

Kinetics of the Reaction between 1,3-Dihydroxybenzene, Hydrogen Peroxide and Copper(II) Ions

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Abstract

The kinetics of the reaction between hydrogen peroxide, 1,3-dihydroxybenzene and copper(II) ion at pH 10.7 and 12.7 have been investigated. The overall rate of reaction appears to be approximately first order in perhydroxyl ion, approximately one third order in 1-hydroxy-3-oxo-1,3-dihydroxybenzene ion and first order in copper(II) ion. The 1,3-dioxybenzene ion does not appear to participate in a rate determining step. The reaction product, postulated to be 4,4'-dihydroxy-2,2'-biquinone seems to form a non-labile complex with copper(II) ion which effectively eliminates its role as a catalyst.

Introduction

The reaction between hydrogen peroxide and various substances catalyzed by suitable metal ions and appropriate ligands have been studied in anticipation that the reactions might serve as models elucidating peroxidases and catalyases [1, 2]. Metal ion catalyzed peroxidase and catalase type reactions of hydrogen peroxide in a suitable substrate system can serve as the basis for kinetic methods of analysis for the catalytic metal ion [3, 4]. The peroxidase like reaction between hydrogen peroxide and 1,3-dihydroxybenzene with copper(II) ion has been recommended for the catalytic thermometric endpoint determination of copper(II) ions by chelometric titration [5]. This is a report of an investigation of the kinetics of the reaction of hydrogen peroxide and 1,3-dihydroxybenzene in the presence of copper(II) ion in higher pH media. Previous investigations of the catalytic effect of copper(II) ion have been in lower pH systems (*i.e.* up to pH 9). It is found that in the higher pH media copper(II) ion does not function as a true catalyst.

Experimental

Reagents

All reagents were analytical grade. The concentration of stock 30% hydrogen peroxide was deter-

mined by titration with standard potassium permanganate solution. Working solutions were prepared by volumetric dilution. Standard copper solutions were prepared by dissolving weighed 99.99% electrolytic copper wire in a minimal amount of nitric acid, allowing excess acid to evaporate and diluting to volume. Kinetic studies were carried out in solutions buffered with dibasic sodium phosphate, sodium phosphate and the pH finally adjusted with 1.0 M sodium hydroxide. The total phosphate concentration was maintained at 0.2 F. Oxygen was removed from solution prior to mixing for kinetic measurements by sweeping with nitrogen gas.

Instrumentation

The reaction between hydrogen peroxide, 1,3-dihydroxybenzene and copper(II) ions produces a colored product which has a strong absorbance in the region of 340 nm. This strong absorbance allows the progress of the reaction to be monitored spectrophotometrically. At the high pH values used here the reaction is relatively rapid and could be completed in a period of 20 to 25 min for the faster reaction experiments and up to 90 min for the slower; consequently in an effort to achieve better precision an apparatus similar to that described by Gibson and Greenwood [6] and also Ahmed and Wilkins [7] was constructed from two hypodermic syringes and the reaction chamber (a cylindrical Spectronic 20 spectrometer cuvette) was mounted in a Beckman DU spectrometer equipped with a Pacific Updated photometer. The reacting solutions could be mixed and the reaction initiated in a period of 3–5 sec and the course of the reaction followed in a very reproducible manner.

Procedure

For each kinetic run 25 or 50 mls. of deoxygenated solutions of (A) hydrogen peroxide buffered to the desired pH and a second solution (B) of 1,3-dihydroxybenzene containing copper(II) ions buffered to the same pH as solution (A) were prepared. The two solutions were transferred under a steady stream of nitrogen gas to the two syringes of the rapid mixing apparatus. The mixing chamber

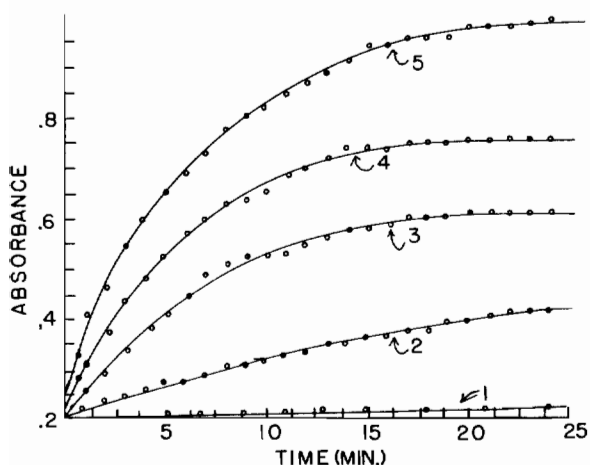


Fig. 1. Absorbance vs. T time for 0.3 F 1,3-dihydroxybenzene reacting with 0.3 F hydrogen peroxide at pH 10.7 with copper(II) ion variable. (a) 0.00 F Cu^{++} , (b) 2.67×10^{-5} F Cu^{++} , (c) 3.93×10^{-5} F Cu^{++} , (d) 5.25×10^{-5} F Cu^{++} , (e) 10.49×10^{-5} F Cu^{++} .

and transfer lines were flushed with the reaction solutions by making preliminary trial mixes of the two solutions. The apparatus was assembled with both hypodermic syringes of the same size: consequently equal volumes of the two solutions were always mixed. The pH of the reaction solution was always measured at the end of a kinetic run to ascertain that the pH of the buffered system had not changed. The absorbance of the reaction mixture was recorded as a function of time. All measurements were carried out at ambient temperature, $24^\circ\text{C} \pm 1^\circ\text{C}$.

Results and Discussion

The concentration dependence of the kinetics of the reaction between hydrogen peroxide, 1,3-dihydroxybenzene, copper(II) ion and pH was studied by monitoring the absorbance of the solutions at a wavelength of 340 nm. A 'one-factor-at-a-time' approach was used to determine the effect of the reactants and pH on the rate dependence. Hydrogen peroxide and 1,3-dihydroxybenzene were each varied in the range of 0.3 M to 0.03 M. The effect of pH at 10.7 and 12.7 was determined. There is a rather radical increase in rate of the reaction between pH 9 and pH 10; the lower pH value was inconveniently slow for the procedure used here. The copper(II) ion was varied in the range of 2.6×10^{-5} M to 10.5×10^{-5} M. In Fig. 1 an example of the data obtained is shown with copper(II) ion as the solution variable. Data similar to Fig. 1, absorbance at 340 nm versus time were obtained with the other reactants serving as the variables.

The extent of reaction as indicated by the absorbance becoming almost constant with respect to time,

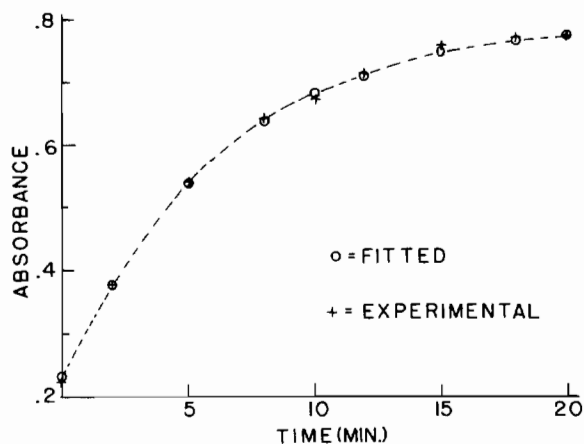


Fig. 2. Comparison of experimental absorbance and calculated absorbance vs. time. Absorbance calculated from fourth degree fitting function. Data from curve (c) of Fig. 1.

as shown in Fig. 1, depends upon the copper(II) ion concentration. The set of kinetic measurements shown in Fig. 1 had the same concentrations of hydrogen peroxide, 1,3-dihydroxybenzene and hydrogen ion; copper(II) ion appears to be the limiting reagent. If it is assumed that the copper(II) ion is limiting the extent of reaction then the ratio of absorbance, when it reached an approximate plateau, to copper(II) ion concentration should be a constant quantity. This is apparently true: the average value for all measurements is 8.88×10^3 liter mol^{-1} corresponds to the molar absorptivity of the product and optical path length assuming one mol of product is formed per mol of copper(II) ions present.

The initial reaction rates for the kinetic experiments were extracted from data of which Fig. 1 is an example. An unweighted least-squares type polynomial regression analysis [8] was carried out on each set of data corresponding to the variation of absorbance with respect to time. The fitting function was,

$$F(A) = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4,$$

and can be used to model the rate data, absorbance (A) vs. time (T) quite well. Fig. 2 illustrates an example of how well the fitting function models the experimental data; absorbance calculated at given time is plotted with experimental absorbance data for comparison. The first derivative, absorbance (DA) with respect to time (DT), of the fitting function represents the rate of the reaction, (*i.e.* slope of absorbance vs. time),

$$DA = C_2 DT + C_3 T DT + C_4 T^2 DT + C_5 T^3 DT$$

and

$$\text{rate} = DA/DT = C_2 + C_3 T + C_4 T^2 + C_5 T^3.$$

TABLE I. Coefficients for Polynominal fitting Function describing Experimental Data with Variable Copper(II) Ion Concentration shown in Fig. 1.

| (Cu ⁺⁺) ^a M × 10 ⁵ | C1 × 10 | C2 × 10 ² | C3 × 10 ³ | C4 × 10 ⁴ | C5 × 10 ⁶ |
|---|------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.00 | 2.008 | 0.4551 | -0.4521 | 0.2326 | -0.425 |
| 2.67 | 2.049 | 1.381 | -0.4172 | 0.2243 | -0.537 |
| 3.93 | 2.093 | 5.615 | -2.934 | 0.7178 | -0.6941 |
| 5.25 | 2.343 | 8.463 | -5.528 | 1.821 | -2.468 |
| 10.49 | 2.733 | 11.37 | -8.346 | 3.244 | -5.003 |

^aIn these experiments hydrogen peroxide was 0.3 F, 1,3-dihydroxybenzene was 0.3 F and pH was 10.7. The fitting function was applied through a 25 min time interval.

At time (*T*) equal to zero the initial rate of reaction (*R_i*) is obtained,

$$R_i = DA/DT = C2.$$

In Table I the data for the experiments which produced the absorbance vs. time curves shown in Fig. 1 is summarized. The initial formal concentrations and pH of the solutions used for each kinetic experiment and the results as the coefficients of the fourth degree polynominal equation describing the absorbance vs. time measurements, are shown. Solution of the polynominal with respect to time faithfully reproduce the absorbance during the time interval of each experiment. The initial rate of each reaction corresponds to the second term (C2 term) of the polynominal shown in the table.

The rate of the reaction in the presence of copper(II) ions (*R_t*) is equal to the sum of two contributions. One contribution is a very slow reaction, proceeding at a rate (*R_i*) and a second contribution, a relatively fast reaction in which copper(II) ion participates of rate (*R_{Cu}*). The over all rate is then,

$$R_t = R_i + R_{Cu}$$

The initial rate of the reaction in which copper(II) ion participates is taken as the difference between initial rates in the presence and in the absence of copper(II) ions, all other factors being held constant:

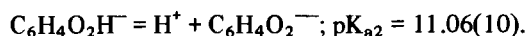
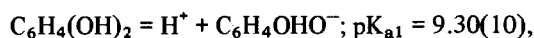
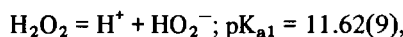
$$R_{Cu'} = R_t' - R_i'$$

where the primes denote initial rates. The initial rates (*R_{Cu'}*) with hydrogen peroxide, 1,3-dihydroxybenzene, copper(II) ion and hydrogen ion concentration as experimental variables were used one variable at a time to determine the rate dependence.

TABLE II. Fraction of Formal Concentration resulting in Each Particular Species at Indicated pH.

| pH | H ₂ O ₂ | HO ₂ ⁻ | C ₆ H ₆ O ₂ | C ₆ H ₅ O ₂ ⁻ | C ₆ H ₄ O ₂ |
|------|-------------------------------|------------------------------|--|---|--|
| 9.0 | 0.997 | 0.0023 | 0.666 | 0.334 | — |
| 10.7 | 0.794 | 0.107 | 0.036 | 0.86 | 0.104 |
| 12.7 | 0.077 | 0.923 | — | 0.077 | 0.923 |

A multiple correlation regression analysis of the logarithm of the initial rate with respect to the logarithm of the initial molar concentrations of the various species present in the solution was carried out to determine the rate-concentration dependence. The initial rates obtained from fitting the absorbance vs. time data, as described above, were converted to concentration vs. time rates using the constant quantity 8.88 × 10³ liter mol⁻¹ which is the molar absorptivity-pathlength for the spectrometer cell used. The use of this absorptivity value assumes that one mol of copper(II) ions is involved in the production of one mol of product. The concentration of species resulting from the pH dependent dissociation of hydrogen peroxide, and 1,3-dihydroxybenzene were calculated from the following equilibrium:



The fractional composition of each species resulting from satisfying these equilibrium are tabulated above (Table II) for the three pH levels investigated.

The copper(II) ion undoubtedly exist as a ternary or quaternary complex in these solutions [11] but the various species present could not be ascertained. The regression analysis was carried out with a general purpose statistical computing system called 'MINI-TAB' [12]. The regression equation produced from sixteen sets of data was,

$$\begin{aligned} \text{Log } R_{Cu'} = & 6.30 + 1.14\text{Log} (HO_2^-) \\ & + 0.358\text{Log} (C_6H_5O_2^-) + 1.03\text{Log} (Cu). \end{aligned}$$

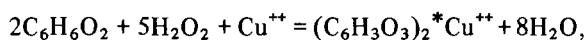
The rate could be expressed in an over-all rate law from the correlation as,

$$R_{Cu'} = \exp 6.30 (HO_2^-)^{1.14} (C_6H_5O_2^-)^{0.358} (Cu^{++})^{1.03}.$$

The over-all rate appears to depend on the 1-hydroxy-3-oxybenzene ion, copper(II) ion and the

perhydroxy ion. The meta dioxybenzene ion does not appear to be involved in a rate determining step.

The oxidation of 1,3-dihydroxybenzene and derivatives of 1,3-dihydroxybenzene have been investigated by Musso and co-workers [13]. They were unable to identify the products of the autoxidation of 1,3-dihydroxybenzene but expected, based on their work with orcinol (methyl-3,5-dihydroxybenzene) to obtain 4,4'-dihydroxy-2,2'-biquinone and 2-hydroxy-5(2,4-dihydroxyphenyl)-quinone. In the investigation reported here the products of the autoxidation and hydrogen peroxide oxidation, both in the presence of copper(II) ion at pH 11 were compared spectrophotometrically and chromatographically (HPLC-octadecyltrichlorosilane, reversed phase and methanol-water gradient, mobile phase). The product had the same spectral and elution characteristics in both cases and is tentatively identified as 4,4'-dihydroxy-2,2'-biquinone [14]. The over all reaction might be written as

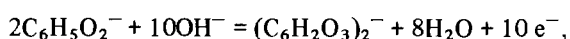


taking place at pH greater than 9 and where copper(II) ion is coordinated to the biquinone.

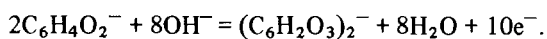
The effect of pH on the reaction rate must be rationalized in terms of both changes in the reduction-oxidation potentials of the oxidant, perhydroxyl ion and the reductants, 1-hydroxy-2-oxybenzene and meta dioxybenzene ions and formation of the appropriate copper(II) ion complex. The half reaction for the oxidant would be,



The half reaction for the reductants would be, written as an oxidation, for the 1-hydroxy-2-oxybenzene ion:



and for the meta dioxybenzene ion:



The effective reduction potential of the perhydroxyl ion decreases with increasing pH,

$$E = 0.88 - (\text{RT}/2\text{F})\log[(\text{OH}^-)^3/(\text{HO}_2^-)].$$

At pH 9, 10.7 and 12.7 the effective reduction potentials, at 25 °C, would be 1.32 V, 1.17 V and 0.99 V respectively. The standard reduction potentials for the reductants are not available, but the effective reduction potential would be computed from the fol-

lowing Nernst equations. For the 1-hydroxy-2-oxybenzene ion,

$$E = E^\circ - (\text{RT}/10\text{F}) \\ \times \log[(\text{C}_6\text{H}_4\text{O}_2^-)^2(\text{OH}^-)10/((\text{C}_6\text{H}_2\text{O}_3)_2^-)]$$

and for the meta dioxybenzene ion,

$$E = E^\circ - (\text{RT}/10\text{F}) \\ \times \log[(\text{C}_6\text{H}_4\text{O}_2^-)^2(\text{OH}^-)8/((\text{C}_6\text{H}_2\text{O}_3)_2^-)]$$

The two Nernst equations indicate that the comparative change in conditional reduction potential per incremental change in pOH is greater for the 1-hydroxy-3-oxybenzene ion. The reduction potential of the perhydroxyl ion changes in the same direction relative to changing hydroxyl ion as the 1-hydroxy-3-oxybenzene and meta dioxybenzene ions. This means that the difference in reduction potential is decreasing or phrased in terms of molecular orbital theory terminology-the difference in energy between the highest occupied and the lowest unoccupied molecular orbitals of the reactants is decreasing [16]. This trend in reduction potential difference has generally, for various phenols, correlated with a decreasing reaction rate [14]. The apparently negative effect of pH upon reaction rate as inferred from oxidation-reduction potential considerations suggest that the formation of copper(II) ion complex and the effect of increasing pH toward facilitating formation of this particular complex over-ride rate effects that correlate with reduction potential differences.

Sigel [17] has made the very logical suggestion that reactions which are accelerated by metal ions take place within the coordination sphere of the metal ion. If the reaction takes place in the coordination sphere at the start of the reaction, copper(II) ion coordinates the reactant species and at the conclusion of the reaction product species remain coordinated to the copper(II) ion and are not exchanged for reactant species. The lack of ability of reactant to compete with product for coordination sites on the copper(II) ion effectively removes copper(II) ion as a catalyst.

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