

Determination of Submicrogram Quantities of Ruthenium(III) by Catalysis of the Cerium(IV)-Formic Acid Reaction in Aqueous Sulphuric Acid Media

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A catalytic kinetic methods of analysis is not really of much value in practice compared to many other methods, but such methods find important applications¹ for the estimation of trace or ultra-trace quantities of different elements which cannot be done by spectrophotometrically or by any other convenient method (except, such ultra-sensitive method as neutron activation). In the title reaction, Ru^{III} can potentially catalyse in the concentration range of ppm or less, and from the measurement of rate of the process, Ru^{III} can be estimated.

Results and Discussion

The uncatalysed cerium(IV)-formic acid reaction leading to quantitative oxidation of formic acid (i.e. $2\text{Ce}^{4+} + \text{HCO}_2\text{H} \rightarrow 2\text{Ce}^{3+} + \text{CO}_2 + 2\text{H}^+$) in aqueous sulphuric acid media is tremendously sluggish², but in presence of catalytic activity of Ru^{III} at the ppm level, the process becomes fairly fast³ to be measured by conventional techniques like spectrophotometric or titrimetric method. In presence of excess formic acid in 1.0 mol dm^{-3} sulphuric acid in the temperature range $30\text{--}50^\circ$, the process is zero-order with respect to cerium(IV) and it follows the following rate law³,

$$-\frac{d[\text{Ce}^{\text{IV}}]}{dt} = k_o = [\text{Ru}]_T [\text{HCO}_2\text{H}]_T \{k_b + k_c [\text{HCO}_2\text{H}]_T\}$$

where $10^2 k_b$ and $10^2 k_c$ are $6.0 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $5.4 \pm 0.1 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ respectively, at 40° . The rate expression shows that the sensitivity of catalytic amount of Ru^{III} determination can be increased by enhancing the concentration of HCO₂H. The linear plot of k_o vs $[\text{Ru}]_T$ at fixed $[\text{HCO}_2\text{H}]_T$ and $[\text{H}_2\text{SO}_4]_T$

(Fig. 1) passing through the origin indicates the non-existence of the uncatalysed path. The plot can be taken as the reference curve from which the unknown concentration of Ru^{III} can be evaluated from the knowledge of k_o .

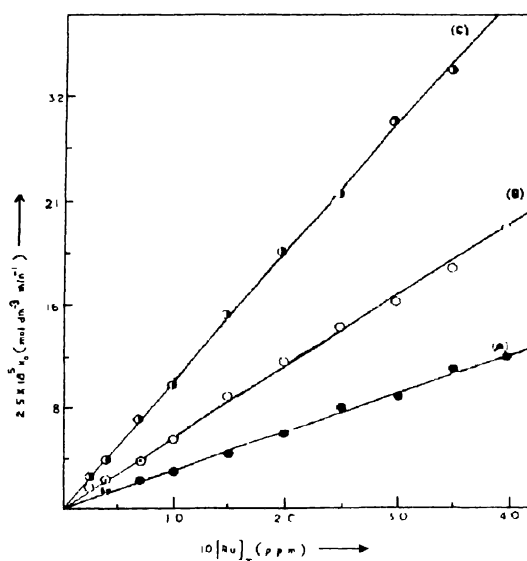


Fig. 1. Dependence of k_o on $[\text{Ru}^{\text{III}}]$ concentration in the oxidation of formic acid by Ce^{IV} in aqueous H_2SO_4 : (A) 30° , (B) 40° and (C) 50° ; $[\text{Ce}^{\text{IV}}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HCO}_2\text{H}]_T = 2.0 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$, $I = 2.75 \text{ mol dm}^{-3}$

Experimental

Standard stock solution of Ru^{III} was prepared³ from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Johnson and Mathey). HCO_2H (G.R., E. Merck) solution was estimated by alkaline permanganate⁴. All other reagents used were of reagent grade. A Beckman DU-6 spectrophotometer was used to follow the process.

Procedure : The reaction was initiated by adding the thermostated oxidant to the reaction mixture pre-equilibrated at the desired temperature. The progress of the reaction was followed by measuring the concentration of cerium(IV) that remained unreacted either spectrophotometrically at 320 nm ($\epsilon = 5.5 \times 10^3 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$) or titrimetrically using a known amount of excess standard iron(II) ammonium sulphate in presence of ferroin indicator. Under the experimental conditions, the zero-order rate constant ($k_0 = \text{slope } [\text{oxidant}] \text{ vs time}$) was calculated as usual.

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