ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 156 (2003) 121–126

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution

Antonio Lopez [a,*], Anna Bozzi [a], Giuseppe Mascolo [a], John Kiwi [b]

[a] *Department of Water Research and Technology, CNR-IRSA, Via F. de Blasio 5, Bari 70123, Italy*
[b] *Laboratory of Photonics and Interfaces, Institute of Molecular Chemistry and Biology, Swiss Federal Institute of Technology, Lausanne 1015, Switzerland*

Accepted 5 December 2002

Abstract

The degradation kinetics of two pharmaceutical intermediates (5-methyl-1,3,4-thiadiazole-2-methylthio (MMTD-Me) and 5-methyl-1,3,4-thiadiazole-2-thiol (MMTD)) have been studied in order to assess the effectiveness and the feasibility of UV processes for the decontamination of water polluted by such intermediates. Experiments were carried out, at 25 °C, treating, in a batch reactor, aqueous solutions (1 and 100 mg/l) of both compounds by UV radiations (254 nm) in the presence or absence of hydrogen peroxide. For both substrates, the results showed that: (i) no degradation occurred when H_2O_2 alone was used; (ii) UV and UV/H_2O_2 processes were both effective for degrading the substrates; (iii) substrates degradation by photo-oxidation was always faster than by direct photolysis; (iv) during direct photolysis, a lower substrate initial concentration lead to a faster and more efficient degradation. The quantum yields of the photolytic process were experimentally measured for both substrates resulting 14.1 ± 1.5 and 12.0 ± 0.7 mmol einstein^{-1} for MMTD-Me and MMTD, respectively. Carrying out photo-oxidation experiments using excess of peroxide (i.e., initial substrate concentration of 1 mg/l and H_2O_2/substrate molar ratios of 50/1, 42/1, 34/1 and 23/1), first- and second-order rate constants for MMTD-Me and MMTD degradation were calculated. In particular, the values of these latter resulted $(8.3 \pm 0.8) \times 10^8$ and $(1.6 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}, respectively. Our results show that to remove 99% of a few μg/l of the pharmaceutical intermediates with a H_2O_2 dose of 1 mg/l, 55 and 2.7 min for MMTD-Me and MMTD are necessary, respectively.

Keywords: Kinetics; Pharmaceutical intermediates; UV; UV/H_2O_2; Water treatment

1. Introduction

Waters contamination by pharmaceuticals is widely documented: estrogens, cholesterol-lowering drugs, pain relievers, antibiotics, caffeine and anti-depressants have been found in lakes, rivers and groundwater [1–4]. These compounds reach waterways mainly through the discharge of wastewaters both rough and treated. Additional pollution sources are direct emissions from production sites, disposal of surplus-drugs in households, excretion after applications for human and animal medical care or therapeutic treatment of livestock on field.

The conventional treatments carried out at wastewater treatments plants (i.e., preliminary, primary and secondary) usually do not effectively remove pharmaceutical derivatives. Therefore, in order to meet the quality's standards required for wastewaters discharge the effluents contaminated by pharmaceutical derivatives must be pre- or post-treated by appropriate physicochemical processes. Recently a growing interest has been observed in the area of UV activated processes due to [5]: (i) the continuous decrease of treatments costs due to the breakthrough into the market of relatively cheap low-energy UV lamps; (ii) the possibility to avoid, by using non-contact reactors, the UV lamp fouling; (iii) the simultaneous use of UV rays and chemical oxidants (e.g., ozone or hydrogen peroxide). Because of their specific technological requirements, UV based treatments are suitable for removing organic pollutants from water or wastewater with a low content of suspended solids and aromatic organic compounds due to the low light scattering and optical absorption.

When UV light is absorbed directly by H_2O_2, $^{\bullet}$OH radicals are generated by photolysis of the –O–O– peroxidic bond ($H_2O_2 + h\nu \rightarrow 2^{\bullet}OH$). Hydrogen peroxide absorbs light (depending on its concentration) in the range of the 185–300 nm, the highest hydroxyl radical yields are obtained when short-wave ultraviolet radiations (200–280 nm) are

* Corresponding author. Tel.: +39-80-5820506; fax: +39-80-5313365.
E-mail address: an.lopez@area.ba.cnr.it (A. Lopez).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1010-6030(02)00435-5

used. Low pressure lamps having an irradiation at 253.7 nm have been found very effective for the degradation of recalcitrant organic pollutants in UV/H_2O_2 mediated processes [6]. The molar absorption of hydrogen peroxide at 253.7 nm is 19.6 M^{-1} cm^{-1} and the quantum yield for the hydroxyl radical production approximately 1.0 [7]. Moreover, at 253.7 nm, the rate of H_2O_2 photolysis in aqueous solutions increases with pH because of the higher molar absorption coefficient of the peroxide anion (240 M^{-1} cm^{-1} beginning at pH 11.63) compared with that of un-dissociated hydrogen peroxide [8–10].

Hydroxyl radicals can react to: oxidize organic compounds; recombine with other hydroxyl species to form hydrogen peroxide or initiate a radical chain degradation of hydrogen peroxide [11,12]. Furthermore, hydroxyl radicals can attack organic molecules by: abstracting a hydrogen atom, adding hydroxyl groups, transferring electrons [13]. UV/H_2O_2 processes have been effective in the degradation of various water contaminants such as benzene [14], trichloroethene [15], MTBE [16], pesticides [17,18] and acetone [19].

In the present paper, the interest has been focused on a pharmaceutical intermediate (5-methyl-1,3,4-thiadiazole-2-methylthio (MMTD-Me)) and its parent compound (5-methyl-1,3,4-thiadiazole-2-thiol (MMTD)). Both compounds have been detected during a groundwater quality survey carried out in Northern Italy [20]. In particular, MMTD is an intermediate used for the synthesis of cefazolin, a cephalosporin antibiotic. MMTD is also a metabolite of this antibiotic [21] and harmful because it plays an important role in the patho-physiology of hypoprothrombinemia [22,23].

As for MMTD-Me, it is a metabolite of MMTD formed during its biological degradation [20]. In two previous papers [24,25] the UV and UV + H_2O_2 degradations pathways of both compounds have been assessed and compared in terms of by-products formation. The present paper, instead, deals with the kinetics of the degradation which is an important point to assess the feasibility of photo-oxidative processes when dealing with these intermediates.

2. Experimental

2.1. Chemicals

MMTD and phenol were from Aldrich (Milwaukee, WI, USA) and used as received (99% purity). MMTD-Me was synthesized according to common procedure for –SH group derivatization. H_2O_2 (30% w/w) was from J.T. Baker (Baker, Gross-Gerau, Germany). HPLC grade solvents (water and methanol) were from Fluka (Sigma-Aldrich, Milwaukee, WI, USA). High purity water from a Milli-Q-Water System (Millipore, Bedford, MA, USA) was used for preparing aqueous solutions. Potassium peroxodisulfate and uridine were from Baker and Aldrich, respectively.

2.2. Photochemical experiments

Experiments were carried out in a thermostated (T = 25 °C) 500 ml cylindrical Pyrex reactor. A 17 W low pressure mercury lamp, from Helios Italquartz (Milan, Italy), emitting at 254 nm was used. The lamp was introduced into the reactor and kept separated from the aqueous solution by a quartz cooling jacket. The light path was 1.9 cm. Aqueous solutions were stirred by a magnetic bar throughout the experiments in order to remain homogeneous. Before each experiment, the lamp was warmed up for 15 min to ensure stable lamp-output. Actinometry was carried out using potassium peroxodisulfate and uridine according to standard procedures [26]. At 25 °C, measured average incident photonic flux was 2.8×10^{-6} einstein/s which corresponds to a power output of 48 W/m^2 and a reactor light path of 1.85 cm. MMTD and MMTD-Me quantum yields were calculated by means of routine procedure [27]. In a typical photochemical experiment, 500 ml of substrate aqueous solution were put in the thermostated reactor and, for UV/H_2O_2 experiments, the appropriate amount of H_2O_2 was added. Afterwards, the warmed up UV-lamp was introduced into the reactor and, at given times, a 5 ml sample was taken and immediately analyzed by high performance liquid chromatography (HPLC).

2.3. Analytical determinations

UV measurements were performed with a Cary 1E UV-Vis spectrophotometer (Varian Inc., Palo Alto, CA, USA). The concentration of unreacted MMTD and MMTD-Me were monitored by HPLC-UV with a 1050-Ti chromatographic system (Agilent Technologies, Palo Alto, CA, USA) equipped with a Chromosphere 5B 5 μm, 250 mm × 3 mm column, a 10 mm × 2 mm pre-column, both from Chromopack (Walnut Creek, CA, USA) and a 1050 series variable wavelength detector set at 285 nm. Samples, injected by a Gilson 234 autosampler (Gilson, Middleton, WI, USA) equipped with a 9010 Rheodyne valve and a 50 μl loop, were eluted by a water/methanol 70/30 mixture at 0.6 ml/min. The detection limit was about 0.005 mg/l and reproducibility was within ±5%.

3. Results and discussion

Fig. 1a and b shows MMTD and MMTD-Me chemical structures together with their recorded decays during UV and UV/H_2O_2 treatments. These figures show that for both substrates no degradation takes place when H_2O_2 was used alone as the oxidant. Instead, UV and UV/H_2O_2 treatments were effective in degrading both substrates with adequate rates. Fig. 1a and b indicates that the substrate more effected by UV direct photolysis is MMTD-Me. Such a result can be mainly ascribed to the difference between the molar absorption at 254 nm (ε_i) for the two substrates, i.e.: 4970 and 2100 M^{-1} cm^{-1} for MMTD-Me and MMTD, respectively.

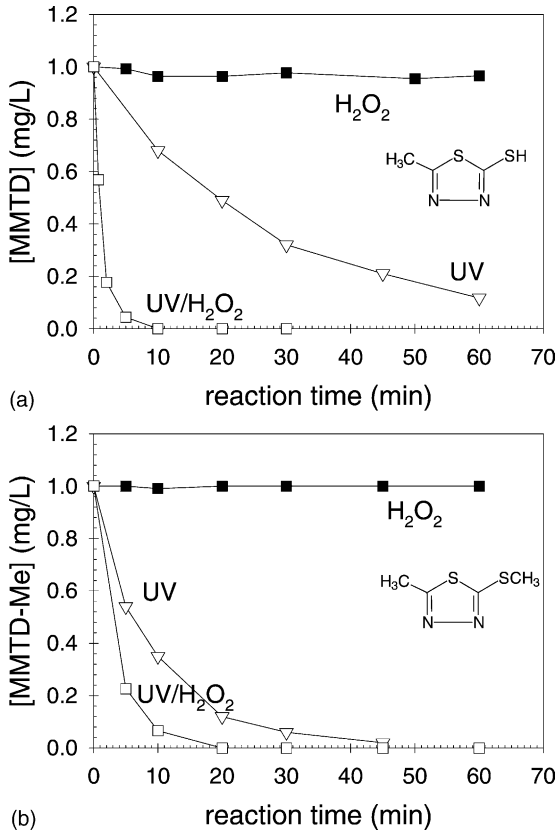

Fig. 1. MMTD (a) and MMTD-Me (b) decays during H_2O_2, UV and UV/H_2O_2 treatments. H_2O_2 initial concentration: 26 mg/l.

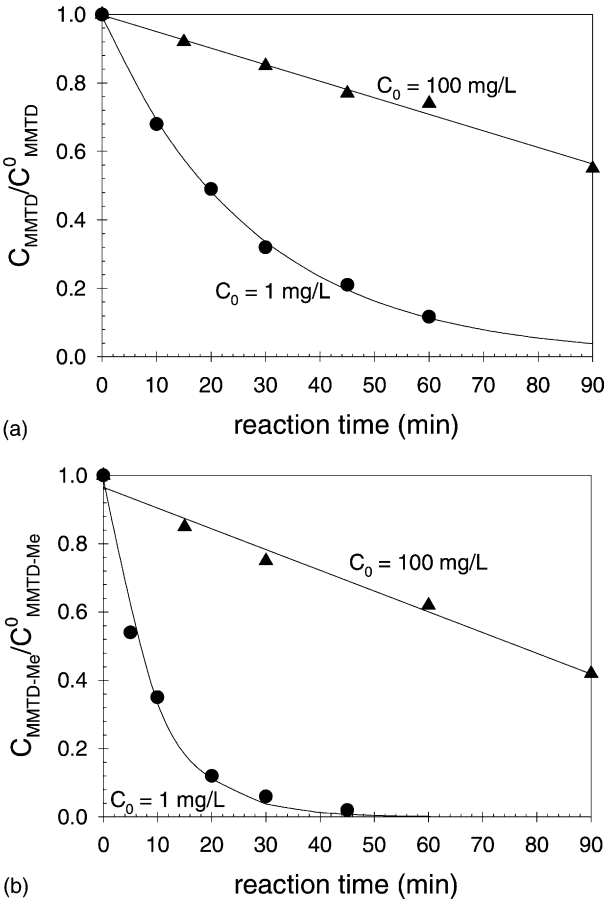

Fig. 2. MMTD (a) and MMTD-Me (b) decays during UV treatment by low pressure mercury lamp.

Furthermore, when using UV treatment alone (i.e., direct photolysis), Fig. 2a and b shows the evolution of residual MMTD and MMTD-Me concentrations versus time at different initial substrate concentrations. For both substrates, Fig. 2a and b indicates that the lower the starting concentration the higher the degradation rate which is expected in homogeneous oxidation processes. This result is consistent with what expected on the basis of the kinetic equation valid for the direct photolysis of an organic compound (i) in the presence of other substances that absorb a radiation at a given wavelength, i.e.:

$$-\frac{dC_i}{dt} = I_0\phi_i f_i \left[1 - \exp\left(-2.3L\sum_{j=1}^{N}\varepsilon_j C_j\right)\right] \quad (1)$$

where C_i is the concentration of the substrate i; I_0 the incident radiation flux; ϕ_i the quantum yield of photolysis; f_i the fraction of total absorbed light absorbed by the substrate ($f_i = \varepsilon_i C_i / \sum \varepsilon_j C_j$); ε_i the molar extinction coefficient; and L the reactor optical light path. In the case of low pressure Hg lamp, if the only compound absorbing UV radiation (254 nm) is the substrate i and the optical density ($L\varepsilon_i C_i$) is greater than 2 (i.e., substrate concentration is relatively high), the exponential term in Eq. (1) is $\ll 1$ and Eq. (1) can be simplified

$$-\frac{dC_i}{dt} = I_0\phi_i \quad (2)$$

Under such conditions, then, substrate decay is linear with time as shown in Fig. 2a and b for the highest (100 mg/l) initial MMTD and MMTD-Me concentrations.

Conversely, in case the optical density is lower than 0.1 (i.e., low substrate concentration) Eq. (1) becomes:

$$-\frac{dC_i}{dt} = 2.3LI_0\phi_i\varepsilon_i C_i \quad (3)$$

Eq. (3) is consistent with the trends in Fig. 2a and b at lower substrate concentrations. Integrating Eqs. (2) and (3), the following expressions are obtained, respectively:

$$\ln\frac{C_i}{C_i^0} = -2.3I_0\phi_i t \quad (2a)$$

$$\ln\frac{C_i}{C_i^0} = -2.3LI_0\phi_i\varepsilon_i t \quad (3a)$$

According to the trends shown in Fig. 2a and b, the most appropriate equation between (2a) and (3a) was selected to calculate the quantum yield values (ϕ_i) for MMTD and MMTD-Me. As expected, regardless to the equation used, for each substrate the same value was obtained, i.e.: 12.0 ± 0.7 and 14.1 ± 1.5 mmol einstein^{-1} for MMTD and MMTD-Me, respectively. These values result particularly

useful in many instances. For example, knowing their ϕ_i values, the extents (%) of MMTD and MMTD-Me degradations in the case of an UV dose of 250 J m^{-2} (i.e., the dose commonly used to disinfect drinking water) were estimated resulting both lower than 1%. This result is important since it confirms that UV disinfection and UV degradation of chemical contaminants is different at different fluence scales [27] and, indirectly, that, as often claimed, no by-products are formed during UV disinfection.

Referring to UV/H_2O_2 treatment, the kinetic equation describing substrate degradation takes into account both its direct photolysis by UV and its degradation by $^{\bullet}$OH radicals formed through hydrogen peroxide photolysis ($H_2O_2 + h\nu \rightarrow 2^{\bullet}OH$):

$$-\frac{dC_i}{dt} = kC_iC_{OH} + 2.3LI_0\phi_i\varepsilon_i f_i C_i \quad (4)$$

where the term kC_iC_{OH} and $2.3LI_0\phi_i\varepsilon_i f_i C_i$ represent the specific contributions of $^{\bullet}$OH radicals and UV radiation to the overall reaction, respectively.

At the beginning of the treatment, i.e., when the extent of substrate degradation is negligible, UV contribution ($2.3LI_0\phi_i\varepsilon_i f_i C_i$) is constant as f_i is constant. Integrating Eq. (4)

$$\ln\frac{C_i}{C_i^0} = -(kC_{OH} + 2.3LI_0\phi_i\varepsilon_i f_i)t \quad (4a)$$

which in the case of negligible UV contribution, becomes

$$\ln\frac{C_i}{C_i^0} = -(kC_{OH})t \quad (5)$$

As previously argued discussing the results shown in Fig. 1a, MMTD degradation by UV/H_2O_2 treatment occurs much more rapidly than by using only UV. Therefore, for this substrate, the UV contribution to the whole UV/H_2O_2 process can be disregarded. On the contrary, in the case of MMTD-Me degradation by UV/H_2O_2 treatment (see Fig. 1b), the UV contribution cannot be ignored.

According to the above considerations, initial substrate decays were successfully fitted by Eqs. (4a) and (5) for MMTD-Me and MMTD, respectively (see Fig. 3a and b). From the slopes of the regression curves in Fig. 3 it is possible to obtain the pseudo-first-order constants (k') values $\{(k' = kC_{OH} + 2.3LI_o\phi_i\varepsilon_i f_i)$ in Eq. (4a) or $(k' = kC_{OH})$ in Eq. (5)$\}$ from which second-order kinetic constant (k) values can be calculated once the C_{OH} values are known. These latter values can be obtained carrying out substrates

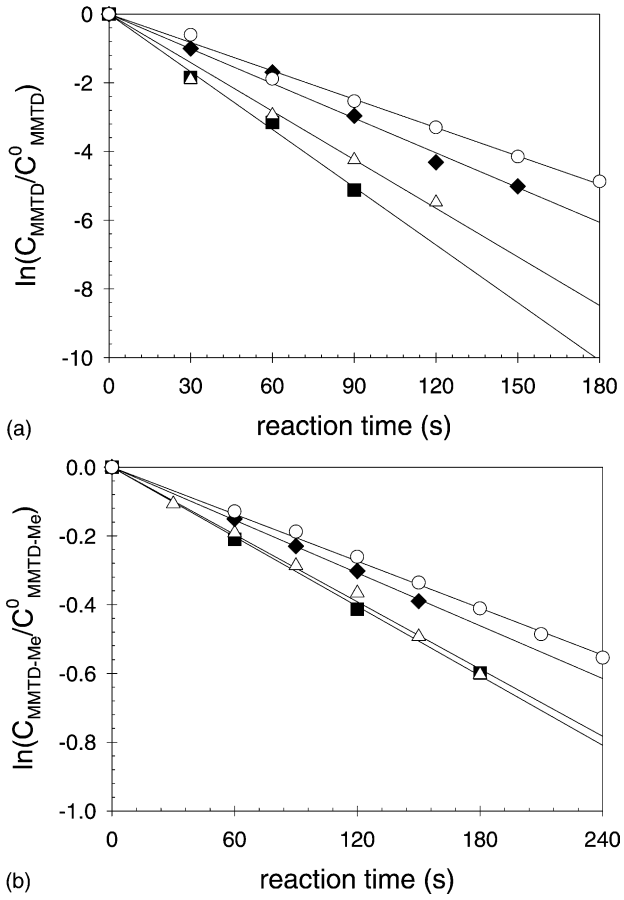

Fig. 3. Initial MMTD (a) and MMTD-Me (b) decay under UV/H_2O_2 irradiation. Experimental conditions: UV low pressure mercury lamp, $[MMTD]_0 = [MMTD\text{-}Me]_0 = 1$ mg/l, (■) H_2O_2/substrate molar ratio 50/1; (△) H_2O_2/substrate molar ratio 42/1; (◆) H_2O_2/substrate molar ratio 34/1; (○) H_2O_2/substrate molar ratio 23/1.

degradation experiments in the presence of a reference compound whose k is already known. From the decay of such a reference compound it is possible to calculate C_{OH} value and, then, the second-order kinetic constant values of investigated compounds. According to such a procedure, during the present investigation, MMTD-Me experiments have been carried out in the presence of phenol [28] ($k = 1.1 \times 10^{10}$ M^{-1} s^{-1}) as reference compound. During MMTD degradation experiments, instead of phenol, as reference compound was used MMTD-Me, because of its suitable chromatographic separation.

In Table 1 are reported the pseudo-first-order kinetic constants calculated from the data in Fig. 3 for MMTD

Table 1
Calculated C_{OH} and pseudo-first-order kinetic constant (k') values for MMTD and MMTD-Me during the reaction with UV/H_2O_2

H_2O_2/substrates	K'_{MMTD} (s^{-1})	C_{OH} (M) (MMTD)	$K'_{MMTD\text{-}Me}$ (s^{-1})	C_{OH} (M) (MMTD-Me)
50/1	$(5.6 \pm 0.6) \times 10^{-2}$	$(3.3 \pm 0.5) \times 10^{-12}$	$(3.3 \pm 0.2) \times 10^{-3}$	$(2.6 \pm 0.2) \times 10^{-12}$
42/1	$(4.4 \pm 0.6) \times 10^{-2}$	$(3.0 \pm 0.5) \times 10^{-12}$	$(3.3 \pm 0.3) \times 10^{-3}$	$(2.3 \pm 0.3) \times 10^{-12}$
34/1	$(3.5 \pm 0.3) \times 10^{-2}$	$(2.4 \pm 0.3) \times 10^{-12}$	$(2.6 \pm 0.2) \times 10^{-3}$	$(1.6 \pm 0.2) \times 10^{-12}$
23/1	$(2.7 \pm 0.4) \times 10^{-2}$	$(1.5 \pm 0.3) \times 10^{-12}$	$(2.3 \pm 0.2) \times 10^{-3}$	$(1.2 \pm 0.2) \times 10^{-12}$

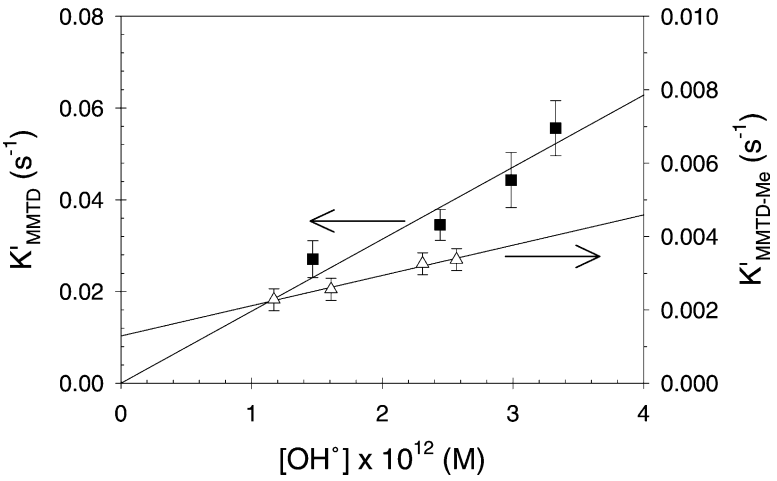

Fig. 4. Linear dependence of pseudo-first-order constants (K'_{MMTD} and $K'_{MMTD\text{-}Me}$) from calculated hydroxyl radical concentration.

($k' = kC_{OH}$) and MMTD-Me ($k' = kC_{OH} + 2.3LI_0\phi_i\varepsilon_i f_i$) as well as the C_{OH} values for each experiment carried out, according to the above procedure, in the presence of a reference compound. For both substrates, as shown in Fig. 4, plotting k' values versus C_{OH} a linear fit is obtained indicating that both degradation kinetics are first-order with respect to hydroxyl radical. The slopes of the second-order kinetic constants are $(1.6\pm0.5)\times10^{10}$ and $(8.3\pm0.8)\times10^{8}\,M^{-1}\,s^{-1}$ for MMTD and MMTD-Me, respectively. These constants are similar to previously studied aromatic compounds [26]. The fact that the MMTD second-order kinetic constant are approximately one order of magnitude greater than that of MMTD-Me, indicates that the latter substrate is less reactive than the former towards •OH radicals attack. This is ascribed to the different reactivity of –SH and $–SCH_3$ groups for these compounds shown in Fig. 1a and b. As shown in Table 1, regardless to the substrate, the higher the amount of H_2O_2 used the higher the resulting C_{OH} value. Fig. 5 demonstrates the linear proportionality for both substrates. Through the mathematical fit of the linear curves in Fig. 5, the following equations $[H_2O_2] = 0.11C_{OH}$ and $[H_2O_2] = 0.132C_{OH}$ have been obtained for MMTD and MMTD-Me, respectively. From these equations, for each substrate, it is possible to calculate: (i) the C_{OH} value for a fixed hydrogen peroxide concentration; (ii) the corresponding k' value (see Fig. 4); (iii) through the Eq. (4a) or (5), the time necessary to achieve a target extent of degradation.

As example, considering the concentration of MMTD or MMTD-Me in contaminated water of a few μg/l, a H_2O_2 concentration of 1 mg/l provides the excess necessary for a pseudo-first reaction involving UV/H_2O_2 activation. The calculated time necessary to achieve a 99% degradation is about 55 and 2.6 min for MMTD-Me and MMTD, respectively. These times as well as the assumed H_2O_2 concentration (i.e., 1 mg/l) pertain to practical processes showing the feasibility of the decontamination process suggested in this study.

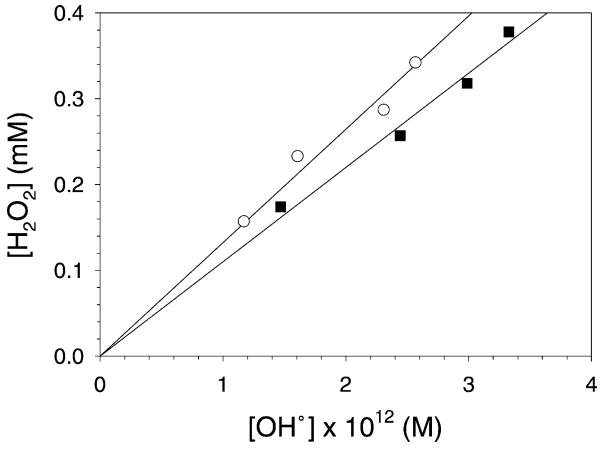

Fig. 5. Linear dependence of H_2O_2 concentration (MMTD (■) and MMTD-Me (○)) from calculated hydroxyl radical concentration.

4. Conclusions

In this paper the degradation kinetics of two pharmaceutical intermediates (MMTD-Me and MMTD) treated by UV and UV/H_2O_2 in aqueous solutions have been investigated. The main results of such an investigation have been the following:

- H_2O_2 alone is not effective for degrading any of the investigated compounds. On the contrary, both UV direct photolysis and UV/H_2O_2 treatments extensively degrade the two substrates with a greater rate in the latter case;
- In case of direct photolysis, MMTD-Me degradation results faster than that of MMTD because of the different values of their molar absorption coefficient (2100 and 4970 $M^{-1}\,cm^{-1}$) and quantum yield (12.0 ± 0.7 and 14.1 ± 1.5 mmol einstein^{-1}) for MMTD and MMTD-Me, respectively;

- Calculated second-order rate constants for the UV/H_2O_2 degradation of MMTD-Me and MMTD [$(8.3 \pm 0.8) \times 10^8$ and $(1.6 \pm 0.5) \times 10^{10}\,M^{-1}\,s^{-1}$, respectively] result of first-order with respect to hydroxyl radicals.

The processes used in this study require UV doses greater than those used to disinfect water indicating that UV inactivation of microorganisms and UV degradation of organic chemicals operate on very different fluence scales. Finally, the kinetic results can be used for assessing the feasibility of UV processes for reclaiming water contaminated with pharmaceutical intermediates.

References

[1] H. Buser, M.D. Muller, N. Theobald, Environ. Sci. Technol. 32 (1988) 188.
[2] B. Halling-Sørensen, S. Nors Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lützhøft, S.E. Jorgensen, Chemosphere 36 (1998) 357.
[3] T. Heberer, Fresenius Environ. Bull. 6 (1997) 438.
[4] T.A. Ternes, Water Res. 32 (1998) 3245.
[5] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[6] G.R. Peyton, Significance and Treatment of Volatile Organic Compounds in Water Supplies, Lewis Publisher, Chelsea, 1990, p. 313.
[7] J.H. Baxendale, J.A. Wilson, Trans. Faraday Soc. 53 (1957) 344.
[8] S. Guittonneau, J. De Laat, M. Dore', J.P. Duguet, C. Bonnel, Environ. Technol. 9 (1988) 1115.
[9] M. Dore', Chimie des oxydants et traitement des eaux, Lavoisier, Paris, 1989.
[10] I. Nicole, J. De Laat, M. Dore, J.P. Duguet, C. Bonnel, Water Res. 24 (1990) 157.
[11] N. Clark, G. Knowles, Effluent Water Treatment J. 22 (1982) 335.
[12] W.H. Glaze, J.W. Kang, D.H. Chapin, Ozone Sci. Eng. 9 (1987) 335.
[13] C.P. Huang, C. Dong, Z. Tang, Waste Manage. 13 (1993) 361.
[14] D.W. Sundstrom, B.A. Weir, H.G. Klei, Haz. Waste Haz. Mater. 14 (1987) 165.
[15] B.A. Weir, D.W. Sundstrom, Chemosphere 27 (1993) 1279.
[16] P.B.L. Chang, T.M. Young, Water Res. 34 (2000) 2233.
[17] F.J. Beltran, G. Ovejero, B. Acedo, Water Res. 27 (1993) 1013.
[18] F.G. Beltran, M. Gonzales, B. Acedo, J. Jarramillo, Chemosphere 32 (1996) 1949.
[19] M.I. Stefan, A.R. Hoy, J.R. Bolton, Environ. Sci. Technol. 30 (1996) 2382.
[20] Guardini, L., Corriere Della Sera, 8 Luglio, 1999.
[21] T.F.L. Ho, J.R. Bolton, Water Res. 32 (1998) 489.
[22] J.J. Lipsky, J.C. Lewis, W.J. Novick, J. Antimicrob. Chemother. 18 (1986) 131.
[23] A.L. Kerremans, J.J. Lipsky, J. Van Loon, M.O. Gallego, R.M. Weinshilboum, J. Pharmacol. Exp. Ther. 235 (1985) 382.
[24] A. Lopez, A. Bozzi, G. Mascolo, R. Ciannarella, R. Passino, Ann. Chim. 92 (2002) 41.
[25] A. Bozzi, A. Lopez, G. Mascolo, G. Tiravanti, Water Sci. Technol.: Water Supply 2 (2002) 19.
[26] G. Mark, M.N. Schuchmann, H.-P. Schuchmann, C. von Sonntag, J. Photochem. Photobiol. A 55 (1990) 157.
[27] K. Nick, H.F. Scholer, G. Mark, T. Soylemez, M.S. Akhlaq, H.P. Schuchmann, C. Von Sonntag, J. Water SRT — Aqua 41 (1992) 82.
[28] G.V. Baxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.