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PORNSAWAN TONGKAEW: KINETICS OF IODIDE-CATALYZED REACTION BETWEEN CERIVM(IV) AND ARSENIC(III) IN SULFURIC ACID

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The kinetics of the iodide-catalyzed reduction of Ce(IV) by As(III) in sulfuric acid solution was studied by the rapid-mixing stopped flow method. By varying the total [Ce(IV)], [As(III)] and [I], but at constant [H₂SO₄] (0.25 M) and temperature (30.0°C), the rate law for the reaction was determined from the initial rate of the decrease of [Ce(IV)]. Concentration change of Ce(IV) was monitored from uv-visible absorbance at 365 nm. The observed rate law is given by:

$$\text{Rate} = -\frac{d[\text{Ce(IV)}]}{dt} = \frac{1.79 \times 10^4 [\text{As(III)}][\text{Ce(IV)}]}{([\text{As(III)}] + (1.06 \times 10^{-4}))} [\text{I}]_{\text{total}}$$

for [Ce(IV)], [As(III)] and [I] in the range $(0.0-0.6) \times 10^{-3}$, $(0.0-12.0) \times 10^{-3}$ and $(0.08-0.48) \times 10^{-6}$ M, respectively. Thus the reaction is first order in [Ce(IV)] and approaches zero order in [As(III)] when $[\text{As(III)}] \gg 1.06 \times 10^{-4}$ M. The rate of reaction is directly proportional to the total iodide concentration, and can thus be employed to determine trace amount of iodide.

The effects of sulfuric concentration and chloride ion, added in the form of HCl, NaCl and KCl, have been examined. It was found that the initial rate increased with increasing sulfuric acid concentration from 0.25 to 0.80 M for a fixed concentration of the reactants for which the rate is zero order in [As(III)]. But at higher concentration of the acid (0.80-2.00 M H₂SO₄), there was a decrease in the initial rate. The formation of various Ce(IV)-sulfate complex ions were indicated from spectrophotometric measurements of solution of Ce(IV). Various species of the Ce(IV) sulfate complex in sulfuric acid may have different kinetic properties, leading to the observed variation of the initial rate.

At the fixed [As(III)], [Ce(IV)] and [H₂SO₄], but varying the [I] and [Cl⁻], it was observed that HCl, NaCl and KCl can also act as catalyst, but the catalytic activity of chloride ion is 10⁶ times less than iodide. The added chloride also affected the rate of the iodide-catalyzed reaction.