

E2-26: Kinetics of the mercuric ion catalyzed reaction of hexacyanoferrate (II) and nitrosobenzene

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The kinetic method involving the catalytic effect of Hg(II) on the reaction of hexacyanoferrate(II) and nitrosobenzene has been used for the determination of trace amounts of Hg(II). A good knowledge of the kinetic of this reaction is essential to select proper experimental conditions and for further improvements to the existing method.

In the present work, kinetics of this reaction was studied by measuring the absorbance (A) of the product $[\text{Fe}(\text{CN})_5(\text{C}_6\text{H}_5\text{NO})]^{3-}$ at 525 nm during the progress of the reaction. Experimental results were fitted by linear least squares to the pseudo first order equation. $\ln(1 - A_t/A_\infty) = -k_1 t$, derived assuming that the reaction is pseudo first order in nitrosobenzene in the presence of excess hexacyanoferrate(II).

The dependence of k_1 on the concentration of hexacyanoferrate(II) indicated that the reaction was first order in hexacyanoferrate (II) when the ratio, $[\text{Fe}(\text{CN})_6^{4-}]/[\text{C}_6\text{H}_5\text{NO}]$, was less than 100 and was zero th order when the ratio was greater than 200. At low concentrations of hexacyanoferrate(II) with trace amounts of Hg(II) the rate of reaction was slow. At higher ratios of $[\text{Fe}(\text{CN})_6^{4-}]/[\text{C}_6\text{H}_5\text{NO}]$, k_1 varied with the concentration of Hg(II) linearly and the rate law was of the form,

$$\text{rate} = (k_a + k_b [\text{Hg}(\text{II})])[\text{C}_6\text{H}_5\text{NO}]$$

with values $3.4 \times 10^{-4} \text{ s}^{-1}$ and $3.5 \times 10^3 \text{ dm}^2\text{mol}^{-1}\text{s}^{-1}$ for k_a and k_b , respectively, at 32°C. For the determination of trace amounts of Hg(II) the ratio, $[\text{Fe}(\text{CN})_6^{4-}]/[\text{C}_6\text{H}_5\text{NO}]$, should be greater than 200.

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