The Effect of Magnetic Field on the Bleaching of Indigo Dyes with Hydrogen Peroxide Catalyzed by Imidazole

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The effect of applying an external magnetic field on the catalytic oxidation of indigo dyes with H_2O_2/imidazole was investigated. It was found that the rate of oxidation, in the presence of imidazole as a catalyst, was enhanced by applying an external magnetic field in the range of 0.035–0.12 T. The magnetic field did not affect the reaction in the absence of imidazole. A mechanism that involves radical intermediates is proposed.

All chemical reactions take place in the ambient magnetic field of earth, which is on the order of 10^{-4} Tesla. The effect of magnetic field on the chemical kinetics has not been studied extensively.[1–3] A magnetic field affects magnetic species each according to its nature (ferromagnetic, paramagnetic, or diamagnetic). Therefore, chemical reactions involving such species will be affected if magnetic field is applied. A significant effect of the magnetic field on radical pair recombination in enzyme kinetics has been observed.[4] The large effect of the applied magnetic field on Vitamin B12 ethanolamine ammonialyase has been taken as evidence for a radical mechanism.[5] Extensive research on the effect of magnetic field on corrosion has also been carried out with corrosion inhibited to different degrees depending on the value of the magnetic field and the amount of surfactant.[6,7] There are also studies on the applications of magnetized water in the fields of water treatment, biological activities and agriculture.[8–11]

The aim of this work is to study the influence of applied magnetic field on the rate of bleaching of indigo dyes by H_2O_2 in solutions. Bleaching is very important process in chemical industries, and hydrogen peroxide under appropriate conditions is a very effective bleaching agent and has been widely used.[12] The oxidation of indigo dyes with H_2O_2 catalyzed with imidazole was studied in the presence and absence of a magnetic field. The rate of oxidation of indigo dye with H_2O_2 increased significantly with an increase in the applied magnetic field in the presence of imidazole.

Experimental

Materials. Indigo (96%), potassium indigotrisulfonate (85%), indigo cumine (90%) dyes, and imidazole (99%) were purchased from Aldrich and used without further purification. Stock solutions of potassium indigotrisulfonate (indigo blue) were prepared in deionized water. The concentration of the stock solutions of indigo blue was determined spectrophotometrically at 600 nm ($\mathcal{E} = 1.9 \times 10^4\,M^{-1}\,s^{-1}$).[13] Stock solutions of hydrogen peroxide (Fischer, 30%) were prepared in water by diluting the commercial solution to 1.0 M and standardized daily by iodometric titration. Stock solutions of imidazoles (0.5–1.0 M), were prepared in CH_3CN or water.

Kinetic Experiments. The kinetic studies were carried out in aqueous solutions at 20 °C. The temperature was kept constant at 20 ± 0.5 °C throughout the entire series of experiments. Air (oxygen) had no effect on the reactions and was not excluded. Quartz cuvettes with optical paths of 1.0 cm were used. The kinetic data were obtained by following the disappearance of the blue color of the indigo dye in the region 580–620 nm using Shimadzu UV-2401 spectrophotometer.

Reaction mixtures were prepared in the spectrophotometer cell with the last reagent added being H_2O_2 to optimize the kinetic conditions. The kinetic data were obtained by applying both initial rate method and pseudo-first-order conditions. In the later case, the pseudo-first-order rate constants were evaluated by nonlinear least-squares fitting of the absorbance–time curves to a single exponential equation, Eq. 2.

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_o - \mathrm{Abs}_\infty)\exp(-k_\psi t), \quad (2)$$

where Abs_t, Abs_∞, and Abs_o are the absorbance at anytime, final, and initial absorbance, respectively, and k_ψ is the first-order rate constant.

Variation of the Magnetic Field. Kinetic experiments on the effect of applying an external magnetic field were carried out under similar conditions to that in the absence of an external magnetic field. These studies were carried out by attaching two to six magnets to the cell holder inside the Shimadzu spectrophotometer. The magnetic field value was measured by inserting a Hall probe in the place of the cell, and the reading was displayed by a Tesla meter. The effect of the applied magnetic field on the instrument optics and reading was tested prior to each run by recording the change in absorbance and its stability during a period of 30–60 min. In these tests, the magnets were attached to the cell holder, which contains a Quartz cell filled with a solution containing indigo blue. Then, the kinetic data from the oxidation of indigo dye with H_2O_2 in the presence and absence of the catalyst (imidazole) were collected by recording the absorbance change with time at 600 nm.

Results and Discussion

Oxidation of Indigo Dyes by H_2O_2. The rate of oxidation of potassium indigotrisulfonate (indigo blue) by H_2O_2 was studied in aqueous solution at 20 °C. In the absence of imidazole, the reaction was very slow. After one hour, less than 10% of the indigo blue was oxidized with 0.01 M [H_2O_2]. The kinetic studies were carried out under pseudo-first-order conditions with the [H_2O_2] much greater than the [indigo]. The pseudo-first-order rate constants, obtained by fitting the absorbance–time curves to Eq. 2, varied linearly with the [H_2O_2] indicating that the reaction is first-order in [H_2O_2] and second-order overall. The slope was the second-order rate constant ($k_{uncat} = 3 \times 10^{-7}\,M^{-1}\,s^{-1}$) for the oxidation of indigo blue by H_2O_2 in aqueous solution at 20 °C.

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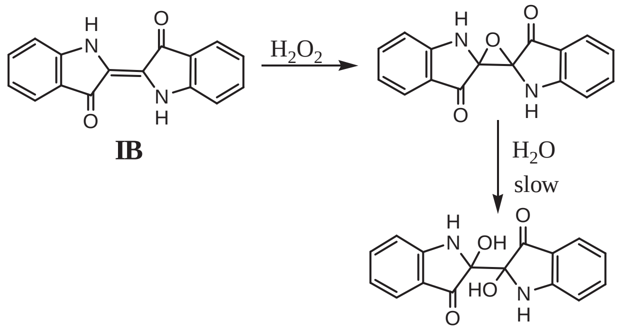


Scheme 1. Oxidation of Indigo Blue with H_2O_2.

The reaction appears mainly to involve oxygen transfer from the peroxide to the dye leading to the formation of an epoxide. The reaction products have been isolated and identified by IR and NMR spectroscopy.[14] The final major product was the epoxide of indigo blue. In addition, the 1,2-diol product was identified as a minor product from this reaction. This product is formed from the ring-opening of the epoxide by water, Scheme 1.

Effect of Imidazole. The addition of imidazole to the reaction of H_2O_2 with indigo blue greatly increased the reaction rate ($k_{cat}/k_{uncat} \approx 10^3$). The rate of oxidation increased linearly with the imidazole concentration in the range 0.005–0.05 M. Imidazole and *N*-methylimidazole have also been found to catalyze the oxidation of indigo dyes with *m*-chloroperoxybenzoic acid (MCPBA). It has been proposed that imidazole increases the activity of MCPBA due to the formation of Im-MCPBA active intermediate. This intermediate, however, has not been identified.

The Magnetic Field Effect. The effect of an applied magnetic field on the oxidation of indigo dye by H_2O_2 was investigated by studying the variation of the reaction rate with the applied magnetic field. The reaction rates in the presence and in the absence of imidazole were determined from the absorbance changes at 600 nm with time due to the loss of the indigo dye.

In the Absence of Imidazole. This study was carried out in aqueous solution at 20 °C under psudeo-first-order conditions with a large excess H_2O_2 (0.02 M) over the indigo dye (0.05 mM). The reaction was second-order or first-order in each reactant. The effect of the applied magnetic field on the oxidation of indigo blue by H_2O_2 was not significant. A slight change in the rate of oxidation was observed, Fig. 1. It was found that the values of the initial rates and the observed-first-order rate constants with and without applying external magnetic field were very close.

In the Presence of Imidazole. The effect of variation of the magnetic field on the oxidation of indigo dye with H_2O_2 in the presence of imidazole was investigated in aqueous solution at 20 °C. The reaction was independent of the [indigo] in the range 0.1–0.02 mM. The rate of oxidation was affected by the applied magnetic field. The absorbance–time curves from the oxidation of indigo blue (0.05 mM) with H_2O_2 (0.02 M) in the presence of imidazole (0.02 M) at different applied magnetic field are shown in Fig. 2. The reaction rate was increased with the magnetic field in the range of 0 to 0.12 T. The initial rate (v_i) values were calculated from the first 2–5% of the absorbance–time curves using Eq. 3.

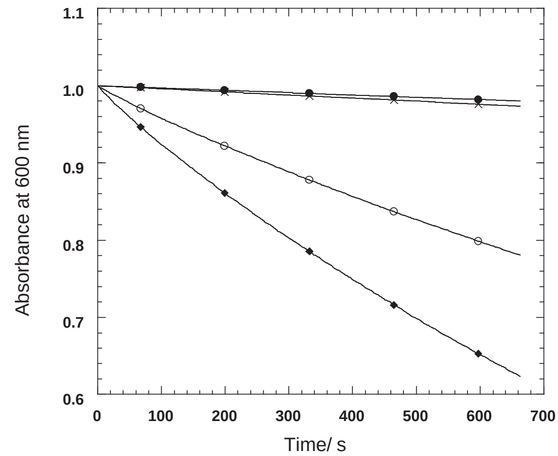


Fig. 1. The reaction profiles for the oxidation of indigo dye (0.05 mM) with H_2O_2 (0.02 M) as catalyzed by imidazole in the presence and absence of magnetic field. The absorbance change due to the loss of indigo dye was recorded at 600 nm ($\mathcal{E}_{600} = 1.9 \times 10^4\ M^{-1}\ cm^{-1}$) in aqueous solution at 20 °C. ● [Im] = 0 and MF = 0, × [Im] = 0 and MF = 0.035 T, ○ [Im] = 0.01 M and MF = 0, ◆ [Im] = 0.01 M and MF = 0.035 T.

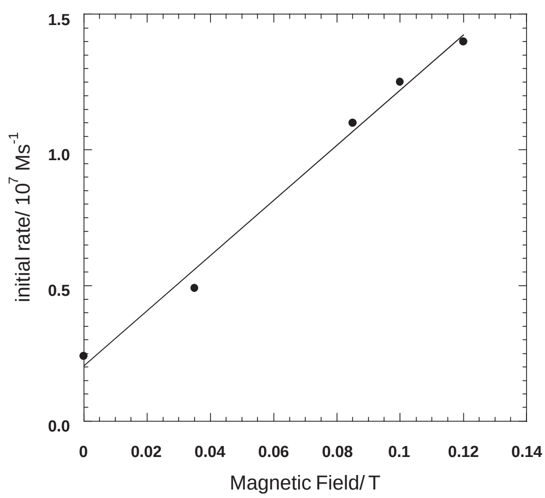


Fig. 2. Variation of the initial rate for the reaction of indigo dye with H_2O_2 as catalyzed by imidazole in a magnetic field in an aqueous solution at 20 °C. [indigo] = 0.05 mM, [Im] = 0.02 M, [H_2O_2] = 0.02 M.

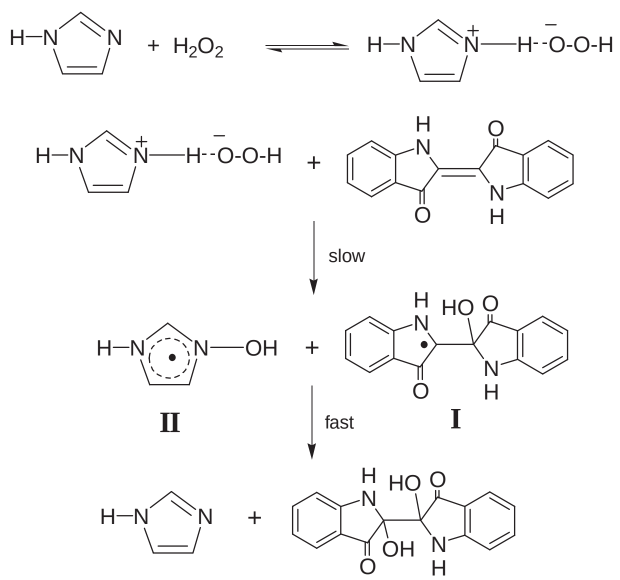
$$v_i = \frac{\Delta \mathrm{Abs_i}}{\Delta t \cdot b \cdot \Delta \mathcal{E}}, \tag{3}$$

where $\Delta \mathrm{Abs_i}$ is the change in the absorbance, b is the pathlength, $\Delta\mathcal{E}$ is the difference in the molar absorptivity of the reactant and product at 600 nm ($\Delta\mathcal{E} = 1.9 \times 10^4\ M^{-1}\ cm^{-1}$), and Δt is the time change. The initial rate values at each magnetic field are listed in Table 1.

A plot of the initial rate against the applied magnetic field showed that the rate increased almost linearly with the magnetic field, Fig. 2. The relative values of the reaction rate in the presence (**rate$_M$**) and absence (**rate$_o$**) of a magnetic field was calculated from the slope and the intercept of Fig. 2;

Table 1. Initial Rates and Pseudo-First-Order Rate Constants for the Reaction of Indigo Blue with H_2O_2 as Catalyzed by Imidazole in Aqueous Solution with Different Magnetic Fileds at 20 °C

Magnetic Field /T	[Imidazole] /M	Initial rate /10^8 M s^{-1}
0	0	0.15
0.035	0	0.20
0	0.02	2.4
0.035	0.02	4.9
0.085	0.02	11.0
0.1	0.02	12.5
0.12	0.02	14.0



Scheme 2. A proposed mechanism for the oxidation of Indigo Blue with H_2O_2 catalyzed by imidazole.

rate$_M$/rate$_o$ ≈ 50.

The Reaction Mechanism. A clear effect of the magnetic field on the rate of oxidation of indigo dye with H_2O_2 in the presence of imidazole as a catalyst may indicate that this reaction involves a radical species.[4] The reaction may involve hydroxyl radical and/or indigo blue radical intermediates. In the absence of imidazole, formation of a free hydroxyl radical would required a high activation energy and is expected to be kinetically unfavorable. Therefore, in the absence of imidazole, the reaction was not affected by the applied magnetic field. In the presence of imidazole, the hydroxyl radical should be stabilized, and the radical path would be kinetically more favorable leading to a faster oxidation reaction. Based on these findings and the other kinetic results, the mechanism in Scheme 2 has been proposed.

The mechanism initially involves acid–base reaction between imidazole and H_2O_2 followed by one-electron oxidation (slow step) of the indigo dye to form radical intermediates I and II. These radicals should be relatively stable since they are involved in highly conjugation systems that have electronegative atoms. The final (very rapid) step involves reaction of these radical intermediates to give the final product and regenerate the imidazole.

The magnetic field is a very important physical factor, like temperature and pressure, that influence the chemical and physical behavior of chemical species. It is obvious that magnetized species, such as paramagnetic and ferromagnetic materials, are affected when a magnetic field is applied. The strength of the interactions of molecules with magnetic fields are much smaller than thermal energies; therefore, chemical and biological processes cannot be influenced by magnetic fields to any measurable degree. However, a chemical reaction is not only influenced by thermal energy barriers, but also by the perturbation of an intermediate quantum mechanical process. For example, the interconversion of a singlet-biradical intermediate to a triplet state is significantly affected by an external magnetic field, which may influence the reaction kinetics.[15]

In this study, although, none of the reactants were paramagnetic, the catalyzed oxidation rate was enhanced by increasing the magnetic field. This may indicate that the oxidation of indigo dyes with H_2O_2 in the presence of imidazole involves radical intermediate(s). Therefore, when the reaction was carried out in a magnetized solution, the reaction was faster. This study showed that investigating the effect of magnetic field on chemical reactions would be a good tool for studying reaction mechanisms and identify possible intermediates, such as radical species. Definitely, additional investigations are necessary on this system, such as identifying intermediates involved during the reaction.

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References

1 K. Shinohara, R. Aogaki, *Electrochemistry* **1999**, *67*, 126.
2 A. Chiba, K. Kawazu, O. Nakano, T. Tamura, S. Yoshihara, E. Sato, *Corros. Sci.* **1994**, *36*, 539.
3 A. M. B. Freitas, F. J. G. Landgraf, J. Nvltý, M. Giulietti, *Cryst. Res. Technol.* **1999**, *34*, 1239.
4 J. C. Scaiano, F. L. Cozens, J. McLean, *Photochem. Photobiol.* **1994**, *59*, 585.
5 T. T. Harkins, C. B. Grissom, *Science* **1994**, *263*, 958.
6 K. Shinohara, R. Aogaki, *Electrochemistry* **1999**, *67*, 126.
7 M. Kaneko, H. S. Isaacs, *Corros. Sci.* **2000**, *42*, 67.
8 J. S. Baker, S. A. Parsons, *Water Waste Treat.* **1996**, *39*, 36.
9 A. S. Ifill, J. S. Baker, S. J. Judd, *Trans. IChemE, (Part B)* **1996**, *74*, 120.
10 S. A. Parsons, B. L. Wang, S. J. Judd, T. Stephenson, *Water Res.* **1997**, *31*, 339.
11 S. A. Parsons, B. L. Wang, S. Udol, S. J. Judd, T. Stephenson, *Trans. IchemE (Part B)* **1996**, *74*, 98.
12 *Congreso Iberoamericano de Investigacion*, ed, by C. Leporini Filho, H. Ulrich Suess, **2002**, pp. 1–37.
13 J. Tokuda, R. Ohura, T. Iwasaki, *Text. Res. J.* **1999**, *69*, 956.
14 K. Q. Shawakfeh, A. M. Al-Ajlouni, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 313.
15 Y. Sakaguchi, *Perkins Review*, **2002**, Vol. 46, pp. 18–21.