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Free radicals generated in photocatalytic oxidation of some organic compounds containing nitrogen atoms

Chen Ciping

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Lu Daohui, Xu Guangzhi

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract— Free radical intermediates generated in photocatalytic oxidation of some organic compound containing nitrogen atoms such as butylamine, piperidine, pyridine and so on were detected by spin trapping technique. The ESR spectra of N-centered radical adduct and C-centered radical adduct were observed. Experiment results reveal that these radicals are participants in the initial steps of photodegradation of these compounds. A mechanism which is consistent with the observation of these radicals species is elucidated.

Keywords: free radicals; photocatalytic oxidation; organic compounds; ESR spectra; spin trapping technique.

1 Introduction

In the recent years attention has been directed toward the photocatalytic degradation of organic compounds in heterogeneous suspensions of metal oxide semiconductors such as TiO_2 and ZnO etc, for the removal of organic pollutants in water (Ollis, 1985; Borello, 1989; D'Oliveira, 1990; Hashimoto, 1984). An advantage of the photocatalytic process is that it can be powered by sunlight to give destruction rates orders of magnitude greater than nature rates. When TiO_2 particles are illuminated with light of wavelength less than 380 nm, an electron-hole pair is created, with the promotion of the electron from the valence band into the conduction band. Some of the electrons and holes migrate to the surface of the particle before recombination occurs. Oxidation reaction will take place if the photogenerated holes react with adsorbed organic molecules whose oxidation potentials lie less positive than the valence band edge.

On the other hand, nitrogen-containing compounds are diverse and play an impor-

tant roles in nature. They comprise different kinds of compounds such as amino acids, proteins and drugs, and figure prominently in herbicides and pesticides. Over the past decade the prolonged and large-scale use of pesticides and herbicides has caused concern because of their toxicity and persistence in the environment.

According to the fact that both ammonia and nitrate ions were formed in TiO_2 mediated photocatalytic degradation of organic compounds containing nitrogen atoms, Low *et al.* (Low, 1991) proposed the degradation process involving a series of intermediates which make the conversion process multicomponent. But little firm evidence is available regard the intermediates in their proposed mechanism and the production of intermediates in the elementary step need to be elucidated. Therefore, it is very important to tackle the formation and elimination of intermediates. The aim of this study is to demonstrate intermediates generated in TiO_2 mediated photocatalytic degradation of some typical organic compounds containing nitrogen atoms by spin trapping technique. The compounds were deliberately chosen primary amines, saturated or aromatic ring nitrogen compounds.

2 Experimental

2.1 Samples

All chemicals used in the experiments were analytical reagents and used as received. The water was double distilled. TiO_2 powder was dispersed ultrasonically in water (50 mg of powder in 5 ml of water). 5, 5-dimethyl-1-pyrroline oxide (DMPO) and nitrosodurene (ND) were used as spin trap. In all experiments, the concentration of the spin trap was 0.05 mol/L. The concentration of compounds containing nitrogen atoms was in the range of $10^{-3}-10^{-4}$ mol/L. The aqueous dispersions were well deaerated with pure nitrogen prior to use.

2.2 Equipment

ESR spectra were recorded on a Bruker ESR 300 spectrometer in a flat quartz cell at room temperature. All samples were illuminated with a GCQ-200W high pressure mercury lamp.

3 Results and discussion

When an aqueous TiO_2 dispersion containing DMPO was irradiated, a quadruplet ESR signal with relative intensities of 1:2:2:1 and hyperfine splittings of $a_N = a_H = 14.90$G was observed immediately. This signal can be attributed to the spin adduct (DMPO-OH). It is well known that when the light of wavelength less than 380 nm is absorbed by TiO_2, an electron is promoted to the conduction band from

the valence band and a hole remains in the valence band. These electrons and holes subsequently undergo interfacial redox-reactions in the heterogeneous systems. If the solvent is water, the hydroxyl radical can be produced from the photooxidation of water.

$$TiO_2 \xrightarrow{h\nu} h^+ + e^-. \quad (1)$$

$$H_2O + h^+ \longrightarrow \cdot OH + H^+. \quad (2)$$

When an aqueous suspension of TiO_2 containing butylamine and DMPO was irradiated, an ESR signal shown in Fig. 1 was obtained. This is a superposition of spectra from two different spin adducts A and B. A and B can be attributed to the Ccentered radical adduct and Ncentered radical adduct respectively. By fitting the calculated spectrum with the observed one, the hyperfine splitting parameters of A and B are given as $a_N = 14.8G$, $a_H = 23.5G$ and $a_N = 14.8G$, $a_H = 18.6G$, $a_{N_2} = 2.4G$, respectively. Nevertheless, the source of the C centered and Ncentered radicals were still unclear. Firstly, it is possible that the photoinduced homogeneous cleavage of butylamine involves an α-CH, or a NH, or an α-CC bond to release proton or carbocations and aminyl or α-amino radicals according to Equation(3).

$$CH_3CH_2CH_2CH_2\text{-}\overset{H}{\underset{|}{N}}\text{-}H \longrightarrow \begin{cases} CH_3CH_2CH_2CH_2\dot{N}H + H\cdot\ ; & (3a) \\ CH_3CH_2CH_2\dot{C}HNH_2 + H\cdot\ ; & (3b) \\ CH_3CH_2\dot{C}H_2 + \dot{C}H_2NH_2. & (3c) \end{cases}$$

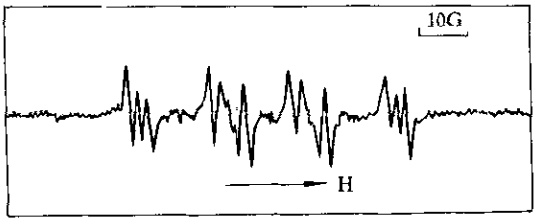


Fig. 1 ESR spectra observed by irradiation of an aqueous TiO_2 suspension containing butylamine and DMPO

Based on comparing the bond energies listed in Table 1 with the energy of photon irradiated the system, ca 75.6 kcal/mol, as well as the result of our experiment that spin adduct $(DMPO\text{-}H)^{\bullet}$ is not observed, we can suggest that various types of free radicals produced in Equation (3) could not be formed. Secondly, it is well known that any substrate whose oxidation potential lies less positive than the valence band edge can act as an effective electron accepter. The oxidation

potential of butylamine and valence band edge of TiO_2 are 1.2 V (vs SCE) and 3.2V (vs SCE) respectively. It is permission thermodynamically that the butylamine may be oxidized to N-centered radical cation by positive hole of valence band of TiO_2. This is well agreement with the observed results.

$$C_4H_9NH_2 + h^+ \longrightarrow C_4H_9\overset{+\cdot}{N}H_2. \quad (4)$$

However, the origination of C-centered radical is still a quite puzzle. It is important to note that the ESR signal of spin adduct $(DMPO\text{-}OH)^{\cdot}$ was not observed when an aqueous suspension of TiO_2 containing DMPO and butylamine was irradiated under the same condition. But the $(DMPO\text{-}OH)^{\cdot}$ appeared in the above system without addition of butylamine, therefore we believe that the $^{\cdot}OH$ could attack the proton at α-C of butylamine, resulting in the formation of C-centered radical.

Table 1 Comparing of the bond energies

Bond	Bond energy, kcal/mol	Bond	Bond energy, kcal/mol
$CH_3(CH_2)N\text{-}CH_3$	84	$CH_3(CH_2)N\text{-}H$	105
$(CH_3)_2N\text{-}CH_3$	88	$(CH_3)_2N\text{-}H$	107
$H_2N\text{-}CH_3$	81	$H_2N\text{-}H$	107
C-C	83		

$$CH_3CH_2CH_2CH_2NH_2 + {}^{\cdot}OH \longrightarrow CH_3CH_2CH_2CHNH_2 + H_2O. \quad (5)$$

It is evident that deprotonate at the α-C to form α-amino radical is also possible.

$$CH_3CH_2CH_2CH_2\overset{+\cdot}{N} \xrightarrow{-H^+} CH_3CH_2CH_2CHNH_2. \quad (6)$$

Since ND is a more efficient trap for C-centered radical, the same experiment was carried out with the replacement of DMPO by ND. The obtained ESRS shows the characteristics of spin adduct $(ND\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}C_3H_7)^{\cdot}$ (Fig. 2), which is consistent with the above mentioned suggestion.

If the same experiment was performed by substituting pentylamine or hyptylamine for butylamine, similar results were obtained. Their hyperfine splitting parameters have slightly different from that of butylamine as shown in Table 2.

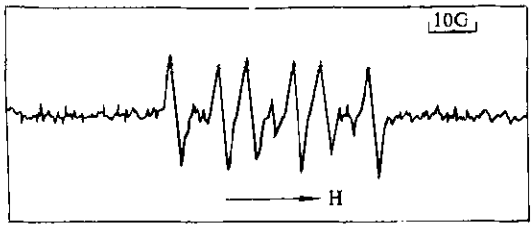
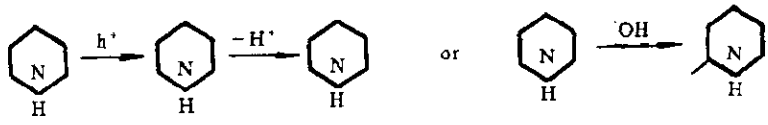


Fig. 2 ESR spectrum generated upon irradiation of an aqueous TiO_2 suspension containing butylamine and ND

When aqueous TiO_2 suspension containing piperidine and DMPO was illuminated, the ESR spectra of spin adducts of both N-centered and C-centered were observed shown in Fig. 3. Based on the ionization potential and oxidation potential of piperidine, it is deducible that the piperidine is similar to alkylamine and could react with positive hole h^+ or $^{\cdot}OH$ to give N-centered and C-centered radicals. These reactions are energetically favorable.



In the cases of aqueous TiO_2 suspension containing pyridine or 2-methylpyridine, or 2, 6-dimethylpyridine was irradiated, the spectra of $^{\cdot}OH$ and C-centered radical adducts were observed (Fig. 4). It is surprised that the N-centered radicals could not be detected. Although the oxidation potential of pyridine and its derivatives used in the experiment are less than the valence band edge of TiO_2, they could be oxidized to N-centered radicals by positive hole. It is probably due to the smaller rates of

Fig. 3 ESR spectra obtained by irradiation of aqueous TiO_2 suspension containing piperidine and DMPO

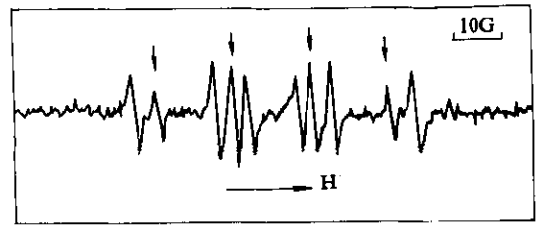
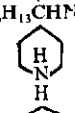
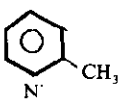
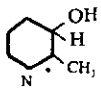
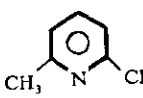
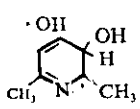


Fig. 4 ESR spectra obtained by irradiation of aqueous TiO_2 suspension containing pyridine and DMPO

Table 2 ESR hyperfine couplings for radical R· adducts

Compounds	R·	(DMPO-R)·			(ND-R)·	
		a_N	$a_{\beta\text{-}H}$	a_{N_2}	a_N	a_H
$C_4H_9NH_2$	$C_4H_9\dot{N}H_2$	15.59	18.45	1.92		
	$C_3H_7\dot{C}HNH_2$				14.16	9.42
$C_5H_{11}NH_2$	$C_5H_{11}\dot{N}H_2$	15.54	18.41	1.94		
	$C_4H_9\dot{C}HNH_2$	15.40	22.49		14.57	8.36
$C_7H_{15}NH_2$	$C_7H_{15}\dot{N}H_2$	15.96	17.98	2.52		
	$C_6H_{13}\dot{C}HNH_2$	15.96	23.02		13.70	6.40
		15.35	18.84	1.87		
		15.34	22.31		14.30	9.11
	·OH	14.86	14.86			
		15.64	22.87			
	·OH	14.88	14.88			
		15.84	22.73			
		14.88 15.58	14.88 27.78			

oxidation reaction between h^+ and pyridine derivatives or smaller rates of addition reactions between DMPO and N-centered radicals. This is consistent with weak intensity of ESRS of C-centered radical adducts.

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