

Thioureas methyl-derivatives photo-induced transformation on titanium dioxide

Paola Calza*, Claudio Medana, Claudio Baiocchi, Ezio Pelizzetti

Dipartimento di Chimica Analitica, Università di Torino, via P. Giuria 5, 10125 Torino, Italy

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Abstract

Thiourea methyl-derivatives photocatalytic degradation has been studied by adopting titanium dioxide as a photocatalyst. A combined study has been performed and had involved: (1) the study of (methyl)thioureas degradation rate; (2) the identification of intermediate compounds, obtained by HPLC tandem mass spectrometry and (3) the assessment of the mineralization process.

Thiourea is mainly transformed into cyanamide and urea and then (very slowly) mineralized (up to 24 h of irradiation are required). For its methyl derivatives, the formation of the corresponding methylureas is realized; in addition, several dimeric compounds have been identified. Methyl thiourea gives the formation of $\text{CH}_3\text{NHC}(\text{NH})\text{CH}_2\text{NHCONHCH}_3$ and methylcyanamide dimeric form, while dimethylthiourea forms $\text{NCNHCH}(\text{OH})\text{CH}_2\text{NHCONHCH}_3$, but no cyano derivatives are observed.

The rate of mineralization gets higher at the increasing of the number of the methyl groups. Sulphur is easily released as sulphate ions in all cases. The nitrogen is preferentially released as ammonium ions, with a ratio ammonium versus nitrate ions of 2:1, observed in all cases but with dimethylthiourea, where instead an initial major formation of ammonium ions, at the increasing of the irradiation time a slight inversion between nitrate and ammonium formation is seen.

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1. Introduction

In previous works, we have investigated the classes of urea and guanidine alkyl-derivatives [1,2], while in the present study we concentrate on the methyl thiourea derivatives. The presence of one or more alky-group on urea induces the formation, as major intermediates, of cyclic compounds, recognized as (methyl)-amino-2,3-dihydro-1,2,4-oxadiazol-3-one, while the demethylation process occurs as a minor transformation pathway [1]. These results are very surprising as they are in contrast with the usual transformation pathways involved in photocatalytic processes, where the transformations lead to more simple structures [3] and, when more complex structures formation is evidenced, they are formed at trace level [4]. By contrast, the photoinduced degradation of methylguanidine derivatives proceeds mainly through a demethylation process [2].

Thiourea methyl derivatives are widespread present as formed during the degradation of more complex structures [5–7]. Moreover, thiourea and its oxides are important reagents in industrial productions [8–10]. The knowledge of the oxidation kinetics for thiourea and its derivatives may also be critical in the understanding of the physiological effect of sulphur-containing species. Recent studies [11] suggest that the reactive oxygen species, superoxide and hydroxyl radicals formed from the cleavage of C–S bond to give the sulfoxylate ion are responsible for the inherent toxicities of thiourea.

In the present study, we have employed heterogeneous photocatalysis to study the thiourea methyl-derivatives transformation pathways, mediated by oxido/reductive species, formed through a sequence of well-known reactions [12–15]. The fate of the intermediates evolution, organic nitrogen and carbon mineralization have been followed, in order to explore the role of electron withdrawing groups on the amino substituents.

A characterization of the formed intermediates has been obtained through an HPLC/tandem MS instrument, while the final products have been identified by ion chromatography and

* Corresponding author. Tel.: +39 0116707626; fax: +39 0116707615.
E-mail address: paola.calza@unito.it (P. Calza).

TOC measurements. Usually, the photocatalytic oxidation of an organic compound containing heteroatoms leads to the total mineralization with the formation of carbon dioxide and inorganic ions [16–20]. While sulphur atom is recovered as sulphate irrespective to its initial oxidation state, nitrogen follows a more interesting fate. Nitrogen moieties in organic compounds can be transformed photocatalytically to either NH_3 (NH_4^+ in acidic media) and/or nitrite and nitrate ions.

2. Experimental

2.1. Materials and photochemical apparatus

Thiourea, methylthiourea, 1,3'-dimethylthiourea, tetramethylthiourea, urea, methylurea, 1,3-dimethylurea and tetramethylurea were all purchased by Aldrich and were used as received. Ammonium chloride (Carlo Erba), potassium nitrate (Merck) and sodium nitrite (Carlo Erba) were used after drying. HPLC grade water was obtained from MilliQ System Academic (Waters, Millipore). Methanol HPLC grade (BDH) was filtered through a 0.45 μm filter before use. Ammonium acetate reagent grade was purchased from Fluka.

When the experiments were carried out using TiO_2 Degussa P25 as the photocatalyst, in order to avoid possible interference from ions adsorbed on the photocatalyst, the TiO_2 powder was irradiated and washed with distilled water until no signal due to chloride, sulphate or sodium ions could be detected by ion chromatography.

The irradiations have been performed using a 1500 W xenon lamp (Solarbox, CO.FO.MEGRA, Milan, Italy) simulating AM1 solar light and equipped with a 340 nm cut-off filter. The total photons flux (340–400 nm) in the cell and the temperature during irradiation has been kept constant for all experiments. They were 1.35×10^{-5} einstein min^{-1} and 50 °C, respectively. The irradiation was carried out on 5 mL of suspension containing 15 mg L^{-1} organic compound and 200 mg L^{-1} TiO_2 . The pH of the solutions was not modified and is approximately 6–6.5. The entire content of the cells was filtered through a 0.45 μm filter and then analyzed by an appropriate technique.

2.2. Analysis of photochemical products

The chromatographic separations were performed by means of a C18 column Phenomenex Luna, 150 mm \times 2.0 mm (Phenomenex, Torrance, CA, USA). Injection volume was 20 μL and flow rate 0.2 mL min^{-1} . Gradient mobile phase composition was adopted: 5:95 to 40:60 in 25 min methanol/aqueous ammonium acetate 5 mM pH 6.8. A LCQ Deca XP PLUS ion trap mass spectrometer (Thermo) equipped with an atmospheric pressure interface and an ESI ion source was used. The LC column effluent was delivered into the ion source using nitrogen as sheath and auxiliary gas (Claind Nitrogen Generator apparatus). The needle voltage was set at the 4.5 kV value. The heated capillary value was maintained at 250 °C. The acquisition method used was previously optimized in the tuning sections for the parent compound (capillary, magnetic lenses and collimating octapoles voltages) in order to achieve the maximum of sensitivity.

A Dionex instrument has been employed equipped with a conductimeter detector. The determination of ammonium ions has been performed by adopting a column CS12A and 25 mM metansulphonic acid as eluant, flow rate of 1 mL min^{-1} . In such conditions, the retention time is 3.9 min. The anions have been analysed by using a AS9HC anionic column and a mixture of NaHCO_3 12 mM and K_2CO_3 5 mM at a flow rate of 1 mL min^{-1} . In such experimental conditions the retention times are 6.63 min, 9.58 min for nitrite and nitrate, respectively.

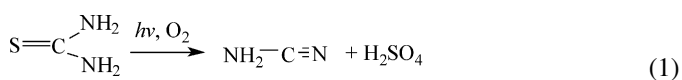
Total organic carbon (TOC) was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C). Calibration was achieved by injecting standards of potassium phthalate.

3. Results and discussion

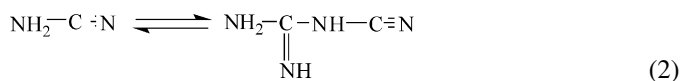
Thiourea (TU), methylthiourea (MTU), dimethylthiourea (DMTU) and tetramethylthiourea (TMTU) have been irradiated by adopting titanium dioxide as a photocatalyst. HPLC/MS analysis, ESI in positive ions, has been performed to recognize the unknown intermediates. In all cases, their MS^n spectra have been analysed and have been taken into account for the identification of the intermediate compounds. Table 1 summarizes all the characteristic MS^n fragments coming from thiourea, its methyl derivatives and the intermediates formed during their transformation processes, together with the supposed structures. Herein the transformation pathways, followed in the different cases, will be described.

3.1. Thiourea

Fig. 1 summarizes the profiles for thiourea disappearance, intermediates formation and the evolution of inorganic ions as a function of the irradiation time. As shown in Fig. 1A, thiourea is rapidly degraded ($t_{1/2}$ 15 min). Along with the TU disappearance, several species have been formed. As assessed by Fig. 1B, it has been recognized the formation of cyanamide as main intermediate compound (maximum after 2 h), in agreement with literature data [21–23]. It is known that thiourea undergoes photochemical degradation, in the presence of oxygen, to form cyanamide and sulphuric acid [23], accordingly to reaction (1):



Alternatively, cyanamide could be formed through the loss of H_2S , as previously suggested [24,25]. In both cases, it is in equilibrium with its dimeric form, dicyandiamide [26].



Cyanamide is revealed by the MS detector as its dimeric form ($[\text{M}+\text{H}]^+$ 85) and its identity is confirmed by the injection of a standard solution.

Concomitantly, a second pathway occurs and involves the cleavage of C–S bond with the formation of urea ($[\text{M}+\text{H}]^+$ 61). Approximately, 13% of the thiourea is converted into urea; it

Table 1

List of retention times, $[M+H]^+$ and main fragments obtained from MS^n spectra for thiourea, methyl thioureas and their intermediate compounds

Compounds	t_R (min)	$[M+H]^+$	MS^2	MS^3
Thiourea	2.77	77	60 ($-NH_3$)	–
1. Cyanamide	2.50	85	–	–
2. Urea	2.35	61	–	–
Methylthiourea	3.01	91	74 ($-NH_3$), 32 ($-SCNH$)	–
1. Methylurea	2.51	75	–	–
2. $CH_3NHC(NH)CH_2NHCONHCH_3$	4.63	145	127 ($-H_2O$) 89 ($-CH_3NHCN$)	71 ($-CH_3NHCN$) 60 ($-CH_2NH$), 30 ($-CHONHCH_3$)
3. Methylcyanamide dimeric form	2.52	113	57 ($-CH_2N_2$), 71 ($-CH_3NHCN$)	–
Dimethylthiourea	3.20	105	74 ($-CH_3NH_2$), 32 ($-SCNHCH_3$)	–
1. Dimethylurea	3.04	89	–	–
2. $NCNHCH(OH)CH_2NHCONHCH_3$	3.56	159	141 ($-H_2O$) 128 ($-NH_2CH_3$) 102 ($-CONCH_3$) 89 ($-NCNHCHO$)	– 71 ($-CH_3NCO$) – 32 ($-CONCH_3$)
Tetramethylthiourea	11.9	133	88 ($-NH(CH_3)_2$)	–
1. Tetramethylurea	10.70	117	72 ($-NH(CH_3)_2$)	–
2. Trimethylurea	4.83	103	–	–
3. Hydroxytetramethyl-thiourea	5.20	149	117 ($-CH_3OH$)	72 ($-NH(CH_3)_2$)

is formed at short times, reaches the maximum after 30 min of irradiation and then very slowly disappears.

When the thiourea is completely disappeared (30 min), up to 95% of the carbon and nitrogen are still present in organic

forms. Conversely, sulphur atom is partially released as sulphate ions (40%). These profiles are in agreement with the identified intermediates, as both require the release of the sulphur atom for their formation. Even if sulphur could be initially released as HS^- or SO_3^{2-} , it is then suddenly oxidized to sulphate [27–29]. This can explain why the rate of increasing sulphate is slower than the thiourea degradation. In addition, some very small and hydrophilic compounds still containing the sulphur atom could also be formed.

After 4 h of irradiation, the sulphur atom is completely mineralized, while 85% of the organic carbon results still bound into intermediate compounds. Also nitrogen is released in a small yield: 20% as ammonium ions and 10% as nitrate ions. Diverse quantities of nitrite, nitrate and ammonium ions may be linked to the different features of the N-containing structure. Nitro groups are converted predominantly to NO_3^- ions [19]. By contrast, secondary, tertiary and quaternary nitrogen atoms are photoconverted predominantly to NH_4^+ ions [20].

After 24 h of irradiation, 80% of the nitrogen is mineralized; ammonium and nitrate are formed in a ratio 2:1, in agreement with literature data [30]. The percentage of missing nitrogen still linked as organic nitrogen is in accordance with the lack of mineralization (30% of organic carbon still present).

Since cyanamide is recognised as the main intermediate, we have performed also its degradation, in order to investigate the fate of organic carbon and the nitrogen. As evidenced in Fig. 2, the TOC slowly decreases and after 16 h of irradiation approximately 20% of the organic carbon is still present. It underlines that both the identified compounds are refractory to mineralization at short time [1,31,32] and are then accountable for the lack of mineralization.

Concomitantly, nitrate and ammonium are formed in a ratio 1:1 and with a rate of evolution that closely resemble the TOC disappearance rate. Taking into account the cyanamide profiles,

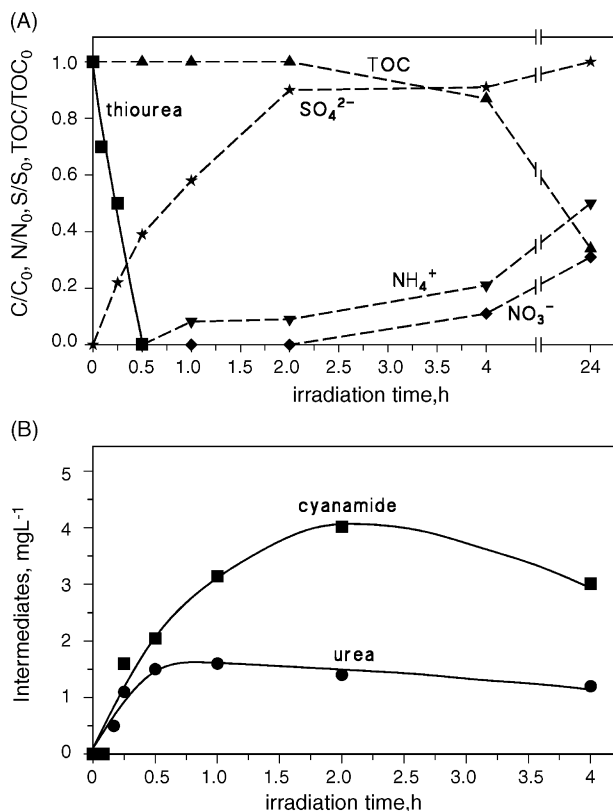


Fig. 1. Degradation of thiourea (15 mg L^{-1}) on titanium dioxide 200 mg L^{-1} : disappearance of initial compound, evolution of inorganic species (nitrate, ammonium and sulphate ions) and TOC disappearance (A) until 1 h of irradiation; (B) until complete mineralization.

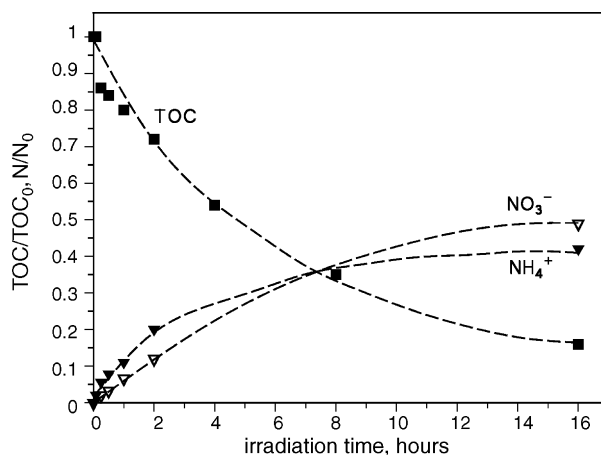


Fig. 2. Degradation of cyanamide (15 mg L^{-1}) on titanium dioxide 200 mg L^{-1} . Evolution of inorganic species (nitrate and ammonium ions) and TOC disappearance until 4 h of irradiation.

it can be concluded that almost all the nitrate formed during thiourea transformation comes from cyanamide degradation, while the ammonium derives from both cyanamide (25%) or other concomitant pathways (20%).

3.2. Methyl-thiourea

The temporal profiles for methylthiourea are shown in Fig. 3. Methyl-thiourea (MTU) is easily degraded ($t_{1/2}$ 10 min, Fig. 3A). Concomitantly, several intermediate compounds come up (see Table 1). On the basis of MS^n spectra analysis, a structure has been proposed for all species.

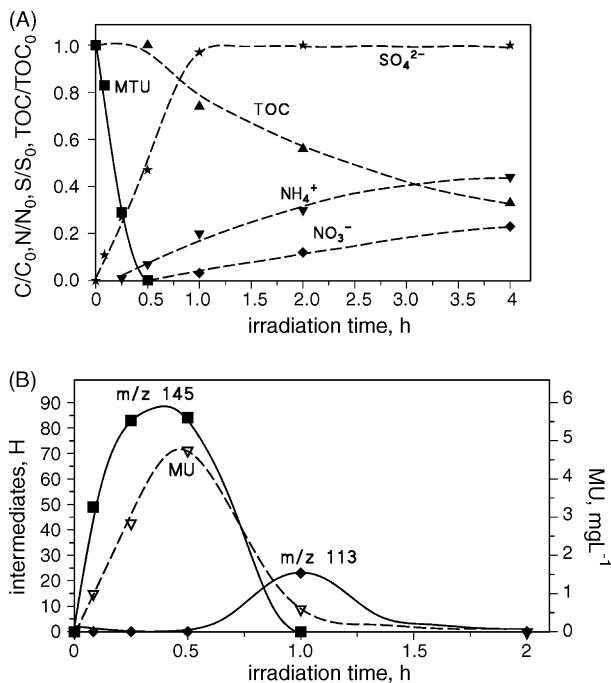


Fig. 3. Degradation of methyl-thiourea (15 mg L^{-1}) on titanium dioxide 200 mg L^{-1} : (A) disappearance of initial compound, evolution of inorganic species (nitrate, ammonium and sulphate ions) and TOC disappearance until 4 h of irradiation; (B) intermediates evolution.

A species at $[\text{M}+\text{H}]^+$ 75 is initially formed and has been identified as methyl-urea, whose identity has been confirmed by the injection of a standard solution. It represents only a secondary pathway, as it is formed in the amount of 0.1 mg L^{-1} .

A parallel transformation leads to a species at $[\text{M}+\text{H}]^+$ 113. The major fragments observed in the MS^n spectra reported in Table 1 can be attributed to NH_2CN and CH_3NHCN losses; they permit to tentatively recognise it as the dimeric form of methylcyanamide.

Similarly to the case of thiourea, also the methyl thiourea photoinduced transformation proceeds through the C–S bond cleavage, with the formation of the oxygen-derivative (methylurea) and cyano derivative (methylcyanamide). Conversely, while for thiourea these two pathways represent the chief transformation route, for methylthiourea they seem to account only for a marginal transformation. In addition another species, holding $[\text{M}+\text{H}]^+$ 145, has been observed at short irradiation times, whose main fragments are shown in Table 1. MS^2 spectrum holds as base fragment m/z 89, formed through a methylcyanamide loss, and a fragment at m/z 127 (loss of a water molecule). A combined analysis of MS^2 and MS^3 spectra permits to assign it to a dimeric form (see Table 1).

When methyl-thiourea is completely disappeared (30 min), 50% of the sulphur has been released as sulphate ions and almost all the organic carbon and nitrogen are still present. At that time, even if the identified intermediates do not contain the sulphur atom, probably some very small (and oxidised) compounds still containing the sulphur atom are also formed, in accord with the high organic carbon content. While for sulphur the complete mineralization is achieved until 1 h of irradiation, after 4 h of irradiation only 70% of the nitrogen has been mineralized, with the formation of ammonium and nitrate ions in the ratio 2:1, in a close analogy with TU. Nevertheless, in this case the TOC disappearance easily occurs than with thiourea. It should be linked to a combination of events. On one side, as the presence of a methyl group on the structure had shown to favour the mineralization of the urea derivatives [1], it should similarly influence the thio derivatives. Moreover, the dimerization products probably evolve rapidly to carbon dioxide.

3.3. Dimethyl-thiourea

Fig. 4 shows the profiles for dimethyl-thiourea (DMTU). It is easily degraded ($t_{1/2}$ 15 min) and in the intermediate compounds, in a close parallelism with the cases of TU and MTU, sulphur atom is displaced by oxygen, so giving the formation of the corresponding urea derivatives. Dimethylurea ($[\text{M}+\text{H}]^+$ 89) is formed in the initial part of the process (in an amount of 0.9 mg L^{-1}) and reaches the maximum after 30' of irradiation. It coincides with 7% of the transformation process. As a consequence of dimethylurea disappearance, the formation of urea ($[\text{M}+\text{H}]^+$ 61) is evidenced. Differently from the MTU and TU, no cyano derivatives have been detected.

A concomitant transformation pathway leads to the formation of the species at $[\text{M}+\text{H}]^+$ 159. On the basis of the MS^n spectra analysis (see Table 1 and Scheme 1 for the fragmentation pathway) it has been attributed to the structure shown on Scheme 1.

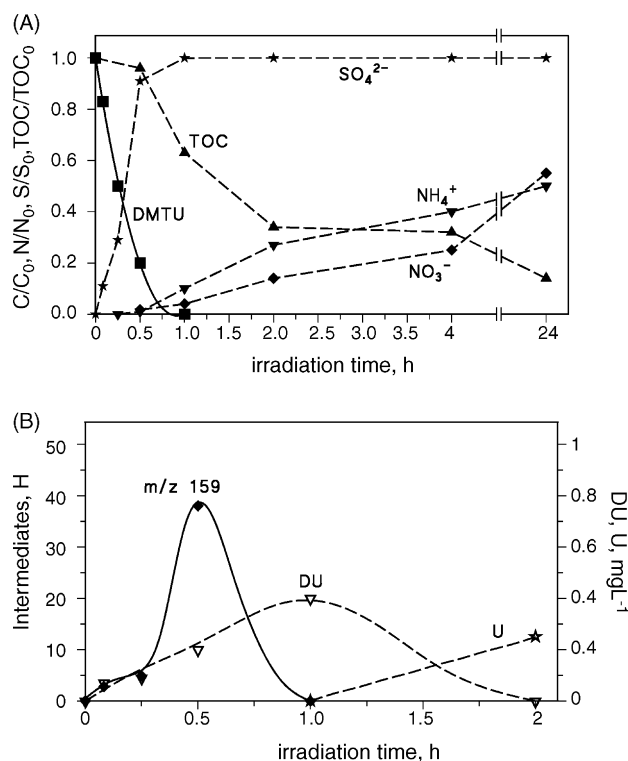


Fig. 4. Degradation of dimethyl-thiourea (15 mg L^{-1}) on titanium dioxide 200 mg L^{-1} : (A) disappearance of initial compound, evolution of inorganic species (nitrate, ammonium and sulphate ions) and TOC disappearance until 4 h of irradiation; (B) intermediates evolution.

MS spectrum reveals the absence of sulphur atom; MS^2 spectrum holds as peculiar fragments m/z 141 (base peak), 128, 102 and 89. They should be reasonably linked together through the fragmentation pathway proposed in Scheme 1.

The rate for carbon mineralization is even increased in respect to MTU and, in the first part of the process, it proceeds faster than the nitrogen mineralization. It has also to be underlined that the absence of cyano derivatives helps in reaching the complete mineralization. When dimethylthiourea is completely disappeared (1 h), sulphur atom has been stoichiometrically released as sul-

phate ions and 35% of the organic carbon has been mineralized; conversely, only 10% of the bound nitrogen has been released. After 4 h of irradiation, when 30% of the carbon is still present, 70% of the nitrogen has been mineralized, with the formation of ammonium and nitrate ions in the ratio 2:1. After 24 h of irradiation, complete mineralization is achieved, with ammonium and nitrate ions formed in a ratio 1:1, so underlining that while the intermediates formed in the first part of the process liberate the nitrogen chiefly as ammonium ions, those formed during the second part of the process release the nitrogen largely as nitrate ions.

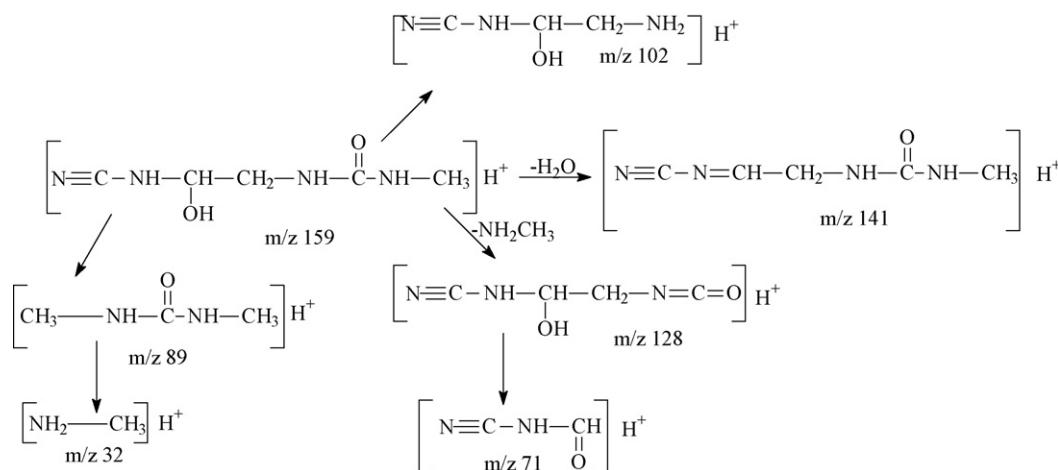
3.4. Tetramethylthiourea

The temporal profiles for tetramethylthiourea disappearance and intermediates formation are summarized in Fig. 5. Tetramethylthiourea is easily degraded ($t_{1/2}$ 10 min). Its MS^2 spectrum presents a fragment at m/z 88, accordingly with a loss of a dimethylamino molecule. This fragmentation pattern will be useful in the identification of intermediates compounds.

In the initial part of the photo-induced transformation process, several peaks have been evidenced, identified and, when possible, quantified. The first step is represented by the formation of a species at $[\text{M}+\text{H}]^+$ 149, recognized as hydroxy-tetramethylthiourea. The attribution to the mentioned structures is supported by the fragments observed from MS^2 spectra, collected in Table 1 and presented in Scheme 2.

At the same time, the formation of a species at $[\text{M}+\text{H}]^+$ 117 is achieved; it has been recognized as tetramethylurea, thanks to the MS^n spectra analysis and a standard solution injection. It is then transformed into a species holding $[\text{M}+\text{H}]^+$ 103, attributed to trimethylurea.

After 30' of irradiation, when tetramethylthiourea has been completely degraded, also sulphur atom has been completely released as sulphate ions, while the nitrogen is still bound (less than 10% forms ammonium ions). It closely resembles the fate followed by the other methyl derivatives. Moreover, in the first part of the process the mineralization proceeds even faster than DMTU (after 1 h of irradiation, up to 70% of the organic carbon



Scheme 1. Fragmentation pathway followed by the species at m/z 159.

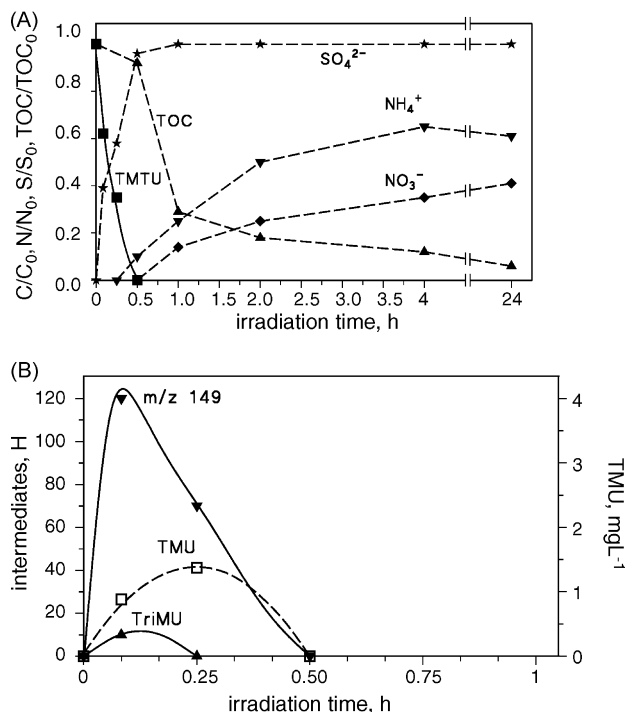
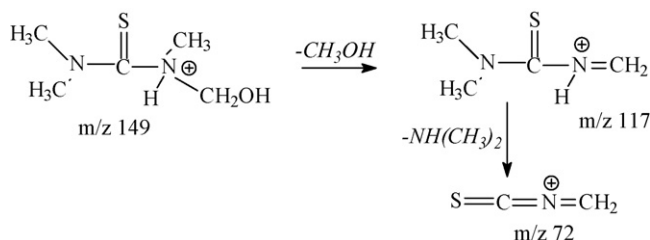


Fig. 5. Degradation of tetramethyl-thiourea (15 mg L^{-1}) on titanium dioxide 200 mg L^{-1} : (A) disappearance of initial compound, evolution of inorganic species (nitrate, ammonium and sulphate ions) and TOC disappearance until 4 h of irradiation; (B) intermediates evolution.



Scheme 2. Fragmentation pathway followed by m/z 149.

has been mineralized). Again, the molecules hardly mineralized are those still containing the nitrogen, i.e. the urea derivatives. Finally, after 4 h of irradiation, complete mineralization has been achieved and nitrogen gives inorganic ions in stoichiometric amount, with the formation of ammonium and nitrate ions in a ratio 2:1.

As intermediate compounds, after 2 h of irradiation neither the UV or MS detectors reveal the presence of intermediate compounds. This is in accordance with the formation of small molecules still containing bound nitrogen, which represent the last step before the carbon mineralization.

4. Conclusions

Thiourea and methylthiourea derivatives disappear at short irradiation times. Along with the disappearance of the thiourea derivatives, several intermediate compounds arise. While thiourea is mainly transformed into cyanamide and urea, different fate is followed by its methyl derivatives. For all of them,

the formation of the corresponding methylureas is realized; in addition the formation of several dimeric compounds occurs. Methyl thiourea gives the formation of $\text{CH}_3\text{NHC}(\text{NH})\text{CH}_2\text{NHCONHCH}_3$ and methylcyanamide dimeric form, while dimethylthiourea forms $\text{NCNHCH}(\text{OH})\text{CH}_2\text{NHCONHCH}_3$, but no cyano derivatives are observed.

The rate of mineralization gets higher at the increasing of the number of the methyl groups. Sulphur atom is photocatalytically transformed into sulphate ions. For all the investigated structures the formation of sulphate ions in stoichiometric amount is realized at short time, ranging from 1 h (MTU, DMTU, TMTU) to 2 h (TU). It is stressed also by the absence of intermediates still containing sulphur in the structure.

The fate of the nitrogen seems not influenced by the number of methyl group linked to the nitrogen atoms. As a matter of fact, the nitrogen is preferentially released as ammonium ions, with a ratio of 2:1 between ammonium and nitrate ions. The only structure where the ratio is only slightly in favour of ammonium release is DMTU, where instead an initial major formation of ammonium ions, at the increasing of the irradiation time a slight inversion between nitrate and ammonium formation is observed. It can be explained on the basis of the identified intermediates. Dimethyl-thiourea gives, in addition to thiourea, also the formation of dimethyl-urea and of a dimeric compound. Dimethylurea had shown to be mainly transformed into nitrate ions [4], so accounting for the increased nitrate formation. Nitrate formation is resulted the main inorganic form observed from all the methylureas. Being only a secondary pathway for tetramethylthiourea and methylurea, the formation of nitrate is limited.

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