Spectral and Mechanistic Investigation of the Osmium(VIII) Catalyzed Oxidation of Diclofenac Sodium by the Copper(III) Periodate Complex in Aqueous Alkaline Medium

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Abstract The kinetics of the osmium(VIII) (Os(VIII)) catalyzed oxidation of diclofenac sodium (DFS) by diperiodatocuprate(III) (DPC) in aqueous alkaline medium has been studied spectrophotometrically at a constant ionic strength of 1.0 mol \cdot dm⁻³. The reaction showed first order kinetics in [Os(VIII)] and [DPC] and less than unit order with respect to [DFS] and [alkali]. The rate decreased with increase in [periodate]. The reaction between DFS and DPC in alkaline medium exhibits 1:2 [DFS]:[DPC] stoichiometry. However, the order in [DFS] and [OH⁻] changes from first order to zero order as their concentration increases. Changes in the ionic strength and dielectric constant did not affect the rate of reaction. The oxidation products were identified by LC-ESI-MS, NMR, and IR spectroscopic studies. A possible mechanism is proposed. The reaction constants involved in the different steps of the mechanism were calculated. The catalytic constant (K_C) was also calculated for Os(VIII) catalysis at the studied temperatures. From plots of $\log_{10} K_{\rm C}$ versus 1/T, values of activation parameters have been evaluated with respect to the catalytic reaction. The activation parameters with respect to the slow step of the mechanism were computed and discussed, and thermodynamic quantities were also determined. The active osmium(VIII) and copper(III) periodate species have been identified.

Keywords Kinetics · Oxidation · Copper(III) · Diclofenac sodium · Os(VIII) catalyst

1 Introduction

Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of some organic compounds [1–3]. Copper(III) was shown to be an intermediate in the copper(II) catalyzed oxidation of amino acids by peroxydisulphate [4]. Oxidation reactions usually involve the copper(II)/copper(I) couple and such aspects have been detailed in different reviews [5, 6]. The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to the fact of its limited solubility

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and stability in aqueous media. DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry [7–9]. Copper(III) is involved in many biological electron transfer reactions [10]. When the copper(III) periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, then it will be interesting to determine which of the possible species is the active oxidant.

Diclofenac, [*o*-(2,6-dichlorophenyl)amino]phenyl] acetic acid (DFS), belongs to a class of drugs called nonsteroidal anti-inflammatory drugs (NSAIDs). In pharmacological studies, diclofenac has shown anti-inflammatory, analgesic, and antipyretic activity [11]. As with other NSAIDs, its mode of action is not known; however its ability to inhibit prostaglandin synthesis may be involved in its anti-inflammatory activity, as well as contributing to its efficiency in relieving pain related to inflammation and primary dysmenorrhea. Diclofenac is used in treating osteoarthritis, rheumatoid arthritis, and ankylosing spondylitis [12, 13]. Due to the low solubility of the acidic form, it is commercially available as its sodium salt.

Transition metals are known to catalyze many oxidation/reduction reactions since some of them involve multiple oxidation states. In recent years, transition metal ions such as those of osmium, ruthenium and iridium, either alone or as binary mixtures, have attracted considerable interest as catalysts in various redox processes [14]. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed [15, 16]. Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and the experimental conditions, it has been shown [17] that metal ions can act as catalysts by several different paths such as the formation of complexes with reactants or oxidation of the substrate itself, or through the formation of free radicals. In an earlier report [18] it was observed that Os(VIII) formed a complex with a substrate, which was then oxidized by the oxidant to form an Os(VII) intermediate, followed by the rapid reaction of Os(VII) with one more mole of oxidant to regenerate the Os(VIII). In another report [19] it was observed that an oxidant-substrate complex reacted with Os(VIII) to form Os(VI) which then reacted with the oxidant in a fast step to regenerate Os(VIII). In another report [20] it was observed that Os(VIII) formed a complex with the substrate that was oxidized by the oxidant with the regeneration of Os(VIII). Hence, understanding the role of Os(VIII) in catalyzed reactions is important.

Osmium(VIII) catalysis in redox reactions can involve several complexes, different oxidation states of osmium, etc. The uncatalyzed oxidation of DFS by DPC has been studied [21]. We have observed that osmium(VIII) catalyzes the oxidation of DFS by DPC in alkaline medium. In order to understand the active species of oxidant and catalyst, and to propose an appropriate mechanism that may contribute to understanding its mode of action in biological systems, the title reaction is investigated here in detail. An understanding of the mechanism allows the chemistry to be interpreted and hence understood and predicted.

2 Experimental

2.1 Materials and Reagents

All chemicals used were of reagent grade and millipore water was used throughout this work. The copper(III) periodate complex was prepared [22, 23] and standardized by a standard procedure [24]. The UV-vis spectrum had a maximum absorption at 415 nm which verified the presence of copper(III). The diclofenac sodium (IP) concentration was checked potentiometrically. The required alkalinity and ionic strength were maintained with KOH

(BDH) and KNO₃ (Analar), respectively. The periodate solution was prepared and standardized iodometrically [25] at neutral pH using a phosphate buffer. An aqueous solution of copper sulfate (BDH) was used to study the effect of the product Cu(II). The temperature was maintained to within ± 0.10 °C.

2.2 Instruments Used

For kinetic measurements, a CARY 50 Bio UV-vis spectrophotometer (Varian, Victoria-3170, Australia) was used. For product analysis, a LC-ESI-MS (liquid chromatography electrospray ionization tandem mass spectrometry; Hewlett-Packard GmbH, Waldbronn, Germany), a Nicollet 5700 FT-IR spectrometer (Thermo, USA), and a 300 MHz ¹H NMR spectrometer (Brucker, Switzerland) were used.

2.3 Kinetic Studies

The oxidation of diclofenac sodium by diperiodatocuprate(III) was followed under pseudofirst order rate conditions where [DFS] \gg [DPC] at 25 ± 0.1 °C, unless otherwise stated. The reaction was initiated by mixing the DPC with a DFS solution that also contained the required concentrations of KNO₃, KOH, KIO₄, and Os(VIII) catalyst. The reaction progress was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC using the molar absorbency index ' ε ' = 6231 ± 100 dm³·mol⁻¹·cm⁻¹. It was verified that there is negligible interference at this wavelength from other species present in the reaction mixture.

The pseudo-first order rate constants, $k_{\mathbb{C}}$, were determined from plots of \log_{10} (absorbance) versus time. The plots were linear up to 80% completion of the reaction over the [OH⁻] range used. During the kinetics measurements a constant concentration of 1.0×10^{-5} mol·dm⁻³ of KIO₄ was used unless otherwise stated. Because periodate is present in excess in the DPC solutions, the possibility of direct oxidation of DFS by periodate at 25 °C was tested in this alkaline medium. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the oxidation of DFS by DPC. The total concentrations of periodate and OH⁻ were calculated by considering the amount present in the DPC solution along with those additionally added. Kinetics runs were also carried out under an N_2 atmosphere in order to detect a possible effect of dissolved oxygen on the rate of reaction. No significant differences were obtained between those obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination by carbonate in basic media, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. The spectral changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases as seen by the changes at 415 nm.

2.4 Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of DPC to DFS in preset constant amounts of OH⁻, KNO₃ and Os(VIII) were kept for 4 h in a closed vessel under the inert atmosphere. The DPC concentration remaining after that interval was estimated by spectrophotometry at 415 nm. The results indicated a 1:2 reaction stoichiometry as shown



in Eq. 1.



The product, [2-(2,6-dicloro-phynylamino)-phenyl]-methanol, was identified by LC-ESI-MS. This LC-ESI-MS analysis was carried out using a reverse-phase high performance liquid chromatography (HPLC) system with a Phenomenes C-18 column, UV/visible detector, and mass analyzer in series. A 12 µL sample of acidified reaction mixture was injected. The mobile phase consisted of 10 mmol·dm⁻³ ammonium acetate at pH = 3.0 (eluent A) and acetic acid (eluent B) at a flow rates of 1 mL·min⁻¹. Gradient elution was run to separate the substrate and reaction products. The LC-ESI-MS analysis indicated the presence of two main products with molecular ions at m/z = 273 (yield ca. 90%) and 598 (yield ca. 5%), respectively, see Fig. 2. The molecular ion of diclofenac sodium occurs at m/z = 299. The m/z = 598 thus corresponds to a dimer product of DFS. The product was further confirmed by its characteristic IR spectrum (Fig. 3). The absence of a sharp band (peak) at 1695 cm^{-1} (due to the acidic carbonyl in DFS) confirms the nature of the product. Further, the secondary amine (-NH) group observed around 3387 cm⁻¹ in DFS is retained in the product. The ¹H-NMR spectrum (in DMSO) shows that of the acidic –OH band disappeared and an alcoholic hydroxyl proton triplet band appears at 6.859 ppm. Further, the secondary amine (-NH) proton singlet band at around 3.69 ppm and other aromatic proton bands in DFS remain in the product, which disappear on D_2O exchange, confirms the formation of [2-(2,6-diclorophynylamino)-phenyl]-methanol (Fig. 4). All of these observations proved the formation of [2-(2,6-dicloro-phynylamino)-phenyl]-methanol as the major product. The dimer structure of DFS is



Fig. 2 Chromatogram and LC-ESI-MS spectra of the product of the Os(VIII) catalyzed oxidation of diclofenac sodium by DPC



Regression analysis of the experimental data to obtain the regression coefficient r and standard deviation S, of points from the regression line, was performed using Microsoft Excel-2003.



Fig. 3 FT-IR spectra of the product of Os(VIII) catalyzed oxidation of diclofenac sodium by DPC

3 Results and Discussion

3.1 Reaction Orders

Inasmuch as the diperiodatocuprate(III) (DPC) oxidation of diclofenac sodium (DFS) in alkaline medium proceeds at a measurable rate in the absence of Os(VIII), the catalyzed reaction is thus understood to occur by two parallel paths with contributions from both catalyzed and uncatalyzed paths. Therefore, the total rate constant k_T is equal to the sum of the rate constants of the catalyzed k_C and uncatalyzed k_U reactions, so $k_C = k_T - k_U$. Hence, the reaction orders were determined from the slopes of $\log_{10} k_C$ versus \log_{10} (concentration) plots by varying the concentrations of diclofenac sodium, osmium(VIII), alkali and periodate in turn, while keeping all other concentrations and conditions constant.

3.2 Effect of the Concentration of Diperiodatocuprate(III)

The diperiodatocuprate(III) concentration was varied in the range 3.0×10^{-5} to 3.0×10^{-4} mol·dm⁻³ while the other concentrations were fixed: diclofenac sodium at 5.0×10^{-4} mol·dm⁻³, periodate at 1.0×10^{-5} mol·dm⁻³, Os(VIII) at 8.0×10^{-7} mol·dm⁻³, and at constant ionic strength of 1.0 mol·dm⁻³. All kinetic runs exhibited identical characteristics. The linearity of log₁₀ (abs) versus time plots (Fig. 5) up to 80% completion of reaction for different concentrations of diperiodatocuprate(III), and the fairly constant $k_{\rm C}$ values, indicate that the reaction order with respect to the diperiodatocuprate(III) concentration is unity (Table 1).



Fig. 4 NMR spectra of the product of Os(VIII) catalyzed oxidation of diclofenac sodium by DPC





| Table 1 Effect of | f [DPC], [DFS], [OH ⁻ |], [IO ⁺] and [C | s(VIII)] on the Os(VI | III) catalyzed oxidation of | DFS by DPC in alkaline | e medium at 298 K and | $I = 1.0 \text{ mol} \cdot \text{dm}$ | -0 - |
|----------------------|----------------------------------|------------------------------|-----------------------|-----------------------------|-------------------------------------|--|---------------------------------------|---------|
| mol·dm ⁻³ | | | | | | | | |
| $[DPC] \times 10^5$ | $[DFS] \times 10^4$ | [HO] | $[IO_4] \times 10^5$ | $[Os(VIII)] \times 10^6$ | $k_{\rm T} \times 10^{2/{\rm s}-1}$ | $k_{\mathrm{U}} 	imes 10^{3} \mathrm{/s^{-1}}$ | $k_{\rm C} \times 10^2/{\rm s}^{-1}$ | ÷ |
| | | | | | | | Found calcu | lated |
| 3.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.1 | 2.8 | 1.8 | 1.7 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.0 | 3.0 | 1.7 | 1.7 |
| 8.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.1 | 3.1 | 1.8 | 1.7 |
| 10 | 5.0 | 0.5 | 1.0 | 0.8 | 2.2 | 2.9 | 1.9 | 1.7 |
| 30 | 5.0 | 0.5 | 1.0 | 0.8 | 2.1 | 3.1 | 1.8 | 1.7 |
| 5.0 | 3.0 | 0.5 | 1.0 | 0.8 | 1.6 | 2.0 | 1.4 | 1.5 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.2 | 3.0 | 1.9 | 2.0 |
| 5.0 | 8.0 | 0.5 | 1.0 | 0.8 | 2.8 | 4.1 | 2.4 | 2.3 |
| 5.0 | 10 | 0.5 | 1.0 | 0.8 | 3.1 | 5.3 | 2.6 | 2.5 |
| 5.0 | 30 | 0.5 | 1.0 | 0.8 | 3.8 | 6.5 | 3.2 | 3.3 |
| 5.0 | 5.0 | 0.1 | 1.0 | 0.8 | 1.0 | 1.2 | 0.94 | 0.96 |
| 5.0 | 5.0 | 0.3 | 1.0 | 0.8 | 1.8 | 2.0 | 1.5 | 1.6 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.2 | 3.0 | 1.9 | 2.0 |
| 5.0 | 5.0 | 0.8 | 1.0 | 0.8 | 2.4 | 3.4 | 2.0 | 2.2 |
| 5.0 | 5.0 | 1.0 | 1.0 | 0.8 | 2.6 | 4.0 | 2.2 | 2.3 |
| | | | | | | | | |

 Table 1 (Continued)

| mol·dm ⁻³ | | | | | | | | |
|----------------------|---------------------|------|----------------------|--------------------------|--------------------------------------|---|---|--------------|
| $[DPC] \times 10^5$ | $[DFS] \times 10^4$ | [HO] | $[10_4] \times 10^5$ | $[Os(VIII)] \times 10^6$ | $k_{\rm T} \times 10^2/{\rm s}^{-1}$ | $k_{\mathrm{U}} 	imes 10^3/\mathrm{s}^{-1}$ | $\frac{k_{\rm C} \times 10^{2/k}}{\text{Found calc}}$ | s-1 mated |
| 5.0 | 5.0 | 0.5 | 0.5 | 0.8 | 4.2 | 4.4 | 3.7 | 3.4 |
| 5.0 | 5.0 | 0.5 | 0.8 | 0.8 | 2.7 | 4.1 | 2.2 | 2.2 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.2 | 3.0 | 1.9 | 2.0 |
| 5.0 | 5.0 | 0.5 | 3.0 | 0.8 | 0.7 | 0.6 | 0.7 | 0.7 |
| 5.0 | 5.0 | 0.5 | 5.0 | 0.8 | 0.5 | 0.5 | 0.4 | 0.4 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.5 | 1.4 | 3.0 | 1.1 | 1.1 |
| 5.0 | 5.0 | 0.5 | 1.0 | 0.8 | 2.0 | 3.0 | 1.7 | 1.8 |
| 5.0 | 5.0 | 0.5 | 1.0 | 1.0 | 2.6 | 3.0 | 2.3 | 2.4 |
| 5.0 | 5.0 | 0.5 | 1.0 | 3.0 | 7.0 | 3.0 | 6.6 | 9.9 |
| 5.0 | 5.0 | 0.5 | 1.0 | 5.0 | 11.5 | 3.0 | 11.2 | 11.0 |
| | | | | | | | | |

3.3 Effect of the Concentration of Diclofenac Sodium

The effect of diclofenac sodium on the rate of reaction was studied at constant concentrations of alkali, DPC, periodate and Os(VIII) at a constant total ionic strength of 1.0 mol·dm⁻³. The concentration of diclofenac sodium was varied from 3.0×10^{-4} to 3.0×10^{-3} mol·dm⁻³. The $k_{\rm C}$ values increased with increasing concentration of diclofenac sodium. The reaction order with respect to diclofenac sodium was found to be less than unity ($r \ge 0.9466$, $S \le 0.008$) (Table 1). However, the order in [DFS] changes from first to zero order as [DFS] is varied.

3.4 Effect of the Concentration of Alkali

The effect of alkali on the reaction has been studied in the range of 0.1 to 1.0 mol·dm⁻³ at constant concentrations of diclofenac sodium, diperiodatocuprate(III) and periodate at a constant total ionic strength of 1.0 mol·dm⁻³ in the presence of the Os(VIII) catalyst. The rate constants increased with increasing [alkali] and the reaction order was found to be less than unity ($r \ge 0.9767$, $S \le 0.006$) (Table 1). As in the case of DFS, the reaction order in [alkali] changes from first to zero order as [OH⁻] is varied.

3.5 Effect of the Concentration of Periodate

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 5.0×10^{-6} to 5.0×10^{-5} mol·dm⁻³ while keeping all other reactant concentrations and the ionic strength fixed. It was found that the added periodate had a retarding effect on the rate of reaction. The reaction order with respect to periodate concentration was negative and less than unity ($r \ge 0.9723$, $S \le 0.005$) as shown in Table 1.

3.6 Effect of Initially Added Products

Externally added products [2-(2,6-dichlorophenylamino)-phenyl]-methanol and copper(II) sulfate did not have any significant effect on the rate of the reaction.

3.7 Effect of Ionic Strength (I) and Dielectric Constant (D) of the Medium

The addition of KNO_3 , at constant concentrations of diperiodatocuprate(III), diclofenac sodium, alkali, periodate and Os(VIII), was used to vary the ionic strength, and *t*-butyl alcohol was used to vary the dielectric constant of the reaction medium. No significant effect was observed on the rate of reaction.

Under the experimental conditions, the rate law constant is given by $k_{\rm C} = 0.020$.

3.8 Effect of the Concentration of Os(VIII)

The [Os(VIII)] concentrations was varied from 5.0×10^{-7} to 5.0×10^{-6} mol·dm⁻³, at constant concentrations of diperiodatocuprate(III), diclofenac sodium, alkali and periodate at a constant ionic strength of 1.0 mol·dm⁻³. The reaction order in [Os(VIII)] was found to be unity based on the linearity of the plot of $k_{\rm C}$ versus [Os(VIII)].

3.9 Polymerization Study

The possible intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed indicating the formation of a polymer by intervention of free radicals in the reaction. Blank experiments with either DPC or DFS alone with acrylonitrile did not produce any polymerization under the same conditions as those used for the reaction mixture. Initially added acrylonitrile decreases the rate of reaction indicating free radical intervention, which was also found to be the case in earlier work [26, 27].

4 Effect of Temperature

The kinetics were studied at four different temperatures with varying concentrations of diclofenac sodium, alkali, periodate and Os(VIII), keeping other conditions constant. The rate constants were found to increase with increasing temperature. The rate constants (k) of the slow step of Scheme 1 were obtained from the slopes and intercepts of plots of [Os(VIII)]/ k_c versus 1/[DFS] at the four different temperatures and their values were used to calculate activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of $\log_{10} k$ versus 1/T ($r \ge 0.8011$), and other activation parameters were also obtained as reported in Tables 2a, 2b, 2c.

4.1 Catalytic Activity

It has been pointed out by Moelwyn-Hughes [28] that in presence of the Os(VIII) catalyst, the uncatalyzed and catalyzed reactions proceeds simultaneously so that

$$k_{\rm T} = k_{\rm U} + K_{\rm C} [\rm Os(VIII)]^x$$
⁽²⁾

Here, $k_{\rm T}$ is the observed pseudo-first order rate constant in the presence Os(VIII), $k_{\rm U}$ the pseudo-first order rate constant for the uncatalyzed reaction, $K_{\rm C}$ is the catalytic constant, and 'x' is the order of the reaction with respect to [Os(VIII)]. In the present investigations, the x value for the standard run was found to be unity. Then, the value of $K_{\rm C}$ was calculated using Eq. 4 as follows

$$K_{\rm C} = \frac{k_{\rm T} - k_{\rm U}}{\left[\mathrm{Os}(\mathrm{VIII})\right]^x} = \frac{k_{\rm C}}{\left[\mathrm{Os}(\mathrm{VIII})\right]} \tag{4}$$

where $k_{\rm T} - k_{\rm U} = k_{\rm C}$. The values of $K_{\rm C}$ were evaluated at the four different temperatures and found to vary with temperature. Furthermore, plots of $\log_{10} K_{\rm C}$ versus 1/T were linear and the values of the energy of activation and other activation parameters, with reference to the catalyst, were computed. These results are summarized in Table 3.

The water soluble copper(III) periodate complex is reported [29] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in aqueous alkaline medium and at the high pHs 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 multiple dissociation equilibria [30], Eqs. 4–6, that depend on the pH of the solution:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{4}$$

$$\mathrm{H}_{4}\mathrm{IO}_{6}^{-} \rightleftharpoons \mathrm{H}_{3}\mathrm{IO}_{6}^{2-} + \mathrm{H}^{+} \tag{5}$$



Scheme 1 Detailed scheme for the Os(VIII) catalyzed oxidation of DFS by diperiodatecuprate(III) in aqueous alkaline medium

$$\mathrm{H}_{3}\mathrm{IO}_{6}^{2-} \rightleftharpoons \mathrm{H}_{2}\mathrm{IO}_{6}^{3-} + \mathrm{H}^{+} \tag{6}$$

Periodic acid exists in acidic media as both H_5IO_6 and $H_4IO_6^-$ around pH = 7. However, under the employed in alkaline conditions, the main species are expected to be $H_3IO_6^{2^-}$ and $H_2IO_6^{3^-}$. At higher concentrations, periodate also tends to dimerize [31]. Hence, at the pHs employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)_2(OH)_2]^{3^-}$, a conclusion that is also supported by earlier work [32, 33].

Osmium(VIII) is known to form different complexes at different OH^- [34] concentrations, $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher OH^- concentrations, $[OsO_5(OH)]^{3-}$ becomes significant. At lower concentrations of OH^- , as employed in the present study, and because the rate of oxidation increased with increasing $[OH^-]$, it is reasonable to assume that $[OsO_4(OH)_2]^{2-}$ was operative and that its formation is important in the reaction [34].

| for the Os(VIII) catalyzed | Effect of temperatur | e | | |
|---|--|---|---|--|
| oxidation of DFS by DPC in | Temperature (K) | | $k \times 10^{-5} c$ | $\text{Im}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ |
| respect to the slow step of | 288 | | 1.3 | |
| Scheme 1 | 298 | | 2.3 | |
| | 308 | | 3.5 | |
| | 318 | | 4.3 | |
| | Activation paramete | rs (Scheme 1) | | |
| | Parameters | | | Values |
| | $E_{\rm a}$ (kJ·mol ⁻¹) | | | 30.7 ± 1.0 |
| | $\Delta H^{\#} (\text{kJ} \cdot \text{mol}^{-1})$ | | | 28.2 ± 1.4 |
| | $\Delta S^{\#} (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathrm{mol}^{-1})$ |) | | -48.9 ± 6.0 |
| | $\Delta G^{\#} (\text{kJ} \cdot \text{mol}^{-1})$ | | | 42.3 ± 4.0 |
| | $\log_{10} A$ | | | 10.7 ± 0.2 |
| Table 2b Effect of temperature on the calculated K_1 , K_2 and K_3 values for the Os(VIII) catalyzed oxidation of DES by DPC in | Temperature (K) | $\frac{K_1}{(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})}$ | $\frac{K_2 \times 10^5}{(\text{mol} \cdot \text{dm}^{-3})}$ | $\frac{K_3 \times 10^{-3}}{(\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})}$ |
| alkaline medium | 288 | 5.8 | 0.28 | 3.0 |
| | 298 | 4.8 | 0.4 | 2.0 |
| | 308 | 3.6 | 0.66 | 1.4 |
| | 318 | 2.4 | 0.9 | 0.9 |
| T-bla 2. The main demonstra | | | | |
| auantities derived from K_1 , K_2 | Thermodynamic | Values from | Values from | Values from |
| and K_3 | quantities | K_1 | K_2 | <i>K</i> ₃ |
| | $\Delta H (\text{kJ} \cdot \text{mol}^{-1})$ | -22 ± 1 | 31.2 ± 2.6 | -30.5 ± 2.2 |
| | $\Delta S (J \cdot K^{-1} \cdot mol^{-1})$ | -63 ± 5 | 4.7 ± 8 | -39 ± 3.0 |
| | $\Delta G \; (\text{kJ} \cdot \text{mol}^{-1})$ | -3.2 ± 0.1 | 30.4 ± 1.2 | -18.8 ± 1.0 |
| | | | | |

Effect of temperature

Table 2a Activation parameters

In an earlier report [18], it was concluded in the Os(VIII) catalyzed reaction, in view of its less than unit order in substrate, and unit order in Os(VIII) and oxidant, that Os(VIII) is regenerated through formation of a Os(VII). In another study [19], it was concluded that Os(VIII) was regenerated by Os(VI) intervention in view of unit orders in osmium, substrate and oxidant. In another report [20] it was observed that Os(VIII) formed a complex with the substrate, which was oxidized by the oxidant with regeneration of the catalyst. Hence, the study of behavior of Os(VIII) in catalyzed reaction becomes significant. To explain the observed orders, the following Scheme 1 is proposed for our osmium(VIII) catalyzed reaction. The reaction between the diperiodatocuprate(III) complex and diclofenac sodium in alka-

line medium has a stoichiometry of 1:2 (DFS:DPC), with a first order reaction dependences on [DPC] and Os(VIII), less then unit apparent orders in [DFS] and $[OH^{-}]$, and a negative fractional order in [periodate]. No effect of added products was observed. Based on these experimental results, a mechanism is proposed for which all the observed reaction orders in [oxidant], [reductant], $[OH^-]$, $[IO_4^-]$, and Os(VIII) may be well accommodated. Lis-

| Table 3 Values of the catalyticconstant (K_C) at different | Temperature (K) | $K_{\rm C} \times 10^{-2}$ |
|---|--|----------------------------|
| temperatures and activation parameters calculated using | 288 | 1.2 |
| the $K_{\rm C}$ values | 298 | 1.9 |
| | 308 | 3.8 |
| | 318 | 4.7 |
| | $E_{\rm a} (\rm kJ \cdot mol^{-1})$ | 34.7 |
| | $\Delta H^{\#} (\text{kJ} \cdot \text{mol}^{-1})$ | 32.2 |
| | $\Delta S^{\#} (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathrm{mol}^{-1})$ | -169 |
| | $\Delta G^{\#} (\text{kJ} \cdot \text{mol}^{-1})$ | 82 |
| | $\log_{10} A$ | 4.4 |

ter [35] proposed that three forms of copper(III) periodate occur in alkaline medium, diperiodatocuprate(III) (DPC), monoperiodatocuprate(III) (MPC), and tetrahydroxycuprate(III). Hence, in the present study, DPC and MPC are considered to be the active forms of the copper(III) periodate complex. In view of the inverse fractional order in $[IO_4^-]$, it may be expected that a lower periodate complex such as MPC is more important than DPC in the reaction. The increase in reaction rate with increasing alkali concentration, and decrease in the rate with increasing periodate concentration, suggest that equilibria of different copper(III) periodate complexes may be involved as shown in Eqs. 7 and 8:

$$\left[\operatorname{Cu}(\mathrm{H}_{2}\mathrm{IO}_{6})(\mathrm{H}_{3}\mathrm{IO}_{6})\right]^{2-} + \mathrm{OH}^{-} \stackrel{K_{1}}{\longleftrightarrow} \left[\operatorname{Cu}(\mathrm{H}_{2}\mathrm{IO}_{6})_{2}\right]^{3-} + \mathrm{H}_{2}\mathrm{O}$$
(7)

$$[Cu(H_2IO_6)_2]^{3-} + 2H_2O \stackrel{K_2}{\rightleftharpoons} [Cu(H_2IO_6)(H_2O)_2] + [H_2IO_6]^{3-}$$
(8)

Anionic species of diclofenac sodium react with osmium(VIII) species to form a complex (C), which then reacts with one mole of MPC in a slow step to give the free radical of diclofenac and a Cu(II) species with regeneration of the catalyst osmium(VIII). Furthermore, this free radical of diclofenac reacts with one more mole of MPC in a fast step to yield the products [2-(2,6-dichlorophenylamino)-phenyl]-methanol, Cu(II) and periodate as given in Scheme 1.

The probable structure of complex (C) is



Spectroscopic evidence for complex formation between the catalyst and substrate was obtained my measuring the UV-vis spectra of DFS ($5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$), Os(VIII) ($8.0 \times 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$), [OH⁻] = 0.5 (mol·dm⁻³), mixtures. A bathochromic shift of about 4 nm was observed from 278 to 282 nm in the spectra of DFS. Attempts to separate and isolate the complex were not successful. A Lineweaver-Burk plot also proved that complex formation

occurred between the catalyst and DFS, which explains the less than unit order concentration dependence on DFS. The rate law for Scheme 1 can then be derived as

$$rate = -\frac{d[DPC]}{dt}$$

$$= \frac{kK_1K_2K_3[DPC][DFS][OH^-][Os(VIII)]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][DFS]} + K_3[H_3IO_6^{2-}][DFS] + K_1K_3[DFS][OH^-][H_3IO_6^{2-}]$$
(9)

$$\frac{\text{rate}}{[\text{DPC}]} = k_{\text{C}} = k_{\text{T}} - K_{\text{U}}$$

$$= \frac{kK_1K_2K_3[\text{DFS}][\text{OH}^-][\text{Os}(\text{VIII})]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{DFS}]} + K_3[\text{H}_3\text{IO}_6^{2-}][\text{DFS}] + K_1K_3[\text{DFS}][\text{OH}^-][\text{H}_3\text{IO}_6^{2-}]$$
(10)

which explains all the observed kinetic orders on the concentrations of the different species.

The rate law Eq. 10 can be rearranged into the following form that is suitable for verification.

$$\frac{[Os(VIII)]}{k_{C}} = \frac{[H_{3}IO_{6}^{2-}]}{kK_{1}K_{2}K_{3}[OH^{-}][DFS]} + \frac{[H_{3}IO_{6}^{2-}]}{kK_{2}K_{3}[DFS]} + \frac{[H_{3}IO_{6}^{2-}]}{kK_{1}K_{2}[OH^{-}]} + \frac{[H_{3}IO_{6}^{2-}]}{kK_{2}} + \frac{1}{kK_{3}[DFS]} + \frac{1}{k}$$
(11)

According to Eq. 11, plots of $[Os(VIII)]/k_C$ versus $1/[OH^-]$ ($r \ge 0.986$), of $[Os(VIII)]/k_C$ versus 1/[DFS] ($r \ge 0.9917$), and of $[Os(VIII)]/k_C$ versus $[H_3IO_6^{2^-}]$ ($r \ge 0.9923$) were linear (Figs. 6a, b and c). From the slopes and intercepts of such plots, the reaction constants K_1, K_2, K_3 and k were calculated as $(4.8 \pm 0.1) \text{ dm}^3 \cdot \text{mol}^{-1}$, $(0.4 \pm 0.02) \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, $(2.0 \pm 0.1) \times 10^3 \text{ dm}^3 \cdot \text{mol}^{-1}$ and $(13.2 \pm 0.5) \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ respectively. The values of K_1 are in good agreement with a literature value [36]. Using these constants, the rate constants under different conditions were regenerated (Table 1).

The thermodynamic quantities for the first, second and third equilibrium steps of Scheme 1 can be evaluated as follows. The $[H_3IO_6^{2-}]$, [DFS] and $[OH^-]$ (as in Table 1) were varied at the four different temperatures. The plots of $[Os(VIII)]/k_c$ versus 1/[DFS], $[Os(VIII)]/k_C$ versus $1/[OH^-]$, and $[Os(VIII)]/k_C$ versus $[H_3IO_6^{2-}]$ were all linear (Figs. 6a, b and c). From their slopes and intercepts, the values of K_1 , K_2 and K_3 were calculated at different temperatures and these values are given in Table 2. The van't Hoff's plots were made for the variation of K_1 , K_2 and K_3 with temperature: $\log_{10} K_1$ versus 1/T $(r \ge 0.8494, S \le 0.004), \log_{10} K_2$ versus 1/T $(r \ge 0.9339, S \le 0.007)$ and $\log_{10} K_3$ versus 1/T ($r \ge 0.8322$, $S \le 0.008$), and the values of enthalpy of reaction ΔH , entropy of reaction ΔS and Gibbs energy of reaction ΔG were calculated for all three equilibrium steps. These values are given in Table 2. A comparison of the ΔH value $(31.2 \pm 2.2 \text{ kJ} \cdot \text{mol}^{-1})$ for second equilibrium step of Scheme 1 with that of $\Delta H^{\#}$ (28.2 ± 1.4 kJ·mol⁻¹) of the rate limiting step supports that the conclusion that the second step of Scheme 1 is fairly slow since it involves a high activation energy. The modest $\Delta H^{\#}$ and $\Delta S^{\#}$ values are favorable for an electron transfer processes. The negative value of $\Delta S^{\#}$ indicates that the intermediate complex (C) is more ordered than the reactants [37].

Fig. 6 (a) Plots of $[Os(VIII)]/k_C$ against 1/[DFS] at four different temperatures (conditions as in Table 1); (b) plots of $[Os(VIII)]/k_C$ against $1/[OH^-]$ at four different temperatures (conditions as in Table 1); (c) plot of $[Os(VIII)]/k_C$ versus $[H_2IO_6^{3-}]$ at 298 K (conditions as in Table 1)



The value of $\Delta S^{\#}$ is within the range for radical reactions, which are ascribed [38] to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of a rigid transition state. The negligible effects from ionic strength and dielectric constant changes are in the right direction as shown in Scheme 1. The observed modest enthalpy of activation and the relatively low entropy of activation, as well as a higher rate constant for the slow step, indicate that the oxidation probably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [39]. The activation parameters evaluated for the catalyzed and un-

1307

catalyzed reaction explain the catalytic effect on the reaction. The Os(VIII) catalyst forms complex (C) with the substrate, which enhances the reducing property of the substrate over that found in the absence of catalyst. Furthermore, Os(VIII) modifies the reaction path by lowering the activation energy.

5 Conclusion

The Os(VIII) catalyzed oxidation of DFS by DPC was studied. Oxidation products were identified. Among the various species of DPC present in alkaline medium, monoperioda-tocuprate(III) (MPC) is considered as the active species for the title reaction. The active species of Os(VIII) is $[OsO_4(OH)_2]^{2-}$. Activation parameters were evaluated for various steps of the proposed mechanism. Catalytic constants and activation parameters with reference to the catalyst were also computed.

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Appendix

According to Scheme 1,

$$Rate = \frac{-d[DPC]}{dt} = -k[C][Cu(H_2IO_6)(H_2O)_2]$$
$$= \frac{kK_1K_2K_3[DFS]_f[Os(VIII)]_f[DPC]_f[OH^-]}{[H_3IO_6^{2^-}]}$$
(11)

The total concentration of DPC [DPC] is given with subscripts T and f (for total and free, respectively).

$$[DPC]_{T} = [DPC]_{f} + [Cu(H_{2}IO_{6})(H_{3}IO_{6})^{2-}] + [Cu(H_{2}IO_{6})(H_{2}O)_{2}]$$

$$= [DPC]_{f} + K_{1}[OH^{-}][DPC]_{f} + \frac{K_{1}K_{2}[DPC]_{f}[OH^{-}]}{[H_{3}IO_{6}^{2-}]}$$

$$= [DPC]_{f} \left\{ 1 + K_{1}[OH^{-}] + \frac{K_{1}K_{2}[OH^{-}]}{[H_{3}IO_{6}^{2-}]} \right\}$$

$$= [DPC]_{f} \left\{ \frac{[H_{3}IO_{6}^{2-}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2-}] + K_{1}K_{2}[OH^{-}]}{[H_{3}IO_{6}^{2-}]} \right\}$$
(12)

Therefore

$$[DPC]_{f} = \frac{[DPC]_{T}[H_{3}IO_{6}^{2^{-}}]}{[H_{3}IO_{6}^{2^{-}}] + K_{1}[OH^{-}][H_{3}IO_{6}^{2^{-}}] + K_{1}K_{2}[OH^{-}]}$$
(13)

Similarly,

$$[DFS]_{T} = [DFS]_{f} + [complex(c)]$$
$$= [DFS]_{f} + K_{3}[DFS][Os(VIII)]$$
$$= [DFS]_{f}\{1 + K_{3}[Os(VIII)]\}$$

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and therefore

$$[DFS]_{\rm f} = \frac{[DFS]_{\rm T}}{1 + K_3[Os(\rm VIII)]}$$
(14)

Because the concentrations of osmium(VIII) used are very small,

$$[DFS]_{T} \cong [DFS]_{f} \tag{15}$$

$$[Os(VIII)]_{T} = [Os(VIII)]_{f} + [complex(C)]$$

= [Os(VIII)]_{f} + K_{3}[DFS][Os(VIII)]_{f}
= [Os(VIII)]_{f} \{1 + K_{3}[DFS]\} (16)

and thus

$$[Os(VIII)]_{f} = \frac{[Os(VIII)]_{T}}{1 + K_{3}[DFS]}$$
(17)

Similarly,

$$[OH^{-}]_{T} = [OH^{-}]_{f} + [Cu(H_{2}IO_{6})(H_{3}IO_{6})^{2-}] + [Cu(H_{3}IO_{6})(H_{2}O)_{2}]$$

=
$$[OH^{-}]_{f} + K_{1}[OH^{-}]_{f}[DPC] + \frac{K_{1}K_{2}[OH^{-}]_{f}[DPC]}{[H_{3}IO_{6}^{-}]}$$
(18)

and thus

$$[OH^{-}]_{f} = \frac{[OH^{-}]_{T}[H_{3}IO_{6}^{2-}]}{[H_{3}IO_{6}^{2-}] + K_{1}[H_{3}IO_{6}^{2-}][DPC] + K_{1}K_{2}[DPC]}$$
(19)

In view of low concentrations of DPC and $H_3IO_6^{2-}$ used,

$$[OH^{-}]_{T} \cong [OH^{-}]_{f} \tag{20}$$

Substituting Eqs. 13, 15, 17 and 20 in Eq. 11 and omitting the T and f subscripts we get

$$rate = -\frac{d[DPC]}{dt}$$

$$= \frac{kK_1K_2K_3[DPC][DFS][OH^-][Os(VIII)]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][DFS]} + K_3[H_3IO_6^{2-}][DFS] + K_1K_3[DFS][OH^-][H_3IO_6^{2-}]$$
(21)

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