THE KINETICS OF THE OXIDATION–REDUCTION REACTION BETWEEN URANIUM(VI) AND TITANIUM(III) IN HCl SOLUTION

MUHAMMAD ABDUL HAMID,* EJAZ UR REHMAN, MUHAMMAD FUZAIL, RIFFAT NAHEED, AMIN-UDDIN AHMED

Applied Chemistry Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad (Pakistan)

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The oxidation–reduction reaction between U(VI) and Ti(III) in HCl solution was studied spectrophotometrically. The reaction is second-order at all concentrations of reactants, HCl, ferrous chloride and mannitol used in this work. In 5M HCl the rate constant \( k \) increases with increasing Ti(III) concentration, whereas it decreases with increasing U(VI) concentration, with increasing HCl concentration from 1.00M to 7.17M and increases thereafter from 7.17M to 11.79M. The addition of mannitol causes a consistent decrease in the rate of reaction, whereas ferrous chloride has no effect. The activation energy for this oxidation–reduction reaction was 47.90 ± 0.11 kJ. mol\(^{-1}\). The values of \( \Delta H^\circ \), \( \Delta G^\circ \) and \( \Delta S^\circ \) were 45.40 ± 0.11 kJ. mol\(^{-1}\), 72.50 ± 0.17 kJ. mol\(^{-1}\) and -91.10 ± 0.22 J. k\(^{-1}\). mol\(^{-1}\), respectively. The mode of reaction is discussed in the light of kinetic results.

Uranium ions show five oxidation states with widely varying oxidation potentials.\(^1\) Thus oxidation–reduction reactions form a very important part of its chemistry. A knowledge of the rates of oxidation–reduction reactions is, therefore, required for designing chemical separation processes and for developing analytical procedures.

LOGAN and BIRK\(^2\) have reported on the reduction of U(VI) by Ti(III) in acid chloride or perchloric media at 25 °C and 0.5M ionic strength. They state that under the given conditions reaction kinetics follow the equation:

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\frac{d[U(VI)]}{dt} = \frac{k_1K_a[Ti(III)][U(VI)]}{(K_a + [H^+])}
\]

where \( K_a \) is the acid dissociation constant of Ti\(^{3+}\). It has been further reported that pseudo-first – order kinetics were always observed for the U(VI)–Ti(III) reaction under the given conditions. It has been, however, reported by various other researchers\(^3–7\) that similar oxidation–reduction reactions follow the integrated form of second order rate law, i.e., first order for each reactant, and the individual experimental second order rate constants are independent of the initial concentrations of the actinides involved. It has

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*To whom correspondence should be addressed.
been further reported by these researchers that the reactants undergo hydrolysis in the acid solution during the process of oxidation and reduction.

The aim of this work was to establish the order of reaction with respect to the reactants and range of acid concentration in which the reactants do not undergo hydrolysis during oxidation–reduction. Therefore, the kinetics of the rapid reaction between U(VI) and Ti(III) in HCl solution were studied spectrophotometrically with high precision, using dilute solutions of the reactants and measuring the principal absorption peak of U(IV) ions at 650 nm. It is worthwhile to mention here that U(V) is formed as an intermediate product in this oxidation–reduction system which disappears very rapidly, therefore the formation of final product U(IV) is monitored to follow the rate of reaction. The effect of added FeCl₂ and mannitol on this oxidation–reduction system was also studied.

Experimental

The stock solution of uranyl chloride was prepared by dissolving uranium trioxide in an excess of hydrochloric acid. The concentration of uranyl chloride solution was determined by potentiometric titration and the residual free acid (HCl) was determined potentiometrically. The desired concentration of uranyl chloride solution for kinetic experiments was prepared by the dilution of stock solutions with known concentration and volume of hydrochloric acid.

Uranous chloride [U(IV)] used to obtain the UV spectrum and the molar extinction coefficient, was prepared by the reaction of uranium metal with concentrated hydrochloric acid. The concentrations of uranium and free acid of the resulting solution were determined as described above for uranyl chloride.

Titanium trichloride (15%) in HCl solution, supplied by Riedel-de Haen, Germany was used as a stock solution. The concentration of titanium in stock solution was determined as described above for uranyl chloride.

Hydrochloric acid fuming, 37%, extra pure, supplied by Merck, Germany was used. Ferrous chloride was prepared by reacting ferric chloride (Merck) with iron powder (Merck) in the presence of dilute hydrochloric acid at 100 °C. On filtration, a clear green solution of ferrous chloride is obtained and stored at 0 °C after flushing the solution with nitrogen gas. The required quantity of this solution was used in the kinetic experiments.

The rate of the oxidation–reduction reaction between U(VI) and Ti(III) in HCl solution was followed by the rate of growth of the U(IV) absorption peak at 650 nm using a DU–64 Spectrophotometer. The optical cells used in this work were calibrated.