Imidazole Catalyzed Oxidations with Organic Peroxides: A Kinetic Study

Khaled Q. Shawakfeh and Ahmad M. Al-Ajlouni*

Department of Applied Chemical Sciences, Jordan University of Science and Technology, Irbid 22110, P.O. Box 3030, Jordan

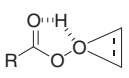
Received April 7, 2003; E-mail: aajlouni@just.edu.jo

Imidazole and 1-methylimidazole catalyze the oxidation of indigo dyes with *m*-chloroperoxybenzoic acid (MCPBA) in organic and mixed aqueous solutions. The kinetics of these reactions were studied in CH_3OH/CH_3CN and CH_3OH/H_2O solvent systems. The reaction rates decreased with the solvent polarity. The catalytically active species is proposed as an MCPBA–Im adduct which is in equilibrium with MCPBA and the imidazole. The equilibrium constant ($K \sim 70$) for the formation of the MCPBA–Im adduct was determined in CH_3OH/H_2O (8:2). The catalyzed rates are at least three-orders of magnitude faster than the uncatalyzed rates. The electron-rich, 1-methylimidazole, increases the rate of oxidation of indigo blue via MCPBA more than imidazole itself. A mechanism similar to the Michaelis–Menten type was proposed for these reactions. The initial products from oxidation of indigo dyes by MCPBA are the epoxides, which undergo a slow ring-opening in the presence of water to form 1,2-diol products.

The most common and cheapest methods for activating hydrogen peroxide and molecular oxygen are to transfer them into organic or inorganic peroxides.[1–5] Organic and inorganic peroxides are widely used in the oxidation of many organic and inorganic substrates. Of these, the epoxidation of olefins by peroxy acids is a very common reaction and useful for the synthesis of many organic compounds. Mimoun[2] has discussed the possible mechanisms for the oxygen transfer from a peroxy acid to an olefin. The most acceptable mechanism is the "butterfly mechanism", which involves a nucleophilic attack of the olefin at the terminal oxygen atom of the hydroperoxide group (**I** in Chart 1).[6]

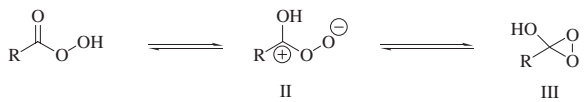
This mechanism is not supported by the fact that these peroxy acids dissociate to their conjugate bases, where this electrophilic oxygen carries a negative charge. In addition, the rate of the epoxidation reaction is greatly enhanced by the acidity of the peroxy acid (i.e., $CF_3CO_3H > CH_3CO_3H$ and *m*-$ClC_6H_5CO_3H > C_6H_5CO_3H$). Furthermore, ab initio calculations have shown that none of the peroxidic oxygen atoms of the peroxy acids are electrophilic.[7] Therefore, a nucleophilic attack on a peroxy acid is more probable to occur at the electrophilic carbon of the CO_3H group. An alternative mechanism considers the intramolecular hydrogen-bonding, which leads to the zwitterion species (**II**) and the dioxirane species (**III**)[2] as shown in Chart 2. Theoretical studies have shown that the most stable species is the dioxirane (**III**).[8] However, a base adduct, such as pyridine, may increase the stability of **II**.

The rate of epoxidation of olefins by transition metal peroxides has been enhanced by the addition of base adducts, such as pyridine derivatives.[9] The activation of H_2O_2 by Mn(III)–porphyrin catalysts towards olefin epoxidation has been accelerated in the presence of pyridine or imidazole axial ligands.[10] It has been demonstrated that the σ-donor ability of imidazole, which is greater than that of pyridine, leads to more stable high valence metal complexes.[11]



I

Chart 1.



II III

Chart 2.

Imidazole, an essential component of many important biological compounds (enzymes), seems to play an important role in enhancing the activity of inorganic and organic peroxides.[12–19] We have found that imidazole increases the reactivity of metal peroxide species and peroxy acids toward oxidation reactions. In addition, imidazole is more resistant to oxidation by peroxides than pyridine.[20]

Here, we are presenting the effect of imidazole and 1-methylimidazole on the oxidation of organic dyes by *m*-chloroperoxybenzoic acid (MCPBA). The reactions of MCPBA with indigo dyes in the presence and absence of imidazole were investigated in organic and mixed aqueous solvents. The effect of each substrate concentration on the reaction rate was studied. A mechanism that involves the formation of an imidazole–peroxide adduct in the initial step, followed by its reaction with the organic reductant has been proposed.

Experimental

Materials. Indigo (96%), tripotassium indigotrisulfonate (85%), and indigo cumine (90%) dyes, 2-phenylpropene, imidazole, and 1-methylimidazole (Aldrich), were used without further

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purification. The percent purity for each dye was considered in the rate constant calculations when necessary. Water was purified by a Milipore deionization system. Methanol and CH_3CN (HPLC grade, Aldrich) were used without further purification. Stock solutions of indigo dyes (0.1–0.2 mM) (1 M = 1 mol dm^{-3}) were prepared in CH_3OH. Solutions of the water-soluble dyes, potassium indigotrisulfonate, and indigo cumine, (1–5 mM) were prepared in deionized water. Stock solutions of *m*-chloroperoxybenzoic acid (Aldrich, 70%), 0.1–0.2 M, were prepared in water and standardized daily by iodometric titration. Stock solutions of imidazoles (0.5–1.0 M) were prepared in CH_3OH.

Equilibrium and Kinetic Experiments. The determination of the equilibrium constant for the formation of the MCPBA–Im adduct was made by scanning the UV spectrum of solutions containing a constant MCPBA concentration (0.5 mM) and different Im concentration, (0.5–200 mM). The reactions were carried out in MeOH/H_2O (8:2) at 25 °C using a 1 cm quartz cuvett. To insure that equilibrium was established, waiting periods of 5–10 min were applied before scanning. Absorbance values were read at several wavelengths in the region 240–300 nm. The data were obtained with a Shimadzu UV-2401 spectrophotometer. All data analysis was carried out with the KaleidaGraph computer program.

Kinetic Studies. The kinetic studies were carried out in CH_3OH/H_2O (8:2) solutions at 25 °C. When the solvent effect was studied, mixtures of CH_3OH/CH_3CN were used. The temperature was kept constant at 25 ± 0.5 °C throughout the entire series of experiments. The ionic strength of the solution was not maintained for these reactions. Air (oxygen) had no effect on the reactions and was not excluded. In all kinetic studies, however, the acid concentration (MCPBA) was held constant. When the effect of [MCPBA] was studied, the H^+ concentration was kept constant by adding *m*-chlorobenzioc acid to the reaction solution. The effect of the pH was studied by adding $HClO_4$ (stock 1.0 M). Quartz cuvettes with optical paths of 0.8 (V_T = 2.0 mL) and 1.0 cm (V_T = 3.0 mL) 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 either a Shimadzu UV-2401 or a Unicam spectrophotometer.

Reaction mixtures were prepared in the spectrophotometer cell with the last reagent added being MCPBA, or the reductant to optimize the kinetic conditions as explained later. The pseudo-first-order rate constants were evaluated by nonlinear least squares fitting of the absorbance–time curves to a single exponential equation, Eq. 1.

$$\mathrm{Abs_t} = \mathrm{Abs_\infty} + (\mathrm{Abs_o} - \mathrm{Abs_\infty})\exp(-k_\psi t) \quad (1)$$

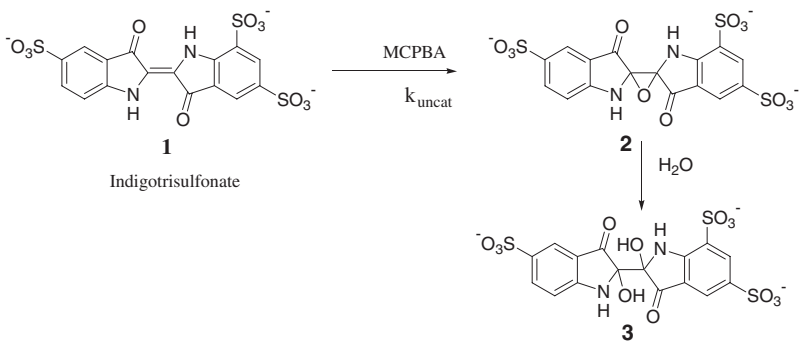
Products. Indigo blue (0.52 g, 1.0 mmol) was mixed with 0.35 g (2 mmol) of MCPB and 0.036 g (0.5 mmol) of imidazole in 25 mL of CH_3OH/H_2O (8:2) solution. The deep blue solution was stirred until the solution color changed to light blue or greenish-yellow. The methanol was removed at 40 °C by a rotary evaporator, and the remaining aqueous solution was washed with ether (5 × 10 mL) to remove imidazole, excess MCPBA, and benzoic acid. Water was then removed by a rotary evaporator at ~70 °C. The product was washed twice with CH_3CN and ether (25 mL each), and characterized by UV–visible, IR, and NMR spectroscopy. The major product was identified as the epoxide of the indigo dye. The 1,2-diol was also observed as a minor product in 5–10% yield. The imidazole oxide was also observed in low yield ~5%. The NMR data for the epoxide product **2** was in good agreement with literature values.[21] ^{1}H NMR (DMSO-d_6, δ/ppm): 9.1 (s, 1H), 8.29 (s, 2H), 7.76 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.1 (d, $J_{H,H}$ = 8.0 Hz, 1H), 4.0 (s, NH). ^{13}C NMR (DMSO-d_6, δ/ppm): 193.2 (C=O), 142.5, 138.5, 132.4, 129.2, 123.2, 118.2 (Aromatic carbons), 81.4 (epoxide carbons).

Results and Discussion

Oxidation of Indigo Dyes by MCPBA—The Uncatalyzed Reaction. All reactions were carried out under pseudo-first-order conditions with MCPBA in large excess over the indigo dye. Kinetic data were collected by following the loss of the dye by recording the absorbance change at a wavelength between 580–620 nm. The reactions were first-order in the [indigo] and in the MCPBA concentrations in CH_3CN/CH_3OH and CH_3OH/H_2O. The pseudo-first-order rate constants obtained by fitting the absorbance–time curves to Eq. 1 varied linearly with the MCPBA concentration, indicating that the reaction is first-order in [MCPBA] and second-order overall. The slope is the second-order rate constant, ($k_2 = 1.1 \times 10^{-4}$ M^{-1} s^{-1}) for the oxidation of tripotassium indigotrisulfonate by MCPBA in MeOH/H_2O (8:2) at 25 °C.

The Products. The reaction products were isolated and identified by IR and NMR spectroscopy. The final major product is the epoxide of indigo blue. The ^{13}C NMR spectra showed two new peaks at 81.1 ppm for the epoxide carbons, where the peaks at ~130 ppm for the alkene carbons disappeared. In addition, the 1,2-diol products were identified as a minor product from this reaction. The epoxide undergoes slow ring opening by water in the solution to give 1,2-diol (Scheme 1). A small amount (<5% based on MCPBA) of imidazole oxide was also observed.

Effect of Imidazoles. The reaction rates for the oxidation of



Scheme 1. Oxidation of indigo blue with MCPBA.

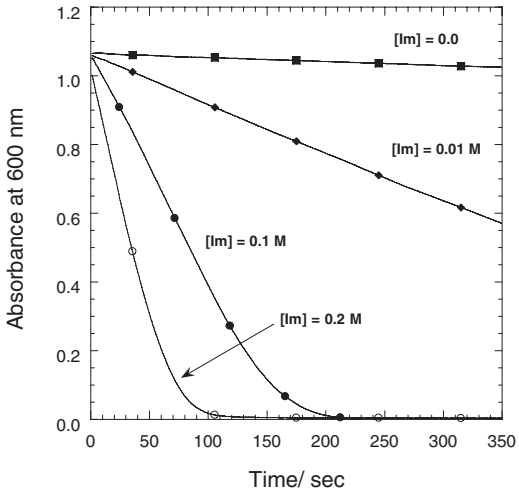


Fig. 1. The absorbance–time curves for the oxidation of indigo blue (0.05 mM) with MCPBA (2.0 mM) in the presence and absence of imidazole. The absorbance change was recorded at 600 nm due to the loss of indigo dye ($\varepsilon_{600} = 1.9 \times 10^4$ $M^{-1}\,cm^{-1}$) in CH_3OH/H_2O (8:2) at 25 °C.

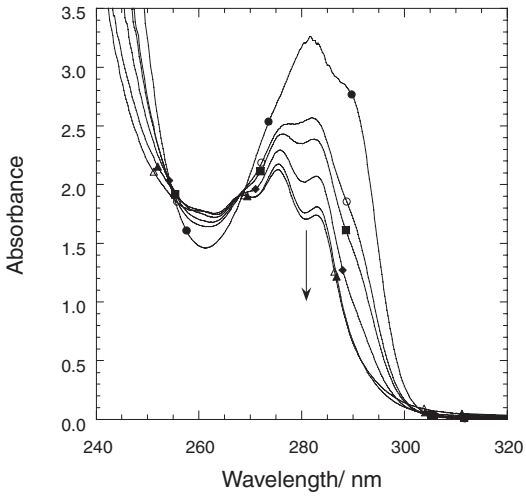
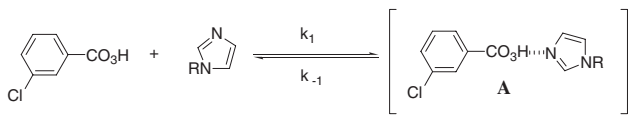


Fig. 2. UV spectra of equilibrated MCPBA/1-MeImidazole mixtures in CH_3OH/H_2O (8:2) at 25 °C. The total MCPBA concentration is 0.5 mM. Reading downward at 282 nm, the 1-MeImidazole concentrations are 0.0 (●), 10 (○), 20 (■), 50 (◆), 100 (▲), 200 (△) mM. Approximate isosbestic point at 269 nm.

indigo dyes with MCPBA were greatly enhanced by the addition of imidazole and 1-methylimidazole to the reaction mixture (Fig. 1). The absorbance changes with time due to the loss of the indigo dye were curved but not exponential. Generally, they exhibit an approach toward linearity during the first one-third of the reaction, but become nearly exponential during the later stages. Both the initial rates (calculated from the first 2–4% of the absorbance–time curves) and the pseudo-first-order rate constants (calculated by fitting the last 10–20% of the absorbance–time curves to Eq. 1) increase linearly with the imidazole concentration even at high concentration ([Im] = 0.05 M). This indicates that the reaction rate is first-order in imidazole concentration in this range.

Reaction of MCPBA with Imidazole: Determination of the Equilibrium Constant. The absorbance–concentration diagram of solutions of MCPBA and imidazole (Fig. 2) is not like a titration curve. It does, however, continue to increase as more imidazole is added, until finally a plateau is reached. This reaction was assumed to form a 1:1 adduct, MCPBA–Im, in equilibrium with MCPBA and Im (Eq. 2).



(2)

The changes in absorbance (Abs) due to the loss of MCPBA and the formation of the MCPBA–Im adduct can be expressed by Eq. 2a (assuming 1.0 cm path length).

$$\text{Abs} = \varepsilon_1[\text{MCPBA}] + \varepsilon_2[\text{MCPBA–Im}] \tag{2a}$$

where ε_1 and ε_2 are the molar extinction coefficients for MCPBA and MCPBA–Im adducts, respectively. Both, ε_1 and ε_2, at each wavelength were determined independently when [Im] = 0 and in the presence of a large excess of Im, respectively. Substituting the equilibrium constant (K) for the formation

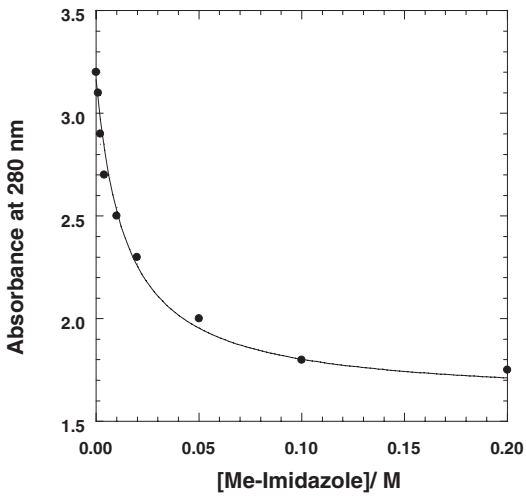


Fig. 3. A plot of the absorbance at 280 nm of MCPBA/1-MeImidazole solutions as a function of [1-MeImidazole] at $[\text{MCPBA}]_T = 0.5$ mM in $MeOH/H_2O$ (8:2) at 25 °C. The solid line is the calculated absorbance using Eq. 6a with the values of K, ε_1, and ε_2 given in Table 1.

of the MCPBA–Im adduct in Eq. 2a, and using the mass balance $[\text{MCPBA}]_T = [\text{MCPBA}] + [\text{MCPBA–Im}]$, we obtain Eq. 2b.

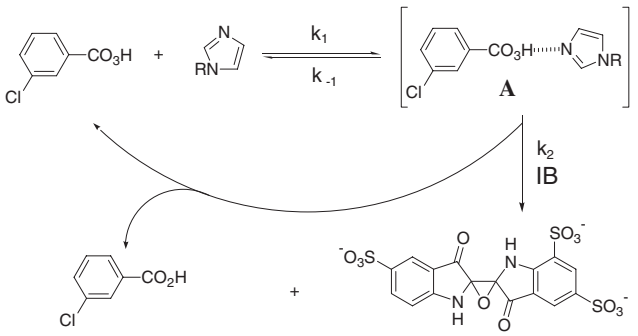
$$\frac{\text{Abs}}{[\text{MCPBA}]_T} = \frac{\varepsilon_1 + \varepsilon_2 K[\text{Im}]}{1 + K[\text{Im}]} \tag{2b}$$

The data were obtained with a constant concentration of MCPBA and over a range of concentrations of imidazole between 0.5 and 200 mM. The data at several wavelengths (270–295 nm) were fit to Eq. 2b (Fig. 3). The calculated equilibrium constants and the values of ε_1 and ε_2 at each wavelength are summarized in Table 1.

Kinetic Studies. The reaction profiles have suggested a

Table 1. Equilibrium Constants for the Formation of MCBPA–Im Adducts in CH_3OH/H_2O (8:2) at 25 °C

Adduct	λ/nm	K_1/M^{-1}	$\varepsilon_1/M^{-1}\,cm^{-1}$	$\varepsilon_2/M^{-1}\,cm^{-1}$
MCBPA–Im	280	68 ± 15	2870 ± 50	1350 ± 35
	290	76 ± 6	1880 ± 32	43 ± 12
MCPBA–MeIm	280	85 ± 15	2970 ± 45	1680 ± 54
	290	83 ± 11	1940 ± 73	175 ± 21



Scheme 2. A reaction scheme for the oxidation of indigo blue with MCPBA as catalyzed by imidazole.

mechanism similar to the Michaelis–Menten mechanism. It involves, first, a reversible (equilibrium) reaction between MCPBA and imidazole to form a reactive intermediate. This step is followed by the reaction of the intermediate with the indigo dye, as shown in Scheme 2.

The rate of oxidation of indigo blue (IB) according to Scheme 2 is expressed by Eq. 3.

$$\text{initial rate } (v_i) = k_2[\mathbf{A}][\text{IB}] \tag{3}$$

The rate equation was derived by means of the steady-state approximation of [**A**]. With the mass balance $[\text{Im}]_T = [\text{Im}] + [\mathbf{A}]$, the rate law can be expressed as follow:

$$v_i = \frac{k_1 k_2 [\text{Im}]_T [\text{MCPBA}][\text{IB}]}{k_1 + k_2[\text{IB}] + k_1[\text{MCPBA}]} \tag{4}$$

Equation 4 can be simplified to Eq. 4a:

$$v_i = \frac{k_2 [\text{Im}]_T [\text{MCPBA}][\text{IB}]}{(K_1)^{-1} + k_2/k_1[\text{IB}][\text{MCPBA}]} \tag{4a}$$

Using the known values of K_1, which were obtained independently from the reaction of the imidazole and MCPBA in the absence of the reluctant, leaves Eq. 4a with two unknown rate constants, k_1 and k_2.

Variation of $[\text{Im}]_T$. The initial rates (v_i) were calculated from experiments in which $[\text{Im}]_T$ varied over the range of 2.0–30 mM. The indigo dye and MCPBA were kept constant at 0.05 and 1.0 mM, respectively. The initial rates showed a linear dependence on $[\text{Im}]_T$, as expected from Eq. 4 (Fig. 4). The rate constants k_1, k_{-1}, and k_2, were determined by studying the variation of the intial rate with IB and MCPBA concentration.

Variation of [IB]. The reaction of indigo blue with MCPBA in the presence of imidazole was studied at constant [MCPBA] (1.0 mM) and [Im] (20 mM). The concentration of IB was varied over the range of 0.002–0.05 mM. The initial rate at each [IB] was calculated from the initial rate of the absorbance change from the loss of IB at 600 nm:

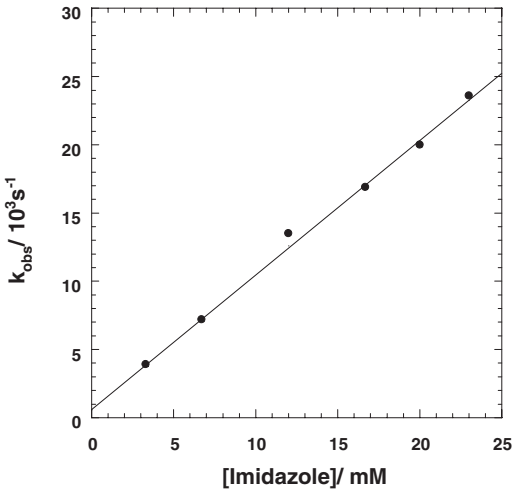


Fig. 4. A plot of the observed-first-order rate constant with [imidazole] for the reaction of MCPBA (2.0 mM) and indigo blue (0.05 mM) in $MeOH/H_2O$ (8:2) at 25 °C.

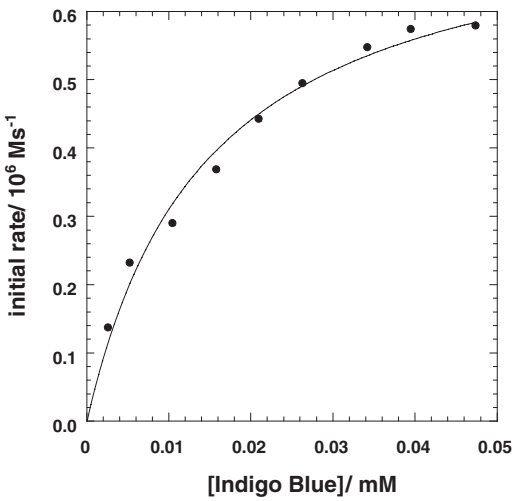


Fig. 5. Variation of the initial rate with [indigo blue] for the reaction of MCPBA (1.0 mM) and indigo blue in the presence of imidazole (20 mM) in $MeOH/H_2O$ (8:2) at 25 °C. The solid line represents the calculated initial rate using Eq. 8 with the values of k_1, k_{-1}, and k_2 given in Table 2.

$$v_i = \frac{\Delta \text{Abs}_i}{\Delta t \cdot b \cdot \Delta \varepsilon} \tag{5}$$

where b is the optical path length and $\Delta\varepsilon$ is the difference in the molar absortivity of the reactants and the products at 600 nm ($\Delta\varepsilon_{600} = 1.9 \times 10^4\ M^{-1}\,cm^{-1}$). The dependence of v_i on [IB], Fig. 5, was linear at [IB] < 0.01 mM. The dependence decreases and reaches a plateau at [IB] > 0.05 mM. This behaviour is common for catalytic reactions in which the ratio $k_1[\text{MCPBA}]/k_2[\text{IB}]$ varies during the reaction due to the decrease in [IB] with time, as shown in Eq. 4a. The data fits very well into Eq. 4a, leading to $k_1 = (0.022 \pm 0.001)\ M^{-1}\,s^{-1}$ and $k_2 = (6.8 \pm 0.4)\ M^{-1}\,s^{-1}$. The rate constant for the deformation of the MCPBA–Im adduct, $k_{-1} = (3.1 \pm 0.3) \times 10^{-4}\ s^{-1}$, was calculated from the value of k_1 and $K_1 = 72\ M^{-1}$.

Variation of [MCPBA]. Values of the initial rates (v_i) for

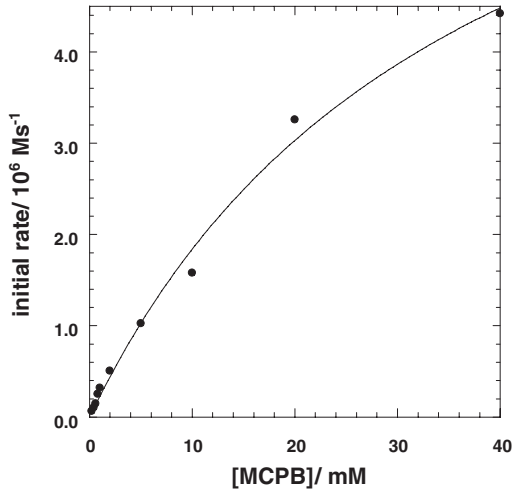


Fig. 6. Variation of the initial rate with [MCPBA] for the reaction of MCPBA and indigo blue (0.05 mM) in the presence of imidazole (20 mM) in MeOH/H_2O (8:2) at 25 °C. The solid line represents the calculated initial rate using Eq. 8 with the values of $k_1 = 0.025$ M^{-1} s^{-1}, $k_{-1} = 3.2 \times 10^{-4}$ s^{-1}, and $k_2 = 7.1$ M^{-1} s^{-1}.

the reaction of MCPBA with indigo blue in the presence of imidazole were calculated over a [MCPBA] range of 0.5–100 mM. Imidazole and indigo blue were held constant at 20 and 0.05 mM, respectively. The variation of the initial rates with [MCPBA] is shown in Fig. 6. The data fits well to Eq. 4, and gave $k_1 = 0.025 \pm 0.005$ M^{-1} s^{-1} and $k_2 = 7.1 \pm 0.3$ M^{-1} s^{-1}. The value of k_{-1} was calculated from k_1 and the equilibrium constant K_1: $k_{-1} = k_1/K_1(3.2 \pm 0.5) \times 10^{-4}$ s^{-1}. The rate constant values obtained from variation of the indigo dye concentration and that obtained from variation of [MCPBA] were in excellent agreement.

Imidazole versus 1-Methylimidazole. Under the same conditions, the oxidation of indigo dye by MCPBA was about 4–5 times faster in the presence of 1-methylimidazole than with imidazole. Fitting the data obtained from variation of the initial rates with the initial concentration of indigo dye to Eq. 4a led to the values of the rate constants k_1 and k_2 for 1-methylimidazole catalyzed reactions. The value of k_{-1} was calculated from the rate constant k_1 and the equilibrium constant K_1. Table 2 summarizes the values of all rate constants for both imidazole and 1-methylimidazole catalytic reactions. The equilibrium constant for the formation of the MCPBA–MeIm adduct was a little higher than that for MCPBA–Im formation, as shown in Table 1. The rate constant k_2 for the oxidation of indigo blue with the MCPBA–MeIm adduct is about 4 times higher than that with the MCPBA–Im adduct. The oxygen-transfer step, rather than the pre-equilibrium step, is responsible for the greater activity of 1-methylimidazole over imidazole.

Solvent Effect. The reaction of MCPBA with indigo dye in the presence of imidazole was carried out in three different solvent mixtures, CH_3OH/H_2O (8:2), CH_3OH/CH_3CN (9:1), and CH_3OH/CH_3CN (1:1). The initial rate and the observed first-order rate constant were found to have the following order (Table 3):

$$CH_3OH/H_2O < CH_3OH/CH_3CN\ (9{:}1) < CH_3OH/CH_3CN\ (1{:}1)$$

The solvent polarity could be the reason for this trend. However, CH_3OH and CH_3CN have similar polarity, but a different ability to form hydrogen bonds with the oxidant and imidazole. This order indicates that the reaction decreases with the solvent ability to form a H-bond and with the solvent nucleophilicity. We think that the solvent nucleophilicity is affecting the reaction. The solvent (as a nucleophile) may compete with imidazole in binding to the carbonyl-carbocation (in the zwitterion species (**II**)), which would be more stable in the presence of a nucleophile, such as imidazole (Eq. 6). It is also possible that protic solvents, such as water or methanol, act as a proton donor to the imidazole and reduce its nucleophilicity.

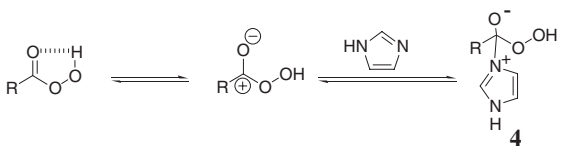


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Table 2. Rate Constants for the Oxidation of Indigo Dye by MCBPA as Catalyzed by Imidazoles in CH_3OH/H_2O (8:2) at 25 °C

Catalyst	k_1/M^{-1} s^{-1}	k_{-1}/s^{-1}	k_2/M^{-1} s^{-1}
Imidazole	0.023 ± 0.002	$(3.1 \pm 0.5) \times 10^{-4}$	7.0 ± 0.6
1-Methylimidazole	0.039 ± 0.005	$(4.6 \pm 1.0) \times 10^{-4}$	32.4 ± 2.9

Table 3. Solvent and Acidity Effect Results on the Oxidation of Indigo Dye with MCPBA as Catalyzed by Imidazole at 25 °C[a)]

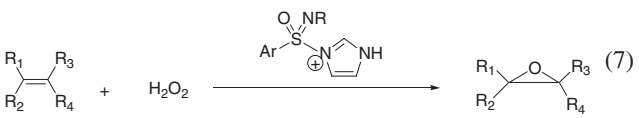
Solvent	$HClO_4$ added	i. r./M s^{-1}	k_{obs}/s^{-1}
CH_3OH/H_2O (8:2)	0	$(1.2 \pm 0.2) \times 10^{-7}$	0.008 ± 0.001
CH_3OH/CH_3CN (9:1)	0	$(3.4 \pm 0.3) \times 10^{-7}$	0.027 ± 0.002
CH_3OH/CH_3CN (1:1)	0	$(6.2 \pm 0.6) \times 10^{-7}$	0.042 ± 0.002
CH_3OH/CH_3CN (1:1)	0.01 M	$(3.6 \pm 0.4) \times 10^{-7}$	0.028 ± 0.002
CH_3OH/CH_3CN (1:1)	0.02 M	$(2.1 \pm 0.3) \times 10^{-7}$	0.017 ± 0.002
CH_3OH/CH_3CN (1:1)	0.05 M	$(1.2 \pm 0.2) \times 10^{-7}$	0.009 ± 0.002

a) [MCPBA] = 1.0 mM, [IB] = 0.05 mM, [Im] = 20 mM.

The exact structure of the active intermediate (**4**) is not known. The structure proposed in Eq. 6 is only one possibility.

Solution Acidity Effect. The effect of pH on the rate of oxidation of indigo blue with MCPBA as catalyzed by imidazole was observed in the presence of different $HClO_4$ concentrations in the range 0.1–0.001 M. The reaction rate decreased with an increase in acidity (Table 3). This result suggests that the binding of imidazole to MCPBA is a necessary step in the activation of MCPBA towards the oxidation of indigo blue dye. The acid reduces both the basicity and the nucleophilicity of imidazoles.

Imidazole Catalysis. It is very clear that imidazoles enhance the activity of MCPBA towards the oxidation of indigo dyes. In addition, imidazoles were not oxidized significantly in these reactions. The imidazole oxide product was less than 10% (based on the [MCPBA]) even at the highest imidazole concentration used in this study, [Im] = 0.2 M ([Im]/[IB] > 2000). Also, the rate of oxidation of indigo dye by MCPBA increases linearly with the Im concentration over the range used, [Im] = 1.0–200 mM (Fig. 4). Imidazole adducts, like all electron-rich bases (or nucleophiles), are known to increase the activity of metal peroxides by enhancing the homolytic or heterolytic cleavage of the peroxide O–O bond "Push Effect".[13] A study on the oxidation of azo dyes by a H_2O_2/Mn^{III}(porphyrin) catalytic system in the presence of imidazoles, pyridines, and benzoic acid found that imidazoles have the highest activity.[14] It has been suggested that imidazoles play a crucial role in coordinating to Mn^{III}, and help in transferring one oxygen atom to the dye.[14] Imidazoles are also reported to enhance the activity and enantiomeric selectivity of the oxidation of olefins by H_2O_2 catalyzed by arenesulfonimido derivatives (Eq. 7).[15] The kinetics and the mechanisms of these reactions were not investigated to understand the role of imidazoles in enhancing the activity.



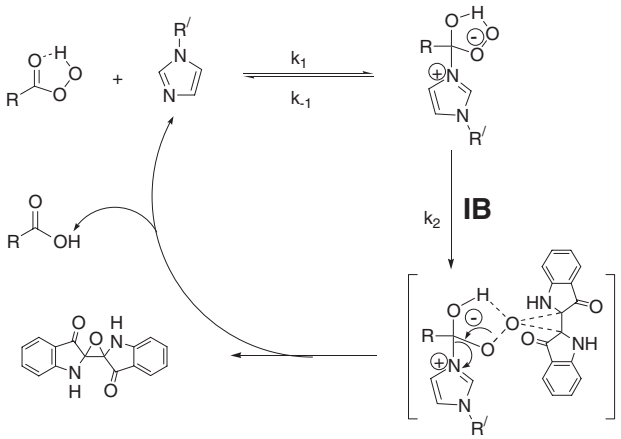
(7)

In our work, the electron-rich imidazoles may play a similar role to the one observed in metal peroxides. Both the metal center and the MCPBA carbonyl are electopositive and can be attacked by the imidazole bases. Therefore, imidazoles may enhance the reactivity of MCPBA by stabilizing the intermediate (**4**) (Eq. 6), and therefore weaken the O–O bond of the MCPBA peroxide. A similar effect has been suggested for the catalytic activation of metal peroxides by imidazoles towards oxidation reactions.[13]

Based on the kinetic results, and the effect of solvent polarity (or nucleophilicity) and the solution pH, the schematic mechanism as described in Scheme 3 is proposed for the oxidation of an olefin (such as indigo dyes) by a MCPBA/imidazole system.

Conclusion

The ability of an imidazole to increase the reactivity of MCPBA to oxidize indigo dyes depends mainly on the electronic nature of the imidazole. Nevertheless, 1-methylimidazole and imidazole were found to have similar equilibrium constants for the formation of MCBPA–Im adducts (Table 1) 1-methylimidazole is about 4–5 times more active than imidazole. It seems that the higher electron-donating ability of 1-methylimidazole is responsible for this higher activity.



Scheme 3. A suggested mechanism for the oxidation of an olefin by MCPBA/imidazole.

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