



Photodegradation of fluorene in aqueous solution: Identification and biological activity testing of degradation products



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ABSTRACT

Degradation of fluorene under UV-vis irradiation in water was investigated and structural elucidation of the main photoproducts was achieved using gas chromatography coupled with mass spectrometry. Twenty-six photoproducts were structurally identified, mainly on the basis of electron ionization mass spectra interpretation. The main generated transformation products are hydroxy derivatives. Some secondary photoproducts including fluorenone, hydroxy fluorenone, 2-biphenyl carboxylic acid, biphenylene, methanol fluorene congeners and hydroxy fluorene dimers were also observed. A photodegradation pathway was suggested on the basis of the chemical structures of photoproducts. Fluorene as well as its main photoproducts for which chemical standards were commercially available were tested for their ability to elicit cytotoxic, estrogenic and dioxin-like activity by using *in vitro* cell-based bioassays. None of the tested compounds was cytotoxic at concentrations up to 100 μ M. However, 2-hydroxyfluorene and 3-hydroxyfluorene exerted significant estrogenic and dioxin-like activity on a concentration range of 3–30 μ M, while fluorene and 9-hydroxyfluorene were weakly or not active, respectively, in our assays. This supports the view that photodegradation processes can generate by-products of higher toxicological concern than the parent compound and strengthens the need to further identify transformation products in the aquatic environment.

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1. Introduction

The industrial and urban development which occurred in the second half of the 20th century allowed the emergence of thousands of organic chemicals into aquatic environment without prior study of their toxicity. Several decades later, a large number of these compounds have shown negative impacts on human health and ecosystems even at very low concentrations. Polycyclic Aromatic Hydrocarbons (PAHs) are among the most widespread pollutants in the environment. They are of special concern due to their negative characteristics, including persistence, mobility in the environment and toxicity. The most environmental PAHs result from incomplete combustion of organic matter: forest fires, automobile exhaust, coal, oil refining processes, etc. [1–3]. Many PAHs are toxic; their mainly adverse health effects are cancers in various tissues such as prostate, breast, pancreatic and cervical [4–7], cardiovascular diseases [8] and immunosuppression [9]. PAHs are also known to

have endocrine disrupting capabilities with consequent alteration of fertility in terrestrial and aquatic organisms [10–12]. A number of PAHs are also found to bind the estrogen, androgen and aryl hydrocarbon receptors and either induce or inhibit the estrogen, antiandrogen and dioxin-like responses [13–15]. For these reasons, PAHs have been listed as priority pollutants by both the US Environmental Protection Agency (US EPA) and the European Union (EU). Despite a reduction in PAHs emissions from fuel combustion, resulting from the substitution of coal by fossil fuels since the 1960s and from the development of clean fuels and catalytic converters for diesel and gasoline engines in the recent years, the amounts of PAHs in aquatic environment remains high [16]. PAHs can be introduced into the aquatic environment through different routes including industrial and municipal wastewater, rainwater runoff, atmospheric deposition and sediment- and air-water exchange [16–18]. The concentration of PAHs in aquatic environments varies widely depending on the nature of water (*i.e.* ground water versus surface water) and the sampling location. In European surface water, the concentrations of PAHs were reported to range from 0.6 to 171.3 ng L^{-1} in rainwater [19,20], from 2 to 587 ng L^{-1} in river water [21,22,26], from 5 to 1930 ng L^{-1}

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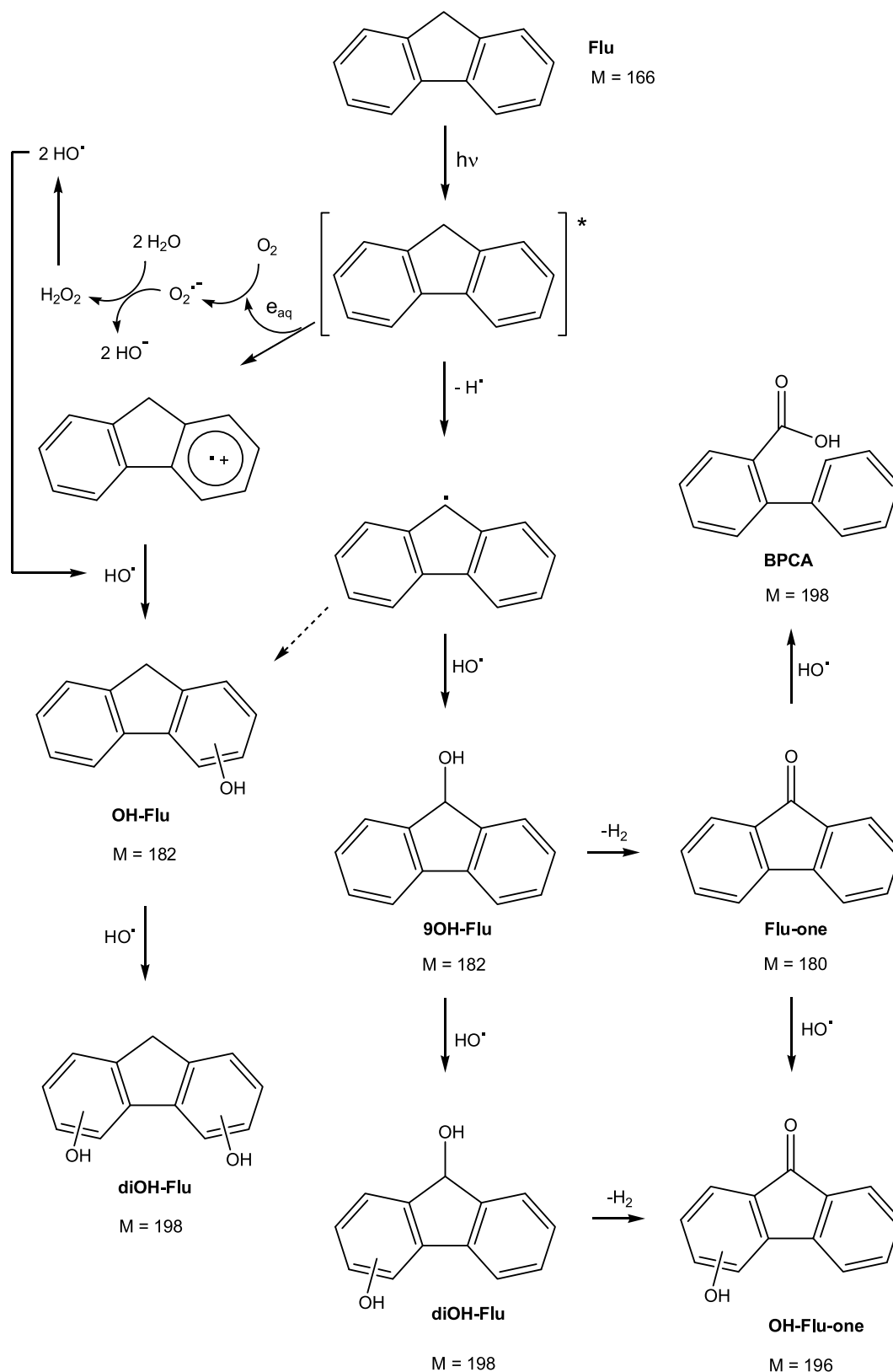


Fig. 1. Reaction pathways proposed for the oxidation of fluorene under UV-vis irradiation in water. BPCA: Biphenyl carboxylic acid.

in seawater [23,24], from 1.4 to 5 ngL⁻¹ in lake and reservoir water [19,22] and from 4 to 1473 ngL⁻¹ in wastewater [20,22]. In natural water environment, the PAHs are eliminated mainly through processes of sorption to sediments, biodegradation and

photodegradation. Photodegradation remains the main route of PAHs degradation, especially for the most recalcitrant ones. It has been reported that photolysis processes induced under natural sunlight can be significantly accelerated by dissolved organic mat-

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