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Kinetic and Mechanism Study of the Oxidative Decolorization of Neutral Red by Bromate in Micellar Medium

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The kinetics of the oxidation of neutral red by bromate was investigated in the presence of cationic surfactant (N-dodecylpyridinium chloride) and strongly acidic media over the temperature range 22-35 °C. The kinetic studies were carried out as a function of different variables like concentration and temperature. The described reaction rate is greatly catalyzed by the presence of trace amount of Fe(II) ions and followed by pseudo-third-order kinetics with respect to dye concentration. A possible mechanism for the catalyzed reaction is offered which is found to be coincidentally congruent with experimental findings. The derived rate equation is in good agreement with the experimental observations. Thermodynamic parameters were also evaluated.

Keywords: Kinetic, Bromate, Neutral red, Surfactant, Mechanism

INTRODUCTION

Potassium bromate is a powerful oxidizing agent [1]. It has been used for the oxidation of various organic compounds. A quick look at the literature shows that bromate has been used as an oxidant for different dyes. The oxidation of dyes has received considerable attention for the past few years [2-4]. The interest has been stimulated by environmental, commercial and social pressures, but particularly by environmental concerns over residual dyes present in wastewater streams which cause aesthetic pollution. Bromate has carcinogenic potential and that is why it has adverse human health effects. It has a moderately strong ability to cause oxidation reactions.

Many kinetic studies have been carried out in which chromogenic reagents were oxidized by BrO_3^- [5]. Although, previous studies have taken important steps forward in generating empirical rules concerning oxidation, further scrutiny is still required to develop a full understanding of the subject.

Neutral red (phenazine, 3-amino-7-(diethylamino)-2-methyl-, hydrochloride) (NR) is a heterocyclic species which belongs to the basic class of dyes. This cationic dye, which is stable for a day with absorption peak at 535 nm, was chosen as a representative species for this study. A number of papers have been published on the oxidation of neutral red (reductive chromogenic agent) by various oxidizing agents [6,7]. However, oxidation by the bromate has not yet been reported. Metal ions have been proved to assist the decolorization of various dyes [8,9].

The aim of this study was to investigate the kinetic aspects of the reaction and the thermodynamic parameters such as the activation energy, the enthalpy $\Delta H^‡$, the entropy $\Delta S^‡$, and the free energy change $\Delta G^‡$. It also describes the effect of temperature, foreign ion and surfactant on the catalyzed oxidation of neutral red (NR) by bromate. A possible reaction mechanism is also offered.

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EXPERIMENTAL

Equipments

All Kinetic and spectrophotometric measurements were performed on a UV-Vis spectrophotometer (shimadzu, Japan 160-A) at 535 nm. The cell compartment of the spectrophotometer was equipped with constant temperature cell holder attached to thermostatic controlled bath with a temperature stability of ±0.05 ºC. A digital Orion 710 pH meter was used for pH measurements with an accuracy of ±0.001.

Reagents

All chemicals were of analytical reagent grade (BDH). Stock of 1.0 × 10^{-2} M neutral red was prepared by accurately weighing 0.288 g and dissolved in 100 ml of pH 2.60 buffer (HCl & KH phthalate). Stock solution of neutral red was stable for a day.

Solution of 0.10 M potassium bromate was prepared by weighing 0.167 gm and diluted up to 100 ml. The working solution of BrO_3^- was prepared just before use.

Stock solution of 0.10 M cationic surfactant (N-Dodecyl pyridiniumchloride) was prepared by weighing 2.800 g and dissolved in 100 ml of water.

Kinetic Run

A dry pyrex 25 ml volumetric flask was used to mix 3.5 ml of $KBrO_3$ (0.10 M), 3.75 ml of 0.10 Mcationic surfactant (N-dodecylpyridinium chloride), and an appropriate amount of Fe(II) standard solution (ammonium Fe(II) sulphate). This mixture was kept in a water bath at 30 ºC for five min. Finally 10.5 ml solution of neutral red (1.00 × 10^{-4} M) was added to the same flask and buffer solution of pH 2.60 was used to dilute the reaction mixture up to the mark. Absorbance of the reaction mixture was measured every 240 seconds at 535 nm in 1-cm glass cells against a buffer reference (Fig. 1).

RESULTS AND DISCUSSION

Effect of pH

The investigated reaction was studied in the range of 2.20 to 3.00. It was observed that at 2.60 pH there was a maximum discrimination between the rate of catalyzed and uncatalyzed reactions as shown in Fig. 2 [11]. Thus, this pH was selected for use in the subsequent studies.

Kinetics of the Catalyzed Reaction

With to the intention of finding effective metal catalysts for the decolorization reaction, the effect of a wide range of cations monovalent, divalent and trivalent cations were investigated. Mg(II), Pb(II), Ce(III), Hg(II), Se(IV), Bi(III), Zn(II), Cu(II), Cr(III), Co(II) and Fe(III) were found to have no effect on the reaction rate with [NR] = 4.2 × 10^{-5} M and [BrO_3^-] = 1.4 × 10^{-2} M. However, Fe(II) demonstrated significant catalyzing ability and hence further studies were made using this as a catalyst.

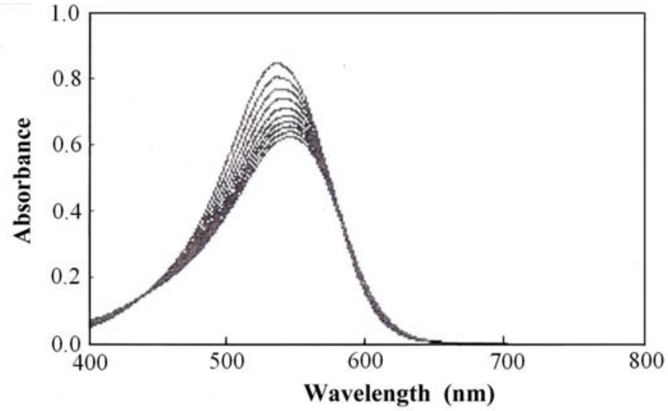

Fig. 1. Variation of the absorbance of neutral red-bromate-cationic surfactant system in the presence of 2 µg ml^{-1} Fe(II) with time for a 120 s interval. Conditions: neutral red concentration, 4.2 × 10^{-5} M; bromate concentration, 1.40 × 10^{-2} M; concentration of N-dodecyl pyridinium chloride, 1.5 × 10^{-2} M; temperature, 30 ºC at pH 2.60.

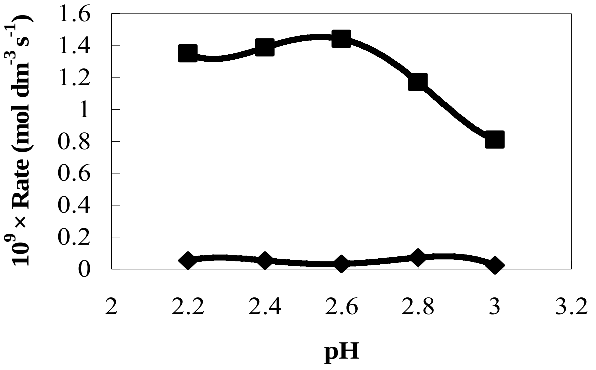

Fig. 2. Effect of pH on blank (■) and catalyzed (◆) reactions at 30 °C. Conditions: 1.4×10^{-2} M BrO_3^- and 4.20×10^{-5} M NR.

Effect of Surfactant

It is well-established that, in many cases, the rate and pathways of all kinds of chemical reactions can be altered by performing the reactions in micellar media instead of pure solvents [12,13]. Micellar effect on the rate of chemical and biochemical processes can be quite varied, ranging from inhibition to activation [14]. These kinetic effects are generally explained in terms of the partition of the substrate between the aqueous and the micellar phase. Surfactants affect reaction rate by incorporating one or both of the reactants into the micellar aggregates. Many research results have been reported in the literature showing the accelerating or inhibitory effects of anionic, cationic and non- ionic surfactants [15-20].

Table 1. Effects of Surfactants Tested for the Enhanced Rate of Neutral Red-Fe(II)-BrO_3^- Reaction

Surfactants	Type	Effect
SDS[a]	Anionic	Negative
Triton X-100	Non-ionic	Negative
N-dodecylpyridinium Chloride	Cationic	Positive

[a]Sodium dodecylsulfate

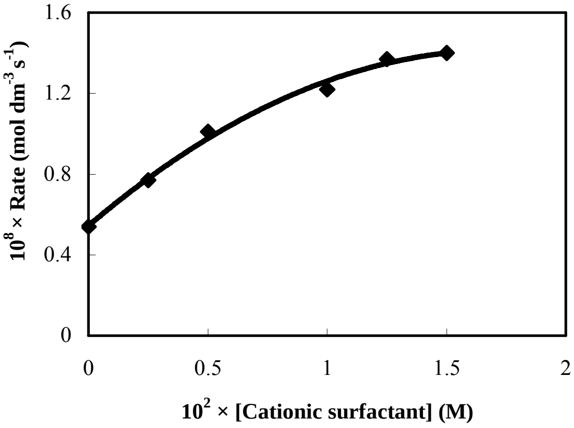

Fig. 3. Effect of concentration of N-dodecylpyridinium chloride on rate at 30 °C. Conditions: 1.4×10^{-2} M BrO_3^-, 4.20×10^{-5} M NR and 3.5×10^{-5} M Fe^{2+} at pH 2.60.

In order to choose an appropriate micellar system for the reaction, one must take into account the type of charge on the reactants, because the accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface [21]. SDS, Triton X-100 and N-dodecylpyridinium chloride are anionic, non-ionic and cationic surfactants, respectively (Table 1). The enhancement effect of cationic surfactant was observed on Fe(II)-catalyzed reaction. Results indicated that NR, which is a cationic dye, was incorporated into the cationic micelles by hydrophobic attraction, which is sufficiently intense to overcome electrostatic repulsion between dyes and micelles of similar charge. This is in agreement with the previous findings [22-24]. In the study of association between anionic dye to different types of surfactants, a similar interaction was observed between anionic micelles and anionic dye in spite of electrostatic repulsion [25]. The kinetic runs were also proceeded for the different concentrations of cationic surfactant to select its appropriate concentration (Fig. 3). Rate of catalyzed reaction in the presence of cationic surfactant was investigated in which 1.5×10^{-2} M has maximum rate. Thus, 1.5×10^{-2} M of N-dodecylpyridinium chloride was chosen to accelerate the rate of Fe(II) catalyzed reaction.

Effect of Temperature

The activation energy (*Ea*) for catalyzed reaction was studied by measuring the rate constants at different temperatures using the Arrhenius equation (Fig. 4). The value of *Ea* was calculated 111.06 kJ mol^{-1} for Fe(II)-catalyzed

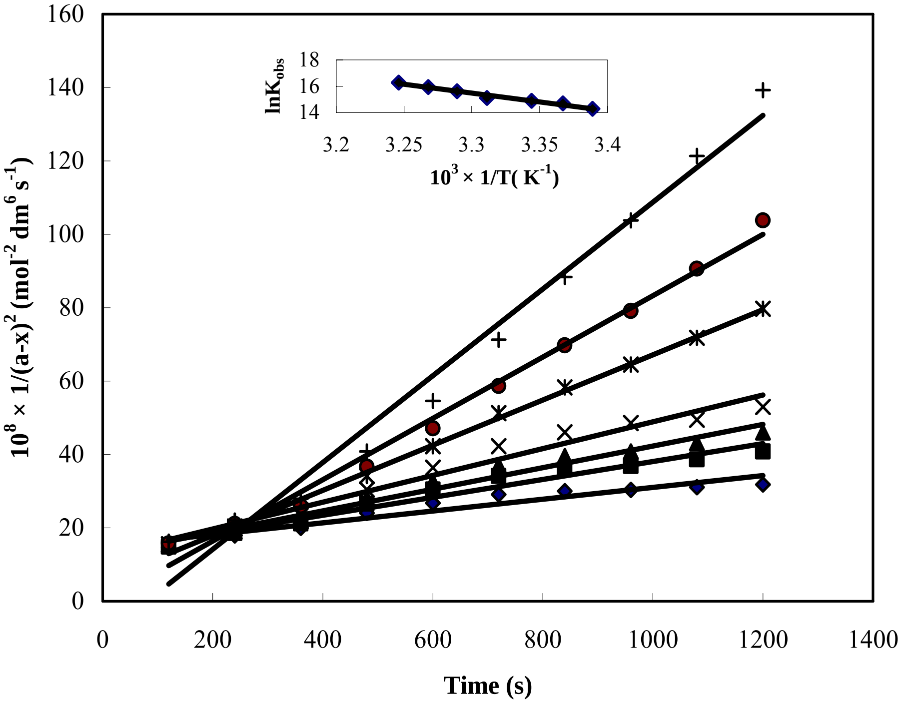

Fig. 4. Effect of temperature on Fe^{2+} catalyzed reaction at pH 2.60 and varying temperatures: (◆) 295 K, (■) 297 K, (▲) 299 K, (×) 302 K, (✳) 304 K, (●) 306 K and (+) 308. Conditions: 1.4×10^{-2} M BrO_3^-, 4.20×10^{-5} M NR and 3.9×10^{-5} M Fe^{2+}. Inset shows the Arrhenius plot for Fe^{2+} catalyzed reaction.

reaction. Values of other parameters at 299 K, namely the enthalpy, entropy and Gibb's free energy are calculated and summarized in Table 2.

In associative reaction, reaction step being bimolecular with two species forming an activated complex resembling a single species, there will be a decrease in entropy and enthalpy on activation. Whereas, dissociative reaction being unimolecular and the activated complex resembling an incipient two (or more) species, increase in entropy and enthalpy would result. A reaction somewhere within these two extremes is termed interchange; the entropy is likely to be small [26] and enthalpy has a value in between. $\Delta S^‡$ is very small, with +ve sign, whereas, $\Delta H^‡$ values are large or slightly large. The values of entropy and enthalpy for the proposed reaction as shown in Table 2 reveal that the proposed reaction may be an interchange reaction. Reaction between ions of unlike signs, expect a gain in entropy. $\Delta S^‡$ and $\Delta H^‡$. Ion-molecule reaction expects a small increase in $\Delta S^‡$ *i.e.* entropy is slightly +ve and it expects a slightly larger value for $\Delta H^‡$. $\Delta G^‡$ was also calculated and illustrated in Table 2. The thermodynamic parameters at 299 K show that reaction was endothermic with positive values of $\Delta H^‡$ and $\Delta G^‡$.

Table 2. Activation Parameters for the Oxidation Reaction of Neutral Red and BrO_3^- at 299 K

Parameter	Value
$^a\Delta H^‡$	108.50 kJ mol^{-1}
$^b\Delta S^‡$	0.241 J mol^{-1} K^{-1}
$^c\Delta G^‡$	36.21 kJ mol^{-1}
E_a	111.06 kJ mol^{-1}

$^a\Delta H^‡ = E_a - RT$. $^b\Delta S^‡ = \Delta H^‡/T - R\ln(T/k) - R\ln(T/h)$. $^c\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$.

Mathematical Justification of the Reaction

To evaluate mathematical relationship two facts must be considered: (a) the uncatalyzed reaction proceeds simultaneously with the catalyzed reaction, and (b) the rate of the catalyzed reaction is directly or nearly proportional to the concentration of catalyst [27].

For the reaction

$$3R + B \xrightarrow{c} P + Y \tag{1}$$

where R and B are reactants (R = monitored species), P and Y are products, and c is the catalyst. On the basis of the observations obtained by the kinetic runs the following general expression can be written:

$$-\frac{d\,[R]}{dt} = k_u\,[R]^3 + k_c\,[R]^3\,[c]_0$$

$$-\frac{d\,[R]}{dt} = [R]^3\,(k_u + k_c\,[c]_0) \tag{2}$$

in which k_u = the rate coefficient for the uncatalyzed reaction (plus some concentration terms), k_c = the rate coefficient for the catalyzed reaction (plus some concentration terms), and $[c]_0$ = the initial concentration of catalyst in the system. For catalytic cycle we can use simplified two-step reaction scheme shown below to develop mathematical relationships between catalytic rate and catalyst concentration.

Another important practical requirement needed for successful application is that concentrations of reactants, other than the catalyst and the species whose change in concentration is monitored, must be kept as to make their effect on the rate pseudo-zero-order. The species whose change in concentration is being monitored is adjusted to third-order dependence.

$$3R + c \xleftrightarrow[k_{-1}]{k_1} (Rc) + Y \tag{3}$$

$$(Rc) + B \xrightarrow{k_2} P + c \tag{4}$$

This simplified mechanism for the catalytic cycle leads to two boundary conditions.

(a) pre-equilibrium case, and

(b) steady-state situation

Pre-equilibrium condition. If $k_1 << k_{-1}$ and $k_2 << k_1$, the reaction represented by Eq. (4) becomes rate determining and we have the pre-equilibrium condition. Under this condition the equilibrium concentration of the species (Rc) can be obtained from Eq. (3).

$$[Rc] = k\,\frac{[c]\,[R]^3}{[Y]} \tag{5}$$

where K = k_1/k_{-1} = equilibrium concentration quotient for reaction 3.

The equilibrium concentration of $[c]_0$ and $[R]_0$ at time t can be defined as

$$[R] = [R]_0 - [(Rc)] \tag{6}$$

$$[c] = [c]_0 - [(Rc)] \tag{7}$$

In catalytic methods, $[R]_0 >> [c]_0$ therefore, $[R]$ can be considered equal to $[R]_0$ and hence

$$[(Rc)] = \frac{k\,(\,[c]_0 - [(Rc)]\,)\,[R]^3}{[Y]}$$

$$[(Rc)] = \frac{k\,[c]_0\,[R]_0^3 - k\,[R]_0^3\,[(Rc)]}{[Y]} \tag{8}$$

$$[(Rc)]\,[Y] + k\,[R]_0^3\,[(Rc)] = k\,[c]_0\,[R]_0^3 \tag{9}$$

$$[(Rc)] = \frac{k\,[R]_0^3\,[c]_0}{[Y] + k\,[R]_0^3} \tag{10}$$

In the pre-equilibrium case Eq. (4) is rate limiting and consequently

$$\text{rate} = k_2\,[Rc]\,[B] \tag{11}$$

$$\text{rate} = k_2\,[B]\,\frac{k\,[R]_0^3\,[c]_0}{[Y] + k\,[R]_0^3} \tag{12}$$

Since measurements were made under conditions for which $[Y] << k\,[R]_0$ (because either Y is not formed at all or, since the catalyst concentration is relatively very low, its concentration is negligible) and $[B]$ = constant, then

$$\text{rate} = \frac{d\,[R]}{dt} = \text{constant x } [c]_0$$

or

$$\text{rate} = \frac{d\,[R]}{dt} = k_2^{'}\,[c]_0 \quad (\text{with } k_2^{'} = \text{k}_2 \text{ x constant})$$

or

$$\text{rate} = \frac{d\,[R]}{dt} \propto [c]_0$$

$$k_2^{'} = \text{k}_2\,[\text{B}]^0 = \text{k}_2 \text{ the rate} = \text{k}_2\,[\text{c}\,]_0 \qquad (13)$$

where $k_2^{'} = \dfrac{k\,k_2\,[B]\,[R]_0^3}{k\,[R]_0^3}$

This relationship reflects the proportionality between the concentration of catalyst and the rate of the reaction.

Steady-state condition. If $k_2 >> k_1 >> k_{-1}$, reaction 3 becomes rate determining, [(*Rc*)] is small because of the substoichiometric amounts of catalyst, and a steady-state condition develops defined by the approximation

$$\frac{d\,[(Rc)]}{dt} = 0 \qquad (14)$$

The rate expression then becomes

$$\text{rate} = k_1\,[R]^3\,[c] - k_{-1}\,[(Rc)]\,[Y] \qquad (15)$$

Since [(*Rc*)] cannot be measured experimentally, we must resort to the steady state approximation to obtain an expression for it:

$$\frac{d[(Rc)]}{dt} = 0 = k_1\,[R]^3\,[c] - k_{-1}\,[(Rc)]\,[Y] - k_2\,[(Rc)]\,[B]^0 \qquad (16)$$

$$\frac{d[(Rc)]}{dt} = 0 = k_1\,[R]^3\,[c] - k_{-1}\,[(Rc)]\,[Y] - k_2\,[(Rc)]$$

By substituting the value of [*R*] as $[R]_0$ and [*c*] as $[c]_0$-[(*Rc*)] (since $R = [R]_0 - [Rc] \cong [R]_0$ due to the large concentration of $[\text{R}]_0$ as compared to [*Rc*]).

$$0 = k_1\,[R]_0^3\,([c]_0 - [(Rc)]) - k_{-1}\,[(Rc)]\,[Y] - k_2\,[(Rc)]$$

$$k_1\,[R]_0^3\,[c]_0 = [(Rc)]\,(k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2)$$

$$[(Rc)] = \frac{k_1\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2} \qquad (17)$$

by putting the value of [*Rc*] in Eq. (15)

$$\text{rate} = k_1\,[R]^3\,[c] - k_{-1}\,[Y]\,\frac{k_1\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2}$$

since $[R] = [R]_0$ and $[c] = [c]_0 - [Rc]$ as stated above, we obtain

$$\text{rate} = k_1\,[R]_0^3\,([c]_0 - [Rc]) - k_{-1}\,[Y]\,\frac{k_1\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2}$$

rate =

$$k_1\,[R]_0^3\,[c]_0 - k_1\,[R]_0^3\,\frac{k_1\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2} - \frac{k_{-1}\,[Y]\,k_1\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2}$$

rate =

$$\frac{k_1\,[R]_0^3\,[c]_0\,(k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2) - k_1^2\,[R]_0^6\,[c]_0 - k_1\,k_{-1}\,[R]_0^3\,[c]_0\,[Y]}{k_1\,[R]_0^3 + k_{-1}\,[Y] + k_2}$$

$$\text{rate} = \frac{k_1\,k_2\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3\,k_{-1}\,[Y] + k_2}$$

since $\text{k}_1\,[R]^3 >> \text{k}_{-1}\,[Y\,]$ so it can be neglected

$$\text{rate} = \frac{k_1\,k_2\,[R]_0^3\,[c]_0}{k_1\,[R]_0^3 + k_2}$$

$$\text{rate} = k_2^{'}\,[c]_0$$

where $k_2^{'} = \dfrac{k_1\,k_2\,[R]_0^3}{k_1\,[R]_0^3 + k_2}$, if $\text{k}_1\,[\text{R}]_0^3 > \text{k}_2$ then $k_2^{'} = \text{k}_2$ therefore the rate = $[c]_0$ (18)

Both approximations (*i.e.* for equilibrium and for steady-state) arrive at the same result. Eq. (13) and Eq. (18) provide the mathematical relation between catalyst and rate of reaction.

Proposed Mechanism of Catalyzed Decolorization Reaction of NR with BrO_3^-

The decolorization kinetics of the neutral red with BrO_3^- catalyzed by Fe^{2+} were investigated with the goal of determining a rate expression. The rate of decolorization was studied by varying different parameters like dye, catalyst, and the BrO_3^- concentration. Initial results demonstrated that BrO_3^- by itself was not able to decolorize NR. Some catalyst was essential to produce BrO_2^* from bromate to initiate the decolorizing of NR. Bromate is necessary for the production of BrO_2^* to initiate the decolorization of NR. The reaction mechanism is illustrated in Table 3.

Table 3. Scheme of the Proposed Mechanism for Catalyzed Reaction

$$2H^+ + Br^- + BrO_3^- \leftrightarrow HOBr + HBrO_2 \tag{I}$$

$$H^+ + Br^- + HBrO_2 \leftrightarrow 2HOBr \tag{II}$$

$$HBrO_2 \leftrightarrow H^+ + HOBr + BrO_3^- \tag{III}$$

$$H^+ + Br^- + HOBr \leftrightarrow Br_2 + H_2O \tag{IV}$$

$$2H^+ + 2BrO_3^- + HBrO_2 \leftrightarrow 3BrO_2^* + H_2O \tag{V}$$

$$Fe^{2+} + BrO_3^- \rightarrow Fe^{3+} + BrO_2^* + 2\bar{e} \tag{VI}$$

$$3NR^+ \xrightarrow{slow} (NR^+)_2 + nr + \bar{e} + 2H^+ \text{ (rate determining step)} \tag{VII}$$

$$(NR^+)_2 + BrO_2^* + H_2O \rightarrow 2P^+ + I + HBrO_2 \tag{VIII}$$

$$2P^+ + HOBr + H_2O \rightarrow P' + Br^- + 3H^+ \tag{IX}$$

$$I + 2\bar{e} + 2HOBr \rightarrow P'' + 2Br^- + H_2O \tag{X}$$

$$nr + Br_2 + 2H^+ + H_2O \rightarrow P' + I + 4H^+ + 2Br^- \tag{XI}$$

$$I + Fe^{3+} + \bar{e} + 2BrO_2^* \rightarrow P'' + HBrO_2 + Fe^{2+} \tag{XII}$$

Over all reaction

$$3NR^+ + 2BrO_3^- \rightarrow 2P' + 2P'' + 2Br^- + 3H^+$$

The basic chemistry of the bromate reactions involves a mechanism of Belousov-Zhebotinsky type oscillators and uncatalysed bromate oscillators. Br^- ion, the control intermediate, switches between high/low concentration conditions [28,29]. A switch from high $[Br^-]$ to low $[Br^-]$ occurs when the $[Br^-]$ is driven below a critical value by reaction with $HBrO_2$ and BrO_3^-. The regeneration of Br^- depends intimately on the nature of the reactions of the reducing substrates. Important reaction steps involving the bromo and oxybromo species, during oxidations involving acidic bromate, are represented in reaction (I - V) [29,30-33]. The oxidation of neutral red results in the disruption of the conjugate structure, possibly the formation of a carbocation. The reaction at the rapid transition involves the direct reaction between bromate and bromide, followed by the oxidation of neutral red by bromine and other oxybromo species. Reaction (VI) shows that Fe^{2+} (catalyst) is responsible for the production of BrO_2^*, which is involved in the oxidation of NR. BrO_2^* also forms from reaction between bromate and bromous acid as mentioned in reaction (V). With no initial concentration of Br^- present, reaction (VII) will be the rate controlling step in which $(NR^+)_2$ was formed by the removal of an electron and other organic species was produced. Other possibilities are the attack by BrO_2^* radicals on neutral red as mentioned in reaction (VIII) and intermediate. An attack by HOBr or bromine results in further oxidation of the intermediate, I, to the product, P'' shown in reaction (X). When $[HBrO_2]$ is low, the rate of reaction (V) becomes significant and $[BrO_2^*]$ increases. It results in the auto- catalytic regeneration of bromous acid, through the reaction of BrO_2^* radicals with the reducing substrate and its intermediates. The increased concentration of bromous acid enhances its disproportionation rate, and bromine and its consequent reaction with the reductant/organic intermediates will increase [bromide], the autocatalyst. This exponentially increases bromine production, resulting in the rapid oxidation of neutral red.

NR was found to compete with bromide for the same oxidizing species. The increase in initial [NR^+] prolonged the induction times. Furthermore, the bromination of aromatic substrates by bromine and hypobromous acid is known [34]. Further oxidation of brominated species regenerates bromide as shown in reaction (IX). Bromine and hypobromous acid react rapidly with dye or other organic species of neutral red mentioned in reaction (XI).

Determination of Rate Expression

Rate expression can be written as,

$$-\frac{d\,[R]}{dt} = k\,[R]^3\,[BrO_3^-]$$

with

$$k_{obs} = k\ \ [BrO_3^-]$$

"R" = dye or neutral red

where, [BrO_3^-] is in excess; therefore, rate expression can be written as,

$$-\frac{d\,[R]}{dt} = k_{obs}\,[R]^3$$

The experimental observations indicate that the decolorization rate is pseudo-third order with respect to monitoring species concentration *i.e.* dye and zero-order with respect to bromate. It is concluded that (i) NR degradation with Fe^{2+} is due exclusively to BrO_2* attack, and (ii) this process is third order with respect to [NR] and zero order with respect to BrO_3^- or BrO_2*.

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