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Impact of Irradiation on *m*-Nitroacetanilide in Presence of a Photocatalyst

J.D. JOSHI*, JABALI VORA†, SANGITA SHARMA†, CHIRAG C. PATEL†, M.P. BRAHMBHATT† and ASHOK B. PATEL†
Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, India

The irradiated semiconductor catalyzed degradation of *m*-nitroacetanilide on zinc oxide powder was carried out. The decomposition of the substrate was observed to be affected by photocatalytic characteristics. The effect of variation of different parameters like concentration of substrate, pH, amount of the semiconductor, light intensity and sensitizer on the rate of photocatalytic degradation was observed. Probable mechanism for the photocatalytic degradation of *m*-nitroacetanilide is proposed.

Key Words: Photocatalytic, *m*-Nitroacetanilide, Zinc oxide.

INTRODUCTION

The photocatalytic reactions are carried out in the presence of light and a semiconductor acts as a photocatalyst. The photocatalyzed transformation of chloroaromatic derivatives such as chlorophenols and dichlorobenzenes on ZnO involving the formation of an adduct between OH radical and aromatic compounds has been studied[1,2]. Efficient photocatalytic degradation of chloral hydrate in aqueous semiconductor suspension has also been observed[3]. Photocatalytic degradation of *p*-nitroaniline in presence of ZnO powder has been observed[4]. Degradation of *o*-nitroacetanilide by heterogeneous photocatalysis has been observed[5]. There are several techniques for removal of organic compounds from industrial effluents[6]. The recent trend of application of photocatytic reaction has given promising outcome in the area of effluent treatment. Important reviews are available on semiconductor photocatalysis[7]. The degradation of nitrophenols and amino phenols on irradiated TiO_2 has been studied[8]. The photocatalytic reactions form a part of important applications of semiconductors[9–12]. In the eighties, researchers began investigating the ability of TiO_2 to photocatalyze organic reactions[13–16].

EXPERIMENTAL

m-Nitroacetanilide was prepared by the usual acetylation of *m*-nitroaniline, crystallized and its purity checked by measuring its m.p. Double distilled water

†Department of Chemistry, North Gujarat University, Patan-384 265, Gujarat, India

was used throughout. Zinc oxide (Merck) was used and other chemicals were of AR grade. A 10 mL 0.20 mM stock solution of *m*-nitroacetanilide and 200 mg of semiconductor (zinc oxide powder, 60 mesh) were taken in a 100 mL beaker and its photocatalytic degradation was observed. This solution was exposed to a 500 W halogen lamp from the top side of a closed beaker. Then the optical density was measured at 355 nm using spectrophotometer (Systronics model 106) in a glass cuvette with path length 1.0 cm and the progress of photocatalytic reaction was observed.

RESULTS AND DISCUSSION

The photocatalytic degradation of *m*-nitro acetanilide was studied using ZnO semiconductor. The results of a typical run are shown in Table-1. A graph of 2 + log O.D. *vs.* exposure time was drawn and its slope determined. According to linear least squares method[17], this graph was plotted. The rate constant of this photocatalytic reaction was determined using the expression K= 2.303 × slope. The photocatalytic degradation of *m*-nitroacetanilide was found to be a two step reaction; in the first step hyperchromic shift was observed without change in λ_{max} value. In the second step the actual degradation reaction occurred.

TABLE-1

Zince oxide = 200 mg	pH = 6.00
Light Intersity = 3.48 m W cm^{-2}	Temperature = 308 K
[*m*-($C_6H_4NHCOCH_3NO_2$)] = 0.20 mM	λ_{max} = 355 nm

Time (min)	O.D.	2 + log O.D.
00	0.026	0.41
30	0.028	0.45
60	0.034	0.53
90	0.033	0.52
120	0.031	0.49
180	0.029	0.46
240	0.028	0.45
300	0.027	0.43
360	0.022	0.34
450	0.018	0.25

$K_1 = 5.00 \times 10^{-3}$ min^{-1}, $K_2 = 1.59 \times 10^{-3}$ min^{-1}

Effect of *m*-nitroacetanilide concentration: The effect of variation of *m*-nitroacetanilide concentration on the rate of its photocatalytic degradation was studied by taking different concentration of *m*-nitroacetanilide (Table-2). The concentration of the substrate was increased, the rate of photocatalytic degradation of *m*-nitroacetanilide decreased the rate of both the step decreased.

TABLE-2
EFFECT OF *m*-NITROACETANILIDE CONCENTRATION

Zinc oxide = 200 mg pH = 6.00
Light Intensity = 3.48 mW cm^{-2} Temperature = 308 K

No.	*m*-nitroacetanilide concentration (mM)	K_1 (min^{-1}) × 10^3 λ_{max} = 355 nm	K_2 (min^{-1}) × 10^3 λ_{max} = 355 nm
1.	0.15	8.82	1.75
2.	0.20	5.00	1.59
3.	0.25	4.61	1.54
4.	0.30	4.31	1.47
5.	0.35	2.00	1.06
6.	0.40	1.68	0.97

Effect of pH variation: The effect of pH on the rate of photocatalytic degradation of *m*-nitroacetanilide was investigated in pH range 4 to 9. The rate of both the steps increased on increasing pH of the solution (Table-3). That is presumably because of the facilitation of the probable intermediates responsible for the advancement of the reaction.

TABLE-3
EFFECT OF pH VARIATION

Zinc oxide = 200 mg ; Light intensity = 3.48 mW cm^{-2}
[*m*-($C_6H_4NHCOCH_3NO_2$)] = 0.20 Mm Temperature = 308 K

No.	pH	K_1 (min^{-1}) × 10^3 λ_{max} = 355 nm	K_2 (min^{-1}) × 10^3 λ_{max} = 355 nm
1.	4	2.53	1.10
2.	5	2.92	1.27
3.	6	5.00	1.59
4.	7	5.36	1.66
5.	8	5.76	1.75
6.	9	6.52	1.77

Effect of amount of phtocatalyst: The effect of variation in the amount of photocatalyst was also observed (Table-4). The value of first rate constant of photocatalytic degradation of *m*-nitroacetanilide increased with increase in the amount of semiconductor but after reaching a certain amount (200 mg) the first rate constant of photocatalytic degradation of *m*-nitro acetanilide becomes almost constant. The value of second rate constant of photocatalytic degradation of *m*-nitroacetanilide decrease with increased in the amount of semiconductor.

TABLE-4
EFFECT OF AMOUNT OF PHOTOCATALYST

[*m*-($C_6H_4NHCOCH_3NO_2$)] = 0.20 mM pH = 6.00
Light Intensity = 3.48 mWcm^{-2} Temperature = 308 K

No.	Amount of photocatalyst (mg)	K_1 (min^{-1}) × 10^3 λ_{max} = 355 nm	K_2 (min^{-1}) × 10^3 λ_{max} = 355 nm
1.	80	3.29	2.28
2.	110	3.45	1.82
3.	140	3.85	1.75
4.	170	4.61	1.63
5.	200	5.00	1.59
6.	250	5.76	1.43
7.	300	5.76	1.17

Effect of light intensity: To observe the effect of light intensity on the photocatalytic degradation of *m*-nitroacetanilide, the distance between the light source and exposed surface of the semiconductor was varied. The intensity was measured using light meter [Make Mastech, Taiwan, Model Lux-1]. The rate of photocatalytic degradation of *m*-nitroacetanilide increase with increased in light intensity. Both the steps show increase in rate with increase in light intensity (Table-5).

TABLE-5
EFFECT OF LIGHT INTENSITY

Zinc oxide = 200 mg pH = 6.00
[*m*-($C_6H_4NHCOCH_3NO_2$)] = 0.20 Mm Temperature = 308 K

No.	Light intensity mW cm^{-2}	K_1 (min^{-1}) × 10^3 λ_{max} = 355 nm	K_2 (min^{-1}) × 10^3 λ_{max} = 355 nm
1.	2.86	4.77	1.43
2.	3.48	5.00	1.59
3.	5.59	9.21	2.69
4.	8.07	9.60	3.94

Effect of sensitizer: Certain dyes and other compounds have a tendency to enhance the reaction rate of photocatalytic reactions[18]. It was therefore an important aspect to observe the addition of similar compounds in the semiconductor catalyzed photo-degradation of *m*-nitroacetanilide. The results are shown in Table-6. Methyl orange, crystal violet and methylene blue were taken up for the study. The first step was totally eliminated in all the three dyes while in case of crystal violet and methyl orange there was a slight increase in the reaction rate indicating the sensitization by them. However, the use of methylene blue resulted in marginal decrease in the rate of second degradation step.

TABLE-6
EFFECT OF SENSITIZER

Zinc oxide = 200 mg pH = 6.00
Light intensity = 3.48 mW cm^{-2} Temperature = 308 K
[*m*-($C_6H_4NHCOCH_3NO_2$)] = 0.20 mM

No.	Sensitizer	K_1 (min^{-1}) × 10^3	K_2 (min^{-1}) × 10^3
1.	Typical run	5.00	1.59
2.	Methyl Orange	—	1.99
3.	Crystal Violet	—	1.80
4.	Methylene Blue	—	1.26

Effect of radical quencher: As alcohols are usually effective in quenching free radicals, methanol and isopropanol were selected for this study. The λ_{max} value, in case of quencher methanol, showed red shift of 5 nm. It was observed that addition of methanol and isopropanol did not reduce the rate of degradation but on the coantrary the reaction rates were found to increase on addition of the alcohol for both the steps (Table-7). Hence it may be inferred that usual free radicals like $^{\bullet}OH$, H^+, $^{\bullet}O_2^-$, H_2O_2, $^{\bullet}HO_2$, O_2 etc. may not play an important role for this degradation reaction but neutral molecules like O_2, H_2O_2 may be responsible.

TABLE-7
EFFECT OF RADICAL QUENCHER

No.	Quencher	λ_{max}	K_1 (min^{-1}) × 10^3	K_2 (min^{-1}) × 10^3
1.	Isopropanol	355	6.15	3.25
2.	Methanol	360	9.21	2.51

Mechanism

Heterogeneous photocatalytic processes typically occurring at solid solution interface when sufficient energy equal to the band gap of the semiconductor is irradiated, the semiconductor forms a pair of valence band hole and conduction band electron.

$$ZnO + h\nu \rightarrow h^+_{(VB)} + e^-_{(CB)}$$

The charge carriers can recombine or be trapped by a defect site or electron transfer with adsorbed electron donors and acceptors can proceed.

$$h^+_{(VB)} + (Red_2)_{ads} \rightarrow (Ox_2)_{ads}$$

$$e^-_{(CB)} + (Ox_1)_{ads} \rightarrow (Red_1)_{ads}$$

The degradation of *m*-nitroacetanilide resulted in virtually all gaseous products. A probable reaction may by written as

$$C_8H_8N_2O_3 + 8.5O_2 \rightarrow 8CO_2 + 4H_2O + N_2$$

Conclusion

The photocatalytic degradation of *m*-nitroacetanilide was found to be a

two-step process. Concentration of substrate, pH of solution, amount of photocatalyst, light intensity, etc. showed their expected impact on the reaction rate. Thus the reaction mechanism is extremely sensitive to some photo-active molecules and its is interesting to extend the study. This method is useful to degrade *m*-nitroacetanilide completely into decomposition products other than solids.

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