



Photodegradation of the steroid hormones 17 β -estradiol (E2) and 17 α -ethinylestradiol (EE2) in dilute aqueous solution

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ABSTRACT

The photochemical transformation of natural estrogenic steroid 17 β -estradiol (E2) and the synthetic oral contraceptive 17 α -ethinylestradiol (EE2) has been studied in dilute non buffered aqueous solution (pH 5.5–6.0) upon monochromatic (254 nm) and polychromatic ($\lambda > 290$ nm) irradiation. Upon irradiation at 254 nm, the quantum yields of E2 and EE2 photolysis were similar and evaluated to be 0.067 ± 0.007 and 0.062 ± 0.007 , respectively. Upon polychromatic excitation, and by using phenol as chemical actinometer, the photolysis efficiencies have been determined to be 0.07 ± 0.01 and 0.08 ± 0.01 for E2 and EE2, respectively.

For both estrogens, photodegradation by-products were identified with GC/MS and LC/MS. In a first step, a model compound – 5,6,7,8-tetrahydro-2-naphthol (THN) –, which represents the photoactive phenolic group, was used to obtain basic photoproduct structural informations. Numerous primary and secondary products were observed, corresponding to hydroxylated phenolic- or quinone-type compounds.

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1. Introduction

Endocrine Disrupting Chemicals (EDCs) are of growing concerns because risks to human and wildlife health they might cause are not clearly assessed (Kavlock et al., 1996). These chemicals include a wide range of compounds such as pesticides, phthalates, alkyl phenols, natural or synthetic estrogens and pharmaceuticals. These molecules can disturb the normal activity of the endocrine system (Sonnenschein and Soto, 1998). Natural estrogens (estrone – E1 and 17 β -estradiol – E2) as well as the synthetic estrogen 17 α -ethinylestradiol – EE2 are known to contribute to a large extent to the estrogenicity of sewage treatment plants (STPs) effluents (Desbrow et al., 1998). E2 is the most important female sexual hormone secreted. EE2 is used for estrogenic deficiencies treatment and oral contraceptive with doses ranging from 15 to 50 μg by tablet. Both E2 and EE2 are released from excretion by humans and animals. (Daughton and Ternes, 1999; Jorgensen and Halling-Sorensen, 2000; D'Ascenzo et al., 2003). Their removal by STPs mainly depends on the behaviour of bacteria (Baronti et al., 2000; D'Ascenzo et al., 2003) and the occurrence of these compounds in aquatic compartments has been reported, with concentration ranging from ng L^{-1} in drinking water or groundwater (Hohenblum et al., 2004, e.g.) to $\mu\text{g L}^{-1}$ in several rivers or STPs effluents (Kolpin et al., 2002, e.g.).

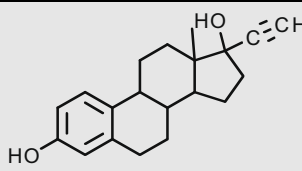
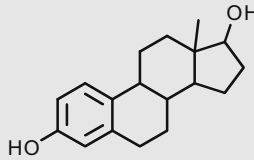
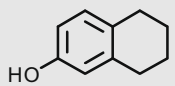
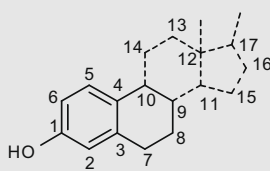
These compounds are considered as the most important compounds responsible for the in vitro estrogenic activity of effluents

of domestic STPs (Cargouët et al., 2004). The decrease of fertilization rate and the alteration of reproductive performance of fishes as well as various development and reproductive parameters of aquatic invertebrates have also been reported (Segner et al., 2003).

In the environment, EE2 was found to be generally resistant to biodegradation compared to E2 (Colucci and Topp, 2001; Colucci et al., 2001; Jürgens et al., 2002). Up to now, the photochemical behaviour and specially the contribution of direct photolysis to the degradation of these compounds have not been deeply studied. Simulated natural light laboratory studies indicated that both E2 and EE2 were photodegraded in river waters with half-lives of at least 10 d under 12 h of bright sunshine per day (Jürgens et al., 2002). In sea water, a half-life lower than 1.5 d has been evaluated (Zuo et al., 2006). The phototransformation of E2 and EE2 has also been studied under UV irradiation (either monochromatic low pressure mercury lamp at 254 nm or polychromatic medium pressure mercury lamp) (Liu et al., 2003; Liu and Liu, 2004; Rosenfeldt and Linden, 2004; Zuo et al., 2006). The quantum yields (in mole/einstein) of photolysis were evaluated to be 0.043 (0.026) and 0.10 (0.061), respectively, with low-pressure and medium pressure lamps for E2 (EE2). Very few and incomplete data are available concerning the photoproducts arising from these hormones, certainly because the initial compounds are very poorly water soluble, which complicate the analysis of photoproducts. The photodegradation of EE2 has been examined at high concentration (4.3 g L^{-1}) in acetonitrile (Segmuller et al., 2000). A hydroperoxide and 6 isomeric dimeric products were identified. These results can be significantly different in water. According to Liu et al. (2003) and Liu and Liu (2004), the monochromatic and polychromatic

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Table 1
Chemical structure of the two hormones and the model compound

Chemicals	Use	Molar mass (g mol ⁻¹)	Structures
17 α -Ethinylestradiol (EE2)	Contraceptive hormone	296.4	
17 β -Estradiol (E2)	Reproductive hormone	272.4	
5,6,7,8-Tetrahydro-2-naphthol (THN)	Model compound	148.2	
Atoms labeling (for photoproducts identification)			

transformations of EE2 result in the breakage and oxidation of aromatic ring to produce compounds containing carbonyl group. However, this direct cleavage is surprising since it is not supposed to occur in the early stages of the photoreaction by analogy with the actual knowledge of the mechanism of photolysis of phenol derivatives (Mazellier and Leverd, 2003). Therefore the question of the identity of photoproducts generated upon photolysis of E2 and EE2 needs to be further investigated and this issue is clearly the major aim of our work.

In this study, we have investigated the photochemical transformation of two endocrine disruptors: the natural estrogen 17 β -estradiol (E2) and the synthetic estrogenic steroid 17 α -ethinylestradiol (EE2). The direct photodegradation of both compounds has been studied under irradiation at $\lambda = 254$ nm (used in water treatment for disinfection) and under simulated sunlight at $\lambda > 290$ nm in purified water. Kinetic studies and quantum yield calculations were performed. We have paid a specific attention to the identification of photoproducts. Some of the structures were identified with the help of a model compound 5,6,7,8-tetrahydro-2-naphthol (THN), which represents the phenolic moiety of E2 and EE2 (Table 1).

2. Experimental

2.1. Chemical and materials

All chemicals were commercial products of the purest grade available. 17 α -ethinylestradiol (EE2), 17 β -estradiol (E2), 5,6,7,8-tetrahydronaphthol (THN) and titanium (IV)-chloride were from Sigma–Aldrich. THN has been used as a model compound for the identification of E2 and EE2 photoproducts as proposed by Huber et al. (2004). Methanol, acetic acid, sulfuric acid were purchased from Carlo Erba and hydrogen peroxide (not stabilized) was provided by Fluka. Purified water was obtained from a Millipore device (Millipore Milli RX75/Synergy 185. pH measurements were

carried out with a MeterLab PHM210 pH-meter. UV–visible spectra were recorded on a Safas double-beam spectrophotometer (Monaco) using either 1 or 5 cm cell.

2.2. Irradiation device

Two identical photochemical reactors were used for ultraviolet photolysis at 254 nm and polychromatic experiments ($\lambda > 290$ nm). The volume of irradiated solution (thermostated at 25 °C) was 4 L and the optical path length was 6.75 cm. Lamps were located at the axis of reactors, in a quartz sleeve. Monochromatic irradiations were performed with a Vilbert et Lourmat 6 W low-pressure Hg lamp T6C. The incident photonic flux at 254 nm was measured weekly by hydrogen peroxide actinometry as described elsewhere (Nicole et al., 1990) and the stability of the photonic flux was also weekly controlled by performing phenol photolysis experiments for the polychromatic lamp. The typical photon fluence rate (per unit volume) varied in the range $6.5\text{--}8.5 \times 10^{-7}$ einstein L⁻¹ s⁻¹ during the period of experiments. A Vilbert et Lourmat 6 W fluorescent lamp T6M was used for polychromatic irradiations as described elsewhere (Zamy et al., 2004).

Up to 10 irradiated samples (3 mL each) were withdrawn at different irradiation times for kinetic studies. The volume variation was thus negligible.

2.3. Chromatographic analyses

During irradiation experiments, the concentrations of target compounds were measured using high performance liquid chromatography (HPLC): Waters 1525 binary pump, Waters 717 auto-sampler, Waters 2487 UV detector (detection wavelength set at 270 nm) and a Waters 2475 fluorescence detector (excitation at 270 nm, emission at 320 nm). A Hypersil BDS C18 250 \times 4.6 mm column, packed with spherical silica particles (particle size:

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