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Spectrophotometric study of photosensitized dechlorination of isomeric mono- and dichloronitrobenzenes

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Abstract

The photosensitized dechlorination of isomeric mono- and dichloronitrobenzenes has been studied in the presence of naphthoxide ion in alkaline medium. The 100 W tungsten lamp was used for irradiation. The effects of pH, concentration of sensitizer, substrate, intensity of light, and temperature on the rate of the dechlorination have been studied. The quantum efficiency of the dechlorination has been evaluated using potassium ferrioxalate actinometer. The removal of chlorine from the substrate was tested with silver nitrate and the formation of nitrobenzene has been confirmed by λ_{max} in UV spectrum. The mechanism of the photodechlorination has been suggested and the rate of the dechlorination follows the order *p*- > *m*- > *o*-chloronitrobenzene.

Keywords: Chloronitrobenzenes; 2-Naphthol; Photosensitized dechlorination; Spectrophotometric; Rate of reaction

1. Introduction

The halogenated aromatic compounds have become a serious environment contamination problem because of their long life, chemical stability and non-biodegradability. The photochemistry of aromatic halo substituted compounds has been studied with considerable interest in recent years due to the toxic impact of these species on the environment by developing special techniques for their dehalogenation like (1) UV irradiation [1], (2) photosensitized sun-simulated light irradiation [2], (3) photocatalysis [3,4].

Aromatic chlorinated compounds are widely used in the manufacture of explosives, pesticides, and dyes. Nitrobenzene and its derivatives are considered to be highly toxic [5]. Chloronitrobenzenes (CNB) and dichloronitrobenzenes (DCNB) which are used as raw materials for dyes manufacturing, show toxicity to skin, eyes, blood and immune system.

The literature survey shows that very little work has been reported on photodechlorination of CNB and DCNB. Xiuhua and Peizhen [6] have reported photodegradation of isomeric monochloronitrobenzenes in pure and river water. Compton et al. [7,8] carried out photoelectrochemical reduction of *p*-halonitrobenzene. Behar and Neta [9] have explained photodehalogenation of halonitroaromatic compounds.

The present study reports photosensitized dechlorination of isomeric mono- and dichloronitrobenzenes in alkaline medium. The naphthoxide ion is used as photosensitizer, which has also been used as sensitizer [10,11] in alkaline medium. The irradiation of sample was carried out in sun-simulated light. The rate of dechlorination, quantum efficiency (ϕ) and effect of different parameters on the rate of the dechlorination have been reported and reaction mechanism has been suggested.

2. Experimental

2.1. Reagents

All chemicals used for the experiments were of AR grade (Aldrich), and no further purification was done. Absolute alcohol (99%) was used after distillation. Double distilled water was used for the dilution.

2.2. Instruments

The 100 W tungsten filament light source (Phillips) was used for the exposure of the sample solution. Glass water jacket and convex lens was used to decrease the temperature of the solution. All spectral measurements were done on

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UV-Vis spectrophotometer (Spectrascan-2800-Cibacorning, England). PH of the solution was measured using pH meter (Systronics, India).

2.3. Stock solutions

The 10^{-3} M monochloronitrobenzenes solutions and dichloronitrobenzenes solutions were prepared by weighing 0.0157 and 0.0192 g of each substrate and dissolved in minimum volume of ethanol and made up to the mark in 100 ml volumetric flask with double distilled water. The 10^{-3} M naphthoxide ion solution was prepared by weighing 0.0144 g 2-naphthol and dissolved in 10 ml of 10^{-1} M NaOH solution and diluted in 100 ml volumetric flask with double distilled water. The aliquots of the stock solution were diluted as required before use.

2.4. Procedure

Four sets of experiment were prepared by withdrawing 2 ml of chloronitrobenzenes solution, 4 ml of 10^{-1} M NaOH in each 50 ml volumetric flask and 5 ml of 10^{-3} M of 2-naphthol solution was added to two flasks and solutions of all four flasks were made up to the mark with double distilled water. The final concentration of chlornitrobenzenes and naphthoxide ion were 4.0×10^{-5} and 1.0×10^{-4} M, respectively. pH of the solution was maintained between 11 and 12.

Two flasks, one of each containing 2-naphthol and without 2-naphthol were kept in the dark for 24 h while remaining similar flasks were exposed to visible light from 100 W tungsten lamp. The course of the reaction was followed by recording the spectrum of the exposed solution with a control solution in the range of 250–350 nm.

The flask kept in the dark and flask exposed without sensitizer did not show any difference in the spectrum when compared to control; while the exposed flask containing sensitizer showed shift in λ_{max} to 265 nm from the original spectrum, confirms that reaction takes place only in the presence of the naphthoxide ion on irradiation. Thus, the reaction is photosensitized dechlorination and not normal or thermal dechlorination.

The change in the absorbance was measured by measuring the absorbance by withdrawing 5 ml aliquot of the reaction solution after different time intervals at 265 nm in the case of *m*-CNB, *p*-CNB and 3,4-DCNB and at 259 nm for 2,5-DCNB for the calculation of the rate of the reaction. Free chloride was tested in the exposed solution with silver nitrate by observing white precipitate of AgCl. The temperature of the solution was maintained at 298 K using water jacket.

3. Results and discussion

A plot of 2+log optical density (OD) versus time was plotted and it was found to be straight line with a positive slope which indicates that the reaction follows first-order reaction kinetics. The increase in the absorbance at 265 nm was measured with time at different time interval; which increased and became constant indicating the completion of the reaction. The molar absorptivity of the product is higher than the molar absorptivity of the substrate. The molar absorptivity of the substrate and the product were calculated by measuring the absorbance of a number of known concentration solutions (Table 1). The increase in the product concentration, increases the absorbance at 265 nm; which has been used to calculate the rate constant for *m*-, *p*-CNB and 3,4-DCNB but the product is *o*-CNB in the case of 2,5-DCNB; which absorbs at 259 nm and the rate is calculated by measuring the increase in the absorbance at 259 nm.

Table 1
Experimental values of λ_{max} and molar absorptivity of chloronitrobenzenes

Compound	Experimental λ_{max} (nm)	Product λ_{max} (nm)	Calculated ε value
o-CNB	259	–	4760
m-CNB	265	265	4930
p-CNB	279	265	8425
2,5-DCNB	255	259	3187
3,4-DCNB	274	265	3433
$Ph\text{-}NO_2$	265	–	6860

The rate constant of the reaction was determined by using the following expression:

$$\text{rate constant} = 2.303 \times \text{slope}$$

The results of a typical run for mono- and dichloronitrobenzenes are presented (Fig. 1). The rates of the dechlorination for *m*-, *p*-CNB and 2,5-, 3,4-DCNB were calculated (Table 2). *o*-CNB does not undergo photodechlorination under the experimental conditions. The molecule of *o*-CNB shows higher stability in the excited state.

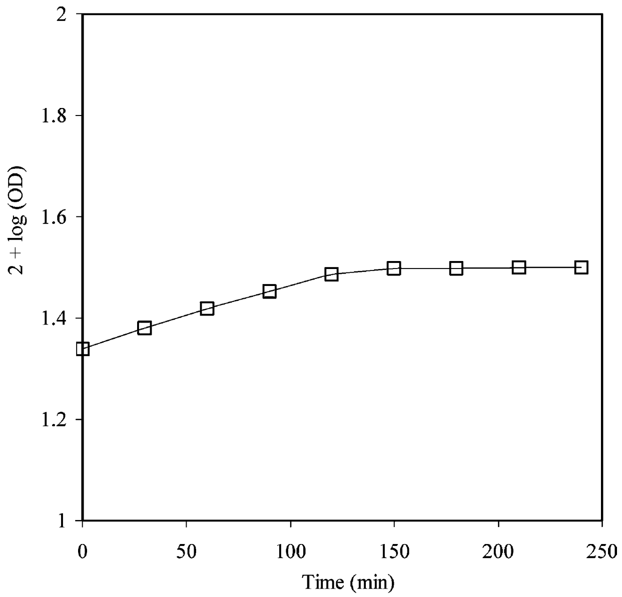


Fig. 1. A typical run.

Table 2
Rate of photosensitized dechlorination of chloronitrobenzenes

Compound	k ($\times 10^3$; min^{-1})
m-CNB[a]	3.3585
p-CNB[b]	6.4950
3,4-DCNB[b]	4.3865
2,5-DCNB[b]	5.8487

[*m*-CNB] = 1.0×10^{-4} M; [*p*-CNB] = 2.5×10^{-5} M; [3, 4-DCNB] = 5.0×10^{-5} M; [2, 5-DCNB] = 8.0×10^{-5} M.

[a] [2-Naphthol] = 4.0×10^{-5} M.

[b] [2-Naphthol] = 2.0×10^{-4} M; light intensity, 11.18×10^{8} E/s; pH 12; temperature, 298 K.

3.1. Spectral characteristics

The spectrum of the exposed solution of the substrates under experimental conditions was recorded between 250 and 350 nm after withdrawing aliquots of the exposed solution at the different time interval. The spectrum of *m*- and *p*-CNB showed change in the spectrum from the original compounds; while exposed solution spectrum of *o*-CNB did not show any change.

The spectrum of *m*-CNB which shows $\lambda_{\max}$ at 265 nm does not show any shift in the $\lambda_{\max}$ but increased absorbance at 265 nm (Fig. 2) which corresponds to the difference in the molar absorptivity of the compound and the product, both absorb at the same wavelength. The spectrum of *p*-CNB, which shows $\lambda_{\max}$ at 279 nm initially, gradually shifts on exposure to 265 nm indicating the formation of single species from the original compound (Fig. 3).

The isomeric 2,5- and 3,4-DCNB undergo shift in their $\lambda_{\max}$ on exposure. The dichloronitrobenzenes show broad absorbance of low molar absorptivity. The spectrum of 2,5-DCNB, which has a broad spectrum of low intensity, shows the new $\lambda_{\max}$ at 259 nm; which corresponds to *o*-CNB (Fig. 4), indicating the removal of only one chlorine atom from the molecule while in the case of 3,4-DCNB, new

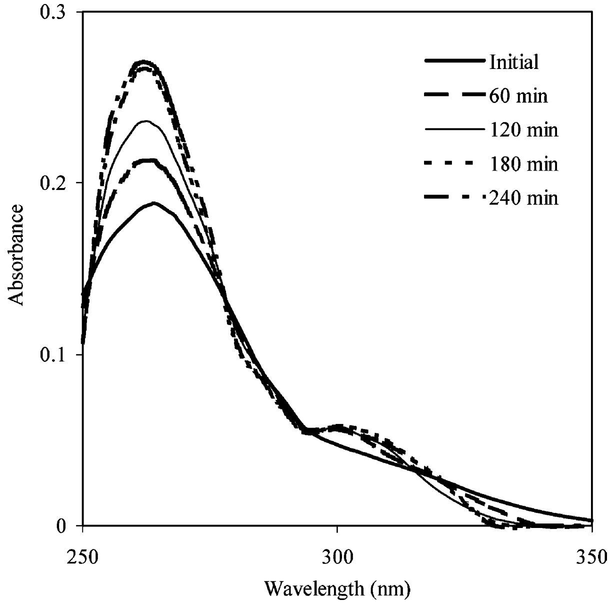


Fig. 2. Spectral changes of *m*-CNB with time, [*m*-CNB] = 4.0×10^{-5} M; [2-naphthol] = 1.0×10^{-4} M; light intensity, 11.18×10^{-8} E/s; pH 12; temperature, 298 K.

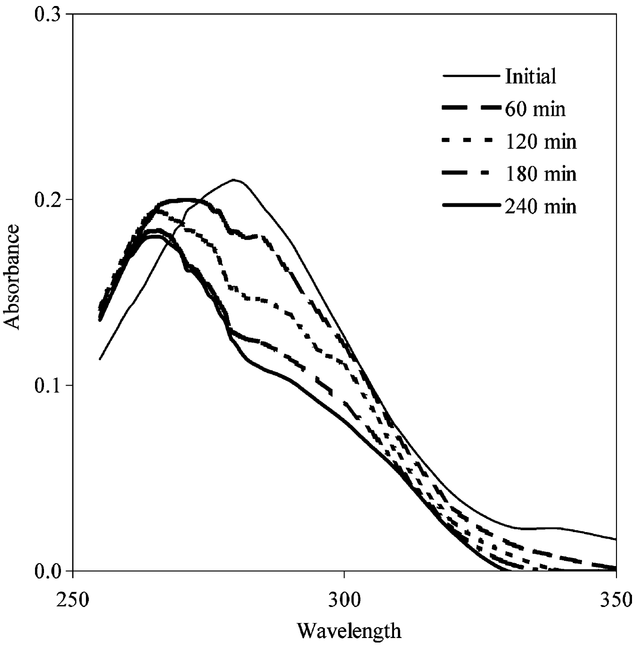


Fig. 3. Spectral changes of *p*-CNB with time, [*p*-CNB] = 2.5×10^{-5} M; [2-naphthol] = 2.0×10^{-4} M; light intensity, 11.18×10^{-8} E/s; pH 12; temperature, 298 K.

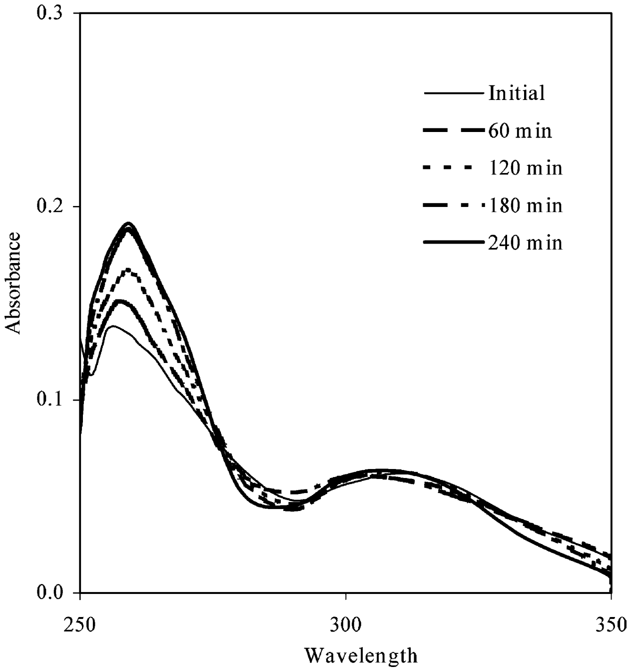


Fig. 4. Spectral changes of 2,5-DCNB with time, [2, 5-DCNB] = 4.0×10^{-5} M; [2-naphthol] = 2.0×10^{-4} M; light intensity, 11.18×10^{-8} E/s; pH 12; temperature, 298 K.

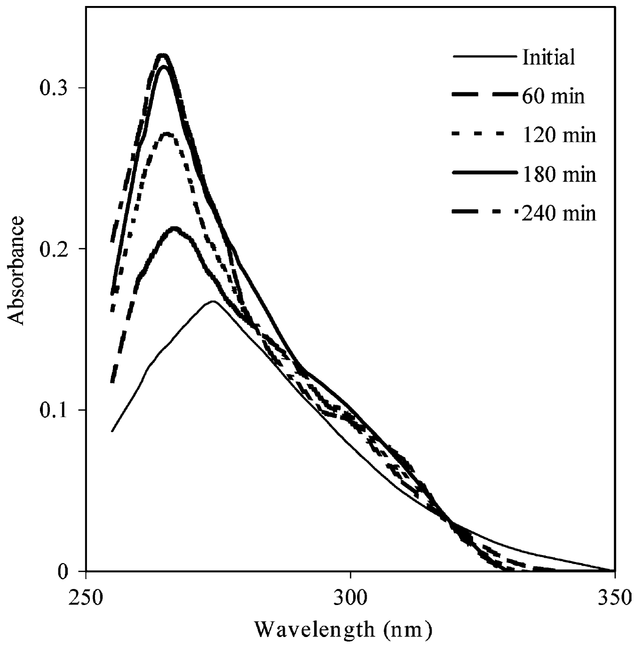


Fig. 5. Spectral changes of 3,4-DCNB with time, [3, 4-DCNB] = 5.0×10^{-5} M; [2-naphthol] = 2.0×10^{-4} M; light intensity, 11.18×10^{-8} E/s; pH 12; temperature, 298 K.

λ_{max} appears at 265 nm (Fig. 5) corresponding to the product obtained from photodechlorination of *m*- and *p*-CNB; which confirms the removal of both chlorine atoms from the molecule.

The molar absorptivity of isomeric mono- and dichloronitrobenzenes shows that spectrum profile of product and of pure nitrobenzene are similar under experimental conditions, confirming the formation of nitrobenzene as major product of the photodechlorination of *m*-, *p*-CNB and 3,4-DCNB; while *o*-CNB in the case of 2,5-DCNB (Table 1).

3.2. Effect of pH

The photosensitizer effect of 2-naphthol was not observed in acidic medium. The rate constant of the photosensitized reaction was calculated for *m*- and *p*-CNB at different pH between 10 and 12.5. It was observed that as pH decreases the rate of the reaction decreases, and it becomes very slow below pH 10 (Fig. 6). The pH 12 gives optimum rate constant value and pH of the solution was maintained at 12 in subsequent study.

The increase in OH^- ion concentration increases the sensitivity of the sensitizer, which shows higher proton transfer of 2-naphthol.

$$C_{10}H_7OH + OH^- \rightleftharpoons C_{10}H_7O^- + H_2O$$

This equilibrium between naphthol and naphthoxide ion is sensitive to OH^- ion concentration of the solution. It is reported that fluorescence of naphthoxide ion is sensitive to pH of the solution. The maximum fluorescence is observed at pH 12 and decreases as pH decreases [12]. Similar effect of OH^- ion concentration is observed in the present study.

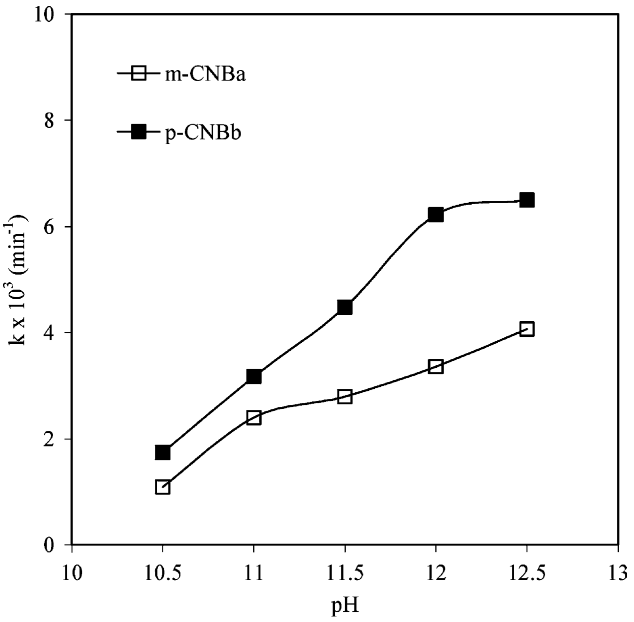


Fig. 6. Effect of pH, [*m*-CNB] = 4.0×10^{-5} M; (a) [2-naphthol] = 1.0×10^{-4} M; [*p*-CNB] = 2.5×10^{-5} M; (b) [2-naphthol] = 2.0×10^{-4} M; light intensity, 11.18×10^{-8} E/s; temperature, 298 K.

3.3. Effect of concentration of the sensitizer

The effect of the concentration of naphthoxide ion on the rate of the dechlorination was studied by calculating the rate constant for *m*- and *p*-CNB by using the different concentration of 2-naphthol in the range of $(0.2–3.0) \times 10^{-4}$ M. The reaction rate increases as the concentration of 2-naphthol increases, but after a limiting value of 1.0×10^{-4} M for *m*-CNB and 2.0×10^{-4} M for *p*-CNB, respectively, it decreases (Fig. 7).

The λ_{max} of all compounds studied lies below 300 nm; which do not absorb visible light. 2-Naphthoxide ions absorb light at 330 nm and get excited; which on collision with the substrate molecules, transfer energy to them, which undergo dechlorination. The increase in the rate of photodechlorination by increasing the concentration of the sensitizer is due to the enhanced collision of excited sensitizer molecules with substrate molecules up to a limiting value. The higher sensitizer concentration increases the deactivation of the excited sensitizer molecule by intermolecular collision.

3.4. Effect of concentration of the substrate

The effect of the initial concentration of *m*- and *p*-CNB on the rate of the reaction was studied. The rate of the reaction was calculated with different initial concentration of the substrate in the range of $(4.0–1.0) \times 10^{-4}$ M, which remains constant with increase in the concentration of the substrate

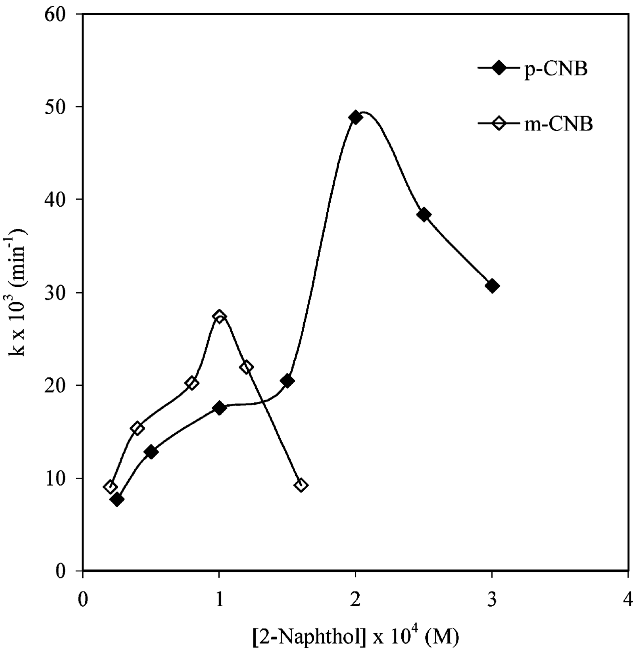


Fig. 7. Effect of concentration of sensitizer, [*m*-CNB] = 4 × 10^{-5} M; [*p*-CNB] = 2.5 × 10^{-5} M; light intensity, 11.18 × 10^{-8} E/s; pH 11.5; temperature, 298 K.

showing that the rate is independent of initial concentration of the substrate (Fig. 8).

3.5. Effect of light intensity

The increase of light intensity shows positive effect and the rate of the dechlorination increases. The number of the excited molecule of the sensitizer increases with higher light intensity as the number of photons increases and corresponding rate of the reaction increases (Table 3). A linear relationship is observed between the light intensity and the rate of the reaction.

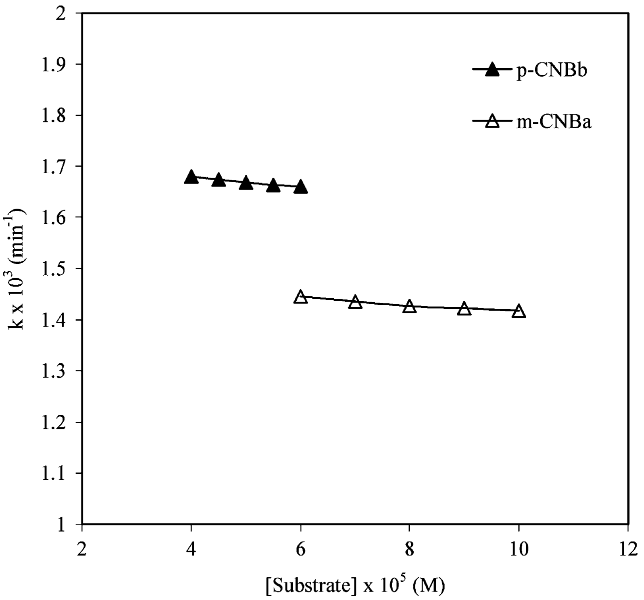


Fig. 8. Effect of concentration of substrate, (a) [2-naphthol] = 2.0 × 10^{-4} M; (b) [2-naphthol] = 3.6 × 10^{-4} M; light intensity, 11.18 × 10^{-8} E/s; pH 11.5; temperature, 298 K.

Table 3
Effect of the light intensity

Light intensity, *I* ($\times 10^8$; E/s)	*k* ($\times 10^3$; min^{-1}) *m*-CNB[a]	*p*-CNB[b]
4.47	0.4652	1.1941
6.72	1.4622	4.1334
11.18	3.3585	6.4956

[a] [*m*-CNB] = 4 × 10^{-5} M; [2-naphthol] = 1 × 10^{-4} M.
[b] [*p*-CNB] = 2.5 × 10^{-5} M; [2-naphthol] = 2.5 × 10^{-5} M; pH 12; temperature, 298 K.

Table 4
Quantum efficiencies of chloronitrobenzenes

Compound	ϕ-Value
o-CNB	–
m-CNB	0.07844
p-CNB	0.16130
2,5-DCNB	0.15370
3,4-DCNB	0.08881

3.6. Effect of temperature

The effect of the variation of the temperature was studied between 298 and 328 K on the rate of the reaction. The fact that the rate of the reaction remains constant with the

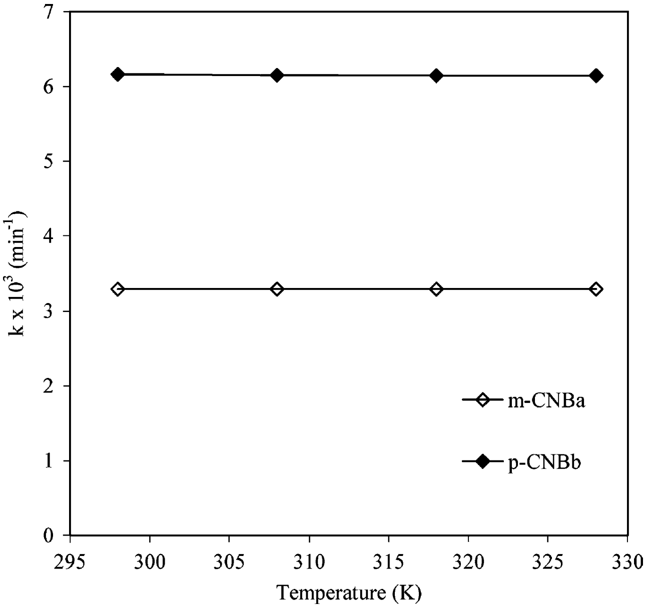


Fig. 9. Effect of temperature, [*m*-CNB] = 4.0 × 10^{-5} M; (a) [2-naphthol] = 1.0 × 10^{-4} M; [*p*-CNB] = 2.5 × 10^{-5} M; (b) [2-naphthol] = 2.0 × 10^{-4} M; light intensity, 11.18 × 10^{-8} E/s; pH 12; temperature, 298 K.

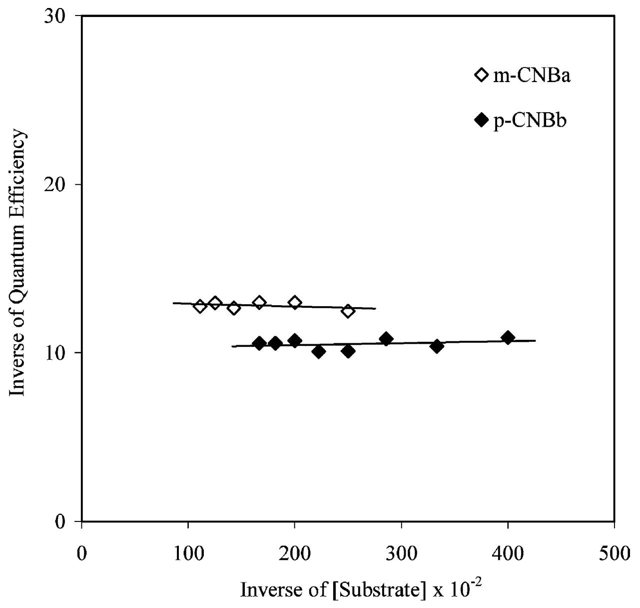


Fig. 10. Inverse of quantum efficiency vs. the inverse of [substrate], (a) [2-naphthol] = 2.0×10^{-4} M; (b) [2-naphthol] = 3.6×10^{-4} M; light intensity, 11.18×10^{-8} E/s; pH 11.5; temperature, 298 K.

$$D \xrightarrow{h\upsilon} D^{*1}$$

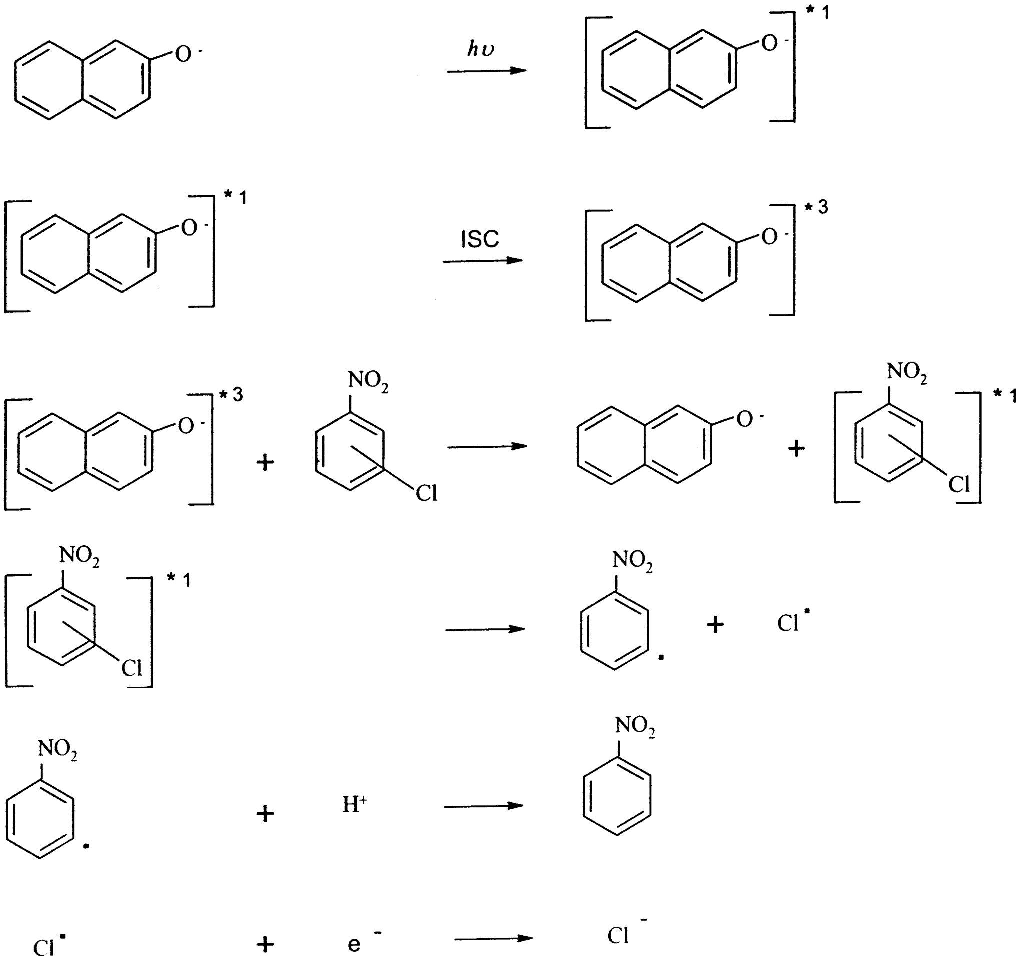
$$D^{*1} \xrightarrow{\text{ISC}} D^{*3}$$

$$D^{*3} + A \longrightarrow A^{*1} + D$$

$$A^{*1} \longrightarrow \text{Product}$$

Scheme 1.

increase in the temperature in the above range indicates that the rate of the reaction is independent of the temperature and thermal condition does not affect the photodechlorination (Fig. 9). The temperature independent nature of the rate of the reaction also indicates that the product formation takes place directly from the excited species without any intermediate stage.



Scheme 2.

3.7. ϕ-Value

The quantum efficiency has been calculated by using standard potassium ferrioxalate actinometer. The ϕ-values calculated for the chloronitrobenzenes are shown in Table 4. The ϕ-values were calculated at different concentrations of the substrate. The plot of inverse of quantum efficiency versus inverse of the concentration of the substrate (CNB) was found linear with zero slope (Fig. 10). The ϕ-values have been found experimentally to be independent of the concentration of the substrate.

4. Mechanism

Isomeric chloronitrobenzenes absorb below 300 nm but naphthoxide ions absorb at 330 nm which is close to visible region. The excited naphthoxide ions, which are in singlet state, undergo inter system crossing (ISC) to triplet state and emit fluorescence [12], in alkaline medium. In the presence of an acceptor (CNB) the naphthoxide ions, which are in triplet state, transfer the energy to acceptor molecules (Scheme 1). The plot of inverse of quantum efficiency versus inverse of concentration of substrate (CNB) (Fig. 10) is linear with zero slope, which indicates the decomposition of first excited state of acceptor molecule to the product [13].

The decomposition of CNB occurred by homolytic fission at C–Cl bond. The nitrobenzene radical accepts a proton from the solution and forms nitrobenzene (Scheme 2). The formation of nitrophenol is not observed which indicates that the C–Cl bond does not undergo complete electron transfer to chlorine. In the case of *o*-CNB, it does not undergo dissociation under experimental condition suggesting a stable excited state.

5. Conclusions

Isomeric mono- and dichlornitrobenzenes undergo photosensitized dechlorination in the presence of naphthoxide ions in alkaline medium in the visible light. The spectral profile of the exposed solution suggests that the product of the reaction is nitrobenzene in the case of *m*-, *p*-CNB and 3,4-DCNB but *o*-CNB in the case of 2,5-DCNB. However, *o*-CNB does not undergo photosensitized dechlorination under experimental condition suggesting a stable excited state.

The rate of the dechlorination is independent of the temperature and initial concentration of the substrate but increases with increase in the sensitizer concentration, OH^- ion concentration and light intensity. The rate of the reaction shows the order *p*- > *m*- > *o*-chloronitrobenzene and ϕ-value also shows similar effect.

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