Kinetics and Mechanism of the Oxidation of Coomassie Brilliant Blue-R Dye by Hypochlorite and Role of Acid Therein

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ABSTRACT

The kinetics of the oxidation of a triphenylmethane dye, Brilliant Blue-R (BB\(^{-}\) Na\(^{+}\)), in aqueous solution by hypochlorite as a function of pH was investigated. While the degradation of dye obeyed \textit{pseudo}-first-order kinetics, the oxidation of the dye occurred through two competitive reactions facilitated by \([\text{OCl}^{-}]\) and \([\text{HOCl}]\). Both reactions exhibited first-order dependence on \([\text{OCl}^{-}]\) and \([\text{HOCl}]\), respectively, but the hypochlorous acid initiated reaction was about ten times faster. The relative importance of the two paths rested on the pH-dependent concentrations of hypochlorite and hypochlorous acid. The overall second-order rate constants for the \([\text{OCl}^{-}]\) and \([\text{HOCl}]\) initiated reactions are 1.2 ± 0.2 M\(^{-1}\) s\(^{-1}\) and 22.2 ± 1.2 M\(^{-1}\) s\(^{-1}\), respectively. The reaction energy parameters were determined as \(E_a = 35.5\) kJ mol\(^{-1}\), \(\Delta H^\circ = 33.1\) kJ mol\(^{-1}\) and \(\Delta S^\circ = -191.9\) J K\(^{-1}\) mol\(^{-1}\) for the \([\text{OCl}^{-}]\) driven oxidation; and \(E_a = 26.8\) kJ mol\(^{-1}\), \(\Delta H^\circ = 29.3\) kJ mol\(^{-1}\) and \(\Delta S^\circ = -204.6\) J K\(^{-1}\) mol\(^{-1}\) for the \([\text{HOCl}]\) facilitated reaction. The governing rate law and probable reaction mechanism were elucidated and validated by simulation. The three main oxidation products were 4-(4-ethoxyphenylamino)benzoic acid, 3-[(ethyl-hydroxyamino)methyl]benzene sulfonic acid and 6’-chloro-5’-hydroxy-bicyclohexyldiene-2,5,2’-triene-4,4’-dione.

KEYWORDS

Brilliant Blue-R, oxidative degradation, hypochlorite, hypochlorous acid, kinetics, simulations.

1. Introduction

The effective treatment of effluent arising from the textile industry is a complex problem as these wastewaters are highly coloured and polluted.\(^{1}\) In this communication we focus on the degradation of Brilliant Blue-R (BB\(^{-}\) Na\(^{+}\)), a triphenylmethane dye.\(^{2}\) It is also known by other names such as Acid Blue 83, Acid Brilliant Blue and Brilliant Indocyanine 6B. It was originally developed for dyeing wool, silk and nylon in the textile industry.\(^{3}\) It is also used extensively in the paint, ink, plastic and leather industries. This dye is water-soluble and readily dissociates into BB\(^{-}\) and Na\(^{+}\). The aqueous dye exhibits two main peaks in its UV-visible absorption spectrum, one at 285 nm and the other at 555 nm (\(\varepsilon = 4.3 \times 10^4\) cm\(^{-1}\) M\(^{-1}\)) that show no shift due to pH change.\(^{4}\)

Hypochlorite is extensively used as a broad-spectrum antimicrobial agent, as a household bleach, as a chlorinating agent (for swimming pools and in wastewater treatment) and also in \textit{endodontic} procedures.\(^{4,5}\) We have previously reported the effect of hypochlorite enriched seawater for the treatment of wastewater.\(^{6}\) We have also reported the oxidation kinetics and mechanisms of reactions of triaryl\(^{11,12}\) (aniline blue and thymol blue), phenothiazine\(^{13}\) (methylene blue) and heterocyclic\(^{14-16}\) (acridine orange and safranine-o) dyes with acidic bromate as oxidant. We also investigated the oxidative degradation kinetics of indigo carmine with hypochlorite\(^{17}\) and the reaction kinetics of triaryl\(^{17}\) (methylene violet), benzophenoxazines\(^{18}\) (Nile blue and Meldola’s blue) and phenothiazine\(^{19}\) (toluidine blue) dyes with chloride under low pH conditions. More recently, we investigated and reported the kinetics and mechanism of oxidation of the toxic dye, amaranth, by hypochlorite and hypochlorous acid under varied pH conditions.\(^{20,21}\)

In this communication we present and describe the details of the kinetics and the reaction mechanisms of decolourization of BB\(^{-}\) by hypochlorite in aqueous solutions as a function of pH. The oxidation products after decolorization of the dye were isolated and characterized immediately.

2. Experimental

2.1. Reagents

All chemicals were of Analar grade and all the solutions were prepared in double-distilled water. Coomassie Brilliant Blue-R (FW = 825) (Aldrich), sodium hydroxide (BDH), 98 % sulfuric acid (BDH) and anhydrous sodium sulfate (Univar) were used as supplied. The hypochlorite solutions were prepared as per the procedure described by Nagypal et al.,\(^{22}\) and were standardized by iodometric titration. Standardized solutions of sulfuric acid (0.1 M) or sodium hydroxide (0.1 M) were used to adjust the pH and sodium sulfate was used to maintain the ionic strength.

2.2. Kinetic Measurements

The kinetic measurements of the reaction between hypochlorite and Brilliant Blue-R (BB\(^{-}\)) were conducted on a Hi-Tech stopped-flow spectrophotometer (Hi-Tech SF-61 DX2 double-mixing micro-volume stopped-flow, Salisbury, UK). The spectrophotometer was interfaced with a computer to collect data as changes in signal volt or absorbance \textit{versus} time. The reaction was monitored at 555 nm. Unless otherwise stated, all
the experiments were carried out at 25.0 ± 0.1 °C. The kinetics data was analyzed by means of the KinetAsyst™ 3.10 software. This involved fitting the data to a suitable model. A HACH EC40 pH/ISE meter, with digital data output, was used to record the pH/potential changes.

2.3. Product Characterization

A mixture of Brilliant Blue-R (500 mg) and a 100-fold molar excess of oxidant with the requisite excess amount of sulfuric acid was continuously stirred with a magnetic stirrer at room temperature. Immediately after decolourisation of the dye, the reaction products from the aqueous reaction mixtures were extracted with diethyl ether (3 × 200 mL). The solvent was dried over anhydrous calcium carbonate and evaporated to dryness. The crude extract was purified by column chromatography on a column (4 cm diameter) containing silica gel (Merck 9385) as the stationary phase and with a hexane:dichloromethane mixture (85:15 v/v) as the eluent. The isolated products were characterized by GC-MS and NMR (1H and 13C), where possible.

3. Results and Discussion

3.1. Product Analysis and Stoichiometry

The crude reaction mixture was extracted with diethyl ether and the products were separated by column chromatography. Only three compounds were observed by TLC, P1, P2 and P3. The separated products were identified by 1H- and 13C-NMR. Scheme 1 illustrates the products obtained.

To the best of our knowledge, P1, is a commercially available compound and P2/P3, have not been reported in the literature. The 1H NMR spectrum of product P1 (Online supplement, Fig. S1) showed the presence of a pair of doublets at δ 8.00 and δ 7.49, attributed to the para-substituted rings of P1. The fact that there is only one pair of doublets indicates that the ortho-coupled protons on one of the rings are equivalent to that of the other, presumably due to similar groups being present on both of the aromatic rings. The ethoxy group is also indicated by the other, presumably due to similar groups being present on both of there is only one pair of doublets indicates that the ortho-

3.2. Kinetic Studies

All the reactions were studied with low initial concentrations of the dye and excess concentrations of all the other reagents. The reaction progress for depletion of [dye] was followed by monitoring the change in its absorbance at 555 nm. Figure 1 shows the repetitive spectra illustrating the depletion of dye as a function of time in a typical reaction with [BB–]0 = 7.0 × 10–5 M, [OCl–]0 = 1.45 × 10–3 M and pH = 9.0. Figure 2 shows the typical depletion curves of BB–, with [BB–]0 = 7.0 × 10–5 M, at varied [OCl–], and constant ionic strength (0.0128 M) at an initial pH of 9.0.

The ln absorbance versus time plots were straight lines confirming the order with respect to dye is unity. The pseudo-first-order rate constant, k, values obtained by analysing the respective kinetic curves for different initial hypochlorite concentrations are summarized in Table 1. Further, the plot of In k' versus In [OCl–] is linear with a slope of 1.03 (R² = 0.97), suggesting that at pH 9.0, the order with respect to hypochlorite ion is one.

3.2.1. Effect of pH on the Reaction Rate

As pH is an important parameter that controls the characteris-

Scheme 1 Oxidation products of Brilliant Blue-R.
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HOCl (pKa = 7.4).

The equilibrium between the two oxidizing species, i.e., OCl– + H +, can be described by a dynamic expression. This suggests that acid may not be directly involved in the rate-limiting step. This can be well explained in terms of a dynamic involvement of HOCl and OCl– ions. Therefore, a linear relationship between the log k' versus [H+] plot gave a slope of 0.27 (R2 = 0.96). The observed partial reaction order with respect to H + clearly enhances k' values with decreasing pH. The large negative entropy values ([BB–]0 = 7.0 × 10−5 M, [OCl–]0 = 0.725 × 10−3 M, pH = 9.0, I = 0.012 M).

The observed partial reaction order with respect to H +, 0.73, b = 1.45, c = 2.18, d = 2.90 and e = 4.35) at pH 9.0 and I (0.012 M).

The ln k' plot gave a slope of 0.27 (R2 = 0.96). The observed partial reaction order with respect to H + clearly enhances k' values with decreasing pH. The large negative entropy values (0.73 0.012, b = 1.45 0.030, c = 2.18 0.037, d = 2.90 0.046, and e = 4.35 0.086) at pH 9.0 and I (0.012 M).

The energy parameters provide valuable information about the nature of the transition state and the reaction mechanism. The kinetics of BB– oxidation were measured over the temperature range of 298–313 K at pH 9.0 to establish the energy parameters for the HOCl and OCl– driven reactions. A plot of log k' versus 1/T data at pH 9.0 gave a linear curve with a slope of 1.03 (R2 = 0.99) suggesting that under alkaline pH, the rate-limiting step involves species of like charges, possibly BB– and OCl– ions.

On the assumption of the occurrence of two competitive reactions, the kinetics data was analysed to estimate the rate constants for the two competitive pseudo-first-order reactions. A perusal of Fig. 3 shows that the computed curve for the occurrence of the two pseudo-first-order reactions agreed fairly well with the experimental kinetic data, as judged by the negligible residual values.

The pseudo-first-order rate constants obtained at different pH conditions are summarized in Table 2, where k1' represents the pseudo-first-order rate constant for the OCl– initiated oxidation and k2' represents the corresponding value for the reaction by HOCl. The ln-ln plots of k1' and [OCl–]eq and k2' and [HOCl]eq gave straight lines (with R2 > 0.97). At low pH conditions, [OCl–]eq will be negligible and the pseudo-first-order conditions do not prevail under those conditions. These results confirm that acid influences the reaction rates by shifting the equilibrium between OCl– and HOCl. Further increase in [H+] below pH 3 exerted marginal increases in the reaction rate as at those pH conditions, all the oxidant already exists in the HOCl form only.

3.2.2. Kinetic Salt Effect at pH 9.0 and 4.0

The influence of the ionic strength on the oxidation of BB– was examined at various ionic strengths (I), between 0.01 and 0.04 M, and at fixed initial concentrations of hypochlorite. At pH 9.0, 85 % of the oxidant exists in the form of the hypochlorite anion and 15 % as HOCl. Hence, the kinetic curves were analyzed for the occurrence of two consecutive reactions and the results obtained are summarized in Table 3. The plot of log k versus I gave a linear curve with a slope of 0.27 (R2 = 0.99) suggesting that under alkaline pH, the rate-limiting step involves species of like charges, possibly BB– and OCl– ions.

At pH 4.0, 99 % of the oxidant will be in the form of the neutral species, HOCl.25,26 Thus, a linear relationship between the log k' and ionic strength can be anticipated theoretically. A plot of log k' versus I gave a linear curve with a gradient of 0.5 (R2 = 0.99), confirming that at acidic pH 4, the rate-limiting reaction involves a neutral molecule (HOCl) and a charged species (BB–) possibly

3.2.3. Activation Parameters

The energy parameters provide valuable information about the nature of the transition state and the reaction mechanism. The kinetics of BB– oxidation were measured over the temperature range of 298–313 K at pH 9.0 to establish the energy parameters for the HOCl and OCl– driven reactions.26,27 The energy parameters for the HOCl and OCl– driven reactions. The ΔH‡ values at 25 °C were estimated to be 33.1 kJ mol–1 and 26.8 kJ mol–1 for the OCl– and HOCl initiated reactions, respectively. The HOCl initiated reaction had a slightly lower energy of activation (29.3 ± 0.1 kJ mol–1) compared with the OCl– initiated reaction (35.5 ± 0.1 kJ mol–1). The large negative entropy values (ΔS‡) of −191.9 and −204.6 J K–1.

Figure 1 Brilliant Blue-R depletion profile (50 scans/min) for the reaction of BB– ([BB–]0 = 7.0 × 10−5 M) with [OCl–]0 = 1.45 × 10−3 M, [H+]0 = 9.96 × 10−7 M and I (0.012 M).

Figure 2 Depletion of Brilliant Blue-R with various hypochlorite concentrations for the reaction of BB– ([BB–]0 = 7.0 × 10−5 M) with [OCl–]0 = 1.45 × 10−3 M, pH = 9.0 and I (0.012 M).

Table 1 The reaction between Brilliant Blue-R and hypochlorite at constant ionic strength ([BB–]0 = 7.0 × 10−5 M, [OCl–]0 = 0.725 × 10−3 M, pH = 9.0, I = 0.012 M).

<table>
<thead>
<tr>
<th>[OCl–]0/10−3 M</th>
<th>k'/s−1 *</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.73</td>
<td>0.012</td>
</tr>
<tr>
<td>1.45</td>
<td>0.030</td>
</tr>
<tr>
<td>2.18</td>
<td>0.037</td>
</tr>
<tr>
<td>2.90</td>
<td>0.046</td>
</tr>
<tr>
<td>4.35</td>
<td>0.086</td>
</tr>
</tbody>
</table>

* Mean of three replicate experiments with relative standard deviation <5 %.
Table 2: Effect of acid on the speciation of hypochlorite and reaction rate.

<table>
<thead>
<tr>
<th>pH</th>
<th>[H⁺]/M</th>
<th>[OCl⁻]/M</th>
<th>[HOCl]/M</th>
<th>k₁'/s⁻¹</th>
<th>k₂'/s⁻¹</th>
<th>k₁/M⁻¹ s⁻¹</th>
<th>k₂/M⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.70</td>
<td>1.99×10⁻⁹</td>
<td>2.76×10⁻²</td>
<td>1.34×10⁻³</td>
<td>0.0390</td>
<td>0.0270</td>
<td>1.41</td>
<td>20.08</td>
</tr>
<tr>
<td>8.35</td>
<td>4.45×10⁻⁹</td>
<td>2.61×10⁻²</td>
<td>2.85×10⁻³</td>
<td>0.0360</td>
<td>0.0610</td>
<td>1.37</td>
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</tr>
<tr>
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<td>2.33×10⁻²</td>
<td>5.68×10⁻³</td>
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<td>0.1400</td>
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<td>24.64</td>
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<tr>
<td>7.70</td>
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<td>9.49×10⁻³</td>
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<td>0.2050</td>
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</tr>
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<td>0.2799</td>
<td>1.22</td>
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<tr>
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<td>1.18</td>
<td>20.88</td>
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<td>8.43×10⁻³</td>
<td>2.06×10⁻²</td>
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<td>0.4275</td>
<td>1.12</td>
<td>20.79</td>
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<td>5.43×10⁻³</td>
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<td>1.10</td>
<td>20.92</td>
</tr>
<tr>
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<td>1.05</td>
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</tr>
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<td>6.00</td>
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<td>0.6459</td>
<td>0.84</td>
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</tr>
<tr>
<td>3.70</td>
<td>1.99×10⁻⁴</td>
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<td>2.90×10⁻¹</td>
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<td>0.6582</td>
<td>–</td>
<td>22.70</td>
</tr>
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<td>2.42×10⁻⁶</td>
<td>2.90×10⁻¹</td>
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<td>0.6652</td>
<td>–</td>
<td>22.94</td>
</tr>
<tr>
<td>3.29</td>
<td>5.12×10⁻⁴</td>
<td>2.32×10⁻⁶</td>
<td>2.90×10⁻¹</td>
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<td>0.6725</td>
<td>–</td>
<td>23.19</td>
</tr>
<tr>
<td>3.22</td>
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<td>–</td>
<td>0.6842</td>
<td>–</td>
<td>23.59</td>
</tr>
<tr>
<td>3.11</td>
<td>7.75×10⁻⁴</td>
<td>1.53×10⁻⁶</td>
<td>2.90×10⁻¹</td>
<td>–</td>
<td>0.6910</td>
<td>–</td>
<td>23.83</td>
</tr>
</tbody>
</table>

Mean and standard deviation: 1.2 ± 0.2 22.0 ± 1.2

* Mean of four replicate experiments with relative standard deviation <5 %. k₁’ and k₂’ are the pseudo-first-order rate constants with respect to OCl⁻ and HOCl, respectively.

Table 3: Effect of ionic strength on the reaction rate ([OCl⁻]₀ = 1.45 × 10⁻³ M, [BB⁻]₀ = 7.0 × 10⁻⁵ M, pH = 9.0).

<table>
<thead>
<tr>
<th>Ionic strength/M</th>
<th>k₁'/s⁻¹</th>
<th>k₂'/s⁻¹</th>
</tr>
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<tbody>
<tr>
<td>0.0099</td>
<td>0.035</td>
<td>0.045</td>
</tr>
<tr>
<td>0.0188</td>
<td>0.035</td>
<td>0.045</td>
</tr>
<tr>
<td>0.0225</td>
<td>0.037</td>
<td>0.047</td>
</tr>
<tr>
<td>0.0263</td>
<td>0.038</td>
<td>0.048</td>
</tr>
<tr>
<td>0.0338</td>
<td>0.040</td>
<td>0.049</td>
</tr>
</tbody>
</table>

* Mean of three replicate experiments with relative standard deviation <5 %.
mol$^{-1}$ for the OCl$^{-}$ and HOCl initiated reactions respectively suggest that the activated complexes formed are compact in nature with a precise configuration.\(^{20}\)

3.2.4. Rate Laws

The first-order dependence of the reaction rate on the reactants and the observed salt effect at pH 9 and pH 4 suggest that the rate-limiting steps for the two competitive reactions involve one each of BB$^{-}$ and OCl$^{-}$ ions and BB$^{-}$ and HOCl respectively. Thus, the major pathways of the reaction involve OCl$^{-}$ or HOCl forming an activated complex, which undergoes decomposition, to form the intermediates and products. The intermediates further undergo oxidation to give the products. Based on these findings the rate law is proposed as:

$$\text{Rate} = k_1[\text{OCl}^{-}][\text{BB}^{-}] + k_2[\text{HOCl}][\text{BB}^{-}]$$

where $k_1$ and $k_2$ represent the rate constants facilitated by OCl$^{-}$ and HOCl respectively.

$$r = \{k_1[\text{OCl}^{-}] + k_2[\text{HOCl}]\}[\text{BB}^{-}] = \{k'_1 + k'_2\}[\text{BB}^{-}] = k'[\text{BB}^{-}]$$

where the pseudo-first-order rate constant, $k'$ equals to $(k'_1 + k'_2)$, while $k_1 = k'_1/[\text{OCl}^{-}]_0$ and $k_2 = k'_2/[\text{HOCl}]_0$. $k'_1$ and $k'_2$ represent the pseudo-first-order rate constants with respect to hypochlorite and HOCl.

3.2.5. Reaction Scheme

A plausible reaction scheme for the oxidation of BB$^{-}$ is presented in Scheme 2. An electron flow originating from the lone pair on the tertiary nitrogen toward the oxygen of the HOCl molecule, results in the addition of a hydroxyl group to the Brilliant Blue-R, intermediate, I$\text{I}_1$. Electrons from the $\pi$ bond in the azo then form a cyclopropane cation with the concomitant loss of the hydroxyl group resulting in I$\text{I}_6$. A hydroxyl ion then attacks the cation resulting in I$\text{I}_5$ from which a proton is abstracted from the hydroxyl group on the cyclopropane ring, resulting in the concurrent opening of the ring to produce I$\text{I}_7$. A hydroxyl ion subsequently attacks the carbonyl group, which ultimately results in P$\text{I}_7$ and the intermediate I$\text{I}_9$.

The lone pair of the nitrogen in I$\text{I}_5$ attacks the oxygen of a further HOCl molecule, resulting in a hydroxy group being attached to the nitrogen in the cationic intermediate I$\text{I}_7$. A water molecule splits the amine portion of I$\text{I}_7$ from the rest of the molecule, resulting in the product P$\text{I}_7$ and the intermediate I$\text{I}_9$. Subsequently, a chloride ion removes a proton from the protonated oxygen to give rise to the neutral intermediate I$\text{I}_7$. The lone pair on the nitrogen in I$\text{I}_7$ attacks the oxygen of a HOCl molecule, resulting in N-hydroxylation in I$\text{I}_8$. Cleavage of the electrons toward the oxygen at the other end results in the benzoquinone intermediate I$\text{I}_5$. Addition of a HOCl molecule across the double bond results in the product P$\text{I}_5$. While the equilibrium between OCl$^{-}$ and HOCl is maintained, the reaction with hypochlorite occurs along similar lines as with HOCl to a large extent, but at a relatively slow rate. The minor differences due to protonation and deprotonation of intermediates and products is accommodated in the simulations.

3.2.6. Reaction Mechanism

Based on the reaction stoichiometry estimated, and the major products identified, the mechanism for the reaction of Brilliant Blue-R with hypochlorite can be expressed in the following steps:

$$\text{H}^+ + \text{OCl}^{-} \rightleftharpoons \text{HOCl}$$

$$\text{HOCl} + \text{Cl}^- + \text{H}^+ \rightleftharpoons \text{L} \text{Cl}_2 + \text{H}_2\text{O}$$

$$\text{BB}^- + \text{OCl}^- \rightarrow \text{PI}_5 + \text{I}_5^+ + \text{H}^+ + \text{Cl}^-$$

$$\text{BB}^- + \text{HOCl} \rightarrow \text{PI}_5 + \text{I}_5^+ + 2\text{H}^+ + \text{Cl}^-$$

$$\text{I}_5^+ + \text{HOCl} \rightarrow \text{PI}_9 + \text{P}_3^+ + \text{Cl}^-$$

$$\text{I}_5 + \text{HOCl} \rightarrow \text{PI}_5 + \text{H}^+ + \text{Cl}^-$$

$$\text{I}_9 + \text{HOCl} \rightarrow \text{PI}_9 + \text{H}^+ + \text{Cl}^-$$

$$\text{I}_9 + \text{HOCl} \rightarrow \text{PI}_9 + \text{H}^+ + \text{Cl}^-$$

$$\text{I}_9 + \text{HOCl} \rightarrow \text{PI}_9 + \text{H}^+ + \text{Cl}^-$$

$$\text{I}_9 + \text{HOCl} \rightarrow \text{PI}_9 + \text{H}^+ + \text{Cl}^-$$

$$\text{I}_9 + \text{HOCl} \rightarrow \text{PI}_9 + \text{H}^+ + \text{Cl}^-$$

The overall reaction mechanism is:

$$2\text{BB}^- + 6\text{HOCl} + 2\text{H}_2\text{O} \rightarrow \text{PI}_5 + 2\text{P}_3^+ + \text{P}_3 + 5\text{HCl}$$

where $\text{P}_3$ is 4-(4-ethoxyphenylamino)benzoic acid; $\text{P}_3$ is 3-[(ethylhydroxyamino)methyl]-benzene sulfonic acid, and $\text{P}_3$ is 6'-chloro-5'-hydroxy-bicyclohexylidene-2,5,2'-triene-4,4'-dione.

3.2.7. Simulation Studies

The Simkin 3 software\(^{26-30}\) was used to simulate the complex multi-step mechanism for the reaction between BB$^{-}$ and the oxidants, by utilizing the proposed mechanism and the experimentally obtained rate coefficients. For the simulations all the steps involving the formation of intermediates, which undergo consecutive reactions with intermediates or other oxidative species were considered. In each elementary step, the overall charge and mass balances were strictly accounted for (Table 5).

The rate constants experimentally obtained were employed for reactions steps R3 and R4. The rate-limiting step of the oxidation mechanism involves the steps initiated by OCl$^{-}$ and/or HOCl on BB$^{-}$ leading to the formation of the reactive intermediate. The reactions R3 and R4 are the rate-controlling steps for dye oxidation. Literature data were used for R1 and R2 and for the reaction equilibrium between OCl$^{-}$ and HOCl\(^{23,31}\) and the values used for R5 to R13 were estimated rate constants from the simulations. The estimated rate constants were optimized so that the simulated curves matched the experimental curves. The rate constants were initially adjusted manually to test the sensitivity and importance of the elementary reactions. Reactions R5 to R13

\begin{table}[ht]
\centering
\caption{Forward and reverse rate constants obtained from literature and simulations.}
\begin{tabular}{lllll}
\hline
Reaction No. & Reaction mechanism & Forward rate & Reverse rate \\
\hline
R1 & $\text{H}^+ + \text{OCl}^- \rightleftharpoons \text{HOCl}$ & $3.97 \times 10^8 \text{M}^{-1} \text{s}^{-1}$ & $1.0 \times 10^4 \text{s}^{-1}$ \\
R2 & $\text{HOCl} + \text{Cl}^- + \text{H}^+ \rightleftharpoons \text{L} \text{Cl}_2 + \text{H}_2\text{O}$ & $3.63 \times 10^8 \text{M}^{-2} \text{s}^{-1}$ & $1.1 \text{s}^{-1}$ \\
R3 & $\text{BB}^- + \text{OCl}^- \rightarrow \text{I}_5^- + \text{P}_1^+$ & $2.2 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R5 & $\text{BB}^- + \text{OCl}^- \rightarrow \text{I}_5^-$ & $1.22 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R6 & $\text{I}_5^- + \text{H}^+ \rightarrow \text{I}_5^0 + \text{P}_1^+$ & $3.30 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R7 & $\text{I}_5^0 + \text{HOCl} \rightarrow \text{I}_5^+ + \text{OCl}^-$ & $2.30 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R8 & $\text{I}_5^+ + \text{OCl}^- \rightarrow \text{I}_5^+ + \text{Cl}^-$ & $4.30 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R9 & $\text{I}_5^+ + \text{HOCl} \rightarrow \text{I}_5^+ + \text{H}^+$ & $3.41 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R10 & $\text{I}_5^+ + \text{HOCl} \rightarrow \text{I}_5^+ + \text{OH}^- + \text{P}_3^+$ & $3.01 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
R11 & $\text{I}_5^+ + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{P}_3^+ + 3\text{HCl}$ & $4.17 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ & – \\
\hline
\end{tabular}
\end{table}
Scheme 2
Plausible mechanism for the oxidation of Brilliant Blue-R.
show the consecutive steps for further oxidation of the reactive intermediates by different species and R8, R12 and R13 represent the reactions leading to the different products identified.

Figure 4 shows the experimental curves for depletion of the dye at different oxidant concentrations and the corresponding simulated curves for those conditions. The experimental and simulated curves are in good agreement. Furthermore, Fig. 5 shows the profiles of the experimental and simulated curves for the depletion of Brilliant Blue-R at the chosen conditions and the profiles of the products and various intermediates as a function of time.

**Supplementary material**

The NMR and MS spectra of the new compounds are provided in the online supplement.

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Figure S1. 1H NMR spectrum for brilliant blue-R major oxidation product P₁ (4-(4-ethoxyphenylamino)-benzoic acid) with hypochlorite.
Figure S2. $^{13}$C NMR spectrum for brilliant blue-R major oxidation product P$_1$ (4-(4-ethoxyphenylamino)-benzoic acid) with hypochlorite.
Figure S3. GC-MS spectrum for brilliant blue-R major oxidation product (P₁ (4-(4-ethoxyphenylamino)-benzoic acid) with hypochlorite.
Figure S4. $^1$H NMR spectrum for brilliant blue-R major oxidation product P$_2$ (3-ethylaminomethylbenzenesulphonic acid) with hypochlorite.
Figure S5. $^{13}$C NMR spectrum for brilliant blue-R major oxidation product P$_2$(3-ethylamino methyl benzenesulphonic acid) with hypochlorite.
Figure S6. GC-MS spectrum for brilliant blue-R major oxidation product P₂(3-ethylaminomethylbenzenesulphonic acid) with hypochlorite.
Figure S7. $^1$H NMR spectrum of brilliant blue-R major oxidation product P$_4$ (6’m-chloro-5’-hydroxy-bicyclohexylidene-2,5,2’-triene-4,4’-dione) with hypochlorite.

Figure S8 $^{13}$C NMR spectrum of brilliant blue-R major oxidation product P$_4$ (6’m-chloro-5’-hydroxy-bicyclohexylidene-2,5,2’-triene-4,4’-dione) with hypochlorite.
Figure S9. GC-MS spectrum of brilliant blue-R major oxidation product P₄ (6'-chloro-5'-hydroxy-bicyclohexylidene-2,5,2'-triene-4,4'-dione) with hypochlorite.