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Catalyst deactivation in the gas phase destruction of nitrogen-containing organic compounds using TiO_2/UV–VIS

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Abstract

Possible application of the TiO_2/UV–VIS photocatalytic process in the destruction of nitrogen-containing malodorous compounds was evaluated. Pyridine (C_5H_5N), propylamine ($C_3H_7NH_2$) and diethylamine ($C_4H_{10}NH$) were photodegraded in the presence and in the absence of oxygen. Degradation of nitrogen-containing organic compounds was confirmed by mass balance taking into consideration NH_4^+ and NO_3^- ions trapped at the TiO_2 surface. Photocatalytic deactivation was observed in all cases. Online mass spectrometry was used to identify byproducts in the gas phase formed during the degradation process. GC–MS analysis of the dichloromethane-extract of aqueous species leached from the surface of deactivated catalyst, as well as pre-concentration in a Tenax column were used to identify intermediates in the gas phase. These byproducts are considered to be the major ones responsible for deactivation of TiO_2. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Titanium dioxide; Photocatalytic destruction; Nitrogen-containing organic compounds; Deactivation; Mass spectrometry (online); Intermediates identification

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1. Introduction

Amines and pyridines are examples of well known malodorous nitrogen-containing compounds and increasing attention has been addressed to removing these compounds from the environment. Recently, heterogeneous photocatalysis using TiO_2 as catalyst and near UV–VIS light has attracted interest due to its potential application for the destruction of a large variety of organic and inorganic pollutants [1,2]. Initially, the emphasis was on the application of photocatalysis for water treatment. In recent years, it has been shown that photocatalytic detoxification of volatile organic compounds (VOCs) is generally more efficient in the gas phase compared to the liquid phase, thus, increasing the attention towards the application of this technology for air treatment. Most of the studies were focused on the photomineralization of hydrocarbon species to CO_2, while reports on the mineralization of heteroatom groups to corresponding inorganic ions have been scarce. Photocatalytic destruction of nitrogen-containing compounds has been carried out in the aqueous phase [3–7], but very little has been published on gas phase degradation [8,9].

Long-term catalytic activity is always desirable in any catalytic process. Although, TiO_2 has proved to be very active in the photo-oxidation of different organic compounds, deactivation has been already reported. According to Sauer and Ollis [10], photocatalyst deactivation is always observed in single-pass fixed-bed photoreactors for cumulative contaminant conversions. Peral and Ollis [11] noted catalyst deactivation

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when photo-oxidizing 1-butanol and butyraldehyde. These authors [12] studied TiO_2-photocatalytic oxidation of decamethyltetrasiloxane, indole, pyrrole and dimethylsulfide, and observed both reversible and irreversible deactivation depending on the organic compound. Deactivation of TiO_2 during the gas phase photo-oxidation of trichloroethylene was reported by Larson and Falconer [13]. Méndez-Román and Cardona-Martínez [14] studied the relationship between the formation of surface species and catalyst deactivation during the gas phase oxidation of toluene. Catalytic deactivation caused by byproducts was observed in the photocatalytic conversion of triethylamine over TiO_2 [15].

As pointed out by Sauer and Ollis [10], every single-pass catalytic process will eventually lead to the deactivation of the catalyst, often not observed in practice due to low levels of substrate or experiments carried out using short periods of time, or both. This may explain why Suzuki [9] did not observe a decrease in the conversion rate of some odorous compounds over illuminated TiO_2.

In this study, the reaction pathways by which pyridine, propylamine, and diethylamine are transformed to nitrate and ammonium ions in the gas phase over irradiated TiO_2 in either oxygen or a nitrogen atmosphere have been investigated. These compounds were selected as they represent primary and secondary amines, as well as pyridine, an nitrogen-containing aromatic compound. The catalyst deactivation process as well as byproduct formation both on the TiO_2 surface and in the gas phase were investigated using online mass spectrometry and liquid–liquid and gas–solid-extraction followed by GC–MS.

2. Experimental

Propylamine, diethylamine and pyridine (all provided by Aldrich) were destroyed in the gas phase using an annular plug flow photoreactor, constructed with a glass cylinder (855 mm × 35 mm i.d.) and a commercially available UV–VIS source (30 W lamp from Sankyo Denki, Japan BLB) with maximum light intensity output at 365 nm. The lamp acts as the inner surface of the annulus. TiO_2 (P25-Degussa) was coated onto the internal glass tube surface using the simple soaking/drying coating method as described by Alberici and Jardim [16]. Experiments were performed in a single-pass mode at a flow rate of 180 to 250 ml/min using synthetic air (21% oxygen and 0.8% relative humidity) or nitrogen (0.8% relative humidity) as carrier gas at room temperature. A more detailed discussion of the experimental apparatus and procedures is found elsewhere [17].

The gaseous mixture was passed through the photoreactor in the absence of UV–VIS illumination until gas–solid adsorption equilibrium under the selected flow was established, as indicated by identical inlet/outlet concentrations of the organic compound. Conversion rates were monitored using a GC–FID (SHIMADZU GC-14B gas chromatograph) equipped with a HP1 ($25\,\mathrm{m} \times 0.25\,\mathrm{mm} \times 0.33\,\mu\mathrm{m}$) capillary column. The destruction of the target compounds and the formation of CO_2 and possible byproducts were also monitored in real time using an online mass spectrometry system and selected ion monitoring (SIM). For this monitoring, the photoreactor outlet was connected directly to the gas inlet of an Extrel (Pittsburg, PA) pentaquadrupole mass spectrometer, that consist of three mass analyzers (Q1, Q3, Q5) and two reaction quadrupoles (q2, q4) [18]. It was also used to identify products of the photocatalytic oxidation through collision induced dissociation (CID) of mass-selected ions in MS–MS experiments [19].

After the photo-oxidation experiments, the reactor was washed with water (3 ml × 50 ml) and the concentration of nitrate was determined by ion chromatography using a Sarasep AN 300 anionic exchange column with a carbonate/bicarbonate buffer mobile phase and a Dionex 200i conductimetric detector. Ammonium ions were analyzed using an ion selective electrode (Metrohn).

Identification of organic intermediates adsorbed onto TiO_2 in the aqueous extracts was accomplished by extraction with dichloromethane and injection in a GC–MS (HP-5890) equipped with an INNOWAX capillary column. Pre-concentration onto a Tenax column following thermodesorption and GC–MS equipped with a HP5 column was used to identify byproducts in the gas phase from diethylamine photo-oxidation.

Sensory analysis was carried out using eight panelists trained according to the flavor profile analysis (FPA) [20]. Panelists were carefully selected based on their sensitivities to detect odor, and were trained

Table 1
Initial conditions and conversion obtained after 2 h of irradiation monitored by GC–FID analysis and nitrogen mass balance in the presence of oxygen

Compounds	C_{inlet}[a] (ppmv)	Flow (ml/min)	Oxidation rate (μmol/min)	Conversion (%)	N-balance (%)	NH_4^+ (%)	NO_3^- (%)
Pyridine	63	188	0.50	90	99	57	43
Propylamine	99	252	0.59	89	93	58	42
Diethylamine	235	240	2.55	90	44	68	32

[a] C_{inlet} is the inlet concentration.

to sample evaluation and description according to the standard methods for the examination of water and wastewater [20]. Panelists were exposed to the treated atmosphere after the TiO_2/UV and the odor intensity was compared to the initial concentration of the compounds kept in a Tedlar bag.

3. Results and discussion

3.1. Photocatalytic destruction of nitrogen-containing compounds

Preliminary experiments showed that both UV–VIS photons and TiO_2 were necessary to destroy the nitrogen-containing compounds. Table 1 summarize the results obtained in the gas phase photocatalytic oxidation in the presence of oxygen for three nitrogen-containing compounds under optimized conditions. The effect of different structures of the nitrogen-containing substrates on the degradation rates was investigated. Degradation yields of 90, 90 and 89% were achieved for pyridine (63 ppmv), diethylamine (235 ppmv) and propylamine (99 ppmv), respectively, taking into consideration the concentrations measured with GC–FID at the inlet and the outlet of the photoreactor.

Panelists scored the smell in the outlet reactor after comparing the odor with odor-free air followed by the air sample collected before irradiation. Results showed that propylamine odor was totally destroyed under the experimental conditions described after irradiation. However, diethylamine produced a new unpleasant odor after 30 min of irradiation. Due the high human olfactive threshold limit (10 ppmv), pyridine was not analyzed by the olfactory panel, since the detection limit for this compound by GC–FID analysis was better.

Table 2 summarizes the results obtained under nitrogen atmosphere. It was observed that oxidation rates in the absence of oxygen were similar to those in the presence of oxygen for propylamine and diethylamine. On the other hand, pyridine is not efficiently destroyed in the absence of oxygen, showing only 6% of conversion. Many reports in the literature have emphasized the importance of oxygen in the photocatalytic reactions of organic compounds, although, the exact role of oxygen in this process has not been yet completely established. It is widely accepted that molecular oxygen is an efficient scavenger of the conduction band electrons of the semiconductor, inhibiting the undesirable e^-/h^+ recombination process. Besides, oxygen is the precursor of various reduced and very reactive species ($O_2^{\bullet -}$, HO_2^-, $HO_2^\bullet$ and H_2O_2). Therefore,

Table 2
Initial conditions and conversion obtained after 2 h of irradiation monitored by GC–FID analysis and nitrogen mass balance in the absence of oxygen

Compounds	C_{inlet}[a] (ppmv)	Flow (ml/min)	Oxidation rate (μmol/min)	Conversion (%)	N-balance (%)	NH_4^+ (%)	NO_3^- (%)
Pyridine	61	180	0.03	6	98	97	3
Propylamine	149	253	1.20	80	78	95	5
Diethylamine	151	240	1.24	90	47	91	9

[a] C_{inlet} is the inlet concentration.

the presence of oxygen was shown to be necessary for the photodestruction of many organic and inorganic compounds [21–24]. However, the effect of oxygen on the degradation rates of diethylamine and propylamine was negligible. According to Fox and Chen [25], since the oxidation potential for both primary and secondary aliphatic amines lies at less positive potentials than the valence band of TiO_2, the adsorbed amine can capture the photogenerated hole, inhibiting the e^-/h^+ recombination process. The decomposition of amines occurs by an electrophilic attack and cleavage of the C–N bond, which may be due to the higher electron density at the nitrogen atom. For pyridine, electrons localized at the nitrogen atom are less available to trap holes (sp^2 orbital) than those of aliphatic amines (sp^3 orbital), explaining why the C–N bond in pyridine is not efficiently broken down in the absence of oxygen.

3.2. Formation of ammonium and nitrate ions

The nitrogen mass balance, including the quantification of ammonium and nitrate ions was investigated under the presence and absence of oxygen (Tables 1 and 2). Nitrite ions were not detected under either experimental condition. It is possible that NO_2^- ions, when formed, are rapidly photo-oxidized to NO_3^-. In the presence of oxygen, the recovery of nitrogen in the degradation of pyridine was 99%, of which 57% corresponds to NH_4^+ and 43% to NO_3^-. For propylamine, 93% nitrogen mass balance was achieved, being 58% from NH_4^+ and 42% as NO_3^-. However, for diethylamine, only 44% were recovered as nitrogen, indicating the possible formation of gaseous or TiO_2 adsorbed nitrogen-containing byproducts. Therefore, all compounds tested yielded nitrate and ammonium ions when exposed to TiO_2/UV–VIS, but at different relative concentrations. In the absence of oxygen, ammonium ions were the main product observed, and the small amount of NO_3^- formed is probably due to adsorbed O_2 or water vapor provided by the carrier gas.

According to Low et al. [4], photocatalytic degradation of nitrogen-containing organic compounds leads to formation of ammonium and nitrate ions. In the aqueous phase, the NH_4^+/NO_3^- ratio after mineralization of the organic compound depends on the nature of the nitrogen atom in the compound and also on the illumination time and the on solute concentration. The authors found that for *n*-pentylamine, piperidine and pyridine, ammonium formation rates were *n*-pentylamine $\gg$ pyridine $>$ piperidine, while the rate for nitrate formation followed pyridine $=$ piperidine $\gg$ *n*-pentylamine. Aliphatic amines produce higher ammonium to nitrate ratios than compounds containing a ring nitrogen.

During illumination, the organic nitrogen is first transformed to NH_4^+, which will act as the precursor of nitrite and nitrate according to the oxidative processes (1) and (2) [26]. Nitrite is often observed as a transient species.

$$2H_2O + NH_4^+ + 6h^+ \rightarrow NO_2^- + 8H^+ \quad (1)$$

$$H_2O + NO_2^- + 2h^+ \rightarrow NO_3^- + 2H^+ \quad (2)$$

In the aqueous phase, photo-oxidation of ammonium to nitrate is a relatively slow process as shown by a low conversion yield (about 3.8%) for an ammonium chloride solution [3]. This behavior was also observed by Maillard-Dupuy et al. [5], when pyridine was mineralized mainly into ammonium ions, and subsequently slowly oxidized to nitrate.

Not much work has been published on the gas phase photocatalytic destruction of nitrogen-containing compounds. In the photocatalytic degradation of gaseous pyridine over TiO_2, Sampath et al. [8] identified no nitrogen-containing byproducts in the gas phase leaving the reactor, and suggested that the major inorganic products could be nitrate and ammonium, although no identification of such species were carried out. In our case, working in the gas phase, it is important to point out that both ammonium and nitrate were identified and measured, and that when compared to aqueous phase, comparatively higher amounts of nitrate were produced.

3.3. Online mass spectrometry analysis

Fig. 1 displays the 70 eV mass spectra obtained before and after UV–VIS irradiation, showing the disappearance of the target compounds with concomitant generation of carbon dioxide (*m/z* 44), the final product identified in gas phase by MS for all compounds tested. For pyridine (Fig. 1a) and propylamine (Fig. 1b), no stable byproducts were detected by online mass spectrometry during 30 min of irradiation. For diethylamine (Fig. 1c), however, acetic acid was identified by its characteristic molecular ion of *m/z* 60.

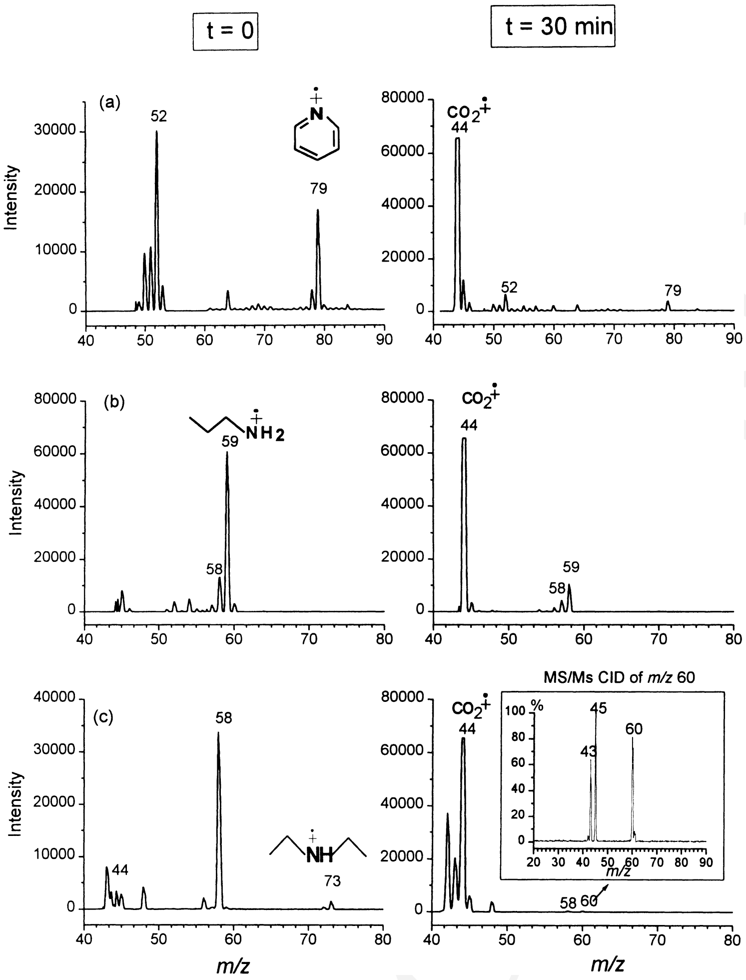


Fig. 1. Electron impact (EI) mass spectra (70 eV) of the gaseous synthetic air mixture containing (a) pyridine, (b) propylamine and (c) diethylamine before and after 30 min of UV-irradiation.

The identity of this ion was investigated using MS–MS collision induced dissociation (CID), the ion *m/z* 60 dissociated to form fragments of *m/z* 43 and 45 (Fig. 1c, insert). Comparing to the CID of the authentic molecular ion, this spectrum confirms the formation of acetic acid as a byproduct [26].

Mass spectrometry–selected ion monitoring (MS–SIM) is a powerful analytical tool since it allows monitoring target compounds destruction as well as any byproduct generation in real time. Fig. 2 shows the MS–SIM profile of the online monitoring of TiO_2/UV–VIS degradation of propylamine (Fig. 2a) and diethylamine (Fig. 2b). As the UV–VIS light is turned on, the concentration of the nitrogen-containing compounds decreases rapidly with the concomitant generation of carbon dioxide. Propylamine is nearly completely destroyed after 8 min of irradiation, while diethylamine was destroyed only 35% in the same time. However, after 2 h (not showed in Fig. 2) the degradation rates for both compounds reached 90%, showing that the degradation kinetics for diethylamine is slower. After 10 min of irradiation the CO_2 production for propylamine was already stable, while for diethylamine it was increasing, as shown in Fig. 2b.

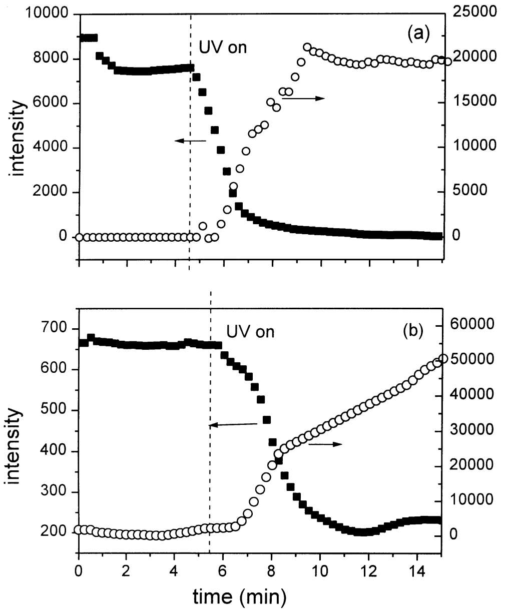


Fig. 2. Selective ion monitoring (SIM–MS) of TiO_2/UV degradation of (a) propylamine and (b) diethylamine: (■) target compounds, (○) *m/z* 44 (CO_2^+). Dashed lines indicate the time when the reactor was turned on.

3.4. Photocatalyst deactivation

The decrease in conversion rates with time most likely indicates that byproducts are adsorbing on the catalyst surface and causing it to deactivate. In some cases, the color of the catalyst also changed during the experiments, as described by Alberici and Jardim [27] for toluene conversion, and by Fu et al. [28] for benzene. Long-term experiments (above 12 h) showed clearly that catalyst deactivation may occur for some of the nitrogen-containing organic compounds. For example, after 17 h of continuous illumination, propylamine conversion rate decreased from 89 to 64%. For diethylamine, the decrease in the conversion rate could be observed after the first 8h (around 78%), dropping to 53% after 24 h. For pyridine, however, no signs of deactivation were observed in numerous 24 h experiments in which the target compound concentration varied from 63 up to 500 ppmv.

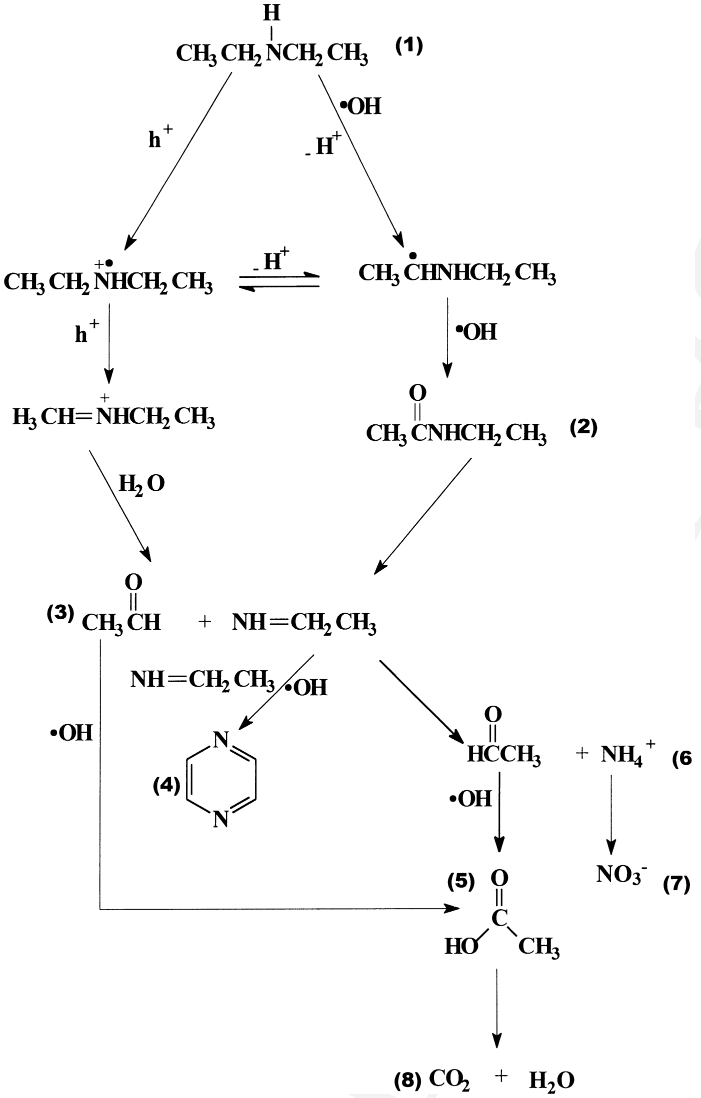
Sauer and Ollis [10] used a conservative approach to explain deactivation, which was based on the cumulative reactant conversion in units of illuminated (active) catalyst surface monolayer equivalents (meq), defined as

$$\text{meq} = \frac{\text{molecules converted}}{\text{(active) catalyst sites}}$$

where meq > 1 indicates that deactivation should occur. Converted molecules are calculated from reaction rate and reaction time. Since the number of active catalyst sites is unknown, then a value of 5×10^{14} sites/cm^2 was adopted from the literature [10] and used as a basis. Assuming that all the catalyst thin film is illuminated, the number of sites per square centimeter equals to 8×10^{17}. The calculated meq range (1–17 h) for pyridine, propylamine and diethylamine were 22–384, 26–452 and 115–1957, respectively, which should lead to catalyst deactivation in a single-path flow reactor from the beginning of the experiment according to the above mentioned authors. However, TiO_2 deactivation was only observed for much higher meq values in all cases.

In this work, identification of surface adsorbed organic species accumulated after 24 h of continuous illumination was carried out using GC–MS analysis. Accumulation for pyridine, dipyridines and 2-acetylpyridine were detected. Maillard-Dupuy et al. [5] also observed the presence of dipyridines as byproducts in aqueous pyridine oxidation. For propylamine, the following products were detected: propanamide, 2,5-dimethyl pyrazine, 1-ethyl propanamine and cyclohexanamine. Ethylacetamide, ethylformamide, diethylacetamide, diethyl urea and pyrazines were detected as byproducts in the diethylamine oxidation. Klare et al. [6] showed that under TiO_2/UV, diethylamine was slightly degraded in the aqueous phase (10% measured as TOC). They also observed that the decrease of diethylamine was faster than the complete mineralization to CO_2. They suggested that the breakdown of diethylamine is more effective than the degradation of the intermediate compounds, because the cleavage of the C–N bond is faster than that of either C–H or C–C bonds in the hydrocarbon residue. With the help of electron impact (EI) mass spectrometry, it was possible to detect the formation of ethylamine, formamide, and acetamide during the degradation experiments.

Although, under a nitrogen atmosphere propylamine and diethylamine were destroyed, many peaks in the chromatograms indicate the formation



Scheme 1. Proposed mechanism for diethylamine photodegradation: ethylacetamide (2), acetaldehyde (3) and pyrazine (5) were identified by GC–MS; acetic acid (4) and carbon dioxide (8) were identified by MS-online; ammonium (6) and nitrate (7) ions were identified by ion selective electrode and ionic chromatography, respectively, in the aqueous phase after washing the photoreactor.

of byproducts due to incomplete mineralization of these amines. Considering that complete mineralization of pyridine, propylamine and diethylamine requires oxygen, it is feasible to assume that under nitrogen, C–N bonds are the first target of the holes of the semiconductor valence band yielding NH_4^+ (nitrogen mass balance), and no CO_2. Huang et al. [15] used Fourier transformed infrared (FTIR) and temperature-programmed desorption followed by mass spectrometry (TPD–MS) to study the deactivation mechanism in triethylamine photo-oxidation. They observed that species such as R–COOH or R–COOR remained at the catalyst surface after reaction. Nitrogen-containing species, in the form of R–N–N=O, were also observed on the surface. They suggested that the accumulation of these surface species and consumption of surface hydroxyl groups were accompanied by the loss of catalytic activity.

During diethylamine photo-oxidation, acetaldehyde, ethylacetamide and pyrizine were detected in the gas phase using Tenax/GC–MS. We were unable to detect these byproducts by online MS during the reaction probably due to low gas phase concentrations. Recent studies showed that TiO_2 rapidly deactivates during photocatalytic processes with acetaldehyde. Acetaldehyde apparently forms surface poisons faster than they can be oxidized photocatalytically [29].

3.5. *Proposed mechanism for the degradation of nitrogen-containing compounds*

Formation of different radicals at the surface of the illuminated semiconductor titanium dioxide is well known. Both holes and hydroxyl radicals have been proposed as the radical/species responsible for initiating the oxidative attack on organic compounds. Low et al. [4] showed that for primary amines (propylamine) in the aqueous phase, both holes and hydroxyl radical paths involve the formation of an ammonium radical cation ($RCH{=}NH_2^{\bullet +}$) followed by hydrolysis, to yield aldehyde and ammonia.

The mechanism for the opening of the pyridine ring is analogous to the rupture of the aromatic ring in the photocatalytic oxidation of benzene. The reaction is initiated by the addition of a hydroxyl radical followed by rapid addition of oxygen to give 2,3-dihydro-2-peroxy-3-hydroxypyridine radical, which finally decomposes in water to produce an aldehyde and formamide [4]. For diethylamine, many byproducts were identified in the gas phase and in the aqueous extract from the catalyst. Based upon these results, a reaction scheme (Scheme 1) is proposed.

4. Conclusion

Total mineralization of nitrogen-containing compounds in the gas phase assisted by TiO_2/UV–VIS showed to be troublesome due to the deactivation of the catalyst. The inorganic species produced, such as ammonium and nitrate, can collaborate in the loss of catalyst activity, as well as can many other identified organic byproducts recalcitrant to the photocatalytic process. However, it is important to mention that catalytic activity could be restored simply by washing the reactor, indicating the reversible nature of the adsorption onto the active surface.

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