Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 323–328
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photocatalytic degradation of a cyanuric acid, a recalcitrant species

Youn-Chul Oh, William S. Jenks*

Department of Chemistry, Iowa State University, 3760 Gilman Hall, Ames, IA 50011-3111 USA

Received 27 May 2003; received in revised form 25 August 2003; accepted 28 August 2003

Abstract

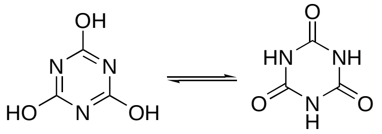
Degradation of cyanuric acid in aqueous suspensions of Degussa P25 TiO_2 has been achieved by the addition of fluoride ion at low pH. Consistent with the work of Minero and Pelizzetti [Langmuir 16 (2000) 2632, Langmuir 16 (2000) 8964], it is suggested that this is due to the formation of homogeneous phase hydroxyl radicals. Support for this hypothesis is brought from successful degradations using other hydroxyl-generating conditions and the successful degradation of 4-*t*-butylpyridine, another organic compound previously shown to be resistant to TiO_2-mediated photocatalytic degradation.

Keywords: Photocatalytic degradation; Titanium dioxide; Fluoride; Cyanuric acid

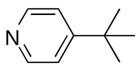
1. Introduction

Nearly every organic molecule ever tested is degraded to CO_2, H_2O, and appropriate inorganic ions when exposed to TiO_2-mediated photocatalytic degradation conditions in oxygenated water. This mineralization process is the basis upon which the use of TiO_2 and other semiconductors for water purification is built.

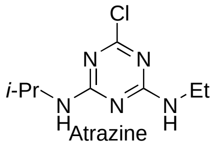
One of the very few organic molecules known to survive such treatment is cyanuric acid, (**1**). This is of both fundamental and practical interest. The latter is true because of the large family of triazine herbicides in popular usage, most notably atrazine. Several studies have all shown that atrazine and other triazine herbicides are all degraded to cyanuric acid in the presence of irradiated TiO_2 suspensions, but that no further degradation takes place [3–8]. While it is known that cyanuric acid is generally difficult to chemically hydrolyze or oxidize [9], this result is still remarkable given the extreme generality of the TiO_2 photocatalytic degradation method. In contrast, biologically based degradations using *Pseudomonas* sp. bacteria have been successful. These degradations proceed through biuret and urea, both of which are intermediates that are formally products of hydrolysis reactions [10–13]. Similarly, hydrolysis can be catalyzed by alumina in the range of 300 °C [14] or in supercritical water at even higher temperature and pressure [15].



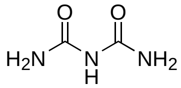
Cyanuric Acid, **1**   Isocyanuric acid



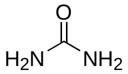
4-*t*-Butylpyridine, **2**



Atrazine



Biuret



Urea

In neutral to acidic solution, (**1**) exists predominantly in the tautomeric form known as isocyanuric acid [9], which is related to cyanuric acid by a series of keto-enol equilibria. (For convenience, we will consistently refer to the mixture of tautomers as cyanuric acid.) The pKa values are 6.9, 11.4, and 13.5, and most evidence suggests that the anion that is formed is that of the cyanuric acid tautomer. This suggests that cyanuric acid, were it adsorbed to TiO_2, would probably be in the enolic form, but there is no direct evidence on this point.

A few reasonable hypotheses might be proposed to account for the stability of (**1**) to TiO_2-mediated photocatalytic degradation, which generally occurs by electron transfer reactions and the action of adsorbed hydroxyl radicals.

---

* Corresponding author. Tel.: +515-294-4711; fax: +515-294-9623.
E-mail address: wsjenks@iastate.edu (W.S. Jenks).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00372-1

First, it might be argued that the principle reaction might simply be removal of one of the phenolic hydrogen atoms, either directly or by sequential electron and proton loss. The resulting phenolic-type radical might be sufficiently stable to survive until it can pick up an electron to return to starting material or its conjugate base. Although it is well known that a great many aromatic compounds (including many phenols) are hydroxylated by irradiated TiO_2 suspensions, we know of no specific evidence to contradict this assertion.

A second hypothesis is that hydroxyl radical addition does occur, but is reversible because loss of water or $HO^{\bullet}$ results in a species that ends up returning to cyanuric acid under the conditions. We refuted this hypothesis a few years ago, showing that ^{18}O in (**1**) is retained, at least on timescales that are relevant to the usual degradation chemistry [5]. It might also be argued that the carbon atoms in cyanuric acid are already fully oxidized and are simply not reactive with the usual species formed in photocatalytic conditions. However, as we have also previously shown [5], urea is sensitive to TiO_2-mediated degradation, even though its carbon atom is also formally at the CO_2 oxidation state. In this paper, we will present circumstantial evidence for what might be the simplest hypothesis of all, that (**1**) does not adsorb significantly to TiO_2, and—given that the great majority of TiO_2-mediated degradation chemistry occurs on the catalyst surface—cyanuric acid is not present where the active oxidizing species are formed.

The factor that suggested this idea to us was the recent report from Nedoloujko that 4-*t*-butylpyridine (**2**) also withstood TiO_2 conditions, but was degraded by Fenton chemistry [16]. This was important in that the degradations of pyridine derivatives have been reported a number of times [17–23] without any evidence that pyridines are particularly hardy species. It thus seemed at least plausible that something similar—presumably a lack of contact between the reactive intermediates and the substrate—was occurring with cyanuric acid. Perhaps it was only the reputation of cyanuric acid as a particularly persistent molecule that made one propose that there would be special chemical explanations.

Here, we report the degradation of cyanuric acid, both using Fenton chemistry and the TiO_2-fluoride system introduced by Minero et al. [1,2]. These authors, on the basis of elegant kinetic studies, proposed that addition of fluoride ion to TiO_2 suspensions under acidic conditions causes the surface coating of the particles by fluoride and the production of homogeneous hydroxyl radicals. For simplicity, we will refer to conditions in which NaF has been added to TiO_2 suspensions as TiO_2/F. The results simultaneously support two hypotheses: (1) that cyanuric acid is not pathologically resistant in principle to this type of degradation, but is not degraded by TiO_2 because it does not bind at or near catalytically active sites, and (2) the Minero–Pelizzetti proposal that the TiO_2/fluoride system is capable of producing mobile—and presumably homogeneous—hydroxyl radicals.

2. Experimental

2.1. Materials

All chemicals were obtained from Aldrich in the highest purity available and used as received, except as noted. The water employed was purified with a Milli-Q UV plus system resulting in a resistivity $= 18\,M\Omega\,cm^{-1}$. TiO_2 was Degussa P-25.

2.2. Degradation and analysis procedures

2.2.1. Photocatalytic degradation

All suspensions were prepared at 100 mg TiO_2 per 100 ml water. The pH was regulated by addition of HCl (pH 2), phosphate buffer (10 mM, pH 7) or NaOH (pH 12). NaF, if used, was added at a concentration of 40 mM. After an hour of stirring and equilibration in the dark, the desired organic (**1** or **2**) was introduced at a concentration of 300 μM. The mixture was dispersed in an ultrasonic bath for 5 min to disperse larger aggregates and then purged with O_2 and stirred for 20 min in the dark before the irradiation was started. The mixture was continuously purged by O_2 throughout the irradiation except as noted. Irradiations were carried out with stirring at ambient temperature using a modified Rayonet mini-reactor equipped with a fan and eight 4 W broadly emitting 365 nm fluorescent tubes. After the reactions, samples were acidified, centrifuged, and filtered to remove the TiO_2. Water was removed by freeze–drying. Anthracene was added after photolysis as an external standard for GC analysis.

2.2.2. H_2O_2 photodegradation

Solutions were prepared as above, leaving out TiO_2. Immediately before photolysis, 1.0 ml of H_2O_2 (30% in water) was added. Photolysis and analysis were carried out in the ordinary way, save that broadly emitting 300 nm fluorescent tubes were used instead.

2.2.3. Fenton reaction

Reactions were conducted at room temperature. Normal conditions were 300 μM of the organic substrate, 8 mM $FeSO_4$ and 80 mM H_2O_2. The pH of solution was regulated as usual. After desired reaction time, the resultant mixture was filtered through 0.2 μm Whatman filters without otherwise quenching the reaction and the water was removed by freeze drying. Ordinary analyses were then used.

2.2.4. Analysis

The dried samples were exhaustively silylated by treatment with 1 ml of anhydrous pyridine, 0.2 ml of hexamethyldisilazane, and 0.1 ml chlorotrimethylsilane. The reactions were carried out in 1.5 ml plastic-stoppered vials. The resulting mixtures were shaken vigorously for about 60 s and then allowed to stand for 5 min at room temperature. Some precipitate was separated by centrifugation prior to chromatographic analysis. The intermediate products were analyzed as their trimethylsilyl (TMS) derivatives using GC–MS on a Varian star 3400CX Gas Chromatograph using 25 m DB-5 column, coupled with a Magnum ion trap detector mass spectrometer (Finnigan MAT, San Jose, CA). The temperature program of column was as follows: at 150 °C, hold time = 2 min; from 150 to 200 °C, rate = 10 °C/min; then raise the rate to 40 °C/min until 280 °C. A HP 5890 series II Gas Chromatograph with a 25 m ZB-5 column and an FID detector was also used for routine analysis.

2.2.5. *Adsorption of cyanuric acid to TiO_2/F and TiO_2*

Equilibrium extents of adsorption onto TiO_2/F and TiO_2 were evaluated after equilibration for fixed periods with vigorous magnetic stirring. The adsorption was evaluated at three different pHs: pH 2, 7, and 11 were held by HCl, and 30 mM phosphate buffer, and NaOH, respectively. Suspensions were prepared containing 50 mg of TiO_2 in 20 ml water and a variable amount of cyanuric acid. For TiO_2/F, 84 mg of NaF was added to each sample. After at least 9 h for equilibration, an aliquot was removed, and syringe filtered twice through Millipore 0.22 μm and Poll 0.20 μm filters to remove TiO_2. The residual concentration of (**1**) was determined by UV-Vis spectroscopy using a Shimadzu UV-2101 spectrometer.

3. Results

The experiments of Nedoloujko and Kiwi [16] were qualitatively reproduced. It was found that 4-*t*-butylpyridine (**2**) was degraded only very, very slowly under typical TiO_2 conditions, regardless of pH. However, at pH 2, using TiO_2/F, (**2**) was degraded over the course of several hours. We do not dwell on the products formed under these conditions, as this compound was not of our primary interest. However, early in the degradation, in addition to the usual trace products, a few major products were partially identified on the basis of mass spectral data. A very small amount of a dimer was formed. What appeared to be a single isomer of a trimethylsilylated hydroxylated product (mass = M + OTMS) the largest new peak at modest degradation conversion. We assume this is the 3-hydroxylated material. An apparently single isomer of a bishydroxylated species (mass = M + 2 OTMS) was also observed. A second dioxygenated species was formed (mass = M + 2 O) that was not silylated, indicating that this was probably a ring-opened product.

Additionally, samples of cyanuric acid (300 μM) were exposed to the standard photocatalytic degradation conditions (100 mg TiO_2 in 100 ml H_2O, broad 365 nm irradiation, O_2-saturated solutions) at pH 2, 7, and 12. Under no conditions was measurable degradation observed, consistent with literature reports.

Treatment of (**1**) at the same concentrations, but with the addition of NaF (i.e., TiO_2/F conditions) were also carried out. At pH 12, no degradation was observed. At pH 7, some degradation was observed over the course of several hours, but degradation was 3–4 times faster at pH 2. A qualitative indication of the relative rates can be seen in Fig. 1, which illustrates the remaining cyanuric acid after a fixed degradation period of 6 h. Degradation kinetics were approximately first order for two half-lives, as is often observed for photocatalytic degradations.

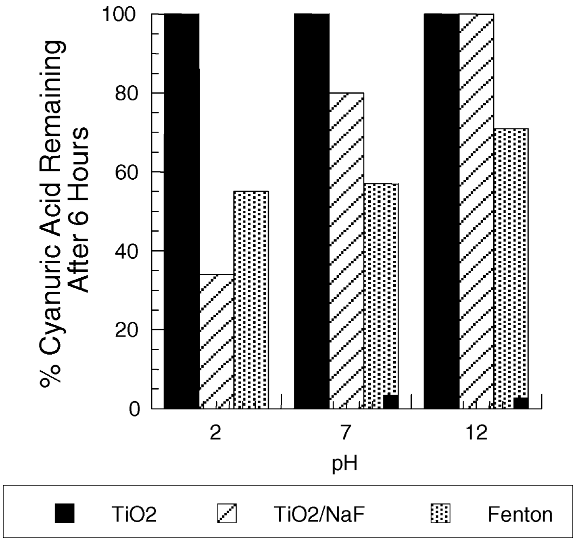


Fig. 1. Cyanuric acid remaining after a fixed period of irradiation under several conditions. The initial concentration was 300 μM for all experiments.

Control experiments using extended irradiation in the absence of NaF indicated that the rate of degradation in the presence of fluoride ion at pH 2 was a minimum of 1000 times faster than in its absence. If either the TiO_2 was left out of the suspension or the sample was flushed with Ar to remove all O_2 and kept anaerobic, no degradation of (**1**) was observed on photolysis.

At appropriate intervals during the degradations using Na/F conditions, samples were removed from the slurry. The TiO_2 was removed, and the residual material remaining after the water was removed was exhaustively silylated and subjected to standard GC–MS analysis. In no case were any intermediates in the degradation observed. Control experiments using potential intermediates urea and biuret ($NH_2CONHCONH_2$) showed that these compounds would have been observed had they been in the mixture.

These results were compared to degradations done under other conditions. Photolysis of oxygen-saturated solutions initially containing 300 μM (**1**) and 8.8 mM H_2O_2 at pH 2, using broadly emitting fluorescent bulbs centered at 300 nm, resulted in successful degradation of cyanuric acid on a timescale similar to the TiO_2/F experiments. An exact rate comparison is meaningless because the output of the lamps (though of the same order of magnitude) was not measured, and the absorption of light in the homogeneous sample is much different than in the highly scattering TiO_2 suspensions. However, as expected, the degradations showed zero-order kinetics, as appropriate for a homogeneous

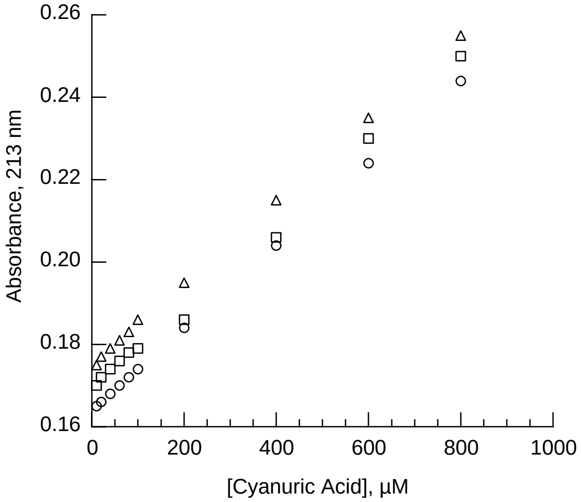


Fig. 2. Residual absorption at 213 nm after removal of TiO_2. Circles: no TiO_2; Squares: TiO_2; Triangles: TiO_2/F.

photochemical reaction limited by photon absorption. As before, no intermediates were detected.

Fenton chemistry using an excess of $Fe(SO_4)$ and H_2O_2 in the dark was also applied to 300 µM solutions of cyanuric acid. As shown in Fig. 1, these degradations were successful at every pH and showed less variation in rate. Again, the comparison of the absolute rates to the TiO_2/F conditions is not particularly meaningful, but what is important is that degradations occur at all pH values tested, indicating that the lack of TiO_2/F-mediated degradation at high pH is not a special feature ot the chemistry of (**1**), *per se*. As usual, no degradation intermediates were observed.

The extent of adsorption of cyanuric acid to TiO_2 was determined by UV-Vis spectroscopy. Samples were prepared using 50 mg TiO_2 in 20 ml water and various concentrations of (**1**). Fig. 2 shows the residual absorptions at 213 nm for three sets of samples: no TiO_2, TiO_2, and TiO_2/F, all at pH 2 after removal of TiO_2 by centrifugation and filtration. The data clearly indicate that there is no more than a few percent of the cyanuric acid adsorbed, even at the highest concentrations. Very similar data were obtained at pH 7 and 12, though the extinction coefficients (and thus the absolute absorptions) vary because of the protonation state of the cyanuric acid.

4. Discussion

Minero, Pelizzetti, and coworkers carried out an elegant set of experiments, based largely on kinetic analyses of the degradation of phenol, using TiO_2 suspensions at various pH values in the presence and absence of fluoride ion [1,2]. At low pH, fluoride displaces OH from the surface of the TiO_2 particles, with a maximum fluoride coverage calculated in the range of approximately pH 2.5 to 4.5, based on reasonable assumptions for the TiOH acid-base equilibria, the fluoride exchange equilibrium constant, and a fixed concentration of TiO_2 and fluoride. For phenol, they determined that at pH 3.6 with 10 mM F^-, virtually all of the reactivity of phenol is with homogeneous hydroxyl radicals formed by oxidation of water. They report a change in the ratio of *ortho* and *para* hydroxylation that occurs when NaF is present, though also note this can be sensitive to many parameters.

We hypothesize here that formation of freely diffusing hydroxyl radicals, caused by addition of fluoride at low pH, facilitates the photocatalytic degradation of cyanuric acid. Consistent with the data in Fig. 2, we suggest that, more than its general resistance to hydrolysis and oxidation, the reason cyanuric acid is not degraded in the presence of “naked” TiO_2 is that it does not adsorb to the surface of TiO_2 to any measurable extent. Therefore, when surface-bound hydroxyl radicals or trapped valence bond holes are formed, it is effectively inert simply because it is virtually never in the immediate vicinity of the reactive species. In contrast to naked TiO_2 conditions, cyanuric acid is degraded on photolysis of hydrogen peroxide or by Fenton chemistry. These results clearly show that it is not solely the inherent unreactivity of cyanuric acid that causes its stability to naked TiO_2 by showing that it is degraded by homogeneously dispersed hydroxyl radicals (or in the case of the Fenton reaction, hydroxyl-like species).

We further infer from the results of the Fenton and hydrogen peroxide photolysis experiments that the relative unreactivity of (**1**) does play a role in the current results, however. That comes from the result that no intermediates such as biuret or urea are observed. If the rate constants for “productive” reactivity between $HO^{\bullet}$ and cyanuric acid are well below the near-diffusion controlled limit that is typical for reactivity between $HO^{\bullet}$ and organic substrates, then any putative stable intermediates should be consumed more rapidly by $HO^{\bullet}$ than is cyanuric acid. In such a case, it is plausible that the intermediates never build up a reasonable steady state concentration because they are degraded faster than they are formed[1].

When cyanuric acid is subjected to TiO_2/F photolysis conditions, formation of freely diffusing hydroxyl radicals is consistent both with the hypothesis of Minero and Pelizzetti regarding hydroxyl radical formation and with our own regarding cyanuric acid adsorption as the root cause for its inertness. Because this logic may be considered somewhat circular, it is important to note that TiO_2-mediated degradation of 4-*t*-butylpyridine is also facilitated by the addition of fluoride. There is no reason to believe that (**2**) possesses any special chemical resistance to hydroxyl-like species or valence bond holes, nor that it is reactive with fluoride ion. Indeed, Nedoloujko and Kiwi showed that it too is subject to oxidation by homogeneously dispersed reagents [16]. Thus, these paired results provide strong supporting evidence for

---

[1] We cannot eliminate the possibility of strongly adsorbed intermediates that we cannot detect, through our previous experience makes this seem unlikely.

the Minero hypothesis, this time using a very simple observable: removal of cyanuric acid from solution at least three orders of magnitude more rapidly than without the fluoride.

Moreover, the observation of "ordinary" hydroxylation intermediates in the TiO_2/F-mediated degradation of (**2**) is consistent with our explanation for the lack of observable intermediates in the degradation of (**1**). There is no reason to believe that compound (**2**) is considerably less reactive than any of its obvious derivatives towards $HO^\bullet$. Thus, the rate of intermediate formation is not grossly lower than that of intermediate degradation early in the course of the reaction, and the steady state concentration initially builds up. In contrast, as in the homogeneous oxidations, the intermediates from TiO_2/F degradation of (**1**) are consumed more rapidly than they are formed and are thus not detected. An unfortunate corollary of this is that, although the expected reactivity of hydroxyl radicals with (**1**) would presumably be by addition to the carbon atoms, any further mechanistic discussion is too speculative to be fruitful.

The pH sensitivity of the degradation of (**1**) under TiO_2/F conditions is also consistent with Minero. By working at pH 2, it is reasonable to suggest that we have not maximized the amount of surface fluoride coverage (which peaks at slightly higher pH according to them), though we used a higher [NaF] than Minero. However, the considerably lower rate at pH 7 is consistent with their prediction of still lower surface coverage by fluoride, and the complete lack of degradation at pH 12 is consistent with their prediction of negligible fluoride coverage. An important secondary conclusion to draw from this work is that the formation of free hydroxyl radicals apparently does not depend on complete fluoride coverage. While undoubtedly more homogeneous $HO^\bullet$ is formed with higher fluoride coverage, some appears to remain even at pH values where coverage is incomplete. The exact form of the pH dependence is beyond the modest scope of this paper, but it is clear that an accurate assessment of the level of fluoride coverage would be required [2]. Finally, it should be noted that we have not optimized the rate of cyanuric acid degradation with respect to lamp output, pH, TiO_2 concentration, [NaF], etc., and it is possible that relative rates could be significantly improved with sufficient effort.

Previous to this, we are aware of only a single report of degradation of cyanuric acid by any TiO_2-mediated system [24]. In contrast to the consistently reported result that cyanuric acid is inert to photocatalytic degradation when using TiO_2 in suspension [3–8,25], these workers report that cyanuric acid could be degraded by use of their proprietary PHOTOPERM membranes. These membranes contain significant quantities of TiO_2 immobilized in a polyester support formed by polymerization around pre-formed TiO_2 particles. The reasons for this apparently anomalous result are not clear. However, it would be consistent with the current results to speculate that their immobilization procedure provides for binding sites that are more attractive to cyanuric acid in addition to immobilizing the TiO_2 particles. Reactions between the TiO_2 and cyanuric acid might then take place.

5. Conclusions

The addition of fluoride to aqueous suspensions of titania has proved to be an important mechanistic tool in unraveling a long-standing conundrum in photocatalytic degradation. By using this method in parallel with other methods for producing homogeneous hydroxyl-type reagents, it is shown that cyanuric acid is susceptible to degradation under easily accessible conditions. The comparatively unrelated, but not as generally unreactive, 4-*t*-butylpyridine (which is also almost untouched by ordinary TiO_2 photolysis conditions) is also degraded by TiO_2/F. It gives predictable hydroxylated intermediates, and thus supports the hypothesis that the induced reactivity is due to the formation of homogeneous $HO^\bullet$. The reason that cyanuric acid is ordinarily inert to TiO_2-mediated photocatalytic degradation appears to be that it simply is not bound to the reactive portions of the TiO_2 surface to any measurable extent, perhaps in combination with its lower reactivity evident from other reactions. Its inherent chemical resistance to degradation is still exhibited in the inability to observe intermediate degradation products, regardless of degradation method, because the intermediates are consumed more rapidly than they are formed.

Acknowledgements

The support of this research by the IPRT Center for Catalysis and, in part, the National Science Foundation is gratefully acknowledged.

References

[1] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, Langmuir 16 (2000) 2632.

[2] C. Minero, G. Mariella, V. Maurino, D. Vione, E. Pelizzetti, Langmuir 16 (2000) 8964.

[3] C. Minero, V. Maurino, E. Pelizzetti, Res. Chem. Intermed. 23 (1997) 291.

[4] E. Pelizzetti, V. Maurino, C. Minero, V. Carlin, M.L. Tosato, E. Pramauro, O. Zerbinati, Environ. Sci. Technol. 24 (1990) 1559.

[5] T. Tetzlaff, W.S. Jenks, Org. Lett. 1 (1999) 463.

[6] V. Héquet, P. Le Cloirec, C. Gonzalez, B. Meunier, Chemosphere 41 (2000) 379.

[7] V. Hequet, C. Gonzalez, P. Le Cloirec, Wat. Res. 35 (2001) 4253.

[8] G. Goutailler, J.C. Valette, C. Guillard, O. Paisse, R. Faure, J. Photochem. Photobiol. A: Chem. 141 (2001) 79.

[9] J.A. Wojtowicz, in: J.I. Kroschwitz, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York, 1991, pp. 835.

[10] A.M. Cook, FEMS Microbiology Rev. 46 (1987) 93.

---

[2] To the extent that cyanuric acid represents a compound that gives very easily distinguished reactivity, its initial rate of degradation might serve as a useful probe to determine the relative $HO^\bullet$ production efficiencies as a function of solution parameters.

[11] M.-S. Lai, A.S. Weber, J.N. Jensen, Water Environ. Res. 67 (1995) 347.

[12] C. Ernst, H.-J. Rehm, Appl. Microbiol. Biotechnol. 43 (1995) 150.

[13] A.M. Cook, P. Beilstein, H. Grossenbacher, R. Hütter, Biochem. J. 231 (1985) 25.

[14] Z. Zhan, M. Müllner, J.A. Lercher, Catal. Today 27 (1996) 167.

[15] S. Horikoshi, H. Hidaka, Chemosphere 51 (2003) 139.

[16] A. Nedoloujko, J. Kiwi, Water Res. 34 (2000) 3277.

[17] I.A. Balcioglu, Y. Inel, J. Environ. Sci. Health, Part A: Environ. Sci. Eng. Toxic Hazard. Subst. Control A31 (1996) 123.

[18] C. Maillard-Dupuy, C. Guillard, H. Courbon, P. Pichat, Environ. Sci. Technol. 28 (1994) 2176.

[19] J. Prousek, A. Klcova, Chem. Listy 91 (1997) 575.

[20] S. Sampath, H. Uchida, H. Yoneyama, J. Catal. 149 (1994) 189.

[21] P. Pichat, L. Cermenati, A. Albini, D. Mas, H. Delprat, C. Guillard, Res. Chem. Int. 26 (2000) 161.

[22] L. Cermenati, A. Albini, P. Pichat, C. Guillard, Res. Chem. Intermed. 26 (2000) 221.

[23] P. Pichat, Water Sci. Technol. 35 (1997) 73.

[24] B.M. Gawlik, A. Moroni, I.R. Bellobono, H.W. Muntau, Global Nest: the Int. J. 1 (1999) 23.

[25] C.M. Maurino, E. Pelizzetti, Res. Chem. Intermed. 23 (1997) 291.