions were prepared by the oxidation of Sn(II) with oxygen. All of the chemicals were of chemically pure grade. Pure water obtained from a Millipore Super-Q system was used for the preparation of samples. A flash photolysis apparatus was the same as that used previously.[10] The main flash lamps dissipated 450 J max. at 15 kV with a flash duration of 10 μs. Solutions for flash photolysis were taken in a quartz cell with a 10-cm path length. Transient absorption changes were recorded on a Textronix 7633 oscilloscope.

Results and Discussion

Photolysis of Sn(II) Solutions. In our previous paper we reported on the absorption spectrum of Sn(III) obtained by using a flash photolysis technique.[10] The spectrum is shown in Fig. 1 together with the absorption spectra of Sn(II) and Sn(IV), measured in a 1 mol dm^{-3} hydrochloric acid solution.

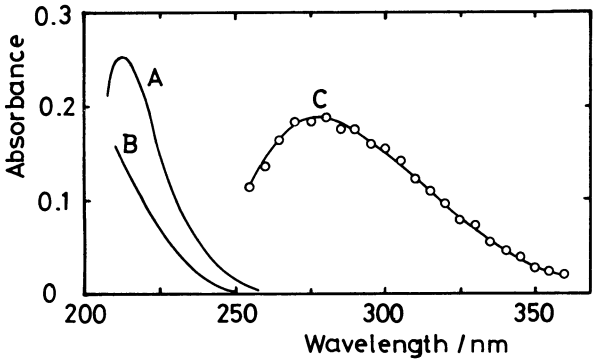

Fig. 1. Absorption spectra of Sn(II), Sn(III), and Sn(IV) in 1 mol dm^{-3} hydrochloric acid solutions. A: 1.0×10^{-5} mol dm^{-3} Sn(II), B: 4.0×10^{-5} mol dm^{-3} Sn(IV), C: Sn(III) obtained in the flash photolysis of 1.0×10^{-4} mol dm^{-3} Sn(II) in the deaerated solution.

Under our experimental conditions, these tin ions exist in chloro complex forms.[11-13] The Sn(II) hydrochloric acid solution, subjected to a flash, showed a transient absorption maximum at 280 nm, which was attributed to the generation of Sn(III), as shown in Reaction (1).

$$Sn(II) + H^+ \xrightarrow{h\nu} Sn(III) + H \quad (1)$$

The resulting H atoms produced H_2 by Reaction (2). However, since Sn(II) can be oxidized by oxygen very easily, the Sn(II) solution usually contains a small amount of Sn(IV) as an impurity. Therefore, some of H atoms react with Sn(IV) very rapidly, according to Reaction (3).[14]

$$H + H \rightarrow H_2 \quad (2)$$
$$Sn(IV) + H \rightarrow Sn(III) + H^+ \quad (3)$$

Photolysis of Sn(IV) solutions. Typical oscillograms obtained by flashing oxygenated Sn(IV) solutions are given in Fig. 2. When the Sn(IV) solution containing a small amount of dissolved oxygen was flashed, there was a fast decay after a rapid increase (within the flash) in absorbance (oscillogram A in Fig. 2). However, the fast decay step could not be observed in the flash photolysis of the oxygen-saturated Sn(IV) solution ($[O_2]=1.38\times10^{-3}$ mol dm^{-3}) (oscillogram B in Fig. 2). Oxygen has a large effect upon the reaction course. Then, flash photolysis was carried out in Sn(IV) solutions under various concentrations of dissolved oxygen, and the obtained absorption spectra are given in Fig. 3. The transient absorption spectrum obtained in the deaerated Sn(IV) solution shows a discernible shoulder at the shorter-wavelength side of the main absorption band at 340 nm. The absorbance near 280 nm decreased with increasing the concentration of dissolved oxygen. The absorption spectrum in an aerated solution is close to that in an oxygen-saturated solution. This fact shows that the amount of oxygen in an aerated solution is sufficient to scavenge the Sn(III) formed by photolysis. The spectrum obtained in the oxygen-saturated solution has an absorption maximum at 340 nm which is attributed to Cl_2^-.[15-18] The difference between the spectrum obtained in the oxygen-free solution and the spectrum obtained in the oxygen-saturated solution (Fig. 3) is similar to the spectrum of Sn(III) in Fig. 1. This suggests that Sn(III) are produced in a flashed Sn(IV) solution. Thus, the reactions in the flashed Sn(IV) solution can be explained by Eqs. 4 and 5, where Sn(IV)-Cl denotes chloro complexes.

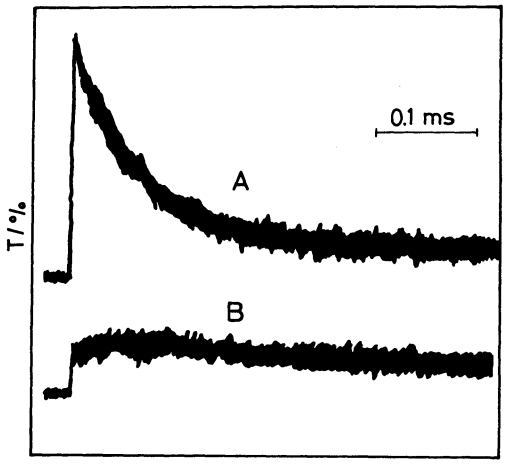

Fig. 2. Oscilloscope traces showing changes in absorption measured at 280 nm after the flash of 5.0×10^{-4} mol dm^{-3} Sn(IV) in 1 mol dm^{-3} hydrochloric acid solutions in the presence of dissolved oxygen.
Concentrations of dissolved oxgen A: 8.83×10^{-5} mol dm^{-3}, B: 1.38×10^{-3} mol dm^{-3}.

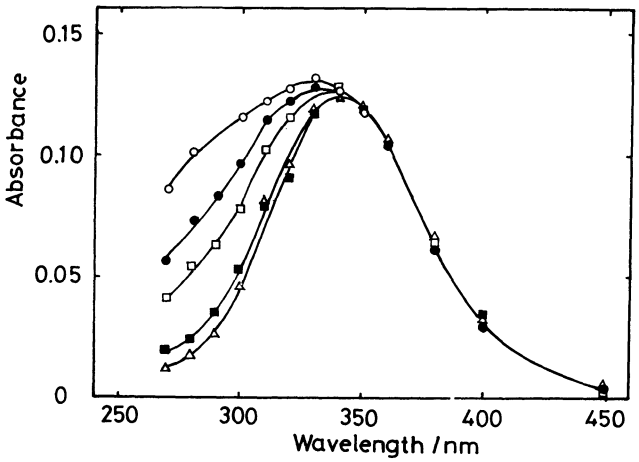

Fig. 3. Transient absorption spectra obtained in the flash photolysis of Sn((IV) solutions in the presence of various concentration of oxygen at 30 μs after the flash.
Concentrations of oxygen; ○: 0, ●: 8.83×10^{-5}, □: 1.60×10^{-4}, ■: 2.84×10^{-4} (aerated), △ 1.38×10^{-3} mol dm^{-3} (oxygen-saturated).

$$Sn(IV)\text{-}Cl \xrightarrow{h\nu} Sn(III) + Cl \quad (4)$$
$$Cl + Cl^- \longrightarrow Cl_2^- \quad (5)$$

The resulting Cl_2^- disappears by Reaction (6), where the rate constant was estimated to be $2k_6=9.7\times10^9$ mol^{-1} dm^3 s^{-1}, as shown in our previous paper.[10]

$$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^- \quad (6)$$

Sn(III) reacts very rapidly with oxygen; the rate constant k_7 was obtained to be 1.7×10^8 mol dm^3 s^{-1}.

$$Sn(III) + O_2 + H^+ \rightarrow Sn(IV) + HO_2 \quad (7)$$

Photolysis of Sn(IV) Solutions Containing Sn(II). The effect of Sn(II) on the generation of Sn(III) in

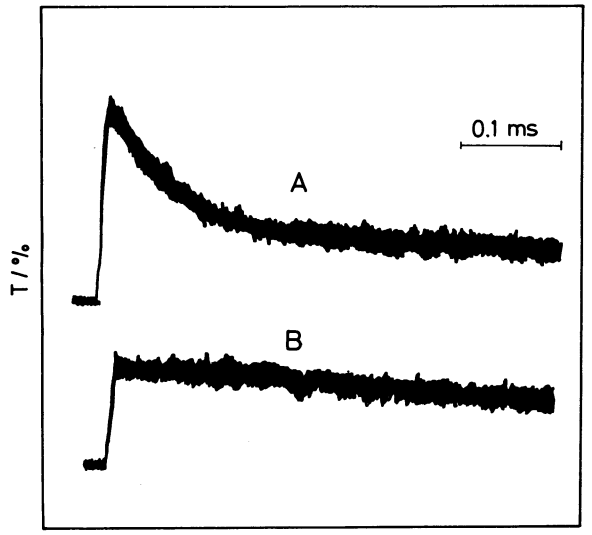

Fig. 4. Oscilloscope traces showing changes in absortion measurd at 350 nm after the flash of 5.0×10^{-4} mol dm^{-3} Sn(IV) containing Sn(II) in the deaerated 1 mol dm^{-3} hydrochloric acid solutions. Concentration of Sn(II); A: 1.7×10^{-5} mol dm^{-3}, B: 8.9×10^{-5} mol dm^{-3}.

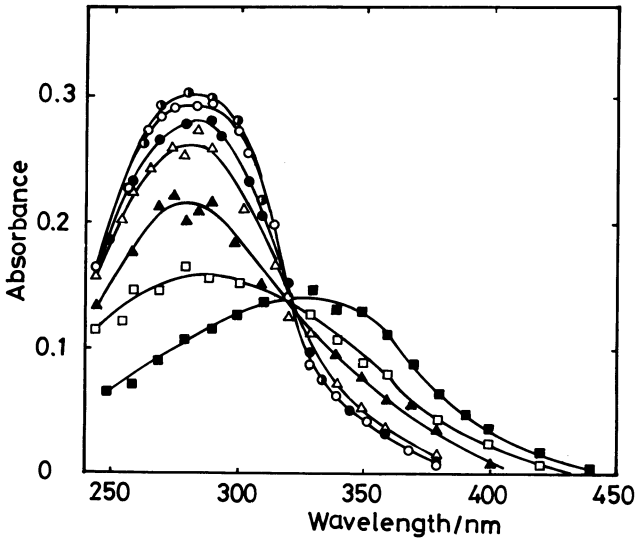

Fig. 5. Transient absorption spectra obtained in the flash photolysis of 5.0×10^{-4} mol dm^{-3} Sn(IV) solutions with various concentration of Sn(II) in deaerated 1 mol dm^{-3} hydrochloric acid solutions. Absorbance were measured 30 μs after the flash. Concentrations of Sn(II); ■: 0, □: 1.7×10^{-5}, ▲: 3.0×10^{-5}, △: 5.0×10^{-5}, ●: 6.9×10^{-5}, ○: 8.9×10^{-5}, ◑: 1.3×10^{-4} mol dm^{-3}.

flash photolysis of a deaerated Sn(IV) solution was studied. Figure 4 shows typical oscillograms obtained in the flash photolysis of Sn(IV) solutions containing Sn(II). Oscillogram A had a fast decay species which did not appear in oscillogram B, measured in a solution containing Sn(II) at a higher concentration. The fast decay is attributed to the reaction of Cl_2^- with

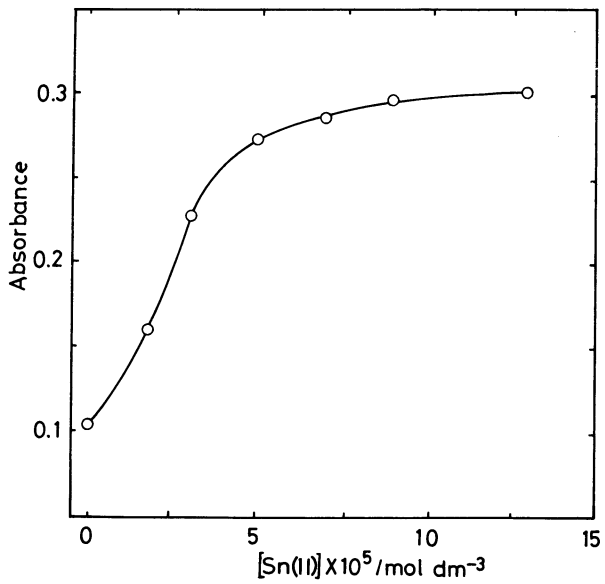

Fig. 6. The dependence of the yields of Sn(III) as a function of the Sn(II) concentration in the deaerated 1 mol dm^{-3} hydrochloric acid solution. The yields are expressed as the absorbances measured at 280 nm 30 μs after the flash. The concentration of Sn(IV) was kept at constant, 5.0×10^{-4} mol dm^{-3}.

Sn(II). The transient absorption spectra obtained in the flash photolysis of Sn(IV) with Sn(II) at various concentrations are shown in Fig. 5. An increase in Sn(II) caused a decrease in the absorbance at 340 nm, followed by an increase in the absorbance at 280 nm. The dependence of the yields of Sn(III) is shown as a function of the Sn(II) concentration in Fig. 6. The yield increases rapidly with an increase in the concentration of the Sn(II), but gradually at higher Sn(II) concentration (> ca. 7×10^{-5} mol dm^{-3}). A pronounced effect on the transient absorption spectrum is caused by the presence of the added Sn(II).

The obtained results can be explained in terms of the following reaction sequence:

$$Sn(II) + H^+ \xrightarrow{h\nu} Sn(III) + H \quad (1)$$

$$Sn(IV) + H \rightarrow Sn(III) + H^+ \quad (3)$$

$$Sn(IV)\text{-}Cl \xrightarrow{h\nu} Sn(III) + Cl \quad (4)$$

$$Cl + Cl^- \rightarrow Cl_2^- \quad (5)$$

$$Sn(II) + Cl_2^- \rightarrow Sn(III) + 2Cl^- \quad (8)$$

An H atom can react rapidly with Sn(IV) to give Sn(III), as already described. The reaction is completed very fast within the flash. The lack of an absorption maximum at 340 nm in the flashed Sn(IV) solution containing Sn(II) at a higher concentration (Fig. 5) can be attributed to the reaction of Cl_2^- with the added Sn(II) (Eq. 8). The rate constant k_8 was estimated to be 8.9×10^8 mol^{-1} dm^3 s^{-1} from a kinetic plot of the curve A in Fig. 4. The Sn(III) yield increases rapidly with increasing Sn(II) concentration,

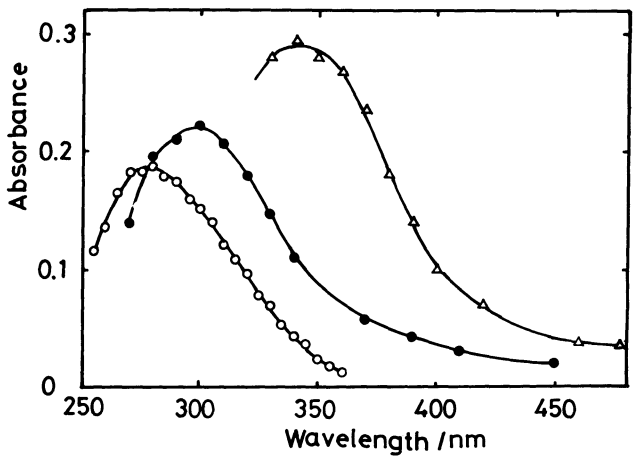

Fig. 7. Transient absorption spectra of Sn(III) obtained in the flash photolysis of 1.0×10^{-4} mol dm^{-3} Sn(II) in 1 mol dm^{-3} acidic solutions.
O: Hydrochloric acid, ●: hydrobromic acid, △: hydroiodic acid.

as shown in Fig. 6. The rapid increase is attributed to the Sn(III) formed by Reactions (1) and (8). Since the Sn(IV) concentration is held constant at 5.0×10^{-4}mol dm^{-3}, the Cl_2^- yield from Reactions (4) and (5) is kept constant. Therefore, the Sn(III) yield from Reaction (8) is also kept constant in the high Sn(II) concentration region (> ca. 7×10^{-5} mol dm^{-3}), in which all the Cl_2^- react with Sn(II). For this reason, a slight increase in the Sn(III) yield in such a concentration region is attributed to the only contribution arising from Reaction (1). Thus, the Sn(III) species can be produced efficiently in the photolysis of an Sn(II)–Sn(IV) mixture.

The transient absorption spectra obtained in the flash photolysis of Sn(II) in hydrobromic and hydroiodic acid solutions are shown in Fig. 7. The spectrum of Sn(III) obtained in a hydrochloric acid solution is also shown for comparison. The spectrum might be attributed to bromo and iodo complex formations of Sn(III), which have the absorption maxima at 300 and 340 nm, respectively.

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