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# Photocatalyzed mineralization of nitrogen-containing compounds at $\text{TiO}_2/\text{H}_2\text{O}$ interfaces

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## Abstract

The photodegradation of two compounds containing multi-nitrogen atoms, azobisformamidoacetic acid (AFAA) and trihydrazinotriazine (THTA), was examined in aerated aqueous  $\text{TiO}_2$  dispersions under UV irradiation. The photocleavage of the conjugated double bond in AFAA and of the ring containing heteronitrogen atoms in THTA was monitored by UV/Vis spectroscopy and the mineralization products ( $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) in the photodegradation processes were determined by gas chromatography and ion liquid chromatography. The photocatalytic kinetics and a possible mechanism for the partial degradation are also discussed on the basis of the experimental results.

**Keywords:** Interfaces; Mineralization; Nitrogen-containing compounds; Photodegradation; Titania; Water

## 1. Introduction

Photocatalytic degradation affords a great potential as an industrial technique of water purification and treatment as mentioned in some review articles [1–5]. In the past decade, the photocatalytic redox of a large and varied number of organic and inorganic pollutants at  $\text{TiO}_2/\text{H}_2\text{O}$  interfaces have been widely investigated. For instance, the  $\text{TiO}_2$  photocatalytic degradations of halogenated aromatics [6,7] and aliphatics [8,9], organometallic compounds [10,11], polymers [12,13], cyanide [14–16], pesticides [17–19] and various kinds of surfactants [20] have been examined. Most of the studies were focused on

the photomineralization of hydrocarbon species to  $\text{CO}_2$ , while the reports on the mineralization of heteroatom groups to corresponding inorganic ions have been scarce in the literature. Recently, we and some other groups therefore have turned attention to the photomineralization of compounds containing heteroatoms. Heteroatoms of phosphorus, sulfur, chlorine in the organics examined are easily photomineralized to  $\text{PO}_4^{3-}$  [21–25],  $\text{SO}_4^{2-}$  [20a,22] and  $\text{Cl}^-$  [6–9] inorganic ion species, respectively. The photodegradation of nitrogen-containing compounds, however, is relatively slow and the mineralization of nitrogen-containing moieties is very complicated since both  $\text{NO}_3^-$  (and/or  $\text{NO}_2^-$ ) ions and  $\text{NH}_4^+$  ions are generated in the photodegradation process [26–28]. The ratio of ammonium to nitrate ions formed in the photodegradation of organic com-

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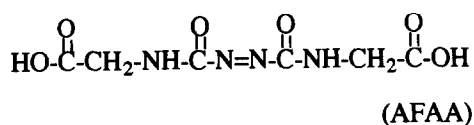
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pounds containing nitrogen atoms is closely related to the structure of compounds examined [27,28]. The photodegradation of those compounds having complicated structures or containing multi-nitrogen atoms has been scarcely published. The mineralization route has not been revealed in detail yet.

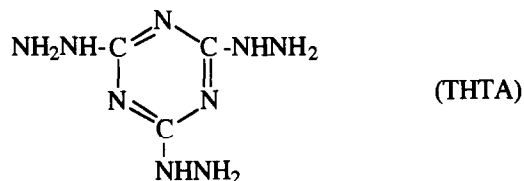
In this paper, the photomineralization of two compounds containing multi-nitrogen atoms, azobisformamido acetic acid (AFAA) and trihydrazinotriazine (THTA) which are used as gas-generating chemicals or pesticides, was investigated in aerated aqueous  $\text{TiO}_2$  dispersions under UV irradiation. The photocleavage of the conjugated double bonds in AFAA and of the heteroatoms-containing ring in THTA and the photomineralization products of  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were examined in the photodegradation processes. The photocatalytic kinetics for the two compounds with different structures and a possible photodegradation mechanism are also proposed on the basis of the experimental results.

## 2. Experimental

Azobisformamidoacetic acid (AFAA) was prepared by condensation of diethyl azodicarboxylate with glycine in a basic aqueous solution according to the procedure in [29]. AFAA formed was recrystallized with a mixed solution ( $\text{H}_2\text{O}:\text{EtOH} = 1:4$  vol/vol) two times. The product was confirmed by elemental analysis and by IR, NMR and UV spectroscopies.



Trihydrazinotriazine (THTA) was synthesized by treatment of cyanuric chloride with hydrazine in a tetrahydrofuran solvent at a temperature of 20–25°C and a normal pressure according to the literature [30,31]. The product was also evidenced by IR and UV spectroscopies and by elemental analysis.



$\text{TiO}_2$  photocatalyst (P-25, mostly anatase powder with a surface of  $55 \text{ m}^2/\text{g}$ ) was kindly supplied by Degussa AG. Deionized and doubly distilled water was used throughout.

A dispersion consisting of a reactant solution (0.1–10 mM, 50 ml) and  $\text{TiO}_2$  (100 mg) particles was contained in a 76 ml Pyrex glass vessel and was irradiated with a mercury lamp (Toshiba SHL-100 UVQ) under continuous magnetic stirring to ensure uniform mixing of the aqueous suspension. The experiments were performed under air-equilibrated conditions unless otherwise mentioned. A 2-ml dispersion after appropriate illumination time was sampled, centrifuged and filtered with a Millipore filter (pore size 0.22  $\mu\text{m}$ ). The photocleavage of the conjugated double bond in AFAA and of the ring containing heteroatoms in THTA was measured by UV/Vis spectroscopy (269 nm for AFAA and 214 nm for THTA). The formation of ammonium ions was determined with a JASCO ion chromatograph equipped with a Y-521 cationic column and a CD-5 conductivity detector using a diluted  $\text{HNO}_3$  solution (4 mM) as an eluent. Nitrate ions were also analyzed by ion chromatographic methods but with an I-524 anionic column using a mixture solution of phthalic acid (2.5 mM)/tris(hydroxymethyl)aminomethane (2.3 mM) as an eluent. When the constituents in the gas phase were analyzed, the vessel containing the dispersion was closed with a rubber septum and was purged with pure oxygen gas for 15 min before illumination. The temporal evolution of  $\text{CO}_2$  and  $\text{N}_2$  during the photodegradation was assayed by gas chromatography with a thermal conductivity detector (TCD); a Porapak Q column was used for  $\text{CO}_2$  and a molecular sieve column for  $\text{N}_2$  measurements. The proton NMR spectra for a AFAA (7 mM)/ $\text{D}_2\text{O}$  solution at several irradiation

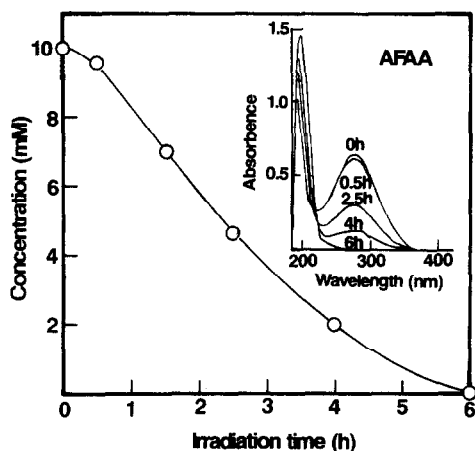


Fig. 1. Photocleavage of the conjugated double bonds in AFAA (10 mM, 50 ml) catalyzed by  $\text{TiO}_2$  particles (100 mg) monitored by UV spectroscopy (269 nm). Inset: variations in the UV absorption spectra of the degraded solution at different irradiation times.

tion intervals were monitored with a JEOL 500-MHz FT proton NMR spectrometer.

### 3. Results and discussion

The photodegradation of AFAA in an aqueous  $\text{TiO}_2$  dispersion is shown in Fig. 1. AFAA was easily decomposed even at a higher initial concentration (10 mM) and the UV absorption peak (269 nm) for the conjugated double bonds ( $-\text{CO}-\text{N}=\text{N}-\text{CO}-$ ) in AFAA disappeared after irradiation for 6 h.

The results of the photocatalytic degradation of AFAA (0.1 mM) are summarized in Fig. 2. The conjugated double bond in AFAA was rapidly photocleaved as indicated by a fast diminution of the intensity of the UV absorption peak (269 nm) within 30 min of irradiation. The total conversion for AFAA disappearance was achieved in a shorter time with an initial concentration  $C_0$  equal to 0.1 mM than with  $C_0$  equal to 10 mM (see Fig. 1) because the number of present molecules to be converted is 100 times smaller in with the same photonic flux. However, the true reaction rate (in moles converted per hour) is higher at  $C_0 = 10$  mM than at  $C_0 = 0.1$  mM, in agreement with a commonly adopted Langmuir–Hinshelwood mechanism. The generation of both  $\text{NH}_4^+$  and

$\text{NO}_3^-$  inorganic species was confirmed in photodegradation of AFAA. No nitrite ions was detected in photodegradation process under our experimental conditions. It is possible that  $\text{NO}_2^-$  ions, if any formed, are (photo)oxidized rapidly into  $\text{NO}_3^-$  ions. The quantities of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions formed increased with increasing the irradiation time and  $\text{NH}_4^+$  ions were produced more than  $\text{NO}_3^-$  ions in the AFAA degradation process. Carbon dioxide was also evolved concomitantly with the photooxidation of AFAA. The amount of  $\text{CO}_2$  evolved increased with an increase in the irradiation time. After 11 h of irradiation, about 0.3 mmol/l of  $\text{CO}_2$  (50% yield), 0.11 mmol/l of  $\text{NH}_4^+$  (27% yield) and 0.07 mmol/l of  $\text{NO}_3^-$  (18% yield) were formed from the AFAA solution (0.1 mM). The decomposition of substrate, the formation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions, and the  $\text{CO}_2$  evolution occur approximately by apparent first order kinetics in the initial photocatalytic processes of AFAA. The integral representation of the apparent first order at the initial degradation stage gives an ascending straight line passing through the origin. The values of the first order rate constants are summarized in Table 1. Since several intermediates form in the degradation process, the kinetics is actually more complicated. It is necessary for detailed kinetic discussion to identify all intermediate compounds and to determine their concentrations quantitatively.

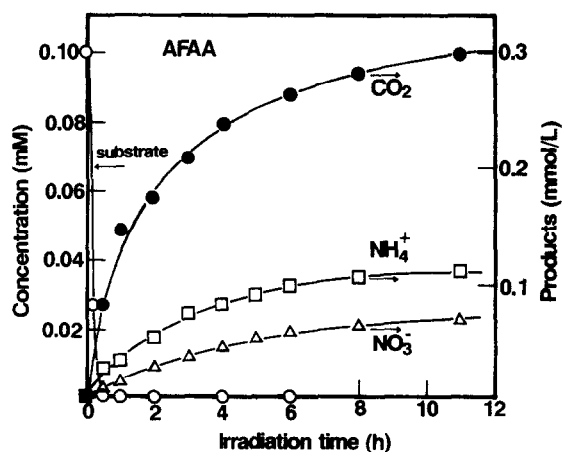


Fig. 2. Photodegradation of AFAA (0.1 mM, 50 ml) in the presence of  $\text{TiO}_2$  particles (100 mg).

Table 1  
Apparent rate constants in the degradation of AFAA and THTA

|   | AFAA                 | THTA                 |
|---|----------------------|----------------------|
| Decomposition $k_s$ ( $\text{min}^{-1}$ )                           | $7.7 \times 10^{-2}$ | $1.7 \times 10^{-2}$ |
| $t_{1/2}$ (min)   | 9.0                  | 40.8                 |
| $\text{CO}_2$ evolution $k_{\text{CO}_2}$ ( $\text{min}^{-1}$ )     | $2.8 \times 10^{-2}$ | $3.9 \times 10^{-3}$ |
| $\text{NH}_4^+$ formation $k_{\text{NH}_4^+}$ ( $\text{min}^{-1}$ ) | $5.1 \times 10^{-3}$ | $9.4 \times 10^{-4}$ |
| $\text{NO}_3^-$ formation $k_{\text{NO}_3^-}$ ( $\text{min}^{-1}$ ) | $2.1 \times 10^{-3}$ |                      |

Fig. 3 gives the results of the photodegradation of THTA (0.1 mM). Similar to the AFAA system,  $\text{CO}_2$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were produced concomitantly with the photocleavage of the ring containing heteronitrogen atoms in the photodegradation of THTA. However, the degradation of THTA was much slower than that of AFAA and the formation of both  $\text{CO}_2$  and  $\text{NO}_3^-$  in the THTA photodegradation exhibited an induction period (about 1 h). After an induction period, the quantities of  $\text{CO}_2$  and  $\text{NO}_3^-$  increased with further increasing the irradiation time. The intensity of UV absorption peak (214 nm) for the heteroatoms-containing ring in THTA decreased with the irradiation time and the absorption peak disappeared after 1.5 h of irradiation. The mineralization yields of THTA to  $\text{CO}_2$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  after irradiation for 10 h were about 11%, 2.5% and 5.1%, respectively. The decomposition of substrate, the evolution of  $\text{CO}_2$  after an induction period and the formation of  $\text{NH}_4^+$  ions occur

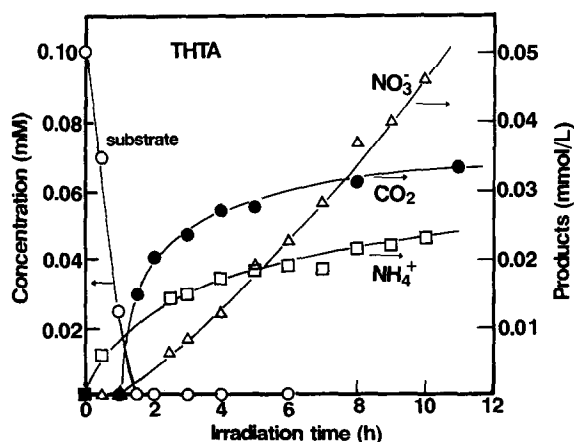


Fig. 3. Photodegradation of THTA (0.1 mM, 50 ml) in the presence of  $\text{TiO}_2$  particles (100 mg).

approximately by apparent first order kinetics in the photocatalytic processes of THTA. The values of the first order constants are also summarized in Table 1. Comparing to the rate constants for AFAA, the photodegradation of THTA is relatively slow. The formation rate for  $\text{NO}_3^-$  ions in the THTA degradation increased significantly with further increasing the irradiation time after an induction period and the amount of  $\text{NO}_3^-$  ions formed became larger than that of  $\text{NH}_4^+$  ions at 5 h of irradiation time. The rate for  $\text{NO}_3^-$  ion formation did not fit first order kinetics.

Besides  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions formed, nitrogen gas was also evolved in the photodegradation of AFAA as assayed by gas chromatography. As listed in Table 2, the amount of  $\text{N}_2$  evolved from 1 mM of AFAA solution reached 0.8 mmol and 0.91 mmol per liter of solution after irradiation for 5 h and 10 h, respectively, which approach the quantity of the  $-\text{N}=\text{N}-$  double bonds in AFAA. We suggest that the  $\text{N}_2$  gas generated mainly from the double  $-\text{N}=\text{N}-$  bonds in the photodegradation of AFAA. No nitrogen gas was evolved in the photodegradation of THTA under the same conditions.

The effect of initial AFAA concentrations on the formation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions in the photodegradation of AFAA is depicted in Fig. 4. At a higher initial concentration (1 mM), the generation of  $\text{NO}_3^-$  ions is inhibited comparing to the degradation at 0.1 mM. Although the amount of  $\text{NH}_4^+$  ions formed in the photodegradation of AFAA at 1.0 mM was larger than at 0.1 mM, the mineralization yield to  $\text{NH}_4^+$  ions (about 7.2%) after 11 h of irradiation was lower than that at an initial concentration of 0.1 mM.

Fig. 5 illustrates the ratios of  $[\text{NO}_3^-]/[\text{NH}_4^+]$  as a function of irradiation time. The ratio of

Table 2  
 $\text{N}_2$  evolution in the photodegradation of AFAA and THTA<sup>a</sup>

| Irradiation time (h)       | 0 | 5    | 10   |
|----------------------------|---|------|------|
| AFAA (mmol/l) <sup>b</sup> | 0 | 0.85 | 0.91 |
| THTA (mmol/l) <sup>b</sup> | 0 | 0    | 0    |

<sup>a</sup> Initial concentration was 1.0 mM.

<sup>b</sup> Represented as millimoles from 1 l of the degraded solution.

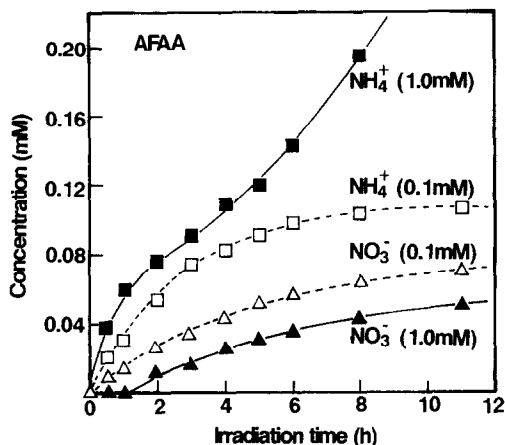
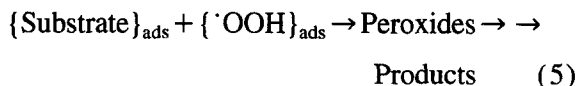
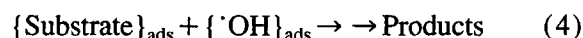
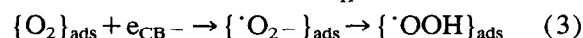
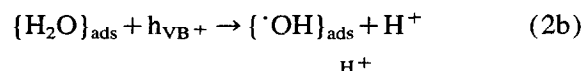
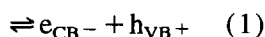
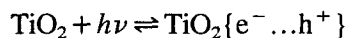


Fig. 4. Formation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions in the photodegradation of AFAA at different initial concentrations (0.1 and 1.0 mM, 50 ml) in the presence of  $\text{TiO}_2$  particles (100 mg).

$[\text{NO}_3^-]/[\text{NH}_4^+]$  increased slightly with increasing the irradiation time to reach a maximum and then decreased slowly by further irradiation for AFAA at an initial concentration of 1.0 mM. More  $\text{NO}_3^-$  ions were formed in the photodegradation of AFAA at 0.1 mM than at 1.0 mM. The increase in the ratio of  $[\text{NO}_3^-]/[\text{NH}_4^+]$  with the irradiation time for THTA (0.1 mM) was more remarkable than that for AFAA (0.1 mM). After 5 h of irradiation, the ratio became larger than one, that is, the quantity of  $\text{NO}_3^-$  ions formed was more than that of  $\text{NH}_4^+$  ions in the photodegradation of THTA.

The photocatalytic process involves attack of  $\cdot\text{OH}$  (and/or  $\cdot\text{OOH}$ ) radicals, generated on the UV-irradiated  $\text{TiO}_2$  surface, on the organic molecules as evidenced by DMPO-spin trapping ESR results and by peroxide measurements [20c,d].



where the  $e_{\text{CB}-}$  and  $h_{\text{VB}+}$  express electrons in the conduction band and holes in the valence band, respectively, and  $\{\}_{\text{ads}}$  stands for the species adsorbed on the irradiated  $\text{TiO}_2$  surface.

The photomineralization of hydrocarbon moieties into carbon dioxide has been investigated in detail [20c,d,25]. The photooxidation of alkyl chain, in general, begins with sequential attack of  $\cdot\text{OH}$  radicals (or other active oxygen species) at the  $\alpha$ -position of a hydrophilic moiety to generate  $\text{CO}_2$  through several intermediates such as hydroxylated compounds (or peroxides), aldehydes (mainly formaldehyde) and carboxylic acids (mainly formic acid). Evolution of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions in the photodegradation of nitrogen-containing compounds can be classified into three types according to the kind of nitrogen groups in compounds from the results reported by Matthews et al. [27], Pelizzetti, et al. [26] and us [28]. Amino groups are predominantly mineralized into  $\text{NH}_4^+$  ions ( $[\text{NH}_4^+] \gg [\text{NO}_3^-]$ ), while the nitro group in several organic compounds is converted mainly into  $\text{NO}_3^-$  ions ( $[\text{NH}_4^+] \ll [\text{NO}_3^-]$ ). In heterocyclic structures, the nitrogen atom is transformed to either or both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  species. The photooxidation of

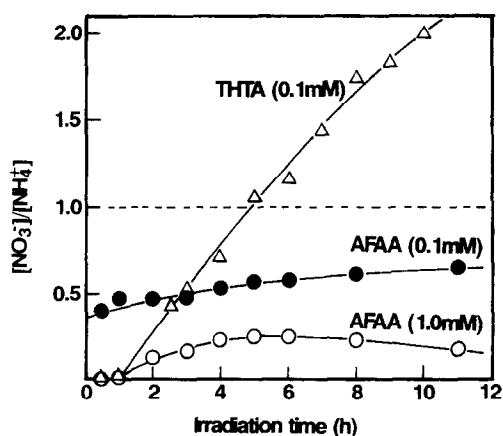


Fig. 5. Ratio of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  ions as a function of irradiation time in the photodegradation of AFAA and THTA. The conditions are the same as those in Figs. 2 and 3.

$\text{NH}_4^+$  ions to  $\text{NO}_3^-$  ions is evidently a relatively slow process as shown by a low conversion yield (about 3.8%) for an ammonium chloride solution (1 mM) under the same experimental conditions. From these results, it is suggested that attack of  $\cdot\text{OH}$  (and/or  $\cdot\text{OOH}$ ) radicals on the  $\alpha$ -carbon atom of the nitrogen-moiety would lead to formation of  $\text{NH}_4^+$  ions via an intermediate of amide and a further hydrolysis step, while an attack of these activated oxygen species directly on the nitrogen atom would produce  $\text{NO}_3^-$  ions. Nitrogen gas results mainly from the photodegradation of the double  $-\text{N}=\text{N}-$  bond moieties. The NMR results for AFAA (7 mM) showed that the peak of methylene protons (4.05 ppm) disappeared quickly within 1 h of irradiation, and a peak of formaldehyde intermediate (8.31 ppm) appeared after irradiation for 1 h to reach a maximum formation at about 2 h of irradiation and then decreased rapidly with further increasing the irradiation time, finally disappeared completely after 6 h of irradiation. Elucidation of the detailed degradation mechanism and the intermediates formed for nitrogen-containing compounds is now in progress. Comparing to the photodegradation of AFAA, the chemical yield of  $\text{NH}_4^+$  ions was relatively low and it became lower than that of  $\text{NO}_3^-$  ions after irradiation for 5 h in the photodegradation of THTA possibly since attack of  $\cdot\text{OH}$  radicals on the  $\alpha$ -carbon of the nitrogen moiety in THTA would be difficult. The rate for conversion of nitrogen moieties (except nitro group) to  $\text{NO}_3^-$  ions was relatively slow in comparison with the  $\text{NH}_4^+$  formation rate in the initial photodegradation stages of both AFAA and THTA. The formation of  $\text{NO}_3^-$  ions from these nitrogen moieties perhaps proceeds by several oxidation steps.

#### 4. Conclusion

The compounds containing multi-nitrogen atoms, azobisformamidoacetic acid (AFAA) and trihydrazinotriazine (THTA), can be totally transformed but only partially photomineralized to  $\text{CO}_2$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in aerated aqueous  $\text{TiO}_2$

dispersions under UV irradiation. Nitrogen gas is also formed in the photodegradation process of AFAA. The formation of  $\text{NH}_4^+$  ions is more than that of  $\text{NO}_3^-$  ions in the AFAA degradation, while the THTA system exhibits an opposite result, which is closely related to the molecular structures of the two compounds.

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