

Oxidation of glycine by diperiodatocuprate(III) in aqueous alkaline medium

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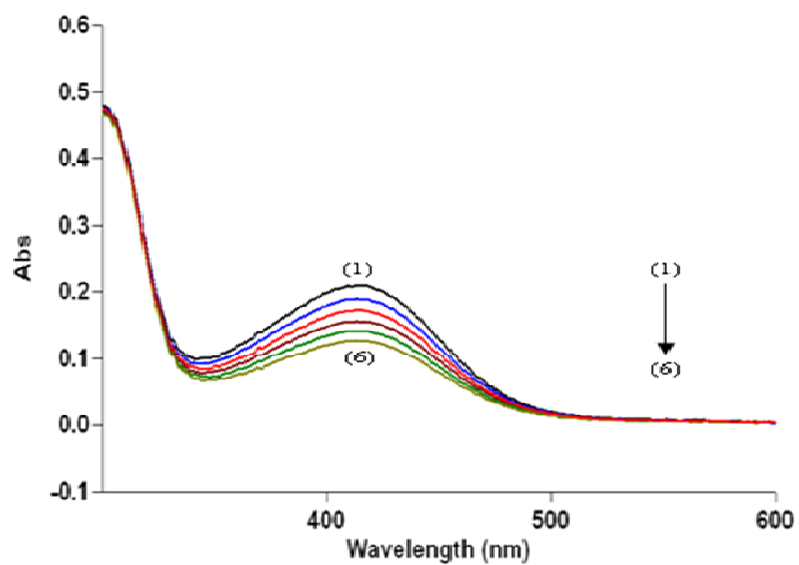


Fig. S1 - Spectroscopic changes occurring in the oxidation of glycine by diperiodatocuprate (III) at 25°C with scanning time interval of 1 minute.

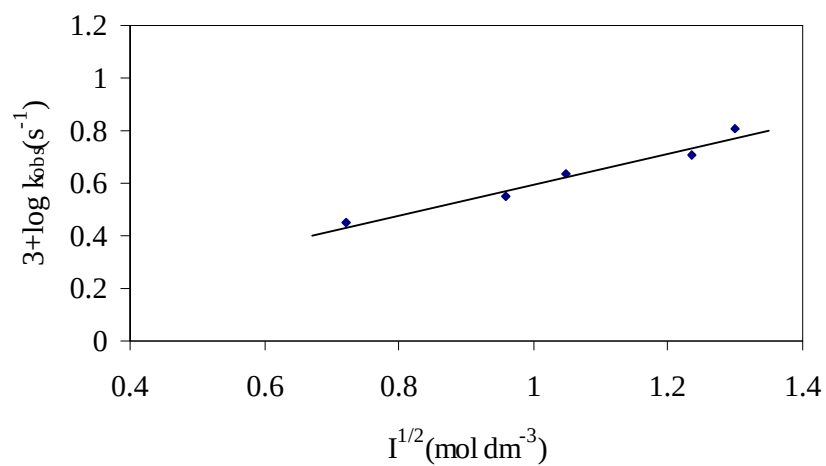


Fig. S2 - The plot of $\log k_{\text{obs}}$ versus $I^{1/2}$ was linear with positive slope.

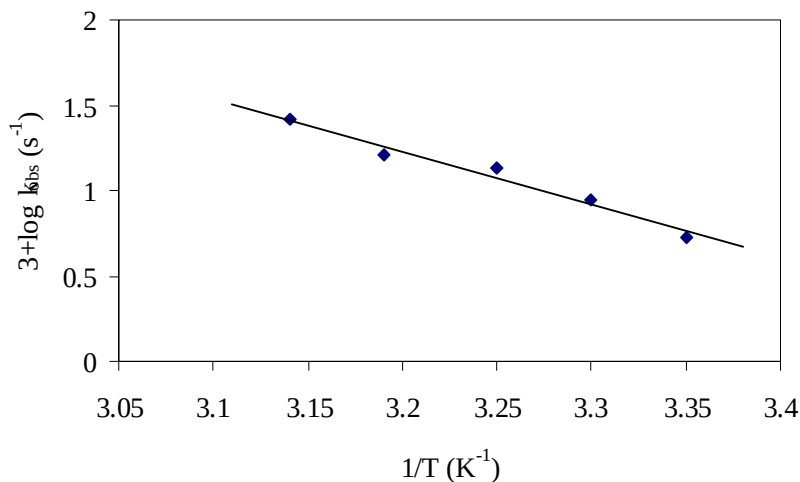


Fig. S3 - Effect of temperature on the oxidation of glycine by diperiodatocuprate (III) in aqueous alkaline medium.

Rate derivation

According to Scheme 1

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = k [\text{Complex}] = \frac{k K_1 K_2 K_3 [\text{GLY}]_f [\text{DPC}]_f [\text{OH}^-]_f}{[\text{H}_3\text{IO}_6^{2-}]} \quad (\text{I})$$

The total concentration of DPC is given by

$$[\text{DPC}]_T = [\text{DPC}]_f + [\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-} + [\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)]^- + \text{Complex (C)}$$

where T and f refer to total and free concentrations.

$$\begin{aligned} &= [\text{DPC}]_f + K_1 [\text{DPC}] [\text{OH}^-] + \frac{K_1 K_2 [\text{OH}^-] [\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}]} + \frac{K_1 K_2 K_3 [\text{DPC}] [\text{OH}^-] [\text{GLY}]}{[\text{H}_3\text{IO}_6^{2-}]} \\ &= [\text{DPC}]_f \left\{ 1 + K_1 [\text{OH}^-] + \frac{K_1 K_2 [\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}]} + \frac{K_1 K_2 K_3 [\text{OH}^-] [\text{GLY}]}{[\text{H}_3\text{IO}_6^{2-}]} \right\} \\ &= [\text{DPC}]_f \left\{ \frac{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 K_3 [\text{OH}^-] [\text{GLY}]}{[\text{H}_3\text{IO}_6^{2-}]} \right\} \\ &[\text{DPC}]_f = \frac{[\text{DPC}]_T [\text{H}_3\text{IO}_6^{2-}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}^-] [\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{GLY}]} \quad (\text{II}) \end{aligned}$$

Similarly,

$$[\text{OH}^-]_T = [\text{OH}^-]_f + [\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{4-} + [\text{Cu}(\text{OH})_2(\text{H}_3\text{IO}_6)_2]^- + \text{Complex (C)}$$

$$[\text{OH}^-]_T = [\text{OH}^-]_f + K_1[\text{OH}^-][\text{DPC}] + \frac{K_1K_2[\text{OH}^-][\text{DPC}]}{[\text{H}_3\text{IO}_6^{2-}]} + \frac{K_1K_2K_3[\text{DPC}][\text{OH}^-][\text{GLY}]}{[\text{H}_3\text{IO}_6^{2-}]}$$

In view of low concentration of DPC used, the second, third and fourth term can be neglected. Hence,

$$[\text{OH}^-]_T = [\text{OH}^-]_f \quad (\text{III}) \quad \text{and} \quad [\text{GLY}]_T = [\text{GLY}]_f \quad (\text{IV})$$

Substituting (II), (III), and (IV) in (I) and omitting the subscripts T and f, we get,

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = \frac{k K_1 K_2 K_3 [\text{DPC}] [\text{GLY}] [\text{OH}^-]}{[\text{H}_3\text{IO}_6^{2-}] + K_1 [\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{OH}^-] [\text{GLY}]} \quad (\text{V})$$