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PHOTOCHEMICAL SUBSTITUTION REACTION IN m–NITROANILINE

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ABSTRACT

The photochemical reaction of m–nitroaniline in presence of nitrite ion has been carried out. The effect of variation of different parameters like pH, concentration of sodium nitrite, intensity of light, etc. were studied. On the basis of these observed data, a tentative mechanism for the nitration of m–nitroaniline has been proposed.

Key words: Photochemical, m–Nitroaniline, Substitution reaction

INTRODUCTION

Electrophilic aromatic substitution reactions are considered as a backbone of organic synthesis but thse reactions, particularly nitration proceed only under–typical conditions like fuming acids, higher temperature, refluxing, etc. which are not eco–friendly and therefore, it is necessary to develop some alternate pathway, like photocatalytic and photochemical to synthesize the desierd product under ambient conditions.

The photochemical reaction of chromium iminie–carbene complexes with heteroatom containing double bonds was investigated by Campos *et al.*[1] The exciation of nitrite ions in the presence of resorcinol leads to the formation of 4–nitrosorsorcinol as the major photoproduct.[2]. The phototransformation of 2–phenylphenol induced in aqueous solution by excitation of nitrate ions was observed by Sarakha *et al.*[3] The photochemical nitration of benzofurane by tetranitrormethane was observed Butts *et al.*[4] THe photochemical reactions of 4–methoxy–1–naphthonitrile and 2–methoxy 1–naphthonitrite with acrylonitrile and 3,4–dihydro–2H–pyran in ethyl acetate solution were studied by Al–Jalal[5]. Photosubstitution and photoredox reaction of some aromatic nitro compounds were studied by Nakagaki and Mutai[6]. The photochemical behavior of 4–nitrophenol in aqueous solution was studied by Pilichowski *et al*[7]. The photochemical reaction fo 1,2,3–trimethylbenzene was studied by Butts *et al.*[8] Mack and Bolton studied the photochemistry of nitrite and nitrate in aqueous solution wheras Sigman *et al.*[10] observed photochemical reaction of trans–stilbene and 1, 1–diphenylethylene on silica gel. The photochemical synthesis of cyclophanes containing tethered benzofuran rings was recently investigated by Park *et al.*[11] The hydroxylation of benzene using titanium dioxide as a semiconductor was studied by Bhatia *et al.*[12]

EXPERIMENTAL

0.0077 g of m–nitroaniline was dissolved in 50.0 mL of absolute alcohol and 0.5 g sodium nitrite was dissolved in 190 mL of doubly distilled water. Then these solutions were mixed, so that the concentration of m–nitroaniline and sodium nitrite was 2.35×10^{-4} M and 3.00×10^{-2} M, respectively. Then the reaction mixture was exposed to a 200 W tungsten lamp. The intensity of light at various distances was measured by Suryamapi (CEL Model SM 201). The optical density of this solution was determined at $\lambda_{max} = 410$ nm with the help of a spectrophotometer (Systronic Model 106). Some control experiments were also carried out and it was observed that the lgiht is necessary for this photochemical substitution reaction in m– nitroaniline. A water filter was used during exposure to cut–off thermal radiations. The role of hydroxyl radicals was also checked using formate ions, where the rate of nitration was also enhanced.

RESULTS AND DISCUSSION

The progress of reaction was observed by taking O.D. of reaction mixture at different time intervals during exposure. An increase in the O.D. indicates the formation of the product. The results for a typical run are given in Table 1 and represented graphically in Fig. 1. The rate cosntants for this reaction were determined using the experssion.

Rate constant (k) = 2.303 x slope.

Table 1 : A Typical run

[m–Nitroaniline] = 2.35×10^{-4} M
[$NaNO_2$] = 3.00×10^{-2} M
pH = 8.0
Light intensity = 70.0 m Wcm^{-2}

Time (hr.)	Optical Density	1+log (O.D.)
1.0	0.451	0.6541
2.0	0.456	0.6589
3.0	0.462	0.6646
4.0	0.476	0.6767
5.0	0.489	0.6893
6.0	0.502	0.7007
7.0	0.519	0.7134
8.0	0.538	0.7307
9.0	0.554	0.7435
10.0	0.570	0.7558

$k = 8.50 \times 10^{-6}$ sec^{-1}

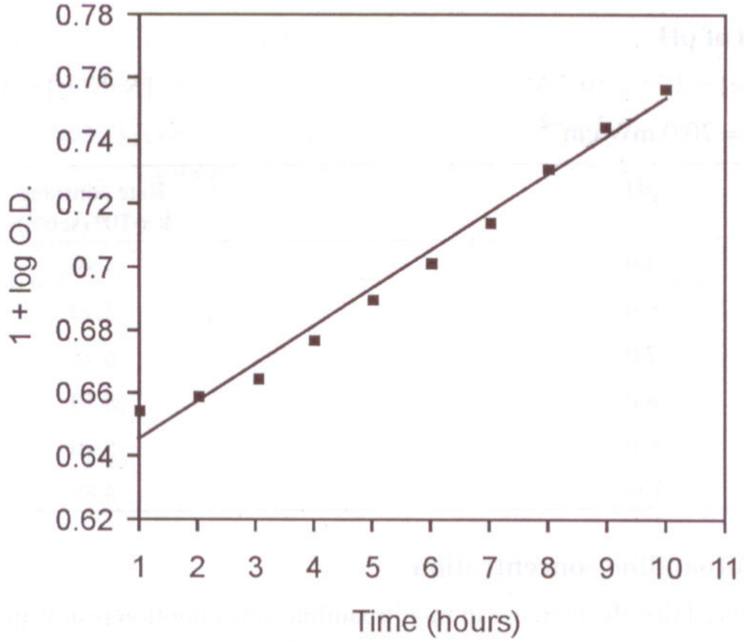


Fig. 1. A Typical Run

Effect of pH

The pH of the medium is likely to affect the rate of the reaction. The reactin rate was meaured in pH range 5–10 and the results are given in Table 2. It is clear that the rate of reaction increases on increasing pH up to 8.0. Thereafter, there is an adverse effect on the rate of the reaction on increasing the pH of the medium further.

Initially, when pH was increased, the reaction rate increases because dinitrogen trioxide N_2O_3 is easily generated by this reaction. This N_2O_3 is considered to be an active species for photonitration of aromatic systems.

$$^{\bullet}NO_2 + {}^{\bullet}NO \longrightarrow N_2O_3 \quad (1)$$

$$N_2O_3 + ArH \longrightarrow ArNO_2 + NO_2^- + H^+ \quad (2)$$

When pH was further increased beyond 8.0, the reaction rate was found to decrease. It is due to the fact that the increasing pH will hinder the generation of $^{\bullet}NO_2$ radicals at higher pH.

$$^{\bullet}OH + NO_2^- \longrightarrow NO_2^{\bullet} + OH^- \quad (3)$$

This reaction generates OH^- ions along with $^{\bullet}NO_2$ radicals, therfore increasing pH will add more OH^- ions to the solution. It will retard the rate of reaction (3) and as a consequence, there will be a corersponding decrease in the rate of reaction.

Table 2. Effect of pH

[m–Nitroaniline] = 2.35 x 10^{-4} M [$NaNO_2$] = 3.00 x 10^{-2} M

Light Intensity = 70.0 mW cm^{-2}

pH	Rate constant k x 10^6 (sec^{-1})
5.0	4.89
6.0	5.49
7.0	6.75
8.0	8.50
9.0	5.70
10.0	4.89

Effect of m–nitoaniline concentration

It was observed that the increase in m–nitroaniline concentration results in a decrese in the rate of reaction. The results are summarized in Table 3. It can be explained on the basis that the m–nitroaniline is coloured and as the concentration of m–nitroaniline was increased, it will act as a filter itself. It will not permit the desired light intensity to reach the molecules present in the bulk of the solution and hence, the reaction rate decreases.

Table 3. Effect of m–nitroaniline concentration

[$NaNO_2$] = 3.00 x 10^{-2} M Light Intensity = 70.0 m W cm^{-2}

pH = 8.0

[m–Nitroaniline] (M)	Rate constant k x 10^6 (sec^{-1})
2.35	8.50
3.14	8.18
3.93	7.21
4.71	5.93
5.50	5.93
6.29	5.45

Effect of $NaNO_2$ concentration

The effect of nitrite ion concentration on rate of reaction was also studied. It was observed that an increase in nitrite ion concentration increases the rate of the reaction up to a limit i.e. 3.00

x 10^{-2} M, beyond which, the rate decreases on increasing the concentration of nitrite ions. The results are tabulated in Table 4.

Table 4. Effect of $NaNO_2$ concentration

[m–Nitroaniline] = 2.35 x 10^{-4} M
Light Intensity – 70.0 m W cm^{-2}

$[NaNO_2]$ x 10^2 M	Rate constant k x 10^6 (sec^{-1})
1.50	3.41
2.25	4.23
3.00	8.50
3.75	4.85
4.50	2.86
5.25	1.89

It can be explained on the basis that as the concentration of sodium nitrite was increased, more NO_2^- ions were available for excitation and consecutive generation of $^{\bullet}NO_2$ readicals and hence, the rate of raection was increased but after a certain limit, these nitrite ions will hinder their own movement, which in turn will decrease the rate of reaction.

Effect of light intensity

The effect of light intensity on the photochemical substitution in m–nitroanline was also observed. The observations are reported in Table 5.

Table 5. Effect of light intensity

[m–Nitroaniline] = 2.35 x 10^{-4} M [$NaNO_2$] = 3.00 x 10^{-2} M
pH = 8.0

Intensity of light (mW cm^{-2})	Rate constant (k x 10^6 (sec^{-1})
40.0	6.74
50.0	7.12
60.0	7.54
70.0	8.50
80.0	7.54
90.0	7.00

It was observed that as the light intensity was increased, the rate of the reaction also increses. This may be attributed to the fact that on increasing the light intensity, more photons are available for excitation of nitrite ions in solution, which ultimately leads to the formation of more $^{\bullet}NO_2$ radicals and hence, the reaction rate increases. However, a slight decrease in the rate was observed on increasing the light intensity above 70 m W cm^{-2}. This may be attributed to the adverse effect of thermal reactions and hence, higher intensities were avoided.

Mechanism

On the basis of observed data and corroborating the existing literature, the following tentative mechansim has been proposed for the nitration.

$$NO_2^- \longrightarrow NO_2^{-*}$$

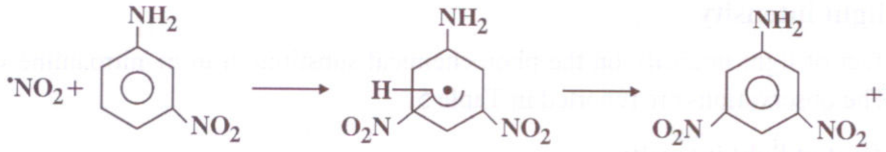
$$NO_2^{-*} \longrightarrow {}^{\bullet}NO + O^{\bullet -}$$

$$O^{-\bullet} + H_2O \longrightarrow OH^- + OH^{\bullet}$$

$$2\,OH^{\bullet} + NO^{\bullet} \longrightarrow NO_2^{\bullet} + H_2O$$

$$OH^{\bullet} + NO_2^- \longrightarrow NO_2^{\bullet} + OH^-$$

$$OH^{\bullet} + NO_2^- \longrightarrow NO_3^- + H^+$$



$$H^{\bullet} + OH^{\bullet} \longrightarrow H_2O$$

First of all, nitrite ion absorbs radiations of suitable wavelength and is excited. These excited nitrite ions dissociate into $^{\bullet}NO$ radical and $O^{-\bullet}$ radical anion. This anion radical decomposes water to give $OH^{\bullet}$ radical and OH^- ion. This $^{\bullet}OH$ radical may react with $NO^{\bullet}$ radical to generate $NO_2^{\bullet}$ radical. Alternatively $^{\bullet}OH$ radical may abstract an e^- from nitrite ion to form the $NO^{\bullet}_2$ radical. $^{\bullet}NO_2$ radical may also undergo in–cage recombination reaction giving nitrate ion. This step seems to dominate in higher pH range. $NO^{\bullet}_2$ radicals now attack the aromatic moiety giving dinitro derivatives. The formation of 3, 5–dinitroaniline was confirmed by usual tests. It was further confimred by its melting piont (observed 160°C, reported 162°C).

There may be hydroxylation also and thus, hydroxyl radical scavenger like formate ion, or isopropanol was used to get better yield of the product.

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