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AQUEOUS CHEMISTRY OF TIN(III). A FLASH PHOTOLYSIS STUDY

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Unstable Sn(III) was produced by ultraviolet irradiation of Sn(II) or Sn(IV) chloride complex in deaerated aqueous hydrochloric acid solution. The optical spectrum of the transient species, Sn(III), observed by using the technique of flash photolysis, has a absorption maximum at 280 nm in 1 mol dm^{-3} HCl and the lifetime is very short. The rate constant of Sn(III) oxidation with oxygen is 1.7×10^8 mol^{-1} dm^3 s^{-1}.

The stable oxidation states of non-transition elements usually differ two units in their mononuclear compounds. Most oxidation-reduction reactions of such elements involve either a two-equivalent change with the direct formation of stable oxidation state, or successive one-equivalent steps. In the latter case, an unstable intermediate oxidation state of non-transition metal is produced and this may show some of the characteristics of a free radical. In Sn(II)-Sn(IV) redox chemistry, unstable Sn(III) is implicated as an intermediate1-4) and supposed to play an important part, but little has been reported about its chemical properties. Only a few studies for the intermediate oxidation state, Sn(III), have been carried out in the radiation chemistry.5-7) Although Sn(II) compounds are often used as a reducing agent, the mechanistic informations are little. It is important to get the information about Sn(III).

A number of metal ions in solution display a strong absorption in the ultraviolet which is attributed to a charge transfer excitation. Absorption of light in such a charge transfer process is known to initiate a number of redox reactions. From the position of absorption of the chloro complexes of Sn(II) and Sn(IV) (Fig. 1 curves A and B),8) it was expected to observe the formation and decay of Sn(III) by the ultraviolet flash photolysis of deaerated aqueous Tin chloride solutions. In fact, a absorption spectrum of a species believed to be Sn(III) has been observed in the flash photolysis of deaerated Sn(II) or Sn(IV) chloride solutions.

A flash photolysis apparatus of the conventional type was used. The main flash lamps dissipated 450 J max. at 15 kV with a flash duaration of 10 μs. The reaction vessel was a fused quartz tube, length 10 cm and I.D. 1 cm with optically flat windows sealed at each end. Transient absorption changes were recorded on a Textronix 7633 oscilloscope. Sn(II) solutions used for flash photolysis were obtained by adding $SnCl_2$ to a deaerated solution of hydrochloric acid. The deaeration was carried out by bubbling with oxygen-free nitrogen. Sn(IV) solutions were prepared by oxidation of Sn(II) with oxygen. Under our experimental conditions, Sn(II) and Sn(IV) exist in chloro complex forms.[9-11]

A solution 1.0×10^{-4} mol dm^{-3} in Sn(II) and 1.0 mol dm^{-3} in HCl, subjected to a flash, showed a transient absorption with absorption maximum at 280 nm. The transient absorbance measured 30 μs after the flash is given in Fig. 1. Absorption of ultraviolet light by Sn(II) solutions would be expected to induce the reactions (1) and (2).

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

$$\mathrm{H} + \mathrm{H} \longrightarrow \mathrm{H}_2 \qquad (2)$$

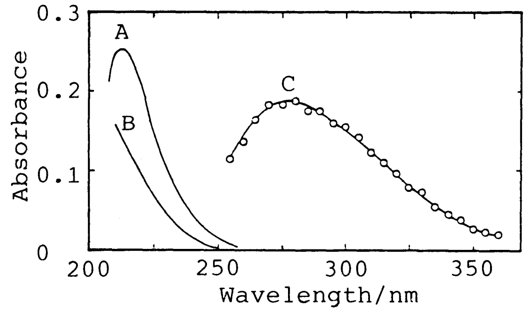

Fig. 1. Absorption spectra of Tin ions in 1.0 mol dm^{-3} HCl (A) 1.0×10^{-5} mol dm^{-3} Tin(II), (B) 4.0×10^{-5} mol dm^{-3} Tin(IV), (C) transient species from 1.0×10^{-4} mol dm^{-3} Tin(II) chloride solution. Absorbance measured 30 μs after flash.

Hydrogen was detected, but the amount was far less than the expected value. It is attributed to a competitive reaction between the reactions (2) and (3), according to the following reason.

$$\mathrm{Sn(IV)} + \mathrm{H} \longrightarrow \mathrm{Sn(III)} + \mathrm{H}^+ \qquad (3)$$

Sn(II) solutions usually contain small amount of Sn(IV) as an impurity, because Sn(II) can be oxidized by oxygen very easily. As H atom reacts with Sn(IV) very rapidly,[12] the reaction (3) may be assumed to occur predominantly, compared with the reaction (2).

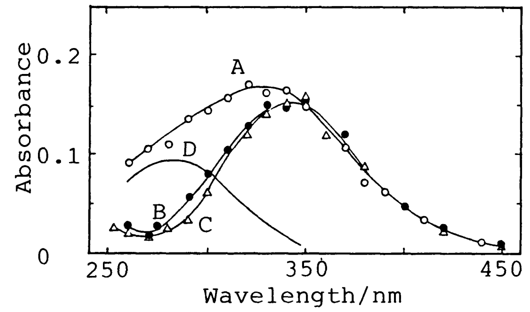

Fig. 2. Absorption spectra of the transient species from 1.0×10^{-4} mol dm^{-3} Tin(IV) chloride solutions in 1.0 mol dm^{-3} HCl. Absorbance measured 30 μs after flash; (A) deaerated, (B) aerated, (C) oxygen-saturated (D) difference of curves A and B.

A solution containing 1.0×10^{-4} mol dm^{-3} Sn(IV) in 1.0 mol dm^{-3} HCl was subjected to a flash. The obtained transient absorption spectrum (curve A in Fig. 2) shows a discernible shoulder at the shorter wavelength side of the main absorption band at 340 nm. Oxygen has a large effect upon the reaction. Flash photolysis was carried out in hydrochloric acid solutions of Sn(IV) in the presence of oxygen. As shown in Fig. 2, the shoulder near 280 nm was decreased with increasing oxygen concentration, but the absorption in wavelength longer than 350 nm did not change. The spectrum obtained in the oxygen-saturated solution has a maximum absorption at 340 nm which is attributed to Cl_2^-.[13-16] Oxygen is a good scavenger for the species which gives the shoulder. The curve D is the difference between the curves A and C, which is very similar to the spectrum C in Fig. 1. From the optical density at 340 nm in Fig. 2 curve C and the extinction coefficient of Cl_2^- ($\varepsilon_{\mathrm{max}}$= 8800 mol^{-1} dm^3 cm^{-1}),[16] the concentration of Cl_2^- is calculated to be 9.1×10^{-6} mol dm^{-3}. Assuming reactions (4) and (5) as the formation scheme of Cl_2^-, the concentration of Sn(III) must equal to that of Cl_2^-. On this basis, the maximum molar extinction coefficient of Sn(III) was found to be 5300 mol^{-1} dm^3 cm^{-1}. From the results given in Fig. 2, the reactions (4) and (5) are suggested for the flashed Sn(IV) solutions, where Sn(IV)-Cl denotes $[\mathrm{SnCl}_n]^{(4-n)+}$.

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

$$\mathrm{Cl} + \mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2^- \qquad (5)$$

Sn(III) reacts rapidly with oxygen, and the rate constant k_6 was 1.7×10^8 mol^{-1} dm^3 s^{-1}.17)

$$\mathrm{Sn(III)} + \mathrm{O}_2 + \mathrm{H}^+ \longrightarrow \mathrm{Sn(IV)} + \mathrm{HO}_2 \qquad (6)$$

Below 270 nm, the spectrum in the oxygen-saturated solution contains a contribution due to $\mathrm{HO}_2$18-21) (curves C and B in Fig. 2). The Cl_2^- species disappears with second-order rate constant equal to $2k_7 = 9.7 \times 10^9$ mol^{-1} dm^3 s^{-1} in 1.0 mol dm^{-3} HCl (the extinction coefficient used for Cl_2^- at 340 nm was 8800 mol^{-1} dm^3 cm^{-1}).16) This value is a little smaller than those ((1.25 – 1.51) X 10^{10} mol^{-1} dm^3 s^{-1}) obtained by Langmuir et al.15)

$$\mathrm{Cl}_2^- + \mathrm{Cl}_2^- \longrightarrow \mathrm{Cl}_2 + 2\mathrm{Cl}^- \qquad (7)$$

The difference is mainly attributed to the extinction coefficient used. They used a larger extinction coefficient, 1.25×10^4 mol^{-1} dm^3 cm^{-1}.

A solution of 1.0×10^{-4} mol dm^{-3} Sn(II) containing Sn(IV) subjected to a flash showed only one large transient absorption in the range of 280 nm, which was attributed to Sn(III). The absorption maximum near 340 nm which was observed in the flashed Sn(IV) solutions was not observed, as shown in Fig. 3. The reaction scheme is proposed as following.

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

$$\mathrm{Sn(IV)} + \mathrm{H} \longrightarrow \mathrm{Sn(III)} + \mathrm{H}^+ \qquad (3)$$

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

$$\mathrm{Cl} + \mathrm{Cl}^- \longrightarrow \mathrm{Cl}_2^- \qquad (5)$$

$$\mathrm{Sn(II)} + \mathrm{Cl}_2^- \longrightarrow \mathrm{Sn(III)} + 2\mathrm{Cl}^- \qquad (8)$$

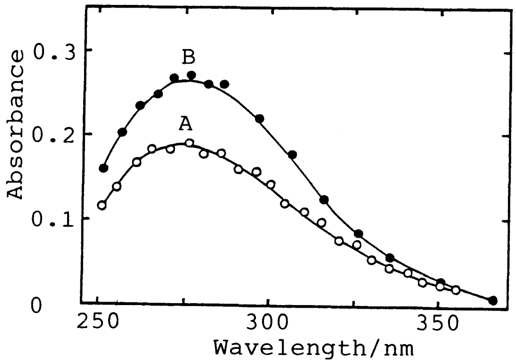

Fig. 3. Absorption spectra of the transient species from Tin(II) chloride with Tin(IV) chloride in 1.0 mol dm^{-3} HCl. Absorbance measured 30 μs after flash; (A) 1.0×10^{-4} mol dm^{-3} Tin(II), (B) 1.0×10^{-4} mol dm^{-3} Tin(II) with 1.0×10^{-4} mol dm^{-3} Tin(IV).

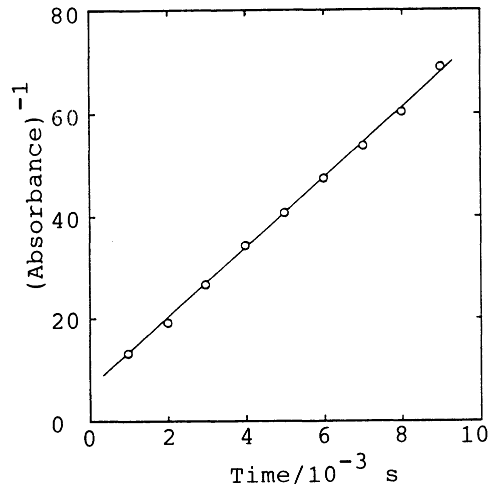

Fig. 4. Second-order plot for the decay of transient species in Fig. 3. curve B. Analyzing light path=10 cm. Wavelength 280 nm.

As described previously, H atom reacts with Sn(IV) in a very rapid reaction, which gives Sn(III) as a product. This reaction is sufficiently fast to be complete during the time of the flash. The lack of absorption maximum at 340 nm in this case suggests that the production of Cl_2^- in the reaction (5) is followed by rapid scavenging of Cl_2^- by added Sn(II). The photolysis of a Sn(II)-Sn(IV) mixture therefore results in the overall initiation reaction (9), and Sn(III) is produced more efficiently.

$$\mathrm{Sn(II)} + \mathrm{Sn(IV)} \underset{}{\overset{h\nu}{\rightleftharpoons}} 2\mathrm{Sn(III)} \qquad (9)$$

The decay of Sn(III) followed a second-order rate low. In solutions containing Sn(II) and Sn(IV), the rate constant for reverse reaction (9), expressed as $2k_{-9}/\varepsilon$ at 280 nm, was 6.9 X 10^4 cm s^{-1} (calculated from the slope of the plot in Fig. 4). By using ε_{max}=5300 mol^{-1} dm^3 cm^{-1} already described, $2k_{-9}$can be estimated to be 3.7 X 10^8 mol^{-1} dm^3 s^{-1}. Similarly, in both Sn(II) and Sn(IV) solutions, Sn(III) disappears by a disproportionation , and the second-order rate constants, k_{-9}, are 5.0 X 10^9 and 2.4 X 10^9 mol^{-1} dm^3 s^{-1}, respectively. The rate constant obtained in the mixed solutions of Sn(II) and Sn(IV) is smaller by about one order than those obtained in each Tin ions solution. The difference may be attributed to the interaction by chloride ion bridging between Tin ions of the different charge.$^{22)}$

References

1) W. C. E. Higginson, R. T. Leigh, and R. Nightingale, J. Chem. Soc., 1962, 435.
2) D. J. Drye, W. C. E. Higginson, and P. Knowles, J. Chem. Soc., 1962, 1137.
3) E. A. M. Wetton and W. C. E. Higginson, J. Chem. Soc., 1965, 5890.
4) A. E. Shilov and A. A. Shteinman, Kinet. Katal., 14, 149 (1973).
5) M. Wolszczak and Cz. Stradowski, Radiochem. Radioanal. Lett., 49, 81 (1981).
6) B. G. Ershov and A. I. Aleksandrov, Radiat. Phys. Chem., 10, 327 (1977).
7) K.-D. Asmus, M. Bonifacic, and P. Toffel, P. O'Neill, D. Schulte-Frohlinde, and S. Steenken, J. Chem. Soc., Faraday Trans. 1, 74, 1820 (1978).
8) M. U. Belyi and B. A. Okhrimenko, Opt. Spektrosk., 26 977 (1969); Opt. Spectry., 26,530 (1969); These spectra in Fig. 2 were measured in this work.
9) P. N. Schatz, P. J. Stephens, G. N. Henning, and A. J. McCaffery, Inorg. Chem., 7, 1246 (1968).
10) R. S. Tobias and Z. Z. Hugus, Jr., J. Phys. Chem., 65, 2165 (1961).
11) S. W. Rabideau and R. H. Moore, J. Phys. Chem., 65, 371 (1961).
12) J. W. Boyle, S. Weiner, and C. J. Hochanadel, J. Phys. Chem., 63, 892 (1959).
13) L. I. Grossweiner and M. S. Matheson, J. Phys. Chem., 61, 1089 (1957).
14) M. Anbar and J. K. Thomas, J. Phys. Chem., 68, 3829 (1964).
15) M. E. Langmuir and E. Hayon, J. Phys. Chem., 71, 3808 (1967).
16) G. G. Jayson, B. J. Parsons, and A. J. Swallow, J. Chem. Soc., Faraday Trans. 1, 69, 1597 (1973).
17) Solutions of Sn(IV) were flashed in the presence of 8 X 10^{-5} – 1.6 X 10^{-4} mol dm^{-3} oxygen. The decay of Sn(III) absorption followed a pseudo-first-order rate low. From the decay, a second-order rate constant for the reaction (6) was calculated.
18) S. Gordon, E. J. Hart, and J. K. Thomas, J. Phys. Chem., 68, 1262 (1964).
19) G. Czapski and L. M. Dorfman, J. Phys. Chem., 68, 1169 (1964).
20) D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, and H. A. Schwarz, J. Phys. Chem., 74, 3209 (1970).
21) B. H. J. Bielski, Photochem. Photobiol., 28, 645 (1978).
22) C. I. Browne, R. P. Craig, and N. Davidson, J. Am. Chem. Soc., 73, 1946 (1951).

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