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Kinetic study of Orange II oxidation using peroxynitrous acid

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The reaction of Orange II with peroxynitrous acid has been studied by a spectrophotometrical method. The reaction rate is complex because the order changes from zero to one in function of substrate and oxidant concentration. The influence of pH and ionic strength has been investigated, but their effect on the reaction rate appears to be negligible under the experimental conditions used. A reaction mechanism based on the experimental results is proposed, involving a radical cage solvent attack from peroxynitrous acid to Orange II. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: peroxynitrous acid; Orange II; oxidation; aqueous; kinetic; dye; radical

INTRODUCTION

Orange II is an azo dye widely used in dyeing textiles, food, and cosmetic industries. Thus, after its use, coloration can be observed in the wastewaters released into the rivers or other water courses.[1] Elimination of this type of pollutant is a matter of major concern for these industries. The current technique for removing this dye involves adsorption on activated carbon but this is an expensive and inefficient process. Another method is oxidation using ozone and hypochlorite, but this yields chlorine as a secondary pollutant agent[2] and, similar to the previous method, it is expensive. Recent progress in eliminating dyes is the Fenton's oxidation, which is not expensive, although it seems to react at low rates and requires special conditions.[3–5]

The goal of this work is to study in depth the oxidation process of Orange II by peroxynitrous acid. The peroxynitrite anion is an important inorganic species, which has been a subject of many studies in recent years due to its outstanding role in several areas of molecular science.[6] In atmospheric chemistry, the photo-isomerization of nitrate to peroxynitrite by UV radiation[7] must be considered as a chemical change that can occur in the atmosphere. In this way, peroxynitrite, due to its strong oxidizing properties, will react with chlorine species (e.g., chlorofluorocarbons) producing Cl atoms which destroy the ozone layer. In biology, it is well known that activated macrophages and neutrophils produce two free radicals (nitrogen monoxide and superoxide) that, under physiological conditions, form peroxynitrite anion.[8]

The peroxynitrite anion is relatively stable and can be preserved for weeks in strongly alkaline media at $-18\,^{\circ}$C. The peroxynitrous acid ($pKa = 6.8$)[6,9–11] is very unstable since it has a half-life of less than 1 s at 37 °C, and can isomerize to nitrate[12] or decompose to nitrite and molecular oxygen.[13–15] Isomerization to nitrate is the main pathway in acidic media. Peroxynitrous acid can oxidize several substrates such as methionine,[10] ascorbate,[16] etc.

The oxidation reactions take place by two main pathways: (1) peroxynitrous acid oxidizes the substrates directly[11] and/or (2) it is converted into a highly reactive intermediate (radical box) that either isomerizes to nitrate, oxidizes the substrate (indirect oxidation), or regenerates HOONO.[6]

The chemistry of peroxynitrous acid is poorly understood but peroxynitrous acid is a very effective oxidizing agent. This is the reason for using this species in the dye pollution remediation.

EXPERIMENTAL

Reactants

The reagents used were Orange II, peroxynitrite, sodium perchlorate, and 0.5 M buffer solutions. All reagents were from A.R. grade and were obtained from Sigma-Aldrich. The solutions were prepared using bidistilled water. Peroxynitrite solution was prepared by following the literature procedure.[17] The purity of stock solutions of peroxynitrite was assessed by measuring the characteristic peak that appears at 302 nm.[17] Buffer solutions were prepared mixing the corresponding pairs of acids and salt, as described by Henderson–Hasselbalch equation. The selected pairs were: sodium acetate/acetic acid from $pH \leq 5$ to pH 3.8 and sodium dihydrogenphosphate/phosphoric acid from $pH \leq 3.5$ to pH 3.

General

Orange II oxidation kinetics was followed by measuring the decrease in the optical absorbance of Orange II (e.g., A) at 484 nm on a Stopped-flow SX18MV from Applied Photophysics Ltd. The initial rates method[18] was used for kinetic analysis because this method is perfectly compatible with the normal standards of experimental accuracy. In certain circumstances this method offers more advantages over the integral method (e.g., the presence of competitive reactions is considerably less important

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when the initial rate method is employed) and since the free radicals may appear during the target reaction process, the initial rate method was used to avoid this problem. The initial rates of disappearance of Orange II were obtained as described previously, using the expression $v_0 = -1/\varepsilon(\mathrm{d}A/\mathrm{d}t)$, where $\varepsilon = 18\,500\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ at 484 nm. The ionic strength was kept constant at 0.5 M, by the addition of sodium perchlorate. The pH was kept constant by the addition of the corresponding buffer solution.

The stoichiometry of the reaction (2:1 [Orange II]/[HOONO]) was obtained by the Yoe and Jones method.[19]

RESULTS

Dependence on substrate concentration

The values of v_0 for four series of kinetic runs at different $[\text{Orange II}]_0$ are shown in Fig. 1. It can be observed that at low Orange II concentration the initial rate is proportional to [Orange II] (first-order kinetics), meanwhile at a higher concentration the initial rate becomes independent of that concentration (zero-order kinetics). The analysis of the experimental data shows a good correlation to the equation

$$v_0 = \frac{B_1[\text{Orange II}]_0}{B_2' + B_3[\text{Orange II}]_0} \tag{1}$$

This result suggests a Micahelis–Menten type dependence of the initial rate on Orange II concentration.

Dependence on oxidant concentration

The dependence of v_0 on $[\text{HOONO}]_0$, while the other parameters are kept constant is shown in Fig. 2, where reaction rate changes from order one to order zero, when peroxynitrous acid concentration increases. These experimental data suggest that the oxidation involves a mixture of two different mechanisms: (1) the peroxynitrous acid solvent cage attack and (2) the peroxynitrous acid direct attack of the Orange II molecule. This study led to the following expression:

$$v_0 = \frac{B_1[\text{HOONO}]_0}{B_3' + B_2[\text{HOONO}]_0} \tag{2}$$

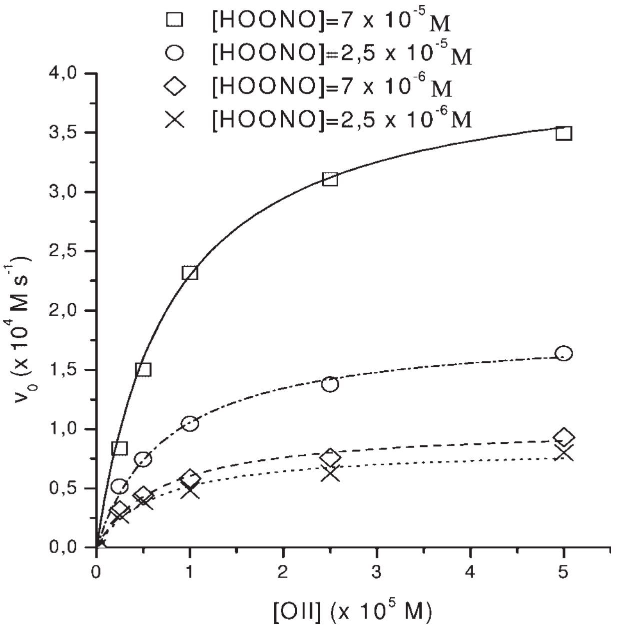


Figure 1. Plot of v_0 *versus* $[\text{Orange II}]_0$ under the experimental conditions $[\text{HOONO}]_0 = 7\times10^{-5}$, 2.5×10^{-5}, 7×10^{-6}, 2.5×10^{-6} M; $[\text{H}^+] = 1\times10^{-5}$ M; $T = 18\,^{\circ}\text{C}$; and $I = 0.5$ M

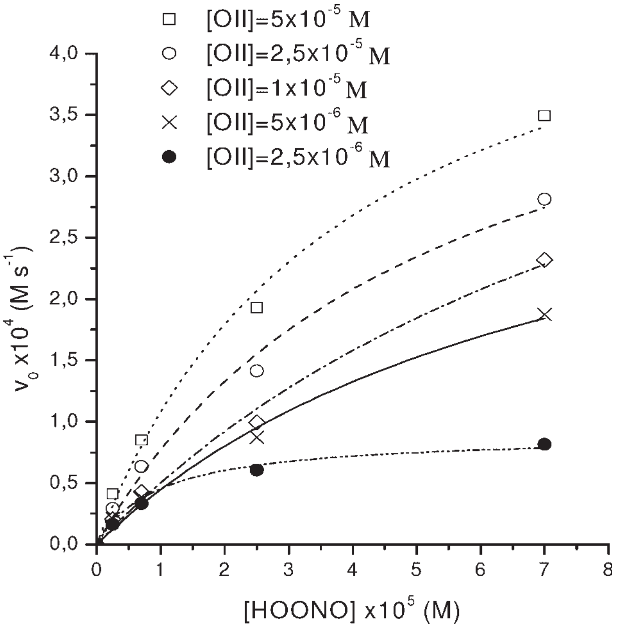


Figure 2. Plot of v_0 *versus* $[\text{HOONO}]_0$, under the experimental conditions $[\text{Orange II}]_0 = 5\times10^{-5}$, 2.5×10^{-5}, 1×10^{-5}, 5×10^{-6}, 2.5×10^{-6} M; $[\text{H}^+] = 1\times10^{-5}$ M; $T = 18\,^{\circ}\text{C}$; and $I = 0.5$ M

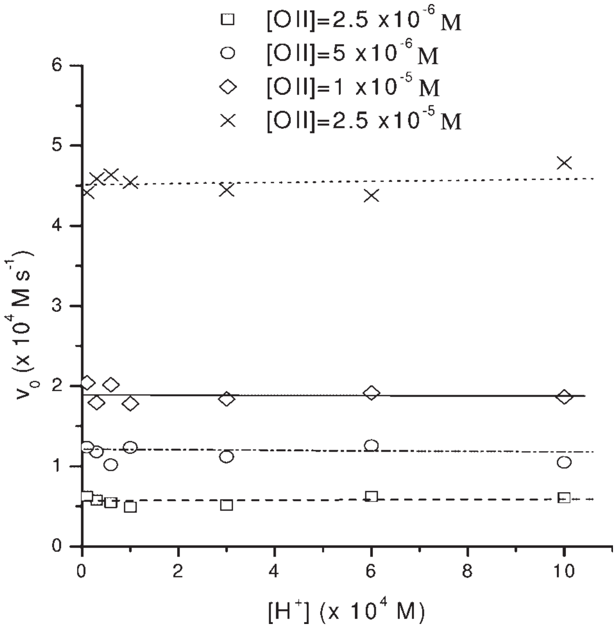


Figure 3. Plot of v_0 *versus* $[\text{H}^+]$, under the experimental conditions $[\text{Orange II}]_0 = 2.5\times10^{-5}$, 1×10^{-5}, 5×10^{-6}, 2.5×10^{-6} M; $[\text{HOONO}] = 2.5\times10^{-4}$ M; $T = 18\,^{\circ}\text{C}$; and $I = 0.5$ M. No pH effect on v_0 is appreciated

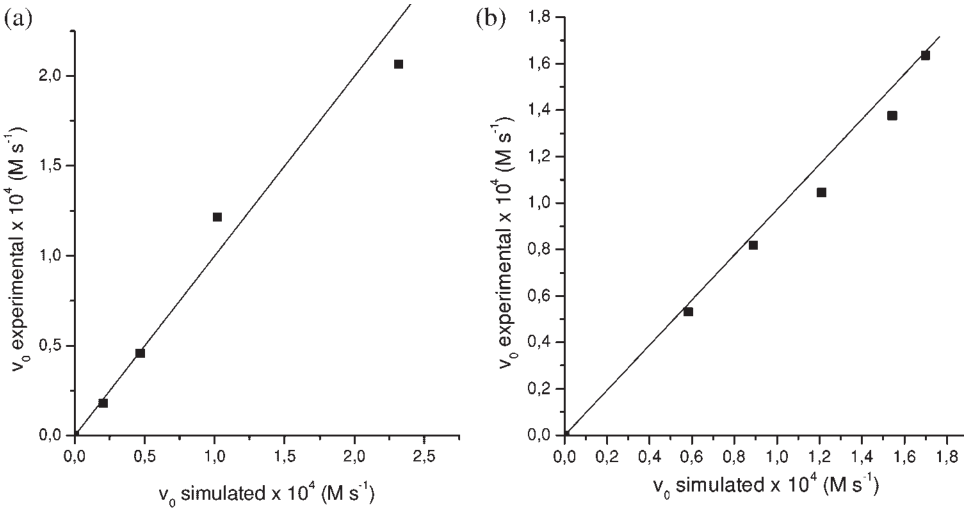


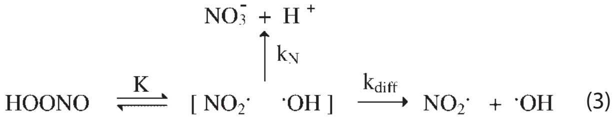
Figure 4. Comparision between simulated and experimental data when: (a) The effect of [HOONO] variation under the conditions: [Orange II] $= 1 \times 10^{-5}$ M; pH = 5; $T = 18\,^{\circ}$C; and $I = 0.5$ M. (b) The effect of [Orange II] variation under the conditions: [HOONO] $= 2.5 \times 10^{-5}$ M; pH = 5; $T = 18\,^{\circ}$C; and $I = 0.5$ M

Dependence on pH and ionic strength

Under the experimental conditions used, no appreciable effect of pH has been observed on the reaction rate (Fig. 3). In the same way, the ionic strength has shown no effect on the reaction rate.

DISCUSSION

First let us review the mechanisms used to explain the oxidation reactions of peroxynitrite.[6–11] The main reaction involves homolysis of HOONO to form $^{\cdot}$HO and $^{\cdot}$NO$_2$ radicals (K), which are the oxidants. These radicals are initially in a solvent cage i.e., surrounded by solvent molecules. We assume that caged radicals pair can: (1) diffuse out of the cage to give free radicals (k_{diff}), (2) re-form ONOOH, or (3) form nitric acid (k_{N}).



$$\begin{tikzcd} & NO_3^- + H^+ & \\ HOONO \arrow[r, shift left, "K"] & {[\,NO_2^{\cdot} \quad {}^{\cdot}OH\,]} \arrow[l, shift left] \arrow[u, "k_N"] \arrow[r, "k_{diff}"] & NO_2^{\cdot} + {}^{\cdot}OH \end{tikzcd} \qquad (3)$$

Experimental data suggest that two molecules of Orange II are implicated in the oxidation reaction, meanwhile only one molecule of peroxynitrous acid participates in the reaction. This fact and the dependence of v_0 on [HOONO]$_0$ can be explained if it is accepted that peroxynitrous acid reacts principally in the way of solvent cage i.e., the main equilibrium is

$$\text{HOONO} \overset{K}{\rightleftharpoons} [\text{NO}_2\cdot \quad \cdot\text{OH}] \qquad (4)$$

Under the experimental conditions, k_{N} is not observed because the plot of v_0 *versus* [HOONO] passes through the origin of Cartesian coordinates, although this process takes place.

So the reaction mechanism involves attack of solvent caged radical pair on the azo dye

$$[\text{OH}\cdot\,\cdot\text{NO}_2] + \text{OII} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate} \qquad (5)$$

where OII represents the Orange II molecule.

This intermediate species, that is supposed to retain color, rearranges into a radical species (R$\cdot$) which in a very fast step collides with another molecule of Orange II giving the final colorless products

$$\text{Intermediate} \xrightarrow{k_2} \text{R}\cdot \qquad (6)$$

$$\text{R}\cdot + \text{OII} \xrightarrow{\text{fast}} \text{Products} \qquad (7)$$

Application of the steady state conditions with respect to the intermediate species, assuming that this intermediate retains the color and that the major reaction channel involves the solvent caged pair, leads to the following theoretical rate equation for the oxidation of Orange II

$$-\frac{d[\text{Orange II}]}{dt} = \frac{2k_1k_2K[\text{Orange II}][\text{HOONO}]}{(k_{-1}+k_2)K + Kk_1[\text{HOONO}] + k_1[\text{Orange II}]} \qquad (8)$$

Equation (8) is similar to the equation described by Chahbane *et al.*[20] for the oxidation process of Orange II by Fentons' reagent in basic media.

The kinetic data were fitted to Eqn (8) using a nonlinear regression in order to obtain the kinetic constants.

The obtained values for these kinetic constants were

$$k_1 = (2.82 \pm 0.07) \times 10^8\ M^{-1}s^{-1}$$
$$k_2 = (29.11 \pm 0.04)\,s^{-1}$$
$$k_{-1} = (7.93 \pm 0.04) \times 10^3 s^{-1}$$
and
$$K = (0.125 \pm 0.09)$$

Finally, as shown in Fig. 4, the experimentally obtained values for the reaction rate were compared with those predicted by Eqn (8). A satisfactory fit between experimental and theoretical values of the reaction rate was achieved (the total average error of Eqn (8) was 8.57%).

CONCLUSION

Kinetics for the oxidation of Orange II by HOONO at different pH values show that HOONO is a convenient oxidant for the treatment of dyes in wastewaters. The decomposition of Orange II takes place in just a few seconds, when the peroxynitrous acid is present in the acidic media. Experimental equations show a change of order from one to zero for both Orange II and HOONO upon increasing their concentrations. The reaction mechanism proposed involves oxidation of Orange II by a solvent caged radical pair with formation of an intermediate species that decomposes to a radical which subsequently reacts with another dye molecule in order to yield products.

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