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PHYSICAL CHEMISTRY | RESEARCH ARTICLE

Spectroscopic and mechanistic investigations into oxidation of aspartame by diperiodatocuprate(III) in aqueous alkaline medium

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Abstract: The oxidation of aspartame (ASP) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at 298 K and a constant ionic strength of 0.30 mol dm^{-3} was studied spectrophotometrically. The reaction between aspartame and diperiodatocuprate(III) in alkaline medium exhibits 1:6 stoichiometry in the reaction. The order of the reaction with respect to [diperiodatocuprate(III)] was unity, while the apparent order with respect to [aspartame] was less than unity over the concentration range studied. The rate of the reaction increased with increase in $[OH^-]$ whereas the rate decreased with increase in $[IO_4^-]$. Increasing the ionic strength of the medium increased the rate. The main products were identified by FT-IR, NMR, and LC-MS spectral studies. The probable mechanism was proposed. The activation parameters with respect to slow step of the mechanism were computed and discussed. Thermodynamic quantities were also calculated. Kinetic studies suggest that $[Cu(H_2IO_6)(H_2O)_2]$ is the reactive species of Cu(III).

Subjects: Science; Food Science & Technology; Physical Sciences; Medicine

Keywords: aspartame; copper(III) complex; spectrophotometer; kinetics; oxidation

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PUBLIC INTEREST STATEMENT

This paper demonstrates the kinetic study of oxidation of an artificial sweetener Aspartame by diperiodatocuprate(III) complex oxidant. In view of the commercial and pharmaceutical importance of aspartame, such oxidation studies may throw some light on the mechanism of conversions of the compounds in biological systems. The present study deals with the title reaction in order to investigate the redox chemistry of DPC in alkaline media and to compute the thermodynamic quantities of various steps involved in the mechanism to those derived on the basis of kinetic and spectroscopic results. Kinetics can be applied to the optimization of process conditions, as in organic syntheses, analytical reactions, and chemical manufacturing. Yet, another practical use of chemical kinetics is for the determination and control of the stability of commercial products such as pharmaceutical dosage forms, foods, paints, and metals.

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1. Introduction

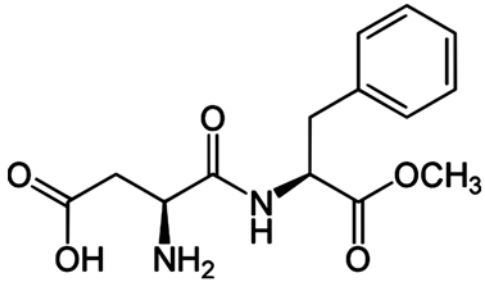
Among sweetening agents, aspartame as a noncaloric compound is widely used in preparation of foods and beverages. Sweetening agents have been reported to enhance the morphine-induced antinociception in the formalin test (Abdollahi, Nikfar, & Habibi, 2000; Nikfar, Abdollahi, Etemad, & Sharifzadeh, 1997). Further studies showed that calcium channel blockers enhance sweetening agent-induced antinociceptive properties (Nikfar, Abdollahi, Sarkarati, & Etemad, 1995). Also it was reported that aspartame-induced antinociception is increased by nitric oxide synthase inhibitor, NG-nitro-L-arginine methyl ester (L-NAME) (Abdollahi, Nikfar, & Abdoli, 2001). However, the exact mechanism of action of sweetening agent-induced antinociception remains uncertain. Aspartame is known to be metabolized in the gastrointestinal tract to aspartate and phenylalanine which enter into the normal metabolic paths for the amino acids (Micromedex International Healthcare Series, 2002; Ranney, Oppermann, & Muldoon, 1976). Aspartame (AT-aspartyl-L-phenylalanine-1-methyl ester, or ASP) is a dipeptide of two amino acids: L-phenylalanine as the methyl ester and L-aspartic acid. The structure of aspartame is shown in Scheme 1.

In recent years, study of the highest oxidation states of transition metals has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatocuprate(III) (Chougale, Hiremath, & Nandibewoor, 1997), diperiodatoargentate(III) (Kumar, Kumar, & Ramamurthy, 1999), and diperiodatonickelate(IV) (Shan, Qian, Gao, & Shen, 2004) are good oxidants in a solvent medium over appropriate pH ranges. Periodate and tellurate complexes of trivalent copper have been extensively used in the analysis of some organic compounds (Niu, Zhu, Hu, Tong, & Yang, 1996).

The kinetics of self-decomposition of these complexes has been studied in detail (Shetti & Nandibewoor, 2009). Copper(III) has been shown to be an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulfate (Ramreddy, Sethuram, & Navaneeth Rao, 1978). The oxidation reaction usually involves the copper(II)/copper(I) couple and other aspects as detailed in different reviews (Karlin & Gultneh, 1997; Tolman, 1997). The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases, due to its limited solubility and stability in aqueous medium. Diperiodatocuprate(III) is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized (Munavalli, Patil, Chimatadar, & Nandibewoor, 2009). Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry (Karlin, Kaderli, & Zuberbühler, 1997). They have also been used (Sethuram, 2003) in the differential titration of organic mixtures, and for the estimation of chromium, calcium, and magnesium concentration from their ores, and for antimony, arsenic, and tin from their alloys. In alkaline media, depending on the pH, the copper(III) periodate complexes exist as multiple copper(III) species (Bailar, Emeleus, Nyholm, & Trotman-Dikenson, 1975). It would be interesting to know which of these species is the active oxidant.

A literature survey reveals that there are no reports on the oxidation of aspartame by diperiodatocuprate(III). In view of the commercial and pharmaceutical importance of aspartame, such oxidation studies may throw some light on the mechanism of conversions of the compounds in

Scheme 1. Chemical structure of aspartame.



biological systems. The present study deals with the title reaction in order to investigate the redox chemistry of diperiodatocuprate(III) in alkaline media, and to compute the thermodynamic quantities of various steps involved in the mechanism to those derived on the basis of kinetic and spectroscopic results.

2. Experimental

2.1. Materials and reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. The copper(III) periodate complex was prepared by a known method (Shetti & Nandibewoor, 2009) and standardized by a standard procedure (Jeffery, Bassett, Mendham, & Denney, 1996). The UV–Visible spectrum with a maximum absorption at 415 nm was used to verify the existence of copper(III) complex. Solutions of aspartame (S.D. Fine Chemicals) and copper sulfate (BDH) were prepared by dissolving known amounts of the samples in distilled water. The periodate solution was prepared and standardized iodometrically (Jeffery et al., 1996). The required alkalinity and ionic strength were maintained with KOH and KNO_3, respectively, in the reaction solutions. t-butyl alcohol (S.D. Fine Chemicals) was used to vary the dielectric constant of the media.

2.2. Kinetic measurements

The kinetic measurements were performed using a Varian Cary 50 Bio UV–visible spectrophotometer. The kinetics was followed under pseudo-first-order conditions where [aspartame] > [diperiodatocuprate(III)] at 25 ± 0.1°C, unless specified. The reaction was initiated by mixing DPC and aspartame solutions which also contained the required concentrations of KNO_3, KOH, and KIO_4. The reaction progress was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance of diperiodatocuprate(III). Prior to the kinetic studies, Beer's law was verified and the extinction coefficient was found to be ε = 6235 ± 100 $dm^3\ mol^{-1}\ cm^{-1}$. It was verified that there is negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo-first-order rate constants, "k_{obs}", were determined from $\log_{10}$ (absorbance) vs. time plots (Figure 1). The plots were linear up to 80% completion of the reaction. The rate constants were the average of three independent sets and reproducible to within ±5%. Regression analysis of experimental data to obtain the regression coefficient r and the standard deviation *S*, of points from the regression line, was performed with Microsoft Excel 2007. In the kinetic studies, a constant concentration was used to fix the concentration of diperiodatocuprate(III) throughout the study unless otherwise stated. In view of the excess periodate concentrations present in reaction mixtures, the possible oxidation of aspartame by periodate in alkaline medium at 25°C was studied. It was found that there was no significant reaction under the experimental conditions employed, compared to the diperiodatocuprate(III) oxidation of aspartame.

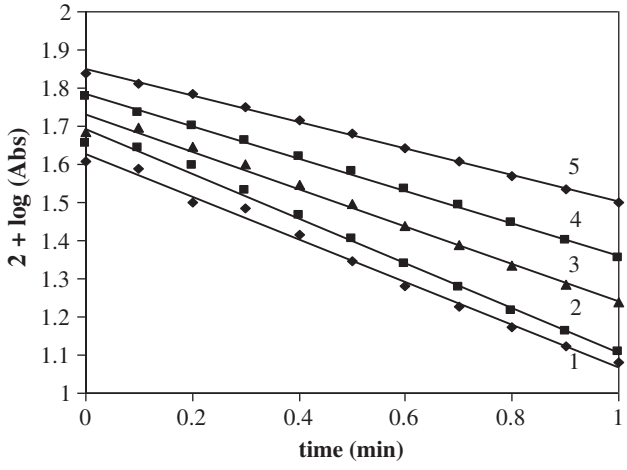


Figure 1. First-order plots for the oxidation of aspartame by diperiodatocuprate(III) in aqueous alkaline medium.

Note: [DPC] = (1) 1.0, (2) 3.0, (3) 5.0, (4) 7.0, and (5) $10.0/10^{-5}$/ mol dm^{-3}.

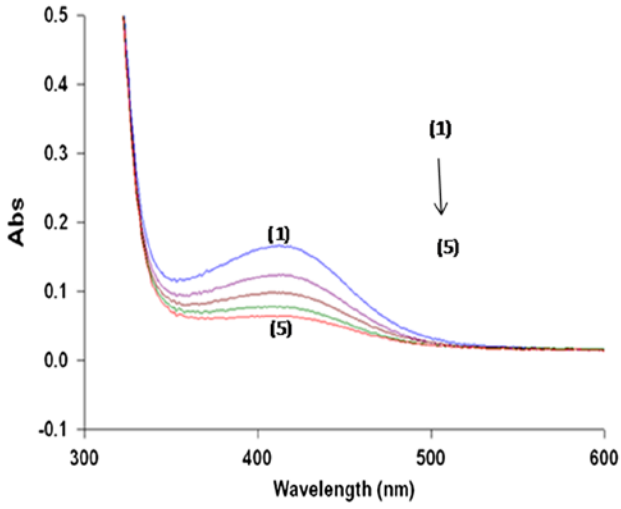


Figure 2. UV–Visible spectral changes during the oxidation of aspartame by diperiodatocuprate(III) in aqueous alkaline medium at 298 K.

Notes: [DPC] = 5.0×10^{-5}; [ASP] = 5.0×10^{-4}; [OH^-] = 0.15 and I = 0.30/mol dm^{-3} with scanning time of: (1) 1.0, (2) 2.0, (3) 3.0, (4) 4.0, and (5) 5.0 min.

The total concentrations of periodate and OH^- were calculated by considering both the amount present in the diperiodatocuprate(III) solution and that additionally added. Kinetic runs were also carried out in an inert N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of the reaction. There was no difference in the kinetic results obtained in the presence and in the absence of nitrogen. The spectral changes during the reaction are shown in Figure 2. It is evident from this figure at 415 nm, the concentration of DPC decreases with increasing time.

2.3. Instruments used

(i) For kinetic measurements, a Peltier Accessory (temperature control) attached to Varian CARY 50 Bio UV–visible spectrophotometer was used.

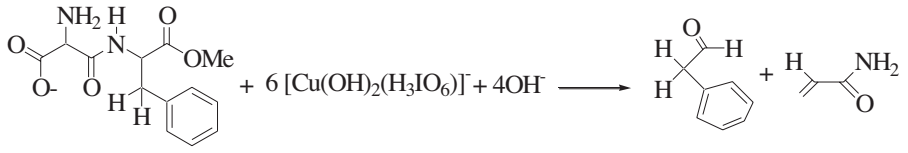
(ii) For product analysis, Nicolet 5700-FT-IR spectrometer (Thermo, USA) and Agilent Technologies-1200 liquid chromatography mass spectrometer were used.

(iii) For pH measurements ELICO pH meter model Li 120 was used.

3. Results

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing various ratios of diperiodatocuprate(III) to aspartame in the presence of constant amounts of OH^- and KNO_3 were kept for two hours in a closed vessel under nitrogen atmosphere. The remaining concentration of diperiodatocuprate(III) was estimated by spectrophotometrically at 415 nm. The results indicate 1:6 stoichiometry as shown in Scheme 2.

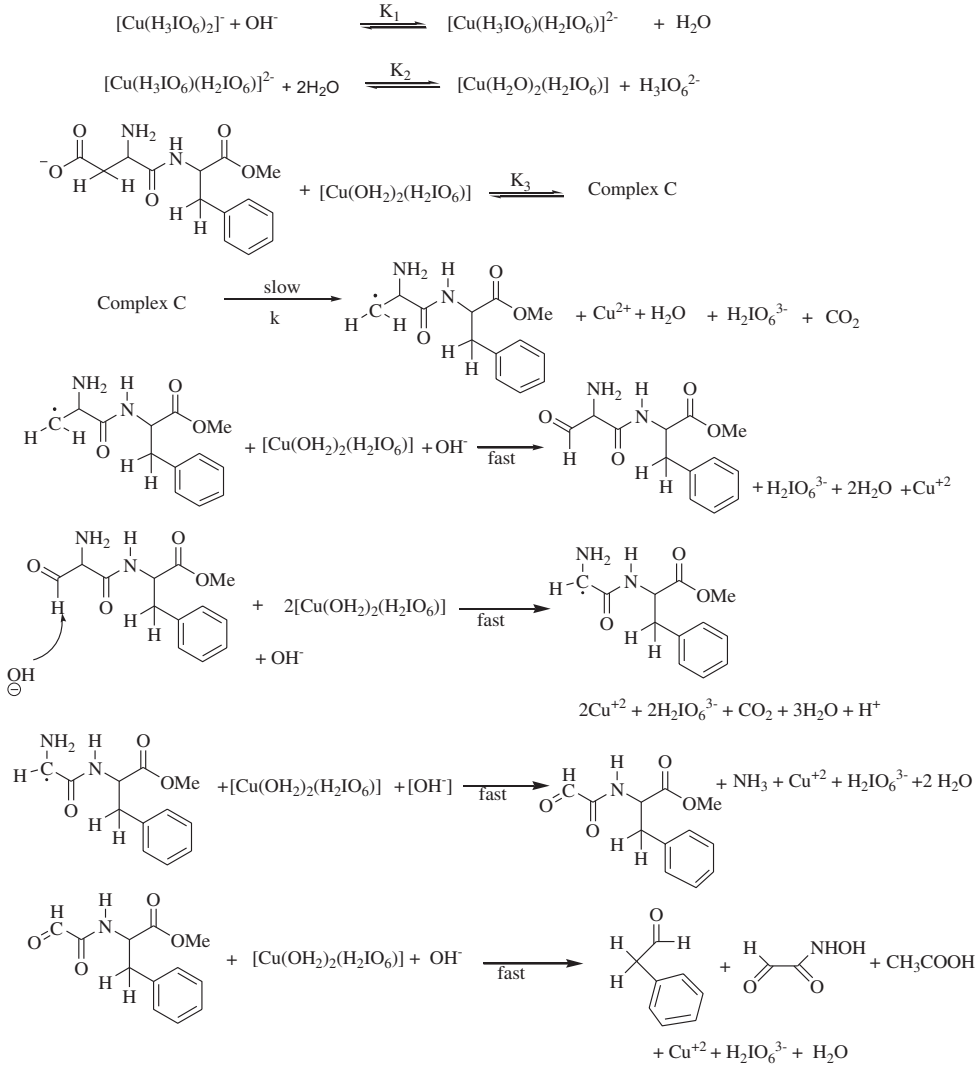


$$CH_3COOH + 6Cu^{2+} + 6H_2IO_6^{3-}$$
$$NH_3 + 9H_2O + 2CO_2$$

---------- (1)

The main product was identified as phenyl acetaldehyde which was confirmed by IR, LC-MS, and NMR spectra. The stretching of the aldehydic carbonyl group (>C=O) of the phenyl acetaldehyde is observed at 1626.05 cm^{-1} (Figure 3(a)). The product was also confirmed by LC-MS analysis data

Scheme 2. Detailed mechanistic pathways for the oxidation of aspartame by alkaline diperiodatocuprate(III).



(Figure 3(b)), mass spectrum showed molecular ion peak at 112 amu. In NMR (Figure 3(c)), {^{1}HNMR (300 MHz, DMSO) δ 4.2 ppm (s, CH_2), δ 8.1 ppm (s, CHO)} confirming the presence of product phenyl acetaldehyde. The formation of free Ag(I) in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that phenyl acetaldehyde did not undergo further oxidation under the present kinetic conditions.

3.2. Reaction orders

The reaction orders were determined from the slopes of $\log_{10} k_{obs}$ vs. log concentration plots while varying the concentrations of aspartame, alkali, and periodate, in turn, also while keeping all other concentrations and conditions constant.

3.3. Effect of [diperiodatocuprate(III)]

The oxidant [diperiodatocuprate(III)] concentration was varied over the range of 1.0×10^{-5}–1.0×10^{-4} mol dm^{-3} and the resulting, fairly constant k_{obs} values (Table 1), indicate that order with respect to the diperiodatocuprate(III) concentration was unity. This was also confirmed by the linearity of the plots of $\log_{10}$ (absorbance) vs. time ($r \geq 0.9986$, $S \leq 0.023$) up to 80% completion of the reaction (Figure 1).

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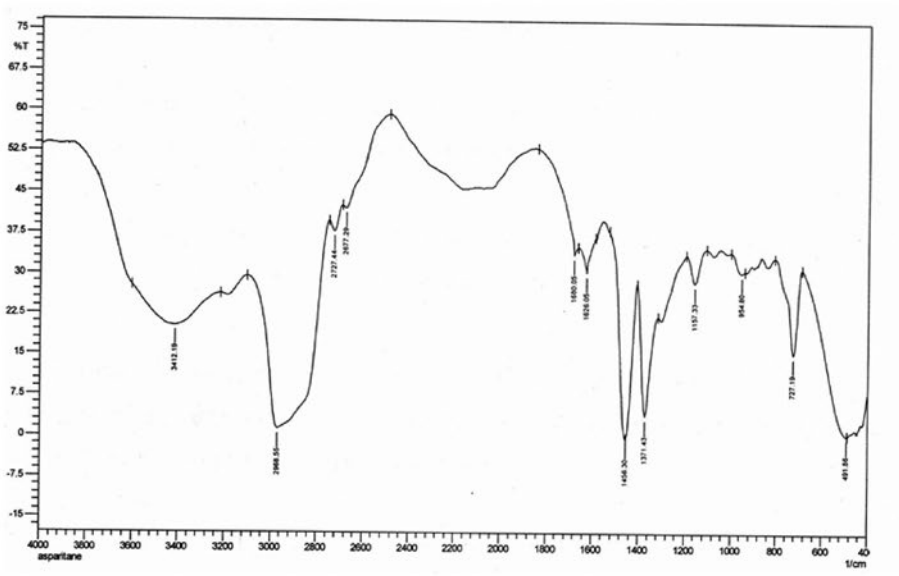
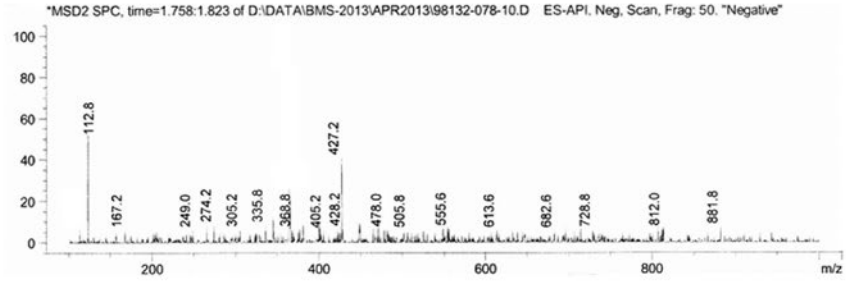
Figure 3. (a) IR spectrum showing carbonyl stretching at 1626.05 cm^{-1}, (b) LC-MS spectrum of phenyl acetaldehyde showing molecular ion peak at 112.8 m/z, and (c) ^{1}HNMR spectrum of phenyl acetaldehyde. (1) δ 4.2 ppm (s, CH_2), (2) δ 8.1 ppm (s, CHO).

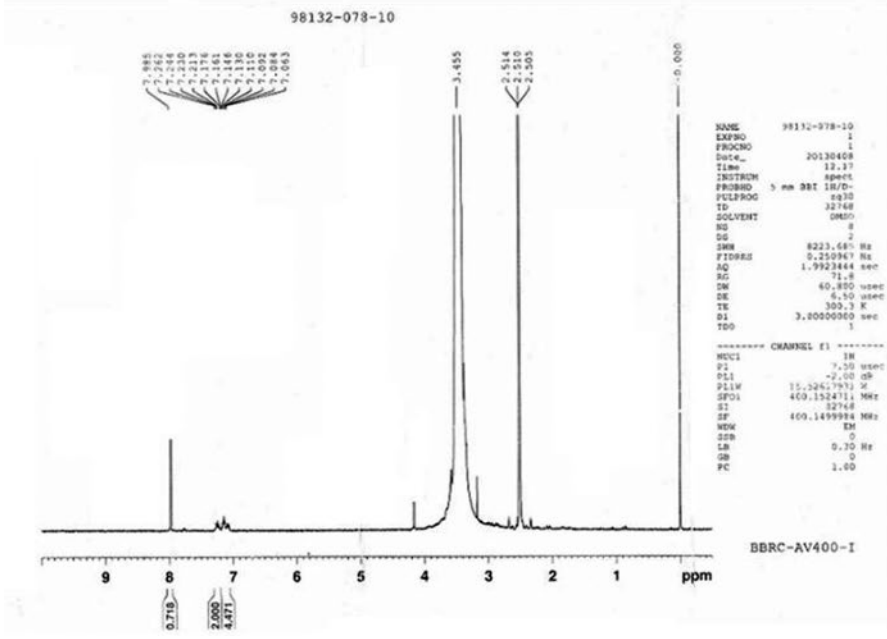
(a) IR spectrum showing carbonyl stretching at 1626.05 cm^{-1}.



(b) LC-MS spectrum of phenyl acetaldehyde showing molecular ion peak at 112.8 m/z



(c) 1HNMRsectrum of phenyl acetaldehyde. 1) δ 4.2 ppm (s, CH_2), 2) δ 8.1 ppm (s, CHO).



3.4. Effect of [aspartame]

The effect of aspartame on the rate of reaction was studied at constant concentrations of diperiodatocuprate(III), alkali, and periodate, all at a constant ionic strength of 0.30 mol dm^{-3}. The concentration of the substrate, aspartame, was varied from 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}. The k_{obs} values increased with increase in concentration of aspartame (Table 1). The order with respect to the concentration of ASP was found to be less than unity (0.82) ($r \geq 0.9985$, $S \leq 0.0062$) at the studied concentrations.

3.5. Effect of [periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} while keeping all other reactant concentrations constant. It was found that periodate had a retarding effect on the rate of reaction. The order with respect to the periodate concentration was negative and less than unity.

3.6. Effect of [alkali]

The effect of alkali concentration on the reaction was studied at constant concentrations of aspartame, diperiodatocuprate(III), and periodate at a constant ionic strength of 0.30 mol dm^{-3} at 25°C. The rate constant increases with an increase in alkali concentration (Table 1). The order with respect to alkali concentration was found to be positive and fractional.

3.7. Effect of ionic strength (I) and dielectric constant of the medium (D)

The effect of ionic strength on the rate of reaction was studied by increasing the concentration of KNO_3 at constant concentrations of DPC, ASP, OH^-, and IO_4^-. It was found that increasing the ionic strength of the reaction medium caused an increase in the reaction rate (Figure 4). The dielectric constant of the medium, D, was studied by varying the t-butyl alcohol and water percentages (V/V).

Table 1. Effect of variation of [DPC], [ASP], [OH^-], and [IO_4^-] on the oxidation of ASP by diperiodatocuprate(III) in aqueous alkaline medium at 25°C and I = 0.30 mol dm^{-3}

[DPC] × 10^5 (mol dm^{-3})	[ASPP] × 10^4 (mol dm^{-3})	[OH^-] (mol dm^{-3})	[IO_4^-] × 10^5 (mol dm^{-3})	k_{obs} × 10^3 (s^{-1})	k_{cal} × 10^3 (s^{-1})
1.0	5.0	0.15	1.0	4.54	4.82
3.0	5.0	0.15	1.0	4.24	4.82
5.0	5.0	0.15	1.0	4.84	4.82
8.0	5.0	0.15	1.0	4.90	4.82
10.0	5.0	0.15	1.0	4.39	4.82
5.0	1.0	0.15	1.0	1.98	1.90
5.0	3.0	0.15	1.0	3.96	3.80
5.0	5.0	0.15	1.0	4.84	4.82
5.0	7.0	0.15	1.0	5.44	5.30
5.0	10.0	0.15	1.0	5.90	5.90
5.0	5.0	0.025	1.0	2.07	2.40
5.0	5.0	0.05	1.0	3.19	3.50
5.0	5.0	0.10	1.0	4.30	4.41
5.0	5.0	0.15	1.0	4.84	4.82
5.0	5.0	0.25	1.0	5.19	5.21
5.0	5.0	0.15	1.0	5.70	5.30
5.0	5.0	0.15	3.0	5.30	5.00
5.0	5.0	0.15	5.0	5.21	4.82
5.0	5.0	0.15	8.0	4.80	3.50
5.0	5.0	0.15	10.0	3.99	2.70

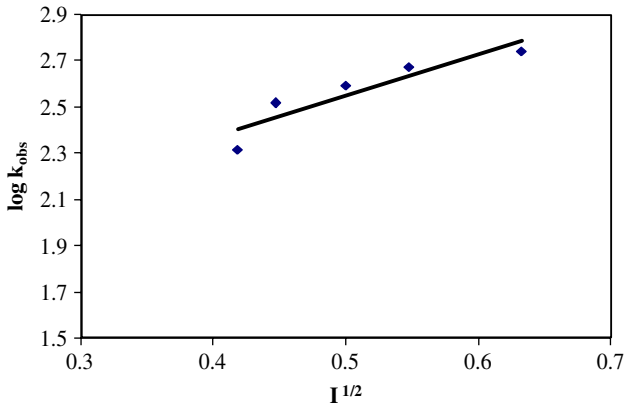


Figure 4. Effect of ionic strength on the oxidation of aspartame by DPC in aqueous alkaline medium at 25°C.

The value of the rate constant remained almost constant. The results indicate that dielectric constant had no significant effect on the reaction rate.

3.8. Effect of added products

Addition of the products, phenyl acetaldehyde or copper(II) (as $CuSO_4$), did not have any significant effect on the reaction rate.

3.9. Polymerization study

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was added, was kept for 6 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals during the reaction (Hiremath, Mulla, & Nandibewoor, 2005). Blank experiments with either diperiodatocuprate(III) or aspartame alone, with acrylonitrile, did not induce any polymerization under the same conditions as those studied for the reaction mixture.

3.10. Effect of temperature (T)

The influence of temperature on the k_{obs} values was studied at, 15, 25, and 35°C under varying concentrations of ASP, alkali, and periodate, keeping other conditions constant. The rate constant was found to increase with increase in temperature. The rate constants, *k*, of the slow step of Scheme 2 were obtained from intercepts of $1/k_{obs}$ vs. 1/[ASP] plots at three different temperatures and used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of log *k* vs. 1/T ($r \geq 0.9955$, $S \leq 0.005$), and the other activation parameters so obtained are tabulated in Table 2.

Table 2. Activation parameters and thermodynamic quantities for the oxidation of ASP by diperiodatocuprate(III) in aqueous alkaline medium with respect to the slow step of Scheme 2

Effect of temperature (K)	**$k \times 10^2$ (s^{-1})**
288	3.07
298	7.65
308	19.02
Activation parameters	Values
E_a (kJ mol^{-1})	67.1 ± 3.2
$\Delta H^{\#}$ (kJ mol^{-1})	64.6 ± 3.5
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−68.1 ± 10.4
$\Delta G^{\#}_{298}$ (kJ mol^{-1})	20.3 ± 1.2
log A	9.6 ± 0.5

Note: [DPC] = 5.0×10^{-5}, [ASP] = 5.0×10^{-4}, [OH^-] = 0.15 and [IO_4^-] = 1.0×10^{-4}/ mol dm^{-3}.

4. Discussion

The water-soluble copper(III) periodate complex is reported (Bhattacharya & Banerjee, 1996) to be $[Cu(HIO_6)_2]^{5-}$. However, in aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as HIO_6^{4-} (as present in the complex) as is evident from its involvement in the multiple equilibria (Bailar et al., 1975) depending on the pH of the solution, as given below.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{2}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \tag{3}$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{4}$$

Periodic acid exists in the acid medium as H_5IO_6 and as $H_4IO_6^-$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerize (Bailar et al., 1975). However, formation of this species is negligible under conditions employed for kinetic study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)(H_2IO_6)]^{2-}$, a conclusion also supported by earlier work (Reddy, Sethuram, & Navneeth Rao, 1984).

4.1. Mechanism for reaction

In this study, OH^- increases the rate of the reaction with increasing the alkali concentration (Table 1), which can be explained in terms of the prevailing equilibrium for the formation of $[Cu(H_3IO_6)(H_2IO_6)]^{2-}$ as given in the following Equation 5:

$$[Cu(H_3IO_6)_2]^- + OH^- \rightleftharpoons [Cu(H_3IO_6)(H_2IO_6)]^{2-} + H_2O \tag{5}$$

Also, the decrease in the reaction rate with increasing $[H_3IO_6^{2-}]$ (Table 1) suggests that the equilibrium of the Cu(III) periodate complex to form monoperiodatocuprate(III) (MPC) species is as given in Equation 6:

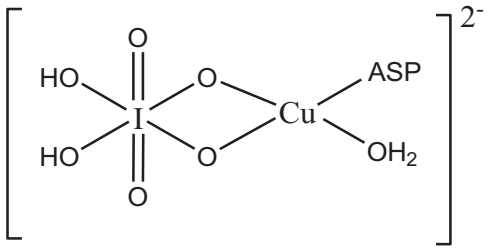
$$[Cu(H_3IO_6)(H_2IO_6)]^{2-} + 2H_2O \rightleftharpoons [Cu(H_2O)_2(H_2IO_6)] + H_3IO_6^{2-} \tag{6}$$

Equilibria as described by Equations 5 and 6 are well described in the literature (Chang, 1981). It may be expected that a lower periodate complex, such as monoperiodatocuprate(III) (MPC), may be more important in the reaction than diperiodatocuprate(III). The inverse fractional order in $H_3IO_6^{2-}$ concentration may also result from this reason. Therefore, MPC may be the main reactive form of the oxidant.

The reaction between diperiodatocuprate(III) and ASP in alkaline medium has the stoichiometry 1:6 [aspartame:diperiodatocuprate(III)] with a first-order dependence on [diperiodatocuprate(III)] and an apparent order of less than unit order in [substrate], a positive fractional order dependence on [alkali] and negative fractional order dependence on [periodate]. No effect of added products was observed. Based on the order with respect to reactants, such as [diperiodatocuprate(III)], $[OH^-]$, [periodate], and [ASP], the following mechanism has been proposed by considering ASP in anionic form which explains all the other experimental observations, as in Scheme 2.

Since Scheme 2 is in accordance with the generally well-accepted principle of noncomplementary oxidations, taking place in sequences of one-electron steps, the reaction between the substrate and oxidant should result to from a radical intermediate. A free radical scavenging experiment revealed such a possibility. Such a radical intermediate has been reported previously (Shetti & Nandibewoor, 2009). A direct plot of k_{obs} vs. [ASP] was drawn in order to determine the presence of a parallel reaction,

Scheme 3. Probable structure of complex.



if any, along with interaction of the oxidant and reductant. However, the plot of k_{obs} vs. [aspartame] was not linear. Thus, in Scheme 2, a parallel reaction and involvement of two molecules of aspartame in the complex are excluded. The probable structure of the complex is given in Scheme 3:

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV–visible spectra of aspartame (5.0×10^{-4} mol dm^{-3}), diperiodatocuprate(III) (5.0×10^{-5} mol dm^{-3}), [OH$^-$] = 0.15 mol dm^{-3}, and mixture of both. A bathochromic shift of about 10.0 nm from 421.0 to 431.0 nm was observed (Figure 5). A Michaelis–Menten plot also proved that complex formation occurs between diperiodatocuprate(III) and ASP, which explains the less than unit-order dependence of the reaction rate on the aspartame concentration. Such a complex between an oxidant and substrate has been observed previously (Naik, Kulkarni, Chimatadar, & Nandibewoor, 2008).

According to Scheme 2

$$\text{Rate} = \frac{-\text{d[DPC]}}{\text{dt}} = k[\text{Complex}]$$

$$\text{Rate} = \frac{kK_1K_2K_3[\text{ASP}]_f[\text{DPC}]_f[\text{OH}^-]_f}{[\text{H}_2\text{IO}_6]^{3-}} \quad \text{(i)}$$

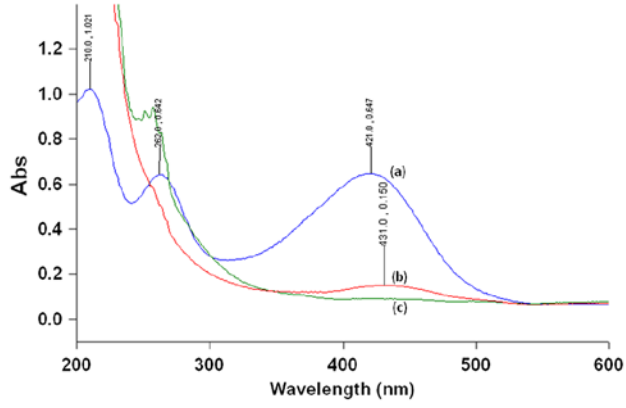
Total concentration of DPC is given by

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

where T and f refer to the total and free concentrations.

$$[\text{DPC}]_T = [\text{DPC}]_f + K_1[\text{DPC}][\text{OH}^-] + \frac{K_1K_2[\text{OH}^-][\text{DPC}]_f}{[\text{H}_2\text{IO}_6]^{3-}} + \frac{K_1K_2K_3[\text{ASP}]_f[\text{DPC}]_f[\text{OH}^-]}{[\text{H}_2\text{IO}_6]^{3-}}$$

Figure 5. Spectroscopic evidence for the complex formation between aspartame and DPC. (a)UV–Vis spectra of DPC complex, (b) UV–Vis spectra of mixture of DPC and aspartame and (c) UV–Vis spectra of aspartame.



$$[DPC]_T = [DPC]_f \left\{ 1 + K_1[OH^-] + \frac{K_1K_2[OH^-]}{[H_2IO_6]^{3-}} + \frac{K_1K_2K_3[ASP]_f[OH^-]}{[H_2IO_6]^{3-}} \right\}$$

$$[DPC]_T = [DPC]_f \left\{ \frac{[H_2IO_6]^{3-} + K_1[OH^-][H_2IO_6]^{3-} + K_1K_2[OH^-] + K_1K_2K_3[ASP][OH^-]}{[H_2IO_6]^{3-}} \right\}$$

$$[DPC]_f = \left\{ \frac{[H_2IO_6]^{3-}[DPC]_T}{[H_2IO_6]^{3-} + K_1[OH^-][H_2IO_6]^{3-} + K_1K_2[OH^-] + K_1K_2K_3[ASP][OH^-]} \right\} \quad \text{(ii)}$$

Similarly

$$[ASP]_T = [ASP]_f + \text{Complex } C_1 = [ASP]_f + \frac{K_1K_2K_3[ASP][OH^-][DPC]}{[H_2IO_6]^{3-}}$$

$$[ASP]_T = [ASP]_f \quad \text{(iii)}$$

Similarly

$$[OH^-]_T = [OH^-]_f \quad \text{(iv)}$$

Substituting Equations ii–iv in Equation i

$$\frac{d[DPC]}{dt} = \frac{kK_1K_2K_3[ASP]\,[DPC]\,[OH^-]}{\left\{[H_2IO_6]^{3-} + K_1[OH^-][H_2IO_6]^{3-} + K_1K_2[OH^-] + K_1K_2K_3[ASP][OH^-]\right\}} \quad \text{(v)}$$

$$k_{obs} = \frac{\text{Rate}}{[DPC]} = \frac{kK_1K_2K_3[ASP]\,[DPC]\,[OH^-]}{\left\{[H_2IO_6]^{3-} + K_1[OH^-][H_2IO_6]^{3-} + K_1K_2[OH^-] + K_1K_2K_3[ASP][OH^-]\right\}} \quad \text{(vi)}$$

The rate law Equation vi can be rearranged into the following form, which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[H_2IO_6]^{3-}}{kK_1K_2K_3[OH^-][ASP]} + \frac{[H_2IO_6]^{3-}}{kK_1K_2[ASP]} + \frac{1}{kK_3[ASP]} + \frac{1}{k} \quad \text{(vii)}$$

According to Equation vii, other conditions being constant, the plots of $1/k_{obs}$ vs. $[H_2IO_6]^{3-}$ ($r \geq 0.9798$, $S \leq 0.011$), $1/k_{obs}$ vs. $1/[OH^-]$ ($r \geq 0.9904$, $S \leq 0.016$), and $1/k_{obs}$ vs. $1/[ASP]$ ($r \geq 0.9964$, $S \leq 0.023$) should be linear, as verified in Figure 6. From the intercepts and slopes of such plots, the reaction constants K_1, K_2, K_3, and k were calculated as 1.98 $dm^3\ mol^{-1}$, 3.25×10^{-4} mol dm^{-3}, 6.9×10^3 $dm^3\ mol^{-1}$, and $0.765 \times 10^{-2}\ s^{-1}$, respectively. The equilibrium constant K_1 is far greater than K_2. This may be attributed to the greater tendency of diperiodatocuprate(III) to undergo deprotonation compared to the formation of hydrolyzed species in alkaline medium. The effect of ionic strength on the rate of reaction explains qualitatively the involvement of same charge molecules, as seen in Scheme 2. Increase the content of t-butanol in the reaction medium leads to negligible effect on the rate of reaction, which seems to be contrary to the expected reaction between the ions having the same charge in media of lower relative permeability.

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The [ASP], $[OH^-]$, and $[H_3IO_6^{2-}]$ (Table 1) were varied at three different temperatures. The plots of $1/k_{obs}$ vs. 1/[ASP], $1/k_{obs}$ vs. 1/ $[OH^-]$, and $1/k_{obs}$ vs. $[H_2IO_6^{3-}]$ should be linear, (Figure 6). From the slopes and intercepts, the values of K_1 were calculated at different temperatures. A van't Hoffs plot was made for the variation of K_1 with temperature [i.e. log K_1 vs. 1/T ($r \geq 0.9851$, $S \leq 0.1121$)], and

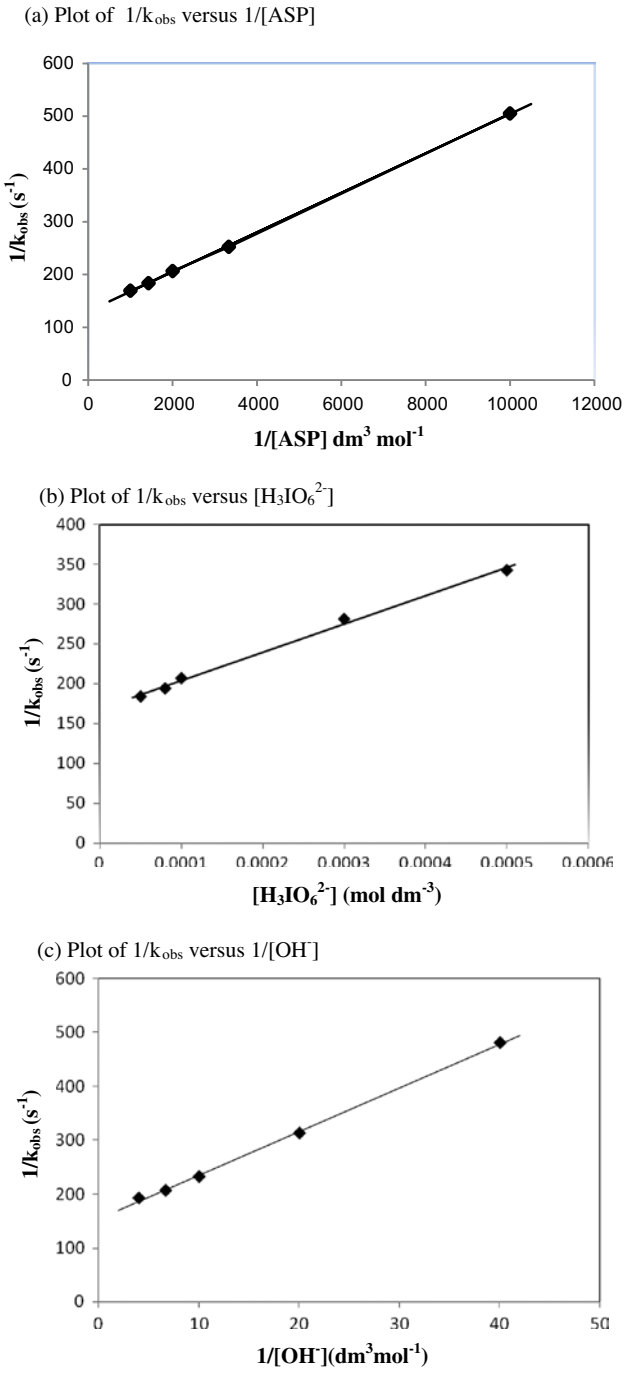


Figure 6. Verification of rate law (vi) in the form of (vii) for the oxidation of aspartame by diperiodatocuprate(III). (a) Plot of $1/k_{obs}$ vs. 1/[ASP]; [ASP] = 1.0 × 10^{-4} to 10.0 × 10^{-4} mol dm^{-3}, (b) Plot of $1/k_{obs}$ vs. $[H_3IO_6^{2-}]$; $[H_3IO_6^{2-}]$ = 1.0 × 10^{-5} to 10.0 × 10^{-5} mol dm^{-3}, (c) Plot of $1/k_{obs}$ vs. $1/[OH^-]$; $[OH^-]$ = 0.025 to 0.25 mol dm^{-3}.

the thermodynamic parameters were calculated. Those values are given in Table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate-limiting step, supporting the fact that the reaction before the rate-determining step is fairly fast and involves high activation energy (Rangappa, Raghavendra, Mahadevappa, & Channegowda, 1998). In the same manner, K_2 and K_3 were calculated at different temperatures and the corresponding thermodynamic quantities are given in Table 2.

The values of $\Delta S^{\#}$ and $\Delta H^{\#}$ were both favorable for electron transfer processes. The favorable enthalpy was due to release of energy on solution changes in the transition state. The low value of

enthalpy of activation obtained might be due to the involvement of prior equilibrium steps as given in Scheme 2 (Weissberger, 1974). A negative value of $\Delta S^{\#}$ (−68.17 JK^{-1} mol^{-1}) suggests that the intermediate complex is more ordered than the reactants. The observed modest enthalpy of activation and higher rate constant for the slow step suggest that the oxidation presumably occurs via an inner sphere mechanism. This conclusion is supported by earlier observations (Farokhi & Nandibewoor, 2003; Martinez, Pitarque, & van Eldik, 1996).

4. Conclusion

The oxidation of aspartame by the cuprate(III) periodate complex is pH dependent. The observed stoichiometry indicates that the oxidation of one mole of aspartame requires six moles of diperiodatocuprate(III). In the present investigation, among the various possible species of the oxidant diperiodatocuprate(III) in alkaline medium, monoperiodatocuprate(III), $[Cu(OH_2)_2(H_2IO_6)]$, is considered to be the active species. Values of equilibrium constants involved in the mechanism, and rate constants with respect to slow step of the mechanism, were determined. The activation parameters with respect to slow step of the mechanism, and thermodynamic quantities, were determined and discussed.

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