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Degradation of *o*-Nitro Acetanilide by Heterogeneous Photocatalysis

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The photocatalytic degradation of *o*-nitro acetanilide, on semiconductor zinc oxide powder in heterogeneous conditions was studied. Concentration of substrate, amount of semiconductor, pH, light intensity, sensitizers, etc. parameters were found to affect the kinetics of the degradation process. A probable mechanism for the process is proposed.

Key words: Photocatalytic, Degradation, *o*-Nitro acetanilide.

INTRODUCTION

The irradiated semiconductor particles are used for treating both organic and inorganic chemical pollutants and micro organisms. A simple experiment demonstrates the efficacy of the use of TiO_2 for the photo oxidation of an organic dye[1]. Reviews on semiconductor photocatalysis are also available. Generally the OH radicals have been frequently implicated in the photo decomposition of organics at oxide semiconductor surfaces[2–4]. Concepts related to the chemistry of semiconductors, the electronic properties of solids and photoelectro chemistry were also discussed recently[5]. Photo degradation of some poly vinyl chloride (PVC) and poly urethane has also been observed[6]. Acyclic chlorinated compounds[7] and chlorobenzenes[8] were photocatalytically degraded in the presence of frequently used semiconductor TiO_2. Attention on several aspects of semiconductor photocatalysis, *viz.*, development of photo active TiO_2 films, panits and paper[9–11], analysis of the kinetics of photo degradation of various organic compounds on TiO_2 films[12] and photo selective destraction of bacteria and cancer cells[13, 14]. Photocatalytic degradation of *p*-nitro aniline[15] and *o*-nitro aniline[16] in presence of oxide semiconductor was found to be effective.

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EXPERIMENTAL

Zinc oxide (Merck) was used and other chemicals were of AR grade. *o*-Nitro acetanilide was prepared by the usual acetylation of *o*-nitro aniline and its purity was checked by measuring its m.p. Double distilled water was used throughout. A 10 mL 0.20 mM stock solution of *o*-nitro acetanilide and 200 mg of semi-conductor (zinc oxide powder, 60 mesh) were taken in a 100 mL beaker and its photocatalytic degradation was observed. This solution was then exposed to 500 W halogen lamp from the top side of a closed beaker. The optical density was measured at 365 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

In Table-1, the results of typical run for photocatalytic degradation of *o*-nitro acetanilide is shown. A graph of 2 + log O.D. versus 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 expression: K = 2.303 × slope. The photocatalytic degradation of *o*-nitro acetanilide was found to be a two step reaction, in the first step hyper chromic shift was observed without change in λ_{max} value. In the second step the actual degradation reaction occurred.

TABLE-1
TYPICAL RUN

Zinc oxide = 200 mg
pH = 7.00
Light Intensity = 4.57 mW cm^{-2}
Temperature = 304 K
[o-$NO_2 \cdot \dot{C}_6H_4 \cdot NHCOCH_3$] = 0.20 mM
λ_{max} = 365 nm

Time (min)	O.D.	2 + log O.D.
00	0.058	0.76
20	0.071	0.85
40	0.082	0.91
60	0.084	0.92
80	0.092	0.96
100	0.086	0.93
120	0.067	0.83
150	0.066	0.82
300	0.032	0.50
360	0.031	0.49
420	0.016	0.20

$K_1 = 5.41 \times 10^{-3}$ Min^{-1}; $K_2 = 4.75 \times 10^{-3}$ Min^{-1}

Effect of *o*-nitro acetanilide concentration: The impact of concentration of *o*-nitro acetanilide upon the rate of the degradation was observed. The results are tabulated in Table-2. As the concentration of the substrate was increased, the rate of both the steps decreased, expectedly due to the e.m.r. cut off as a result of increased absorption by the substrate.

TABLE-2
EFFECT OF *o*-NITRO ACETANILIDE CONCENTRATION

Zinc oxide = 200 mg
Light Intensity = 4.57 mW cm^{-2}
pH = 7.00
Temperature = 304 K
λ_{max} = 365 nm

No.	*o*-nitro acetanilide concentration (mM)	$K_1(min^{-1}) \times 10^3$ λ_{max} = 365 nm	$K_2(min^{-1}) \times 10^3$ λ_{max} = 365 nm
1.	0.10	12.09	6.75
2.	0.15	5.76	6.70
3.	0.20	5.41	4.75
4.	0.25	4.61	4.33
5.	0.30	2.88	4.09
6.	0.35	1.73	3.45

Effect of pH variation: It was important to observe the impact of the pH of the solution of the degradation reaction. The rate of both the steps increased on increasing pH of the solution 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 = 4.57 mW cm^{-2}
[o-$NO_2 \cdot C_6H_4 \cdot NHCOCH_3$] = 0.20 mM
Temperature = 304 K
λ_{max} = 365 nm

NO.	pH	$K_1(min^{-1}) \times 10^3$ λ_{max} = 365 nm	$K_2(min^{-1}) \times 10^3$ λ_{max} = 365 nm
1.	4	4.03	2.53
2.	5	4.60	2.99
3.	6	5.18	3.27
4.	7	5.41	4.75
5.	8	6.33	5.13
6.	9	8.64	5.53
7.	10	9.79	6.49
8.	11	11.51	8.63

Effect of amount of photocatalyst: The effect of variation in the amount of photocatalyst was also observed and the results are tabulated in Table-4. The data indicates that the rate of photocatalytic degradation of *o*-nitro acetanilide increased with increase in the amount of semiconductor but after reaching a certain amount (200 mg) the rate of photocatalytic degradation of *o*-nitro acetanilide did not increase. It is due to the saturation of semiconductor surface exposed to e.m.r. when quantity was increased beyond 200 mg.

TABLE-4
EFFECT OF AMOUNT OF PHOTOCATALYST

$[o\text{-}NO_2\cdot C_6H_4\cdot NHCOCH_3]$ = 0.20 mM
Light Intensity = 4.57 mW cm^{-2}
pH = 7.00
Temperature = 304 K
λ_{max} = 365 nm

No.	Amount of photocatalyst (mg)	$K_1(min^{-1}) \times 10^3$ λ_{max} = 365 nm	$K_2(min^{-1}) \times 10^3$ λ_{max} = 365 nm
1.	50	4.03	1.79
2.	100	4.60	4.33
3.	150	5.18	4.35
4.	200	5.41	4.75
5.	250	5.06	3.93
6.	300	4.72	2.92

Effect of light intensity: The distance between light source and the surface of the semiconductor was varied and the effect of light intensity variation on the photocatalytic degradation of *o*-nitro acetanilide was observed. The intensity of light was measured using light meter [make Mastech, Taiwan, model Lux-1]. The results obtained are shown in Table-5. It is obvious to expect an increase in reaction rate on increasing light intensity. In the degradation of *o*-nitro acetanilide, the value of K_2 was found to increase with increase in light intensity. However, an unexpected observation was noticed for the values of K_1 which decreased with increase in light intensity. Furthermore, it was also observed that the onset of the second step, *i.e.*, actual degradation step was delayed on increasing the light intensity, because of the decrease in the kinetics of the first step. The delay of the onset of the second step could be anticipated as a result of delayed completeness of the first step on increasing the light intensity.

TABLE-5
EFFECT OF LIGHT INTENSITY

Zinc oxide = 200 mg
$[o\text{-}NO_2\cdot C_6H_4\cdot NHCOCH_3]$ = 0.20 mM
pH = 7.00
Temperature = 304 K
λ_{max} = 365 nm

No.	Light intensity (mW cm^{-2})	$K_1 (min^{-1}) \times 10^3$ λ_{max} = 365 nm	$K_2 (min^{-1}) \times 10^3$ λ_{max} = 365 nm
1.	2.13	11.50	3.13
2.	3.50	5.87	4.35
3.	4.57	5.41	4.75
4.	8.16	4.83	13.38
5.	8.79	3.68	18.50

Effect of sensitizer: Sensitizers are usually known to increase the photocatalytic reaction rate by initially absorbing e.m.r and then passing the energy to the reaction system. In the present investigation the sensitizers selected were methylene blue, methyl orange and crystal violet. When methylene blue (10 ppm) was used as a sensitizer, an interesting result was found that the first step process already vanished and the second step, *i.e.*, degradation process started immediately on irradiation with decreased reaction rate ($K = 9.60 \times 10^{-4}$ min^{-1}). In case of methyl orange and crystal violet, it was found that either of the degradation reactions could not be observed possibly due to the e.m.r absorption by the dyes. Hence, these two dyes were not found to be useful as sensitizer.

Impact of free radical quencher: Excited semiconductor especially in aquenous medium can generate several ionic or radical species in solution. It was therefore required to see the effect of radical quencher on this degradation reaction. Two sets were studied for this purpose. One set contained respectively 2 mL and 4 mL isopropanol which is usually regarded as a good radical quencher. The results are mentioned in Table-6. It was observed that addition of isopropanol did not reduce the rate of degradation, on the coantrary the reaction rates were found to increase on addition of the alcohol for both the steps. Hence it may be concluded that free radicals may not be responsible for this degradation reaction.

TABLE-6
EFFECT OF RADICAL QUENCHER

Zinc oxide = 200 mg | pH = 7.00
Light Intensity = 4.57 mW cm^{-2} | Temperature = 304 K
[o-$NO_2 \cdot C_6H_4 \cdot NHCOCH_3$] = 0.20 mM | λ_{max} = 365 nm

No.	Isopropanol (mL)	$K_1(\text{min}^{-1}) \times 10^3$ λ_{max} = 365 nm	$K_2(\text{min}^{-1}) \times 10^3$ λ_{max} = 365 nm
1.	4	7.14	10.34
2.	2	2.50	13.58

Mechanism

Heterogeneous photocatalytic processes typically occuring 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 conductance band electron.

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

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

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

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

The degradation of *o*-nitro acetanilide resulted virtually in all gaseous products. A probable reaction may be written as.

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

Conclusion

The photocatalytic degradation of *o*-nitro acetanilide was found to be a two step process. The pH of solution, substrate concentration, amount of semiconductor, light intensity etc showed their expected impact on the reaction rate. The use of methylene blue did not increase the rate of the reaction however it eliminated the first step. Thus the reaction mechanism is extremely sensitive to some photo active molecules and it is interesting to extend the study. This method is useful to degrade *o*-nitro acetanilide completely into no solid residue decomposition products.

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