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Osmium(VIII)-Catalyzed Kinetics and Mechanism of Indigo Carmine Oxidation by Chloramine-B in Basic Medium

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Indigo carmine (IC) or sodium indigotin disulfonate is a natural dye that finds applications in clinical diagnosis, chemistry and biology. The osmium(VIII)-catalyzed oxidation of IC by chloramine-B (CAB) in alkaline solutions has been spectrophotometrically monitored at the indigo carmine λ_{max} of 610 nm at 298 K. The reaction stoichiometry has been found to be 1:4 (mol:mol), resulting in the formation of major products that are the sodium salt of sulfonated anthranilic acid (SAA) and benzenesulfonamide (BSA). The reaction shows a first-order dependence of the rate on [IC], a fractional-order dependence each on [Os(VIII)] and [OH$^-$], and a zero-order dependence each on [CAB], [BSA], and [SAA]. The variation of the ionic strength of the reaction medium has a negligible effect on the rate. Based on the effect of temperature in the range 288–313 K, activation parameters are evaluated from Arrhenius and Eyring plots. A mechanism consistent with the observed kinetic and activation data has been proposed and a rate law has been derived.

Keywords benzenesulfonamide, catalyst, chloramine-B, indigo carmine, mechanism, osmium(VIII), oxidation, product, rate law, reduction, stoichiometry, sulfonated anthranilic acid

INTRODUCTION

Indigo carmine (IC or 2,2′-bis(2,3-dihydro-3-oxoindolyliden)) is also called indigotin, indigo dye, and Saxon blue, which is a chemical derivative of indigo. Pharmaceutical applications of IC include the preparation of stable chitosan nanoparticle films.[1] Results of the study of Laccase activity using IC indicated that a high concentration of NaCl would be beneficial to textile industries, and IC was used in the detoxification of effluent waste with excess NaCl and other metal salts.[2] Moreover, it is used in the determination of cationic surfactant present in wastewater.[3] In ophthalmology, during vitreoretinal surgery, dyes such as IC are commonly used to differentiate and facilitate the delicate removal of intraocular membranes. Indigo carmine was found to be very safe for retinal staining with minimum toxicity.[4] Indigotin disulfonate is also used as a dye in renal function testing and as a reagent for the detection of hypochlorites and chlorates in milk.[5] In the cosmetic industry, indigo combined with henna yields a brunette color, which is widely used in hair dyeing.[6] The denim textile industry widely uses IC for blue coloring of jeans.[7] In analytical chemistry and biology, it finds application as a redox indicator and microscopic stain, respectively. Rodd has reviewed the chemistry of IC and indigotin compounds.[8] Using the inhibitory effect on the oxidation of IC by $KBrO_3$ in micellar media, a rapid, sensitive spectrophotometric method based on kinetics for the determination of I$^-$ has been developed.[9] It is also used in the determination of selenium(IV).[10]. The reported oxidation products of IC are istain sulfonate (IS) and sulfonated anthranilic acid (SAA). Anthranilic acid derivatives are used as intermediates for production of dyes and pigments. Their esters are used in the preparation of perfumes, pharmaceuticals, and ultraviolet (UV) absorbers, as well as corrosion inhibitors for metals, and mold inhibitors in soya sauce.[6,7]

The major sources of inorganic chloramines, such as NH_2Cl, $NHCl_2$, and NCl_3, in water are the reactions of ammonia and its derivatives with added chlorine.[11] Organic chloramines are poorer disinfectants than inorganic chloramines.[12] The oxidation reactions of aromatic sulfonylhaloamines such as chloramine-B (CAB) and chloramine-T (CAT) have been extensively studied.[13–19]

Oxidations of IC by CAT, dichloramine-T, bromamine-T, and hypochlorites in acidic and basic solutions have been reported.[19-22] In these studies, a pseudo-first-order condition of [IC] >> [oxidant] have been used. There is no report on the oxidation of IC by CAB in basic medium. In this study, we report the kinetics and mechanism of Os(VIII)-catalyzed IC oxidation by CAB in NaOH medium using a pseudo-first-order condition of [CAB] >> [IC].

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EXPERIMENTAL

Indigo carmine and CAB used were from Aldrich Chemical Co. Sodium thiosulfate (Spectrum Chemicals, USA), potassium iodide and iodate (MCB reagents), and potassium hydrogen phthalate and osmium tetroxide (Fisher Chemical Co.) were used. All chemicals were of accepted analytical grades of purity. Double-distilled water was used in all solutions.

Stock aqueous solutions of approximately decimolar CAB were prepared, iodometrically standardized, and stored in amber-colored bottles. A fresh aqueous solution of decimolar IC was prepared in an amber bottle to prevent photochemical effects. A stock solution of 0.0100 *M* OsO_4 in 0.0100 *M* NaOH was prepared. While studying the catalyst effect on the reaction rate, the amount of NaOH added in the form of the OsO_4 solution was taken into consideration in calculating the overall [NaOH] in the reaction mixture.

Kinetic Measurement

Kinetic runs were performed under pseudo-first-order conditions of a large excess of the oxidant (CAB) over IC at 25°C. For each run, requisite amounts of solutions of IC, OsO_4 (when necessary), and NaOH (to maintain a constant base strength) were mixed in a stoppered glass tube. The required amount of water was added to maintain a constant total volume. The tube was thermostated in a water bath at a given temperature. To initiate the reaction, a measured amount of the preequilibrated

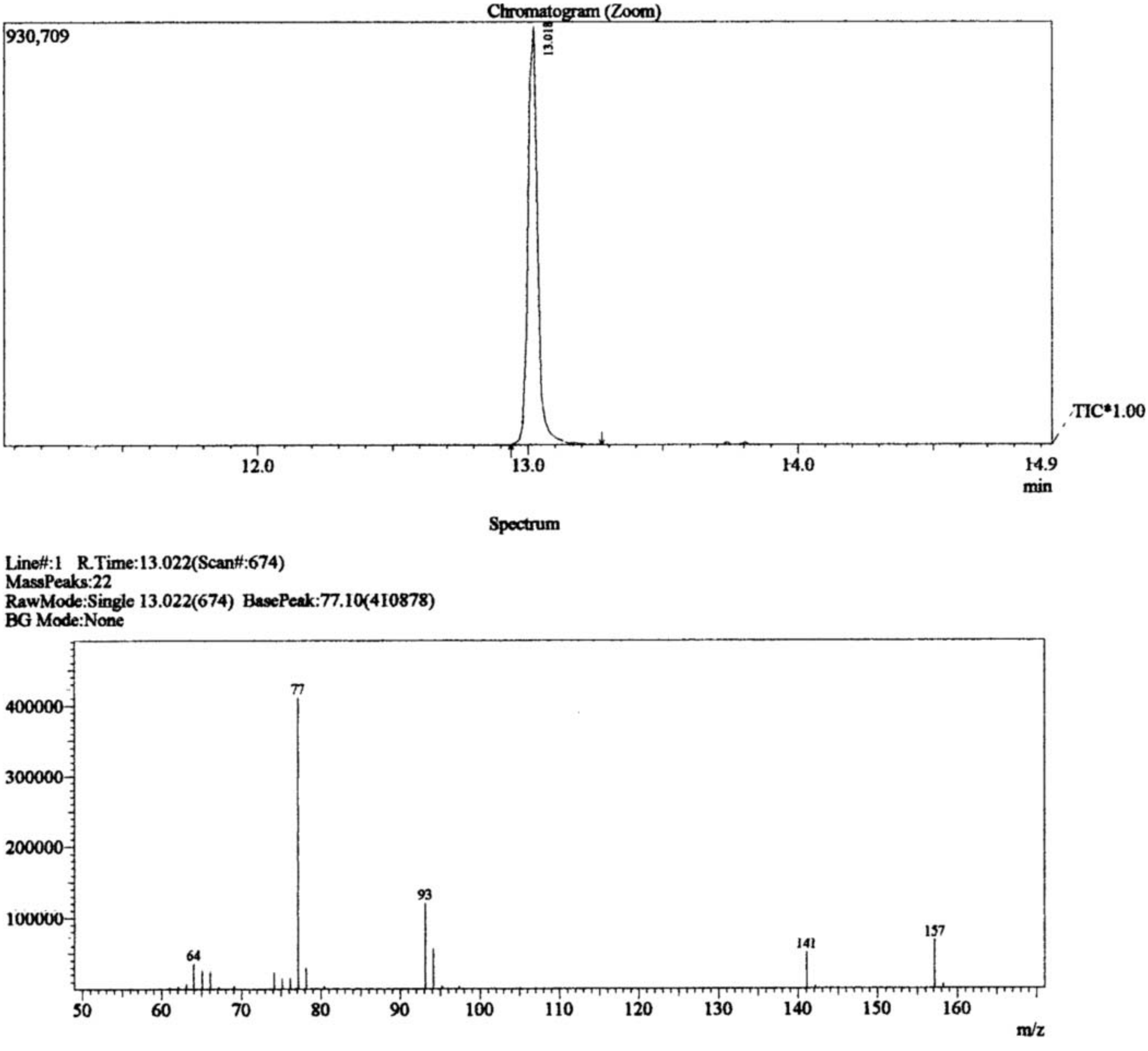


FIG. 1. Chromatogram (top) and mass spectrum (bottom) of the reduction product, BSA.

standard CAB solution was added to give a known overall concentration in the reaction mixture. The reaction mixture was taken in a cuvette of 1 cm pathlength to monitor the reaction on a Shimadzu ultraviolet–visible (UV-Vis) model 1601 spectrophotometer fitted with a temperature controlling unit or thermostat. Absorbances were measured at the IC λ_{max} of 610 nm at varying time intervals for 5 h. Pseudo-first-order plots of ln(abs) versus time were plotted where each slope gave the pseudo-first-order rate constant, k' or k_{obs}. Each run was performed in duplicate and the mean of two values was taken. The calculated k' values were reproducible within an error of ±3%.

Determination of Stoichiometry for the IC Oxidation by CAB

Reaction mixtures containing varying compositions maintaining [CAB] >> [IC] in 0.100 *N* NaOH were prepared and kept at 25°C with stirring for varying time intervals: 1, 5, 10, 20, 30, 40, and 48 h. At the end of the time period, [CAB] in each reaction mixture was iodometrically determined using starch indicator near the end point.

Product Analysis

Reaction mixtures containing $[CAB]_o >> [IC]_o$ in 0.100 *N* NaOH were kept stirring for 48 h at 25°C. The aqueous reaction mixture was thrice subjected to liquid–liquid extraction with dichloromethane–petroleum ether mixtures (1:1 v/v). The less polar organic layer had benzenesulfonamide (BSA), which was the reduction product of CAB, while the aqueous layer contained the polar compounds, including the oxidation product of IC, sodium salt of sulfonated anthranilic acid (SAA), unreacted CAB, and one of the reduction products NaCl. The combined organic layer was concentrated with a rotary evaporator to separate BSA, which was then recrystallized from hot MeOH. Of the reaction products, BSA was identified by thin-layer chromatography (TLC) using *n*-BuOH–glacial acetic acid–water (4:1:5 v/v/v) as the solvent mixture and iodine as the developing agent ($R_f = 0.17$).[19] Furthermore, BSA was analyzed on Shimadzu GC/MS (model 5050) with the following conditions: temperature = 80–250°C and pressure = 72 kPa. The mass spectrum showed a parent M^+ ion peak at 157 amu, confirming BSA (Figure 1). The formation of the oxidation product, SAA, is indicated by a shift in the λ_{max} of IC in the visible spectrum of the IC–CAB reaction mixture (Figure 2). Furthermore, amounts of SAA present in the reaction mixtures were quantitatively analyzed using a standard method[22] involving the precipitation of SAA as its zinc(II) salt, $Zn(C_7H_6O_5NS)_2$. Another oxidation product, CO_2, was detected by the conventional lime–water test[19].

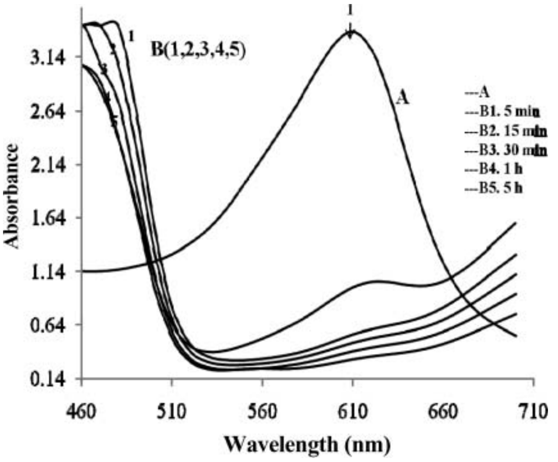


FIG. 2. Electronic absorption spectra: (A) Curve with λ_{max} at 610 nm, indigo carmine (IC) solution. (B) Curves 1–5 are for the IC–CAB reaction mixture at various reaction times. Conditions: $[IC]_o = 1.00 \times 10^{-4}\,M$; $[CAB]_o = 5.00 \times 10^{-3}\,M$; $[NaOH] = 0.100\,M$; temperature 298 K.

Test for Free Radicals

Alkene monomers such as acrylonitrile and acrylamide (a freshly prepared 10% solution), under nitrogen atmosphere, were added to the IC–CAB reaction mixtures in 0.10 *M* NaOH to initiate polymerization in the presence of free radicals formed *in situ.* Flasks were kept overnight in dark. A suitable control without the IC–CAB mixture was also run under the same conditions.

RESULTS AND DISCUSSION

Reaction Stoichiometry

Preliminary results of the reaction in 0.100 *N* NaOH solutions showed that 4 moles of CAB were consumed per mole of IC. The reaction forms sodium salt of sulfonated anthranilic acid (SAA) derivative and CO_2 as the oxidation products of IC, and BSA and NaCl as the reduction products of CAB. The reaction stoichiometry is represented by the following equation:

$$\underset{(IC)}{C_{16}H_8O_8S_2N_2Na_2} + \underset{(\text{anion of CAB})}{4PhSO_2NCl^-} + 6H_2O \longrightarrow \underset{(SAA)}{2C_7H_6O_5NSNa} + \underset{(BSA)}{4PhSO_2NH_2} + 2CO_2 + 4Cl^-. \quad [1]$$

Kinetics

Effect of Indigo Carmine Concentration

Under pseudo-first-order conditions, $[CAB]_o >> [IC]_o$, at constant [NaOH] and temperature; the $[IC]_o$ was varied. Plots of ln Abs versus time were linear, indicating a first-order dependence of the rate on $[IC]_o$. The pseudo-first-order rate constants (k') calculated from the slopes of Ln (Abs)-time plots are presented in Table 1. The values of k' were unaltered with the variation of $[IC]_o$ further confirming the first-order dependence of the rate on $[\text{substrate IC}]_o$.

TABLE 1
Effect of varying concentrations of CAB, indigo carmine (IC), and NaOH on the reaction rate at 298 K

$[CAB]_o$ (10^{-3}M)	$[IC]_o$ (10^{-4}M)	[NaOH] (10^{-1}M)	k′ (10^{-4} s^{-1})
1.00	1.00	1.00	7.40
5.00	1.00	1.00	7.48
7.50	1.00	1.00	7.50
25.0	1.00	1.00	7.55
50.0	1.00	1.00	7.58
10.0	1.00	1.00	1.82 (2.47)[a]
10.0	1.00	1.00	1.82 (2.10)[a]
10.0	1.00	1.00	1.82 (1.84)[b]
10.0	1.00	1.00	1.82 (2.03)[b]
10.0	1.00	1.00	1.82 (1.72)[c]
10.0	1.00	1.00	1.82 (1.90)[c]
10.0	1.00	1.00	1.82
10.0	2.00	1.00	1.89
10.0	5.00	1.00	1.84
10.0	10.0	1.00	2.11
10.0	15.0	1.00	1.76
10.0	6.0	0.0100	0.817
10.0	6.0	0.0500	1.20
10.0	6.0	0.100	1.72
10.0	6.0	0.500	4.44
10.0	6.0	2.00	9.72

[a] Values in parentheses refer to ionic strength variation: $[NaClO_4] = 0.010$ *M* and 0.25 *M*.

[b] Values in parentheses refer to variation of $[BSA] = 1.0 \times 10^{-4}$ *M* and 5.0×10^{-3} *M*.

[c] Values in parentheses refer to variation of $[SAA] = 1.0 \times 10^{-3}$ *M* and 7.50×10^{-3} *M*.

Effect of Chloramine-B Concentration

When the initial concentration of CAB was varied while keeping all other conditions the same, the rate did not change with the increase in $[CAB]_o$ (Table 1). This indicated a zero-order dependence of the rate on $[CAB]_o$ (Figure 3).

Effect of Hydroxide Ion Concentration

An increase in the NaOH concentration in the reaction mixture, when all other conditions were kept constant, increased the reaction rate. A linear plot of ln k′ versus ln $[OH^-]$ was obtained with the slope showing a fractional order (0.400) dependence on $[OH^-]_o$ (Figure 4).

Effect of Ionic Strength

The rate constant was determined at various concentrations of $NaClO_4$ in the range 0.010–0.25 *M*. The other reaction conditions were the same. The rate did not change, suggesting zero effect of the ionic strength on the rate (Table 1). As a result, the ionic strength in the reaction mixture was not maintained constant for all other runs.

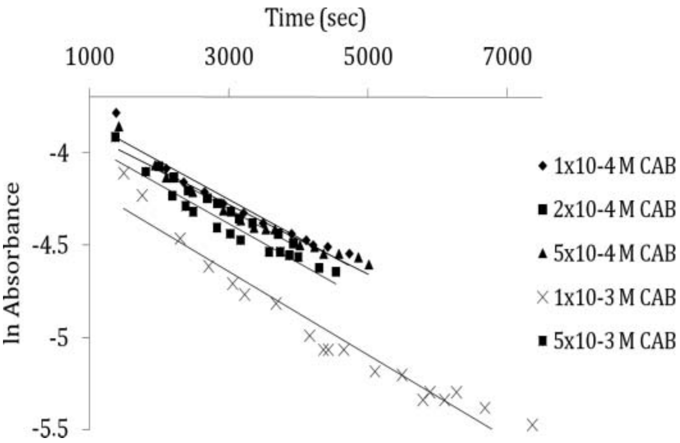


FIG. 3. Pseudo-first-order plots with approximately constant slopes for different concentrations of oxidant: $[CAB]_o = 1.00 \times 10^{-4}$ *M* to 5.00×10^{-3} *M*; $[IC]_o = 1.00 \times 10^{-4}$ *M*; [NaOH] = 0.100 *M*; temperature 298 K.

Effect of Concentration of Products

The effect of varying concentrations of the products, BSA and SAA, on the reaction rate was studied. Isatin sulfonate (IS), which is an intermediate in the reaction, has been used in place of the end product, SAA, to test the effect of SAA. Increasing concentrations of BSA or IS (SAA) had no significant effect on the rate, showing zero order in each case (Table 1).

Effect of Varying Dielectric Constant

The rate of reaction decreased slowly when the permittivity (D) of the medium was decreased by adding MeOH (0–30%, v/v) to the reaction mixtures.

Effect of Osmium Tetroxide Concentration

The rate of reaction increased with increasing [Os(VIII)]. A plot of ln k′ versus ln [Os(VIII)] was linear with a slope of

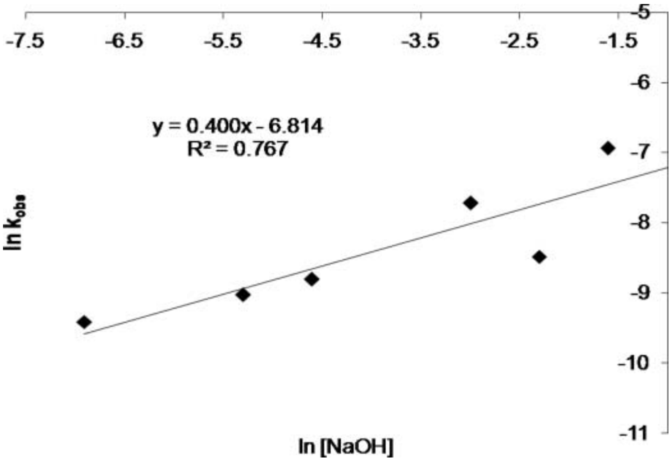


FIG. 4. A ln–ln plot for the determination of the hydroxide ion order.

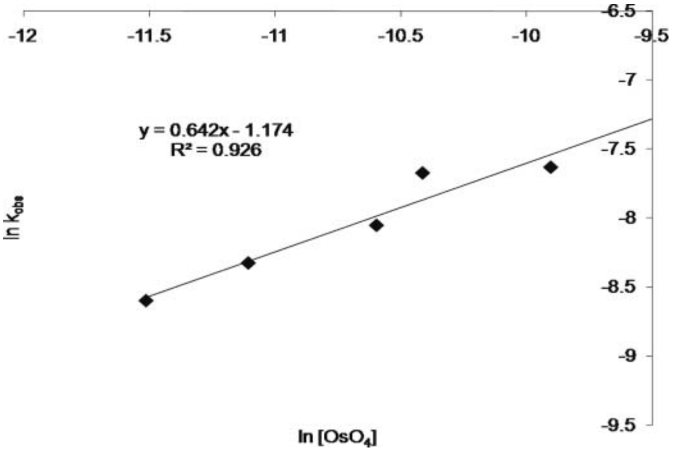


FIG. 5. A ln–ln plot for the determination of the OsO_4 order.

0.64, indicating a fractional order dependence on $[Os(VIII)]_o$ (Figure 5).

Effect of Temperature

Kinetic runs were performed at various temperatures ranging from 288 to 313 K, while keeping the other experimental conditions the same. Based on the linear Arrhenius plot of log k′ versus 1/T and the Eyring plot of ln *k*′/T versus 1/T (Figure 6), activation parameters, namely, energy of activation (E_a), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$), were calculated. These results are summarized in Table 2.

Detection of Free Radicals

The free radical sensitive test with monomers, acrylamide and acrylonitrile, was found to be negative. The absence of *in situ* formation of free radicals in the reaction mixtures was confirmed by a lack of turbidity or precipitation of the polymer product.

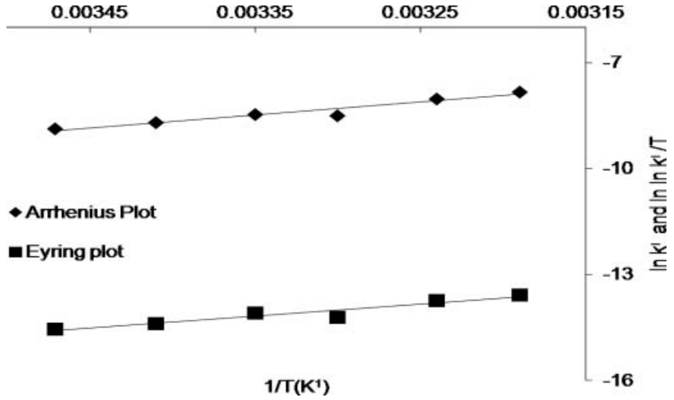


FIG. 6. Effect of temperature on the rate: (A) Arrhenius plot; (B) Eyring plot.

TABLE 2

Rate constants (k′) at different temperatures and activation parameters for the indigo carmine (IC) oxidation by CAB in alkaline solutions[a]

Temperature (K)	k′ (10^{-4} s^{-1})
288	1.38
293	1.65
298	2.10
308	3.30
313	3.96
E_a (kJ mol^{-1})	3.06
$\Delta H^{\neq}$ (kJ mol^{-1})	28.4
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	–220
$\Delta G^{\neq}$ (kJ mol^{-1})	94.0[b]

[a] Reaction conditions: $[CAB]_o = 1.00 \times 10^{-2}$ *M*; $[IC]_o = 1.00 \times 10^{-4}$ *M*; [NaOH] = 0.100 *M*.

[b] $\Delta G^{\neq}$ value at 298 K.

Reaction Mechanism

The observed 1:4 stoichiometry of the oxidation of IC by CAB in basic medium results in the formation of major products SAA and BSA, is shown in Eq. (1).

In aqueous solutions, CAB and CAT behave as electrolytes. Some of the important equilibria exhibited by them include Eqs. (2)–(6).[3–14,22]

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad [2]$$

$$ArSO_2NCl^- + H^+ \rightleftharpoons ArSO_2NHCl \quad [3]$$

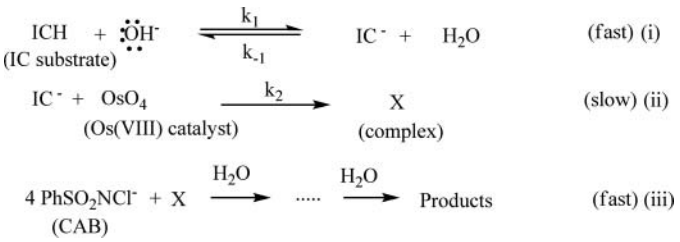
$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NHCl + OH^- \quad [4]$$

$$ArSO_2NCl^- + H_2O \rightleftharpoons ArSO_2NH_2 + OCl^- \quad [5]$$

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-, \quad [6]$$

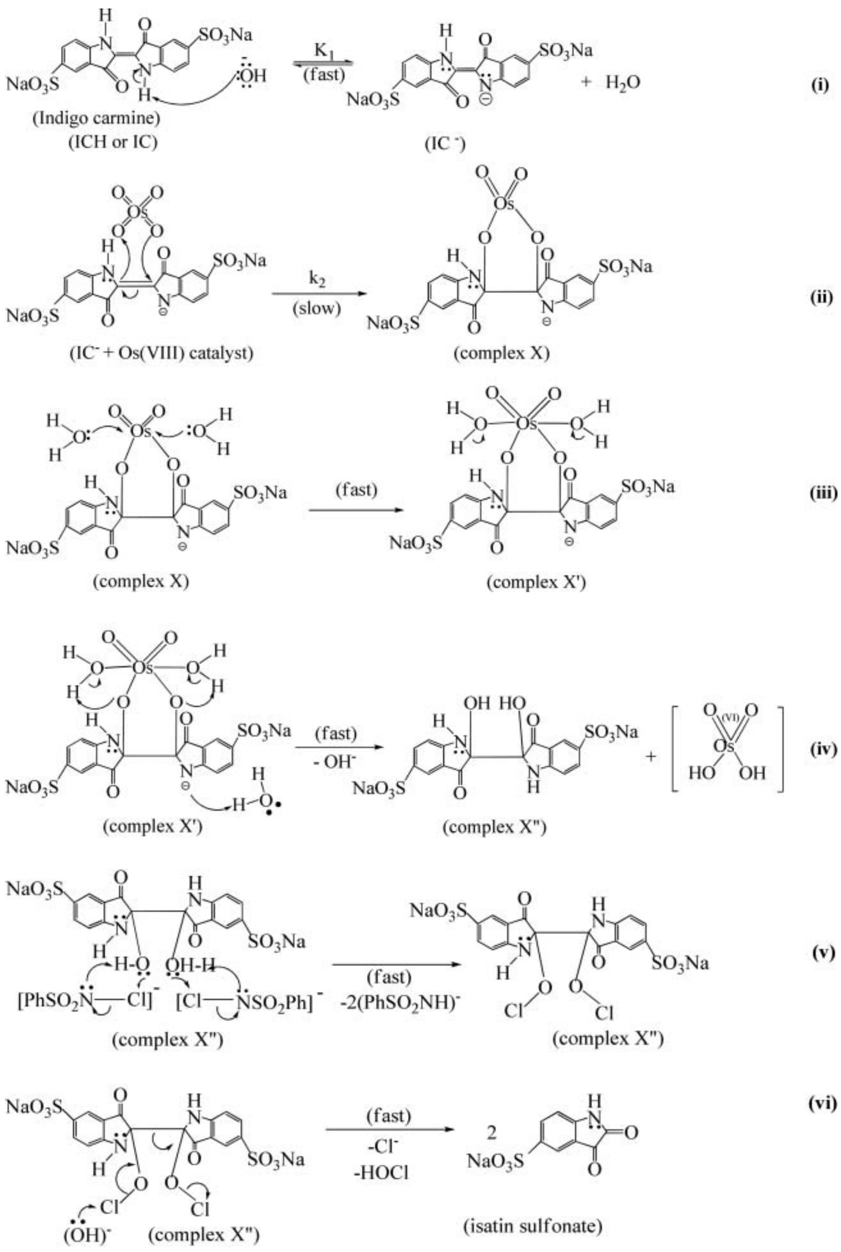
where Ar = Ph or C_6H_5- for CAB and *p*-Me-C_6H_4- for CAT

In acid solutions, the first two equilibria [Eqs. (2) and (3)] predominate. In alkaline medium, the other three equilibria exist, leading to the possible reactive species $ArSO_2NCl^-$, $ArSO_2NHCl$, OCl^-, and HOCl. The species $ArSO_2NCl^-$ and OCl^- could be transformed into more reactive oxidizing species, $ArSO_2NHCl$ and HOCl, through reactions Eqs. (4)–(6). If OCl^- and HOCl were the primary oxidizing species as shown in Eqs. (5) and (6), a first-order retardation of the rate by the added $ArSO_2NH_2$ (sulfonamide) would be expected. This is contrary to the experimental observations. A retarding influence of OH^- ions on the reaction rate, observed in many reactions of CAB and CAT, has been attributed to the formation of the conjugate acid $ArSO_2NHCl$ from $ArSO_2NCl^-$ through the reaction in Eq. (4). The catalyzing effect of OH^- ions (a positive fractional order) observed here suggests the $ArSO_2NCl^-$ ion to be the reactive oxidizing species involved in the oxidation of IC. The weak N-Cl bond in haloamines is implicated in the oxidizing effect through their ability to release Cl^+ species.

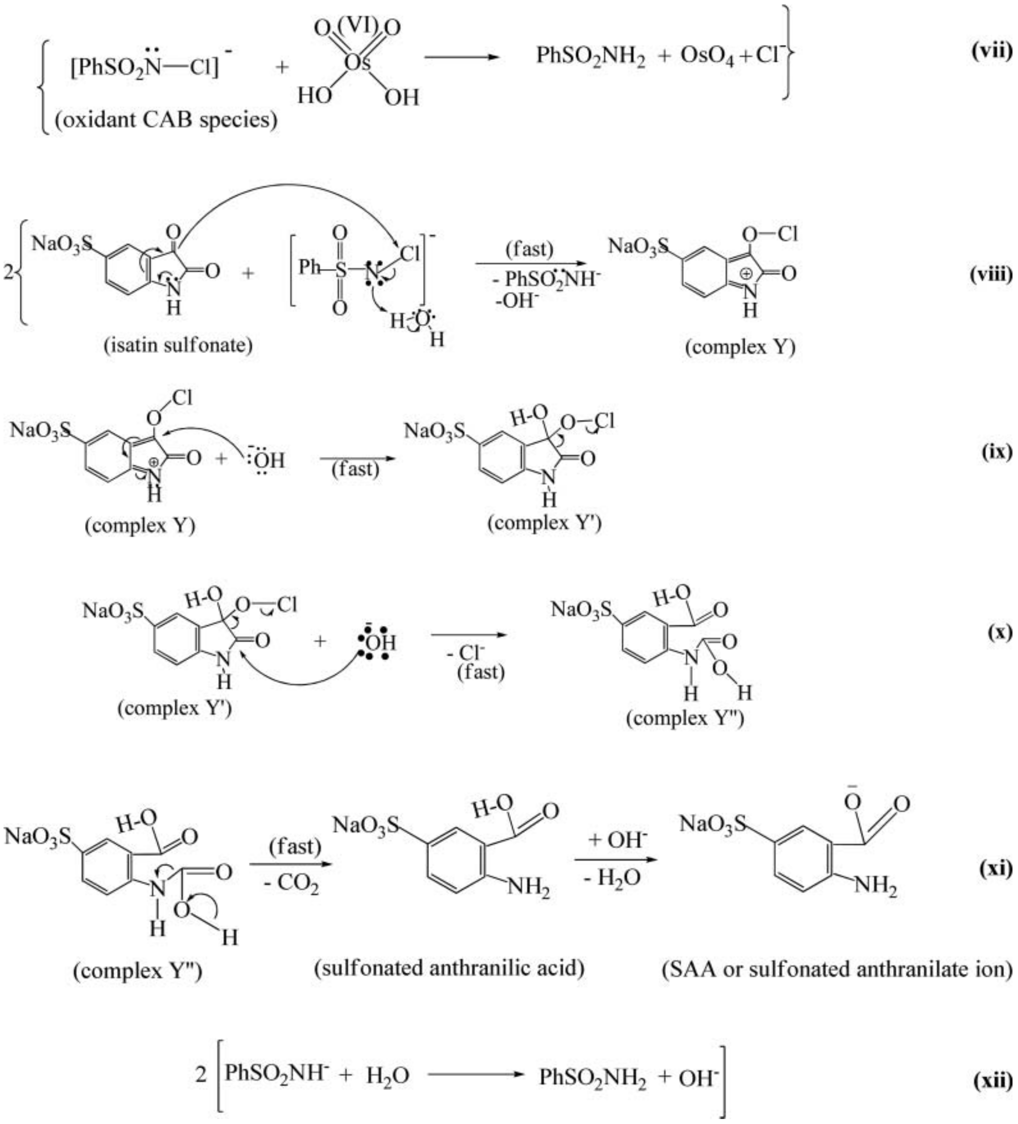


SCH. 1. A simple mechanistic scheme for the Os(VIII)-catalyzed IC–CAB reaction in basic medium.

Kinetic data show that the reaction follows a first-order dependence of the rate on $[IC]_o$; a fractional-order each on $[OH^-]$ and [Os(VIII) catalyst]; and a zero-order each on [CAB], [BSA], and [SAA]. Free radicals were not formed in the reaction mixtures. The rate showed a negative effect on the solvent dielectric constant. Furthermore, the rate was not affected by the variation of ionic strength. On the basis of the preceding discussion, a simple mechanism (Scheme 1) has been proposed for the reaction in basic solutions.



SCH. 2. A detailed mechanism for the Os(VIII)-catalyzed indigo carmine oxidation by CAB in NaOH solutions.



SCH. 2. (Continued).

Structures of the complex X presented in Scheme 1 and other intermediate species are shown in Scheme 2, where a detailed mechanistic interpretation of Os(VIII)-catalyzed IC-CAB reaction in alkaline medium is illustrated. In the fast preequilibrium (step (i)), an OH^- ion abstracts a proton from the amino group of ICH or IC to form an IC^- ion and H_2O. In the rate-determining process (slow step (ii)), the IC^- ion interacts with the catalyst, OsO_4, to form the complex intermediate (X). The reaction of the catalyst–IC complex with the reactive oxidant species, $(PhSO_2NCl)^-$, yields in several fast steps [(iii)–(xii)] the oxidation end product, a salt of sulfonated anthranilic acid (SAA). Scheme 2 is consistent with the reported mechanisms for similar reactions.[18,23]

Rate Law Derivation

From slow step (ii) of Scheme I,

$$\text{rate} = k_2[IC^-][Os(VIII)] \qquad [7]$$

Application of the steady state concept to the intermediate IC^- species leads to eq. (8)

$$\frac{d[IC^-]}{dt} = k_1[IC][OH^-] - k_{-1}[IC^-][H_2O] - k_2[IC^-] \times [Os(VIII)] = 0 \qquad [8]$$

$$[IC]_o = [IC] + [IC^-] \quad \text{or} \quad [IC] = [IC]_o - [IC^-] \qquad [9]$$

Substitution for [IC] from eq. (9) into eq. (8) and solving for $[IC^-]$ leads to eq. (10).

$$[IC^-] = \frac{k_1[IC]_o\,[OH^-]}{k_1[OH^-] + k_{-1}[H_2O] + k_2\,[Os(VIII)]} \qquad [10]$$

Substitution for $[IC^-]$ from eq. (10) in eq. (7) gives eq. (11).

$$\text{rate} = \frac{k_1 k_2[IC]_o[OH^-][Os(VIII)]}{k_{-1}[H_2O] + k_1[OH^-] + k_2[Os(VIII)]} \qquad [11]$$

If both the numberator and the denominator of eq. (11) are divided by k_{-1}, the rate law below (eq. (12)) is obtained. $[H_2O]$ is nearly constant.

$$\text{rate} = \frac{K_1 k_2[IC]_o[OH^-][Os(VIII)]}{1 + K_1[OH^-] + k_2/k_{-1}[Os(VIII)]} \qquad [12]$$

As the reaction is performed in aqueous solutions, the constant $[H_2O]$ is omitted in the rate law. The rate law (Eq. (12)) reduces to the following pseudo-first-order form, as $[CAB]_o >> [IC]_o$, at known concentrations of reactants and catalyst: rate $= k_{obs}\,[IC]_o$, which leads to the following equation:

$$k_{obs} = k' = \frac{K_1 k_2[OH]^-\,[Os(VIII)]}{1 + K_1[OH^-] + k_2/k_{-1}\,[Os(VIII)]} \qquad [13]$$

Since k_{-1} is larger than k_2 and [Os(VIII)] is low, the last term becomes smaller as compared to the magnitudes of the first two terms. Hence it can be neglected.

$$k' = \frac{K_1 k_2[OH^-]\,[Os(VIII)]}{1 + K_1[OH^-]}$$

Or

$$1/k' = \frac{1}{K_1 k_2[OH^-]\,[Os(VIII)]} + \frac{1}{k_2\,[Os(VIII)]} \qquad [14]$$

To test the validity of Eq. (14), the reaction was performed at varying $[OH^-]$ with $[Os(VIII)] = 2.50 \times 10^{-5}$ *M*. A linear double reciprocal plot of $1/k'$ versus $1/[OH^-]$ yielded a slope $= 1/\{K_1k_2[Os(VIII)]\}$ and an intercept $= 1/k_2[Os(VIII)]$. Calculated values of equilibrium constant, K_1 (fast step (i)) and the complex formation rate constant, k_2 (slow step (ii)) are 404.4 and 10.8 $M^{-1}\,s^{-1}$, respectively. These values are supportive of Scheme 1 and 2.

The derived rate law (Eq. (12)) is in good agreement with the experimental kinetic results such as a first-order dependence on [IC], a fractional-order dependence each on [Os(VIII)] and $[OH^-]$, and a zero-order dependence each on [CAB], [BSA], and [SAA]. The zero-effect of the ionic strength indicates the involvement of a neutral species in the rate-determining step (slow step (ii)) in Scheme 1. Both the reduction product of the oxidant, benzenesulfonamide (BSA or $PhSO_2NH_2$), and the oxidation product of IC, SAA, do not influence the rate, showing that they are not involved in any preequilibrium. These observations are supportive of the proposed mechanism.

The proposed reaction mechanism and the derived rate law are also supported by the following experimental facts: Bronsted and Bjerrum[24] have explained the primary salt effect on the reaction rates through the following relation:

$$\log k' = \log k_o + 1.02\,Z_A Z_B \mu^{1/2}, \qquad [15]$$

where μ is the ionic strength of the medium, A and B are the reacting ions, Z_A and Z_B are charges on the respective species, and k' and k_o are rate constants in the presence and absence of the added electrolyte, respectively. According to Eq. (15), a plot of log k' versus $\mu^{1/2}$ should be linear with a slope of 1.02 Z_AZ_B and intercept of log k_o. As the slope of the line depends on Z_AZ_B, the reaction rate may increase, decrease, or remain unaffected with the ionic strength of the medium. In the present case, variation of ionic strength of the medium (0.010–0.25 *M* $NaClO_4$) does not alter the rate, which signifies that at least one of the reactants is a neutral molecule as shown in step (ii) of Scheme 1. Hence, the observed ionic strength effect is consistent with the Bronsted–Bjerrum concept[24] for the proposed scheme.

The MeOH effect also provides support to the proposed mechanism (Schemes 1 and 2). The effect of solvents on the reaction kinetics has been described by House,[25] Entelis and Tiger,[26], Amis,[27] and Richardt.[28] For a limiting case of zero angle of approach between two dipoles or an ion–dipole system, Amis[27] has shown that a plot of log k' versus 1/D is linear with a negative slope for interactions between a negative ion and a dipole or between two diploes, while a positive slope results for the positive ion–dipole interactions. The negative dielectric effect observed in the present studies clearly supports the anion–dipole interactions in the rate determining step (step (ii) of Scheme 1).

Solvent isotope studies have shown that the rate of reaction is higher in D_2O medium for acid- or base-catalyzed reactions.[29,30] For a reaction involving a fast preequilibrium with H_3O^+ or OH^- ion transfer, the rate increases in D_2O medium since D_3O^+ and OD^- are stronger acid and stronger base, respectively, than H_3O^+ and OH^- ions. In the present case, the observed solvent isotope effect $k'(D_2O)/k'(H_2O) > 1$ is due to the greater basicity of OD^- compared to OH^-. However, the magnitude of acceleration in D_2O is small as compared with the expected value of 2 to 3 times greater, which is reflective of the fractional-order dependence of the rate on $[OH^-]$.

The mechanism is supported by moderate values of energy of activation and other activation parameters. The fairly high positive values of free energy of activation and enthalpy of activation indicate that the transition state is highly solvated, while the negative entropy of activation suggests an associative, rigid transition state with less degrees of freedom. Furthermore, the negative $\Delta S^{\neq}$ suggests that the redox reaction is controlled by entropy instead of enthalpy.

CONCLUSIONS

The redox reaction involving CAB oxidation of IC in the presence of the Os(VIII) catalyst in basic solutions has been investigated. The reaction stoichiometry has been found to be 1:4 (mol/mol).

The Os(VIII)–IC complex formation in the IC–CAB reaction in NaOH solutions has been monitored spectrophotometrically at the IC λ_{max} of 610 nm at constant temperature to generate kinetic data.

The experimental rate law has been found to be: rate $= k'[\mathrm{IC}][\mathrm{OH^-}]^{0.40}\,[\mathrm{Os(VIII)}]^{0.64}$. A suitable mechanism consistent with the experimental data has been proposed, based on which a rate law has been derived.

The activation parameters E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ have been determined to understand whether the reaction is controlled by entropy or enthalpy. The negative $\Delta S^{\neq}$ indicates the rigid transition-state formation and the entropy-controlled reaction.

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