

Photocatalytic Degradation of Michler's Ketone in Water by UV Light Illumination Using TiO₂ Photocatalyst: Identification of Intermediates and the Reaction Pathway

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The TiO₂/UV photocatalytic degradation of Michler's Ketone (MK) has been investigated in aqueous heterogeneous suspensions. Results obtained show rapid and complete oxidation of MK after 24-h, and more than 97.5% of MK was mineralized after a 32-h exposure to UV-365 nm irradiation. Establishment of the reaction pathway was made possible by a thorough analysis of the reaction mixture identifying the main intermediate products generated. Nine intermediates have been detected by HPLC/ESI-MS and GC/MS techniques. The photocatalytic degradation of MK proceeds through competitive reactions such as *N*-de-methylation and destruction of the bis-aminobenzophenone structure. The former reaction took place in a stepwise manner to yield mono-, di-, tri-, tetra-demethylated species, while the latter reaction yielded *N*-methylaminobenzene and aminobenzene. The reaction mechanisms of TiO₂/UV proposed in this study should shed some light on future applications of the technology to the destruction of organic pollutants.

Keywords: Michler's Ketone; TiO₂; Photocatalytic.

INTRODUCTION

4-(*N,N*-dimethylamino)-4'-(*N',N'*-dimethylamino)-benzophenone (Michler's Ketone, MK) can be used in printing systems for carton-board used for food packaging. It acts as a curing agent which hardens the ink when it is exposed to ultraviolet light during the printing process. MK is thought to be a potential carcinogen, and the UK printing industry has voluntarily placed it on a list of substances that it does not recommend for use in carton-board packaging inks.¹ MK has been found to induce hepatocellular carcinomas and hemangiosarcomas in rats and mice. The genotoxicity of paper and paperboard extracts and the compounds found in them have been investigated by *Rec*-assay and comet assay. The results showed that most recycled paper products containing chemicals like Michler's Ketone possess genotoxicity.² MK is an important intermediate in the production of triphenylmethane dyes. A large number of investigations have been carried out on the use of MK as a

photosensitizer.³ MK is also used in certain screen printing inks because of its ability to extend the durability of the coating. It is commonly used in the manufacture of road signs and signs mounted on commercial vehicles. The massive use of MK has well-known noxious consequences for the human environment. Because of the importance of this compound, an urgent need for more enhanced technologies that can reduce its presence in the environment has become evident.

Degradation and purification processes for the organic compound in polluted water include adsorption on various adsorbents,⁴⁻⁶ chemical oxidation,⁷ biodegradation,^{8,9} photolysis¹⁰⁻¹² and photocatalysis.¹³⁻²¹ However each has limitations and disadvantages. Adsorption involves only phase transfer of pollutants without degradation; chemical oxidation is unable to mineralize all organic substances; and in biological treatment the slow reaction rates and the disposal of activated sludge are the drawbacks

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to be considered.^{22,23} The photocatalytic processes have received increasing attention in recent years because they are not burdened by the above disadvantages. The photooxidation of organic compounds on photocatalyst particle surfaces has been examined extensively and is being exploited widely to mineralize a variety of environmentally harmful organic compounds. The efficiency of such processes has been demonstrated by several authors and ideally, the end products are carbon dioxide, water and inorganic mineral ions.^{24,25}

Photocatalytic processes use light to generate conduction band electrons and valence band holes (e^- and h^+) capable of initiating redox chemical reactions on semiconductors.^{26,27} Many researchers have used different aqueous suspensions of semiconductor slurries irradiated by UV light to generate highly reactive intermediates, usually hydroxyl radical ($\cdot OH$), that initiate a sequence of reactions leading to the partial or total destruction of organic pollutants such as chlorophenols, nitrogen-containing pesticides, and aromatic compounds.²⁸⁻³² Among the semiconductors used, titanium dioxide (TiO_2) is considered a very efficient catalyst that, unlike other semiconductors, is nontoxic, stable to photocorrosion, and low cost.^{33,34} The photocatalytic process is highly promising because it operates at ambient temperature and pressure with low energy photons ($\lambda < 388$ nm for anatase TiO_2) and requires no expensive catalysts or chemical reagents (except O_2 in the ambient air). Therefore, the photocatalytic method can be developed into a safe and economically viable remediating system.³⁵

Muneer et al.³⁶ have investigated the degradation of gentian violet in a TiO_2 heterogeneous aqueous system. They found MK to be the primary oxidation product, which further degrades to *N*-methylaminobenzene and *p*-aminobenzoic acid. Only two photodegradation intermediates of MK have been separated and identified, and the detailed mechanisms are still unclear. Therefore, this research focused on the identification of the reaction intermediates and understanding of the mechanistic details of the photodegradation of MK in the TiO_2 /UV light process as a foundation for future application of this promising technology.

EXPERIMENTAL

Materials

TiO_2 nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20-30 nm; BET area, ca. $55\text{ m}^2\text{g}^{-1}$) were supplied by Degussa Co. and used in all the photocatalytic

experiments. Michler's Ketone was obtained from Acros Organics Co. and used without any further purification. Sample solutions containing 10 mgL^{-1} of MK in water were prepared, protected from light, and stored at $4\text{ }^\circ\text{C}$. HPLC analysis confirmed the presence of MK as a pure organic compound. Reagent-grade ammonium acetate and HPLC-grade methanol were purchased from Merck. De-ionized water was used throughout this study. The water was purified with a Milli-Q ion-exchange system (Millipore Co.) to give a resistivity of $1.8 \times 10^7\ \Omega\text{-cm}$.

Apparatus and instruments

The LC/MS system used in the study consisted of Waters 1525 HPLC pump connected with Waters 2996 Photodiode Array Detector and Micromass ZQ-4000 Mass spectrometer with electrospray ionization source. An Empower software workstation was used for the LC/MS instrument control, data acquisition, and data processing. GC/MS analyses were run on a Perkin-Elmer AutoSystem-XL gas chromatograph interfaced to a TurboMass selective mass detector. The mineralization of the MK was monitored by measuring the total organic carbon (TOC) content with a Dohrmann Phoenix 8000 Carbon Analyzer, which employs a u.v./persulfate oxidation method by directly injecting the aqueous solution. The apparatus for studying the photocatalytic degradation of MK has been described elsewhere.²⁰ The reactor, a C-75 Chromato-Vue Cabinet of UVP, provides a wide area of illumination from the 15-Watt UV-365 nm tubes positioned on two sides of the cabinet interior.

Procedures and analyses

An aqueous TiO_2 dispersion was prepared by adding 10 mg of TiO_2 powder to a 100 mL solution containing the MK at an appropriate concentration. Before being irradiated, the dispersions were allowed to stay in the dark for 30 min under stirring to reach adsorption equilibrium on to the TiO_2 surface. Irradiations were carried out using two UV-365 nm lamps (15 watt). At given irradiation time intervals, the dispersion was sampled and centrifuged to separate the TiO_2 particles.

After each irradiation cycle, the amount of residual MK was determined by HPLC. The analysis of organic intermediates was accomplished by HPLC/ESI-MS after readjustment of chromatographic conditions in order to make the mobile phase compatible with the working conditions of the mass spectrometer. Solvent A was 25 mM aqueous ammonium acetate buffer (pH 6.9), and solvent B was

Table 1. The chromatographic condition for gradient elution of Michler's Ketone

Time (min)	% Solvent A	% Solvent B
0	95	5
20	50	50
35	10	90
40	10	90
45	95	5

methanol. LC was carried out on an Atlantis™ dC₁₈ column (250 mm × 4.6 mm i.d., dp = 5 μm). The mobile phase flow rate was 1.0 mL/min. The chromatographic conditions for gradient elution of MK are shown in Table 1. The column effluent was introduced into the ESI source of the mass spectrometer. The quadrupole mass spectrometer, equipped with an ESI interface with heated nebulizer probe at 350 °C, was used with an ion source temperature of 80 °C. ESI was carried out with the vaporizer at 350 °C, and nitrogen was used as sheath (80 psi) and auxiliary (20 psi) gas to assist with the preliminary nebulization and to initiate the ionization process. A discharge current of 5 μA was applied. Tube lens and capillary voltages were optimized for maximum response during the perfusion of the MK standard.

Solid-phase extraction (SPE) was employed for pre-concentration of irradiated samples prior to GC/MS analysis. Oasis HLB (hydrophilic/lipophilic balance) was used as the sorbent, and this ensures good recovery of compounds in a wide range of polarities. The cartridges were placed in a vacuum cube (provided by Supelco) and conditioned with 5 mL of methanol and 5 mL of deionized water. After the conditioning step, 1000 mL aliquots of the irradiated samples were loaded at a flow rate of approximately 10 mL/min. Elution was performed with 8 mL of methanol. The eluates obtained were concentrated by solvent evaporation with a gentle nitrogen stream and recomposed to a final volume of 1 mL in methanol. The extracts were stored in amber vials and refrigerated until chromatographic analysis to prevent further degradation.

GC/MS analyses were run on a Perkin-Elmer Auto-System-XL gas chromatograph interfaced to a TurboMass selective mass detector. Separation was carried out in a DB-5 capillary column (5% diphenyl/95% dimethyl-siloxane), 60 m, 0.25-mm i.d., and 1.0-μm thick film. A split-splitless injector was used under the following conditions: injection volume 1 μL, injector temperature 280 °C, split

flow 10 mL/min. The helium carrier gas flow was 1 mL/min. The oven temperature program was 4.0 min at 40 °C, 4 °C/min to 80 °C (2 min), 8 °C/min to 280 °C (9 min). Electron impact (EI) mass spectra were monitored from 10 to 300 *m/z*. The ion source and inlet line temperatures were set at 220 and 280 °C, respectively.

RESULTS AND DISCUSSION

Photocatalytic degradation and mineralization evaluation

To confirm the role of TiO₂ in the photocatalysis reaction, three sets of experiments were performed to compare MK degradation rates with and without catalysts. One set was performed with MK (10 mgL⁻¹) exposed to TiO₂ (100 mgL⁻¹) but no UV (the TiO₂-only condition). The second set was performed by exposing MK (10 mgL⁻¹) to UV without TiO₂ (the photolysis condition). Then, the third set was performed by exposing MK to TiO₂ (100 mgL⁻¹) in the presence of UV illumination (the photocatalysis condition). The results are presented in Fig. 1. First, the experiment with TiO₂ showed only that a small amount of MK (about 11%) was adsorbed on the TiO₂ surface. Next, the results of the photolysis and photocatalytic experiments showed that the photolysis reaction resulted in 81% decrease in the MK concentration after 24 h while the MK was 99.9% removed after 24 h in the case of the photocatalytic reaction. These

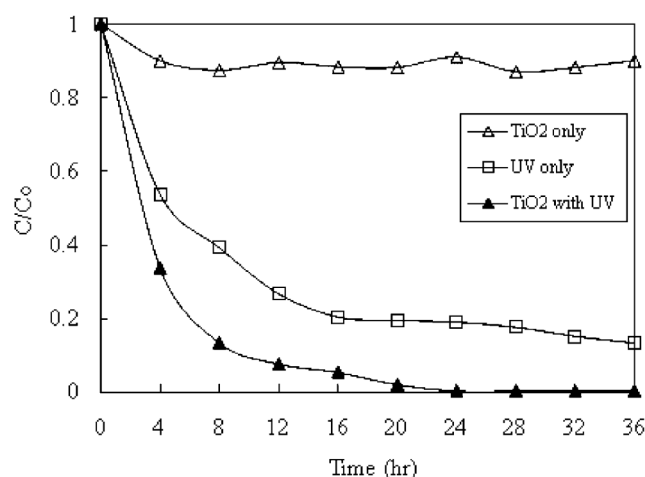


Fig. 1. MK degradation under control conditions (TiO₂ only and UV only) and photocatalytic conditions (experimental conditions: MK = 10 mgL⁻¹, TiO₂ = 0 mgL⁻¹ in photolysis, 100 mgL⁻¹ in photocatalysis, UV-365 nm = 5.2 W/m² in photolysis and photocatalysis conditions).

results indicate that photocatalysis is more effective than direct photolysis for MK degradation.

The complete degradation of an organic molecule by photocatalysis normally leads to the conversion of all its carbon atoms to gaseous CO₂ and of the heteroatoms into inorganic anions that remain in solution. In order to study the total mineralization of MK, the determination of total organic carbon (TOC) was carried out as a function of the irradiation time. The decrease in the TOC percentage of MK during the photocatalytic degradation is depicted in

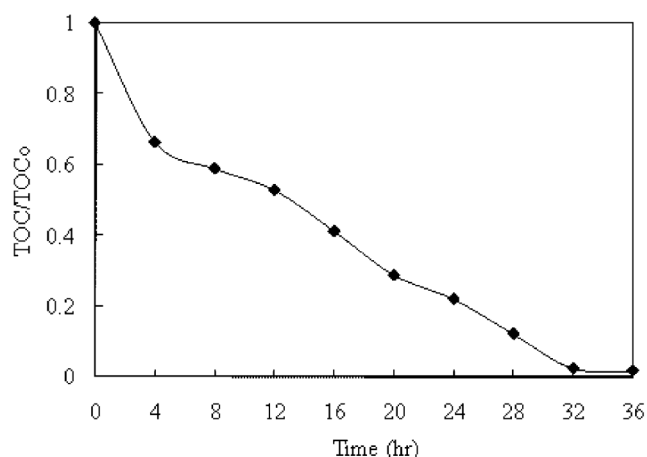


Fig. 2. Depletion in TOC measured as a function of irradiation time for an aqueous solution of MK in the presence of TiO₂.

Fig. 2. It was found that more than 97.5% of the MK was mineralized within 32 h by the photocatalytic reaction. The TOC data suggests that given sufficient reaction time MK can be mineralized in TiO₂ slurries.

Identification of intermediates

Considering the environmental concerns regarding MK and the limited data in the literature with regard to the reaction intermediates generated during the removal of this pollutant, a thorough product study on the degradation of MK in dilute aqueous solution using the TiO₂/UV process was undertaken. A relatively low intensity UV-365 lamp (15 watt) was used in this study for the identification of organic intermediates. This enabled us to obtain slower degradation rates and provide favorable conditions for the determination of photoproducts. Additionally, the initial MK concentration (10 mgL⁻¹) was selected to be high enough to facilitate the identification of intermediate products.

Various approaches to intermediate evaluation have been developed, but the most effective are based on the GC/MS and LC/MS techniques.³⁷⁻³⁹ To get a better understanding of the mechanistic details of this TiO₂-assisted photodegradation of MK with UV light irradiation, nine intermediates of the process were identified and examined by the HPLC/ESI-MS and GC/MS techniques in this research. Table 2 presents the retention times and the fragmentation

Table 2. Identification of the intermediates from the photodegradation of MK by HPLC/ESI-MS and GC/MS

Peaks	Photodegradation intermediates	Abbreviation	R.T. (min)	MS peaks (<i>m/z</i>)
A	4-(<i>N,N</i> -dimethylamino)-4'-(<i>N,N</i> -dimethylamino)benzophenone	DDBP (MK)	38.90 ^a	269.04, 147.89
B	4-(<i>N,N</i> -dimethylamino)-4'-(<i>N</i> -methylamino)benzophenone	DMBP	36.22 ^a	255.01, 147.89, 133.86
C	4-(<i>N</i> -methylamino)-4'-(<i>N</i> -methylamino)benzophenone	MMBP	33.06 ^a	240.98, 133.86
D	4-(<i>N,N</i> -dimethylamino)-4'-amino-benzophenone	DBP	32.64 ^a	240.98, 148.02, 119.89
E	4-(<i>N</i> -methylamino)-4'-amino-benzophenone	MBP	28.82 ^a	226.96, 133.92, 119.89
F	4,4'-Bis-aminobenzophenone	BP	23.52 ^a	212.86, 119.83
A'	<i>N</i> -methylaminobenzene	MBz	32.48 ^b	107, 106, 77, 51
B'	aminobenzene	Bz	30.39 ^b	93, 66
C'	1-hydroxy-2-propanone	Hp	12.64 ^b	74, 43, 31, 15
D'	acetic acid	AAc	9.39 ^b	60, 45, 43, 15

^a The intermediates were identified by HPLC/ESI-MS.

^b The intermediates were identified by GC/MS.

patterns of the intermediates and the corresponding compounds identified by interpretation of their MS spectra. The results reported here show that the combination of GC/MS with EI, and of LC/MS with electrospray ionization, represent a powerful analytical approach for the confirmation of the molecular structure of photocatalytic intermediates. Using these methods, several families of intermediates can be distinguished. The first family of intermediates arise from the de-methylation of 4-(*N,N*-dimethylamino)-4'-(*N',N'*-dimethylamino)benzophenone (MK) and include compounds B-F, which were found for the first time in the TiO₂-mediated photocatalysis process. Muneer et al.³⁶ failed to identify the *N*-de-methylated intermediates formed in the photocatalytic degradation of MK through GC/MS analysis. It is likely that the volatility of these intermediates is too small to be eluted out under the gas chromatographic conditions used, and the polarity so great that they were eluted with the solvent phase in our HPLC analysis. The second family of intermediates (compounds A'-B') are the results of the cleavage of the MK and *N*-de-methylated MK species, leading to *N*-methylaminobenzene and aminobenzene. A similar observation was made in the previous study,³⁶ in which *p*-aminobenzoic acid and *N*-methylaminobenzene were detected as intermediates. The last family of intermediates consists of compounds C'-D' formed by cleavage of the aromatic derivatives, leading to aliphatic products.

Fig. 3 displays a typical HPLC chromatogram of the MK solution during irradiation in the presence of TiO₂. The solution contained at least six identified components at retention times of less than 45 min. One of the peaks was the initial MK (peak A); the other five (new) peaks are those of the intermediates formed. We denoted the MK and its related intermediates as compounds A-F. Except for the initial MK, the other peaks increased at first and subsequently decreased, indicating formation and subsequent transformation of the intermediates.

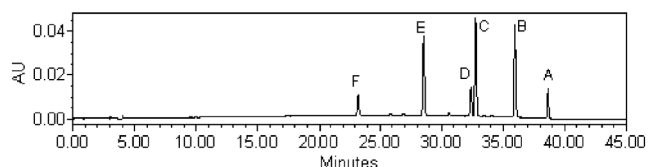


Fig. 3. HPLC chromatogram of the photodegradation intermediates at 8 h of irradiation, recorded at 373 nm.

The absorption spectra of these intermediate products are measured and depicted in Fig. 4. The absorption maximum of the spectral bands shifts hypsochromically from 373.5 nm (Fig. 4, spectrum A) to 342.6 nm (Fig. 4, spectrum F). The *N*-de-methylation of the 4-(*N,N*-dimethylamino)-4'-(*N',N'*-dimethylamino)benzophenone (MK) has the wavelength position of its major absorption band moved toward the blue region, λ_{\max} , MK, 373.5 nm; DMBP, 366.3 nm; MMBP, 362.9 nm; DBP, 362.9 nm; MBP, 358.9 nm; BP, 342.6 nm. These hypsochromic shifts of the absorption bands are presumed to result from the formation of a series of *N*-de-methylated intermediates in a stepwise manner. Similar phenomena were also observed during the photodegradation of sulfan blue²⁰ and crystal violet²¹ under UV irradiation.

The relative distribution of these intermediates (compounds B-F) obtained is illustrated in Fig. 5. To minimize errors, the relative intensities were recorded at the maximum absorption wavelength for each intermediate. This was done even though the complete quantitative determination of all of the photogenerated intermediates was not achieved, owing to the lack of both appropriate molar extinction coefficients for these intermediates and reference standards. Nonetheless, we clearly observed the changes in the distribution of each intermediate during the photodegradation of MK.

The first product (DMBP) of *N*-de-methylation reached its maximum concentration after a 2-h irradiation period (Fig. 5, curve B). The *N*-di-de-methylated intermediates

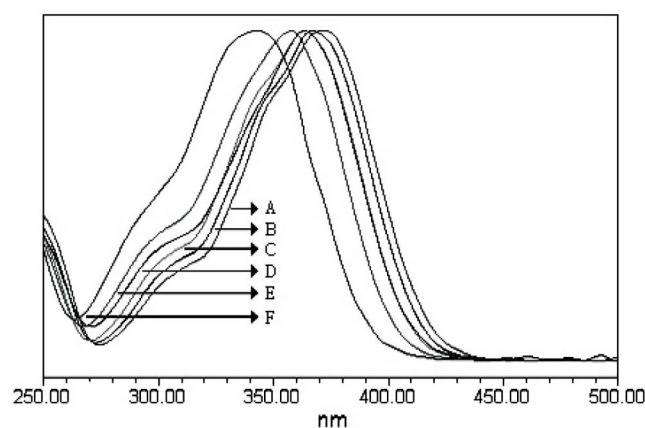


Fig. 4. Absorption spectra of *N*-de-methylated intermediates formed after irradiation for 8 h during the photodegradation of MK. Spectra were recorded using the photodiode array detector.

(MMBP and DBP) were clearly observed (Fig. 5, curve C-D) to reach their maximum concentrations after 6-h and 5-h irradiation periods, respectively. Considering that the *N,N*-dimethyl group is bulkier than the *N*-methyl group in DMBP molecules, nucleophilic attack by $\cdot\text{OH}$ on the *N*-methyl group should be favored at the expense of the *N,N*-dimethyl group. In accord with this notion, the HPLC results showed that the DBP intermediate reached maximal concentration before the MMBP intermediate did. The *N*-tri-de-methylated intermediate (MBP) was clearly observed (Fig. 5, curve E) to reach its maximum concentration after an 8-h irradiation period. The final *N*-de-methylated intermediate (BP) was clearly observed (Fig. 5, curve F) to reach its maximum concentration after a 12-h irradiation period. The successive appearance of the maximal quantity of each intermediate indicates that the *N*-de-methylation of MK is a stepwise photochemical process.

The *N*-de-methylated intermediates were further identified using HPLC-ESI mass spectrometric method; the relevant mass spectra are illustrated in Fig. 6. These compounds were identified by interpretation of the mass spectra. The molecular ion peaks appeared in the acid forms of the intermediates. Compound A was identified as 4-(*N,N*-dimethylamino)-4'-(*N,N'*-dimethylamino)benzophenone (MK) and exhibited a protonated molecular ion peak at $m/z = 269.04$ and a fragment ion at $m/z = 147.89$, which corresponded to the main fragment of the *N,N*-dimethylaminobenzoyl group. Compound B was identified as 4-(*N,N*-di-

methylamino)-4'-(*N'*-methylamino)benzophenone (DMBP) and exhibited a protonated molecular ion peak at $m/z = 255.01$, which corresponded to the loss of one methyl group from MK. It also exhibited fragment ions at $m/z = 147.89$ and 133.86 which corresponded to the main fragments of the *N,N*-dimethylaminobenzoyl and *N*-methylaminobenzoyl groups, respectively.

Two species had protonated molecules of $m/z = 240.98$ eluted at retention times of 32.64 min (compound D) and 33.06 min (compound C) during LC/MS, suggesting the formation of di-*N*-de-methylated products of MK. Both intermediates display similar HPLC/ESI-MS characteristics. The intermediates were identified by interpretation of their fragment ions in the mass spectra. Compound C was identified as 4-(*N*-methylamino)-4'-(*N'*-methylamino)benzophenone (MMBP) and exhibited a protonated molecular ion peak at $m/z = 240.98$ and a fragment ion at $m/z = 133.86$ which corresponded to the main fragment of the *N*-methylaminobenzoyl group. Compound D was identified as 4-(*N,N*-dimethylamino)-4'-aminobenzophenone (DBP) and exhibited a protonated molecular ion peak at $m/z = 240.98$ and fragment ions at $m/z = 148.02$ and 119.89 which corresponded to the main fragments of the *N,N*-dimethylaminobenzoyl and aminobenzoyl groups, respectively. The LC chromatogram revealed a shorter retention time for compound D than for compound C, suggesting compound D was more polar. Considering that the polarity of the DBP species exceeds that of the MMBP intermediate, we expected the latter to be eluted after the DBP species.

Compound E was identified as 4-(*N*-methylamino)-4'-aminobenzophenone (MBP) and exhibited a protonated molecular ion peak at $m/z = 226.96$ which corresponded to the loss of three methyl groups from MK and fragment ions at $m/z = 133.92$ and 119.89 which corresponded to the main fragments of the *N*-methylaminobenzoyl and aminobenzoyl groups, respectively. Compound F was identified as 4,4'-Bis-aminobenzophenone (BP) and exhibited a protonated molecular ion peak at $m/z = 212.86$ which corresponded to the loss of four methyl groups from MK and a fragment ion at $m/z = 119.83$ which corresponded to the main fragment of the aminobenzoyl group.

The identification of intermediates was also performed by solid phase extraction (SPE) followed by GC/MS analysis. SPE has been demonstrated to be more efficient than

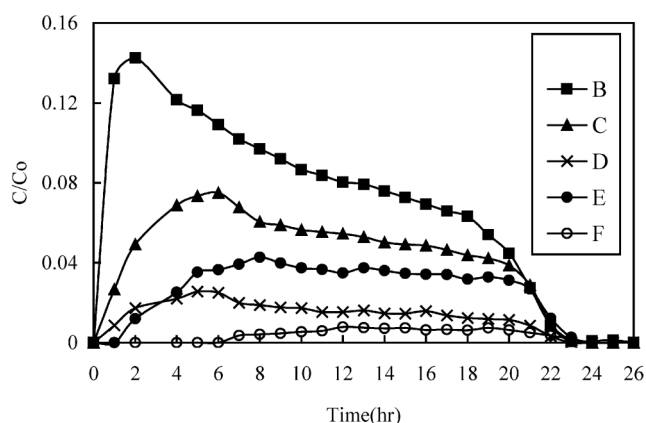


Fig. 5. Variation in the relative distribution of the *N*-de-methylated intermediates obtained from the photodegradation of MK as a function of irradiation time. Curves B-F correspond to the peaks B-F in the Fig. 3, respectively.

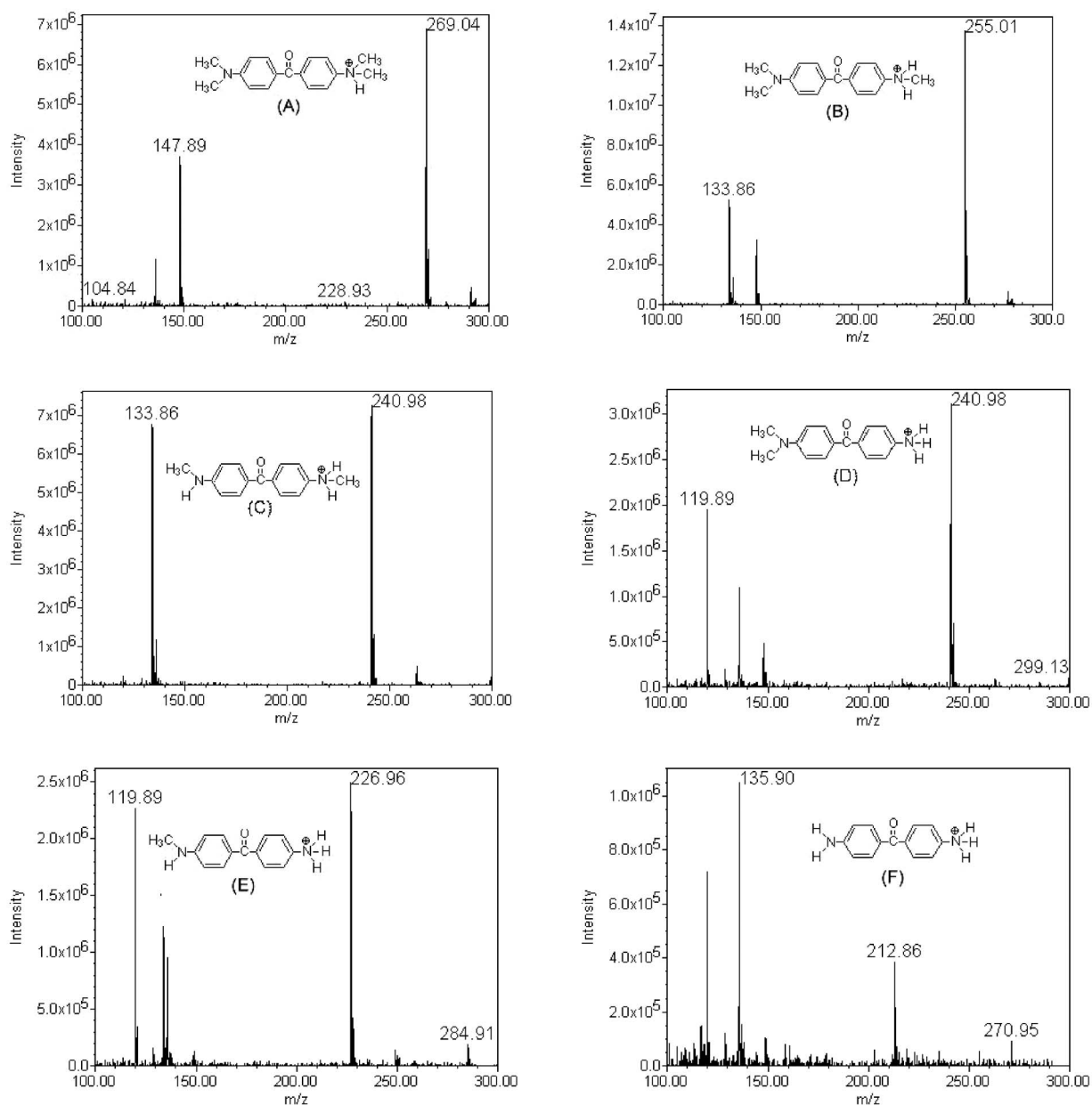


Fig. 6. ESI mass spectra of *N*-de-methylated intermediates formed during the photodegradation of the MK after they were separated by HPLC/ESI-MS method.

traditional liquid-liquid extraction (LLE) in the analysis of water samples containing very polar intermediates resulting from the photocatalytic degradation process.⁴⁰ Fig. 7(a) shows the GC/MS chromatogram obtained for a SPE extract of MK solution after 8 h of irradiation. Blank analysis helped us to discard those peaks coming from the sample handling procedure and chromatographic system. The GC/MS analysis of the irradiated mixture of MK/TiO₂ solution showed the formation of several intermediate products.

Out of these, four intermediates have been identified by using an identification program of the NIST library with a fit value higher than 80% in all cases. Analyses by GC/MS led to the identification of these compounds (A'-D') which did not possess the bis-aminobenzophenone group. The mass spectra of these intermediates are shown in Fig. 7(b). The peaks eluting at 32.48 min, 30.39 min, 12.64 min, and 9.39 min during GC/MS were identified as *N*-methylaminobenzene, aminobenzene, 1-hydroxy-2-propanone and acetic

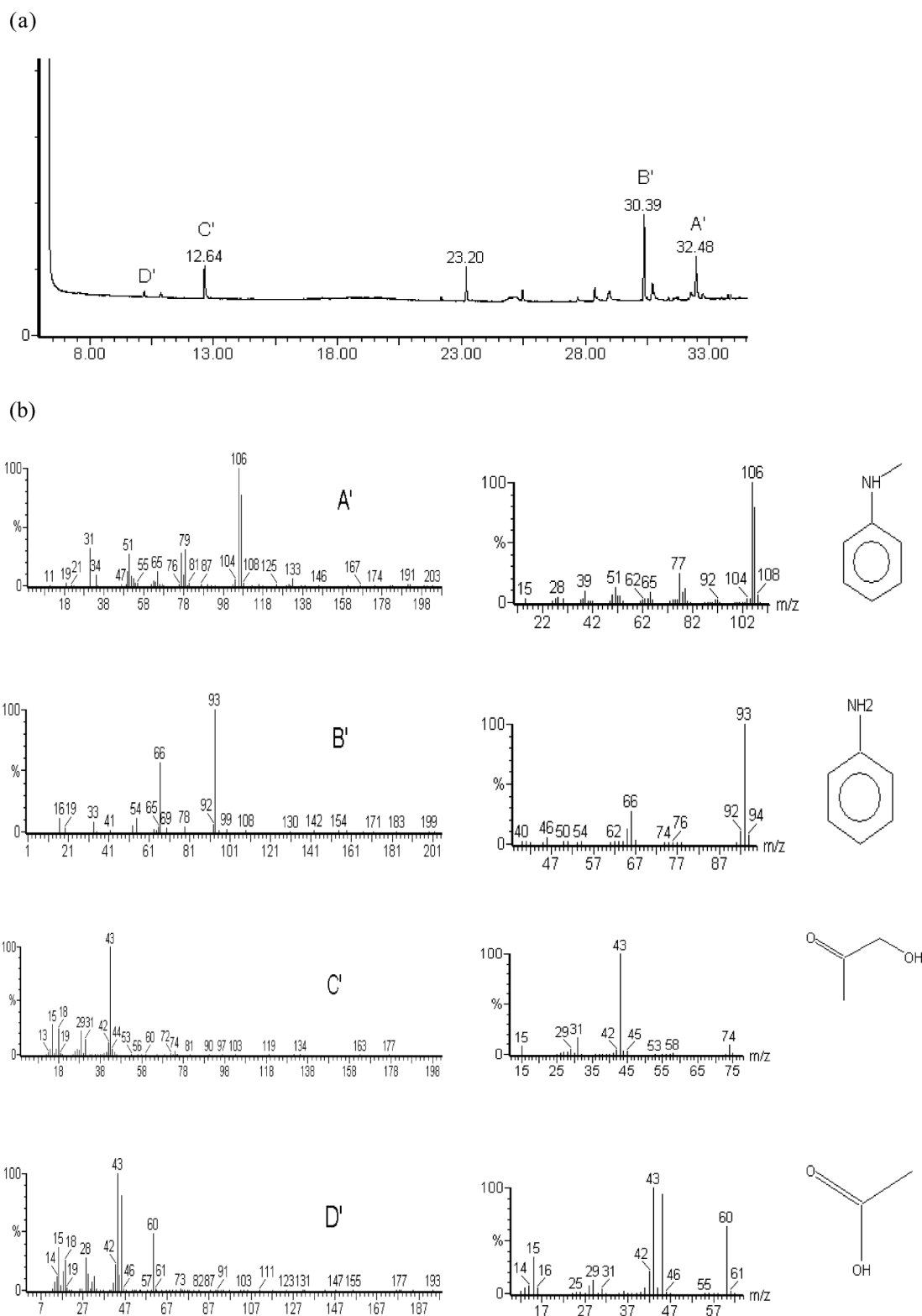


Fig. 7. (a) GC/MS chromatogram obtained for a SPE extract of MK solution after 8 h of irradiation with UV light in the presence of TiO_2 (100 mgL^{-1}). (b) Mass spectra of intermediates formed during the photodegradation of the MK after they were separated by GC/MS method. Left: mass spectra of the irradiated solution. Right: mass spectra of the NIST library.

acid with fit values of 92%, 83%, 97% and 97%, respectively, found by searching the mass spectra library. The former intermediates (compounds A'-B') are the results of the cleavage of the MK and *N*-de-methylated MK species, leading to *N*-methylaminobenzene and aminobenzene. The findings confirm other authors' work. These results are coherent with some given by Muneer.³⁶ The latter intermediates consist of compounds C'-D' formed by cleavage of the aromatic derivatives, leading to aliphatic products.

Concentration of compounds A' and B' can be determined from SPE and GC/FID experiment. The mean recovery values of *N*-methylaminobenzene (compound A') and aminobenzene (compound B') were 75.5% and 51.2% with R.S.D. values of 9.8% and 15.8% ($n = 3$) respectively, which made estimated quantitation feasible. The concentration of *N*-methylaminobenzene and aminobenzene in MK/TiO₂ solution after 8 h of irradiation, determined by SPE-GC/FID method, were 10.1 and 33.8 μgL^{-1} , respectively.

Initial photooxidation pathway

It is well accepted that oxidation in photocatalytic systems (TiO₂, O₂, hv) is mediated to a large extent by the hydroxyl radical ($\cdot\text{OH}$) formed when either adsorbed water or hydroxide is oxidized at a valence band hole.^{41,42} Based on the LC/MS and GC/MS analyses of the various photocatalytic intermediates, the degradation pathways for MK are proposed in Scheme I. It involves two different pathways (routes A and B, respectively), corresponding to the two possible sites for the attack of the $\cdot\text{OH}$ radicals on the MK molecule.

The *N*-de-methylation of the MK occurs mostly by the attack of the $\cdot\text{OH}$ species on the *N,N*-dimethyl groups of the MK, as shown in Scheme I (route A). Hydroxyl radicals yield carbon-centered radicals upon the H-atom abstraction from the methyl group, or they react with the lone-pair electron on the N atom to generate cationic radicals, which subsequently convert into carbon-centered radicals.¹⁹ The carbon-centered radicals react rapidly with O₂ to produce peroxy radicals that subsequently transform into alkoxy radicals through the bimolecular Russell mechanism.⁴³ The fragmentation of the alkoxy radical produces a de-methylated product. The mono-de-methylated species, DMBP, can also be attacked by $\cdot\text{OH}$ species and be implicated in other similar events (H-atom abstraction, oxygen attack, and the bimolecular Russell mechanism) to yield the bi-

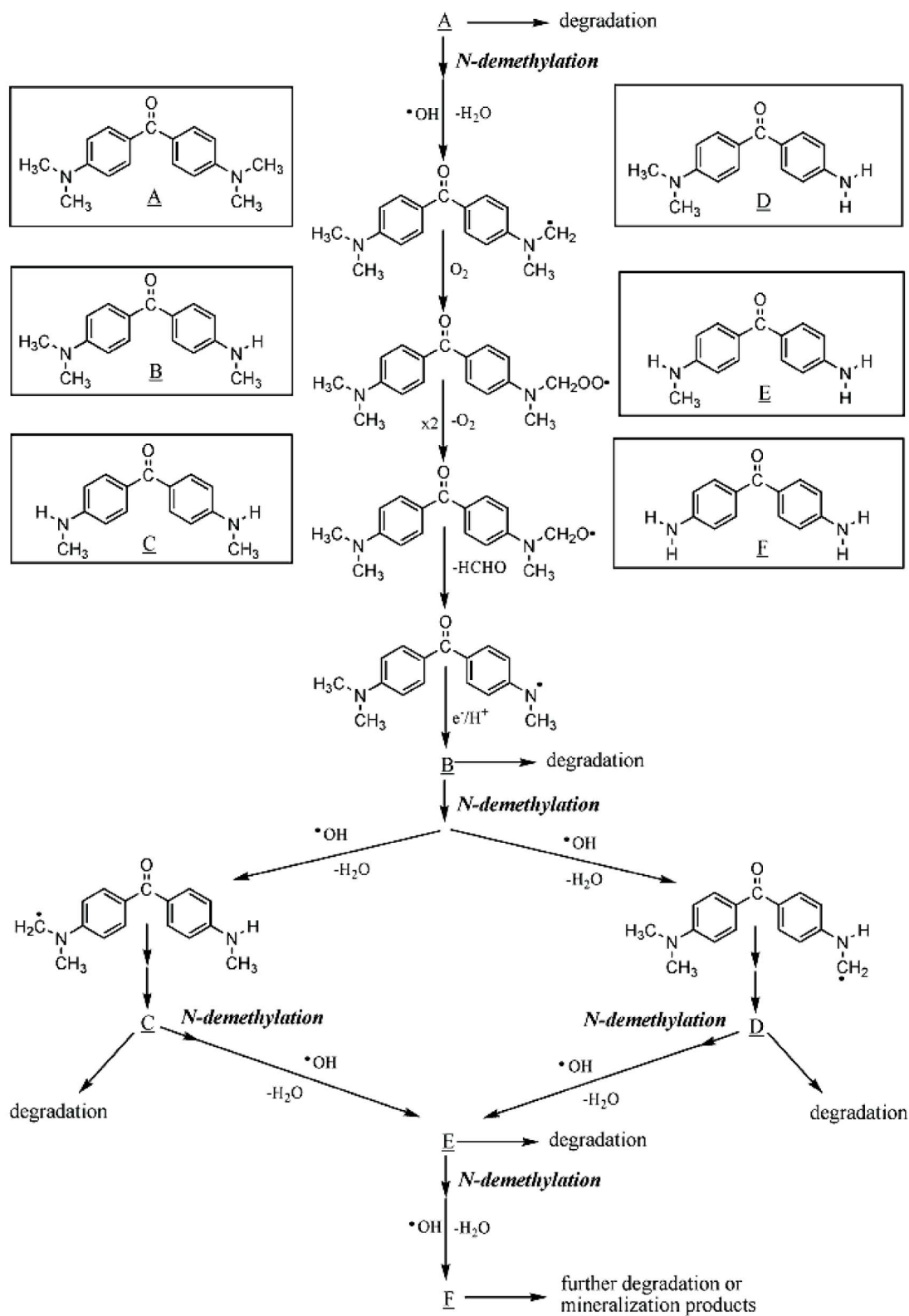
de-methylated intermediates, MMBP and DBP. The de-methylation process as described above continues until formation of the completely de-methylated species, BP.

In addition to the *N*-de-methylation degradation route, an alternative pathway was also identified. A plausible mechanism for the formation of degradation products A'-B' involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme I (route B). Upon the transfer of an electron the MK and its *N*-de-methylated species can form the radical anion, which can undergo the addition of a hydroxyl radical and form the anionic species, which upon cleavage can lead to the formation of *N*-methylaminobenzene and aminobenzene. This is in agreement with mechanisms proposed by Muneer et al. for gentian violet.³⁶

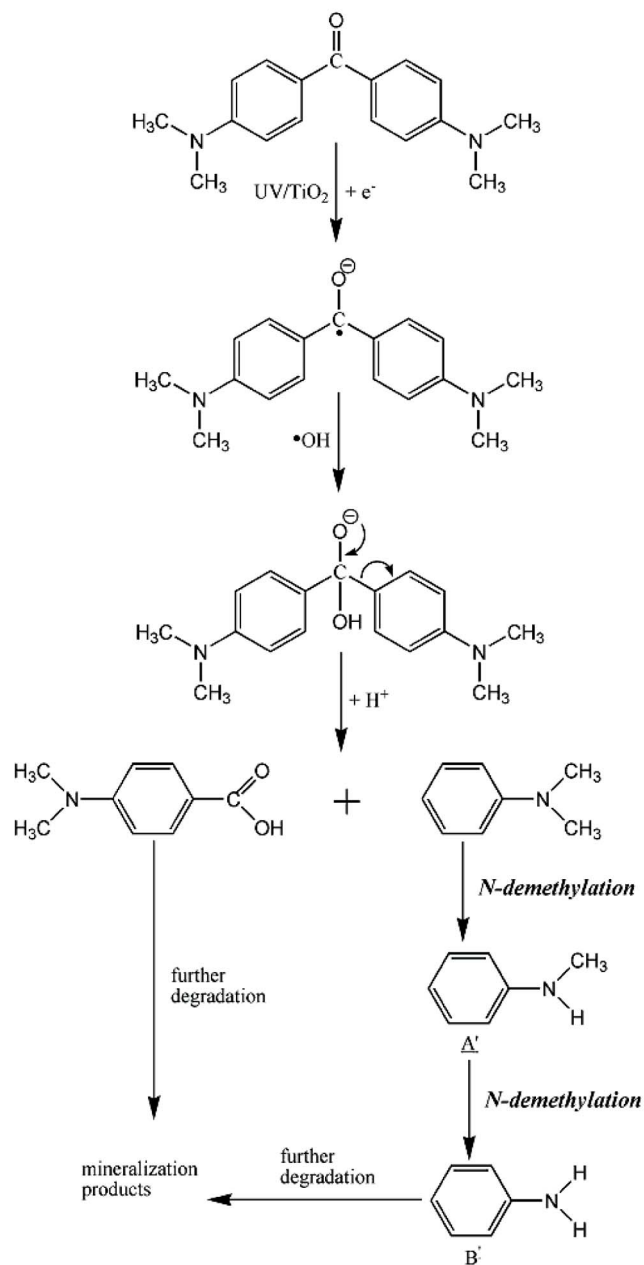
It is known from previous photocatalytic studies that, after the formation of various aromatic derivatives, cleavage of the benzene or other organic rings takes place, and different aliphatic products are subsequently formed before complete mineralization.²⁵ Even though further oxidation leads to the ring-opening and the formation of aliphatic oxidation products (compounds C'-D'), these species will not be discussed here.

CONCLUSION

Our studies suggest that TiO₂ photocatalysis should be an effective technique for the destruction of the MK in aqueous solutions. The percentage decreases in MK concentration, resulting from the photocatalytic reactions conducted for 20 h, was 98.1%. Nine intermediates have been identified and characterized using LC/MS and GC/MS techniques, giving insight into the early steps of the degradation process. The photocatalytic degradation of MK proceeds through competitive reactions such as *N*-de-methylation and destruction of the bis-aminobenzophenone structure. The former path generates a carbon-centered radical upon H-atom abstraction, which further reacts with O₂ generating peroxy and alkoxy radical intermediates to result in a series of *N*-de-methylated products. The hypsochromic effects resulting from *N*-de-methylated intermediates of MK occurred concomitantly during irradiation. In the latter path, the electron in the conduction band of TiO₂ can be picked up by the adsorbed MK, leading to the formation of radical anion, which can undergo addition of a hydroxyl radical forming the anionic species, which upon cleavage can lead to the formation of *N*-methylaminobenzene and

Scheme I (route A) Proposed *N*-de-methylation pathway of the MK under UV irradiation in aqueous TiO₂ dispersions

Scheme I (route B) Proposed destruction bis-amino-benzophenone structure pathway of the MK under UV irradiation in aqueous TiO₂ dispersions



aminobenzene. The reaction mechanisms of TiO₂/UV proposed in this research should prove useful in future efforts to breakdown the organic compounds in wastewater.

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REFERENCES

- National Toxicology Program, Bioassay of Michler's Ketone for Possible Carcinogenicity, *Natl. Toxicol. Program Tech. Rep. Ser.* **1979**, 181, 1.
- Ozaki, A.; Yamaguchi, Y.; Fujita, T.; Kuroda, K.; Endo, G. *Food Chem. Toxicol.* **2004**, 42, 1323.
- Brinker, C. J.; Cornils, B.; Bonet, M. *Ullmann's Encyclopedia of Industrial Chemistry. Part A27. Triarylmethane and Diarylmethane Dyes*, 6th ed.; Wiley-VCH: New York, 2001.
- Pollard, S. J. T.; Fowler, G. D.; Sollars, C. J.; Perry, R. *Sci. Total Environ.* **1992**, 116, 31.
- Banerjee, K.; Cheremisinoff, P. N.; Cheng, S. L. *Environ. Sci. Technol.* **1995**, 29, 2243.
- Namasivayam, C.; Kavitha, D. *J. Environ. Sci. Eng.* **2004**, 46, 217.
- Mascolo, G.; Lopez, A.; Foldenyi, R.; Passino, R.; Tiravanti, G. *Environ. Sci. Technol.* **1995**, 29, 2987.
- Wittich, R. M. *Appl. Microbiol. Biotechnol.* **1998**, 49, 489.
- Ballerstedt, H.; Kraus, A.; Lechner, U. *Environ. Sci. Technol.* **1997**, 31, 1749.
- Konstantinov, A. D.; Johnston, A. M.; Cox, B. J.; Petrusis, J. R.; Orzechowski, M. T.; Bunce, N. J.; Tashiro, C. H. M.; Chittim, B. G. *Environ. Sci. Technol.* **2000**, 34, 143.
- Qin, Z. *Chemosphere* **1996**, 33, 91.
- Friesen, K. J.; Foga, M. M.; Loewen, M. D. *Environ. Sci. Technol.* **1996**, 30, 2504.
- Konstantinou, I. K.; Albanis, T. A. *Appl. Catal. B: Environ.* **2004**, 49, 1.
- Watanabe, N.; Horikoshi, S.; Kawabe, H.; Sugie, Y.; Zhao, J.; Hidaka, H. *Chemosphere* **2003**, 52, 851.
- Kouloumbos, V. N.; Tsipi, D. F.; Hiskia, A. E.; Nikolic, D.; Breemen, R. B. *J. Am. Soc. Mass Spectrom.* **2003**, 14, 803.
- Liu, I.; Lawton, L. A.; Robertson, P. K. J. *Environ. Sci. Technol.* **2003**, 37, 3214.
- Chen, C.; Lei, P.; Ji, H.; Ma, W.; Zhao, J.; Hidaka, H.; Serpone, N. *Environ. Sci. Technol.* **2004**, 38, 329.
- Daneshvar, N.; Rabbani, M.; Modirshahla, N.; Behnajady, M. A. *J. Photochem. Photobiol. A: Chem.* **2004**, 168, 39.
- Lee, J.; Choi, W. *Environ. Sci. Technol.* **2004**, 38, 4026.
- Chen, C. C.; Lu, C. S.; Mai, F. D.; Weng, C. S. *J. Hazard. Mater. B* **2006**, 137, 1600.
- Chen, C. C.; Mai, F. D.; Chen, K. T.; Wu, C. W.; Lu, C. S. *Dyes and Pigments* **2007**, 75, 434.
- Pelizzetti, E.; Maurino, V.; Minero, C.; Carlin, V.; Pramauro, E.; Zerbinati, O.; Tosato, M. *Environ. Sci. Technol.* **1990**, 24, 1559.
- Wang, K. H.; Hsieh, Y. H.; Chou, M. Y.; Chang, C. Y. *Appl.*

- Catal. B: Environ.* **1999**, *21*, 1.
24. Konstantinou, I. K.; Sakkas, V. A.; Albanis, T. A. *Water Res.* **2002**, *36*, 2733.
25. Bianco, P. A.; Vincenti, M.; Banciotto, A.; Pramauro, E. *Appl. Catal. B: Environ.* **1999**, *22*, 149.
26. *Photocatalysis-Fundamentals and Applications*, Serpone, N.; Pelizzetti, E. Eds.; Wiley-Interscience: New York, 1989.
27. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
28. Richard, C.; Bengana, S. *Chemosphere* **1996**, *33*, 635.
29. Tang, W. Z.; Huang, C. P. *Water Res.* **1995**, *29*, 745.
30. Percherancier, J. P.; Chapelon, R.; Poyet, B. *J. Photochem. Photobiol. A: Chem.* **1995**, *72*, 261.
31. Zaleska, A.; Hupka, J.; Wierowski, M.; Biziuk, M. *J. Photochem. Photobiol. A: Chem.* **2000**, *135*, 213.
32. Hermann, J. M.; Disdier, J.; Pichat, P.; Malato, S.; Blanco, J. *Appl. Catal. B: Environ.* **1998**, *17*, 15.
33. Hermann, J. M.; Guillard, C.; Arguello, M.; Aguera, A.; Tejedor, A.; Piedra, L.; Fernandez-Alba, A. *Catal. Today* **1999**, *54*, 353.
34. Poullos, I.; Kositzi, M.; Kouras, A. *J. Photochem. Photobiol. A: Chem.* **1998**, *115*, 175.
35. Choi, W.; Hong, S. J.; Chang, Y. S.; Cho, Y. *Environ. Sci. Technol.* **2000**, *34*, 4810.
36. Saquib, M.; Muneer, M. *Dyes Pigm.* **2003**, *56*, 37.
37. Chiron, S.; Fernandez-Alba, A.; Rodriguez, A. *Trends Anal. Chem.* **1997**, *16*, 518.
38. Malato, S.; Caceres, J.; Fernandez-Alba, A. R.; Piedra, L.; Hernando, M. D.; Aguera, A.; Vial, J. *Environ. Sci. Technol.* **2003**, *37*, 2516.
39. Wong, C. C.; Chu, W. *Environ. Sci. Technol.* **2003**, *37*, 2310.
40. Fernandez-Alba, A. R.; Aguera, A.; Contreras, M.; Penuela, G.; Ferrer, I.; Barcelo, D. *J. Chromatogr. A* **1998**, *823*, 35.
41. Turchi, C. S.; Ollis, D. F. *J. Catal.* **1990**, *122*, 178.
42. Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, *95*, 5261.
43. Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.