

Ionic Strength Effects on the Oxidation of Vitamin C

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Abstract

- The kinetics of the reaction between vitamin C, L-ascorbic acid, and hexacyanoferrare (III), Fe(CN),³, in aqueous acidic media at different temperatures has been studied by following the absorbance with time at 420 nm. The mechanism of the oxidation of L-ascorbic acid had been proposed to be multi-step and the rate determining step was between ascobate anion, which would be produced in the initial reversible step, and hexacyanoferrare (III). This reaction has been well established to be first order with respect to L-ascorbic acid and Fe(CN)₆³. The overall second order rate constant, k_{obs}, was observed to show an inverse dependence on [H⁺] for the range of pH studied at temperatures from 293 to 313 K. In this study k_2 , the rate constant for the rate-determining step, was determined by its relationship to k_{obs}, the experimentally measured overall rate constant, at various temperatures and different concentrations of NaNO₃. The experimental value for k_2 was found to vary from 52.6 to 202 dm³ mol⁻¹ min⁻¹ when NaNO₃ concentration was changed from zero to 0.200 mol dm⁻³ at 302 K. The effect of ionic strength on the kinetics of this reaction was investigated by substituting NaNO₃ with KNO₃, K2SO₄, NaCl, KCl, Na₂SO₄, $MgCl_2$, $MgSO_4$, $Mg(NO_3)_2$, $Al_2(SO_4)_3$ and $Al(NO_3)_3$. It was deduced by the primary kinetic salt effect, that the rate determining step involved species of like charges. Thermodynamic parameters of activation at different ionic strengths were calculated by using the Eyring equation.

Keywords: entropy of activation, ionic strength, rate-determining step, reaction mechanism.

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