Photochemical Reaction of Technetium(IV) Chlorocomplexes

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During the investigation of ultraviolet and visible spectra of Tc(IV) chlorocomplexes in hydrochloric acid solutions, we observed the fact that the changes in spectra depending upon the concentration of hydrochloric acid were induced by the irradiation of light. Although several publications[1-8] have dealt with spectroscopic and/or magnetic properties of hexachlorotechnetate-($TcCl_6^{2-}$), the photochemical nature of Tc(IV) chlorocomplexes has not been studied so far.

Technetium used here was ^{99}Tc obtained from the Oak Ridge National Laboratory: Batch No. Tc-99-p. $TcCl_6^{2-}$ was prepared by refluxing 200 mg of technetium in the form of NH_4 TcO_4 with 20 m*l* of concentrated hydrochloric acid for 15 hr on a steam bath. The colorless solution turned yellow on the addition of hydrochloric acid. After the solution was evaporated almost to dryness with gentle heating by steam, refluxing wtih concentrated hydrochloric acid was repeated for another 15 hr to make sure that all TcO_4^- was converted into $TcCl_6^{2-}$. The ordinary procedure to obtain $TcCl_6^{2-}$ is to reduce TcO_4^- with iodide or bromide ions, followed by repeated heating with concentrated hydrochloric acid. The procedure was compared with ours and similar absorption spectra were obtained for both the cases.

The $TcCl_6^{2-}$ was dissolved in hydrochloric acid of varying concentrations between 11.8 N and 0.025 N. Duplicate samples were prepared with

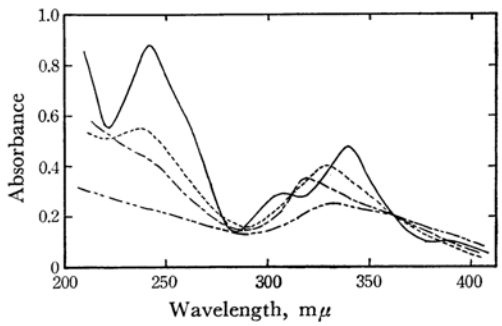

Fig. 1. Absorption spectra of Tc(IV) chlorocomplexes in hydrochloric acid.

—— in 12, 6, 3 and 1 N HCl kept in dark for two weeks
---- in 6 N HCl after irradiation for two weeks
—— in 3 N HCl after irradiation for two weeks
—— in 1 N HCl after irradiation for two weeks

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respect to the concentration of hydrochloric acid. One series was kept in a dark box and the other was irradiated with four 10 W fluorecent lamps in a thermostat at 20°C. The absorption spectra of both series were occasionally measured for two weeks in quartz cells with Shimadzu's automatic recording spectrophotometer SV-50A.

The spectra of the samples which were kept in the dark box remained unchanged regardless of their hydrochloric acid concentrations. On the other hand, those of the irradiated ones changed gradually to reach equilibria depending on the concentration of hydrochloric acid in a given sample. In Fig. 1, some of the spectra after equilibria have been established are shown, together with those of the solutions kept in the dark. Two isosbestic points appear, one for the samples in more than 3 N hydrochloric acid with a molar extinction coefficient 6280 at 311 mμ, the other with a molar extinction coefficient 4370 at 362 mμ. However, the latter is not certain whether it is really isosbestic or not. From the analytical point of view, one may utilize the absorption at the isosbestic points to measure the concentration of Tc(IV) in the solution.

According to our measurement, molar extinction coefficients of $TcCl_6^{2-}$ at 241 and 340 mμ are 19650 and 11040, respectively, which are a little greater than those previously reported.

No kinetic studies and measurements of quantum yields have been carried out at the present stage. The species in the solution, however, have been separated by means of ion exchange and electrophoresis. From the determination of charge and Cl/Tc ratio in the separated complexes, we concluded that $TcCl_6^{2-}$ is photochemically aquated to give $TcCl_{6-x}(H_2O)_x^{x-2}$, as Eq. (1).

$$TcCl_6^{2-} + X\,H_2O \rightarrow TcCl_{6-x}(H_2O)_x^{x-2} + X\,Cl^- \quad (1)$$

More details will be published elsewhere.