Behavior and prediction of photochemical degradation of chlorinated polycyclic aromatic hydrocarbons in cyclohexane

Takeshi Ohura [*], Takashi Amagai, Masakazu Makino

Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

Abstract

The photochemical degradation of 11 chlorinated polycyclic aromatic hydrocarbons (ClPAHs) and the corresponding 5 parent PAHs was examined to simulate the compound's fate on aerosol surfaces. All the ClPAHs and PAHs decayed according to the first-order reaction rate kinetics. The photolysis rates of ClPAHs varied greatly according to the skeleton of PAHs; the rates of chlorophenanthrenes (ClPhes) and 1-chloropyrene were higher than those of corresponding parent PAHs, whereas chlorofluoranthenes, 7-chloro-benz[*a*]anthracene and 6-chlorobenzo[*a*]pyrene were more stable under irradiation compared to respective parent PAH. Considering the photoproducts of ClPhes detected, the oxidation could occur immediately at positions of the highest frontier electron density. Finally, the quantitative structure-property relationship models were developed for direct photolysis half-lives and average quantum yields of the ClPAHs and parent PAHs, in which the significant factors affecting photolysis were E_{LUMO+1}, total energy and surface area, and E_{LUMO}, $E_{LUMO} - E_{HOMO}$ and total energy, respectively.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hazardous materials because of their mutagenic and carcinogenic properties, and are distributed in the environment through combustion, discharge of fossil fuels, automobile emissions, and subsequent atmospheric transport and deposition (Bidleman, 1988; Baek et al., 1991; Mantis et al., 2005; Lönnermark and Blomqvist, 2006; Pekey et al., 2007). Therefore, determination of the environmental fate of PAHs is important for human risk assessment (Menzie et al., 1992; Finlayson-Pitts and Pitts, 1997; Sabljic, 2001). The dominant degradation pathway of PAHs associated to graphitic particles in the atmosphere is suggested to be photolysis (Nielsen, 1984; Kamens et al., 1988; McDow et al., 1994; Finlayson-Pitts and Pitts, 1997). The

photochemical reaction of PAHs adsorbed to particles could also occur in an organic layer surrounding the particle core (McDow et al., 1994; Ohura et al., 2004, 2005). That is, the direct photolytic pathways of pollutant degradation can be simulated in the laboratory by irradiation of the compound in an organic solvent. The photostability of various PAHs has been investigated in organic solvents such as toluene (Jang and McDow, 1995, 1997), benzene (Jang and McDow, 1997), and cyclohexane (Lamotte et al., 1987).

Environmental occurrences, behavior and toxicity of PAH derivatives have been studied by many researchers. As typical PAH derivatives, nitrated PAHs have been well studied in the fields of environmental behavior because of their high level of toxicity (Finlayson-Pitts and Pitts, 2000). Recently, the focus of attention has been on the effect on the environment of chlorinated polycyclic aromatic hydrocarbons (ClPAHs) with more than 3 rings, which have been found in urban air, snow, tap water, and sediment (Ohura, 2007). Ohura and co-workers

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[*] Corresponding author. Tel.: +81 54 264 5789; fax: +81 54 264 5798.
E-mail address: ooura@smail.u-shizuoka-ken.ac.jp (T. Ohura).

(Ohura et al., 2004, 2005; Kitazawa et al., 2006) have detected various ClPAHs associated with particles in urban air, and discussed the fates and possible sources of emission. However, the characteristics of ClPAHs such as environmental fate remain uncertain in comparison with those of the parent PAHs. In this study, we first investigated the photostability of ClPAHs using a chemical model system, followed by comparison to the corresponding parent PAHs. The effects of chlorination of PAHs are discussed on the basis of the photolysis rates and products of each test compound. Note that we used an inert solvent, cyclohexane, for the investigation of photostability to reduce the effects of reactivity of the solvent itself. Finally, the photolysis rate and average quantum yield of each ClPAH and PAH were predicted via a quantitative structure–property relationships (QSPRs) model, which indicated the significant molecular descriptors of the photodegradation.

2. Experimental

2.1. Chemicals

We selected 5 PAH species as reference substances and chlorinated each by the procedure of Dewhurst and Kitchen (1972). The PAHs were selected because of their atmospheric and toxicological relevance. A solution of 20 g of *N*-chlorosuccinimide (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in 20 ml of propylene carbonate (PC, Wako Pure Chemical Industries) and a solution of each PAH (~0.1 M) in 20 ml of PC were mixed and incubated at 100 °C for ~3 h in the dark. The reaction solvent for each PAH was fractionated by high-pressure liquid chromatography (HPLC) (column, COSMOSIL 5C18-AR; eluent, methanol), and the fractions corresponding to the dominant peaks were isolated and analyzed by gas chromatography–mass spectrometry (GC–MS) and by ^{1}H NMR spectroscopy (500 MHz, CDCl$_3$), yielding 11 ClPAH

species. The ClPAHs tested in this study are abbreviated as follows: 9-chlorophenanthrene (9-ClPhe), 3,9-dichlorophenanthrene (3,9-Cl$_2$Phe), 9,10-dichlorophenanthrene (9,10-Cl$_2$Phe), 3,9,10-trichlorophenanthrene (3,9,10-Cl$_3$Phe), 3-chlorofluoranthene (3-ClFluor), 8-chlorofluoranthene (8-ClFluor), 3,4-dichlorofluoranthene (3,4-Cl$_2$Fluor), 3,8-dichlorofluoranthene (3,8-Cl$_2$Fluor), 1-chloropyrene (1-ClPy), 7-chlorobenz[*a*]anthracene (7-ClBaA), and 6-chlorobenzo[*a*]pyrene (6-ClBaP). The structural formulae of these ClPAHs are illustrated in Fig. 1. The synthesized ClPAHs were >95% pure (as determined by GC–MS).

2.2. Photodegradation experiments

Photodegradation experiments were performed with a turntable photoreactor (Ace Glass Inc., Vineland, NJ) using a 450 W high-pressure mercury lamp (Ushio Co., Ltd., Tokyo, Japan, maximum wavelengths 313, 334, 365, 404, 435, 546, and 578 nm) as the light source, and a quartz immersion well with circulating water. The immersion well was surrounded by a Pyrex sleeve to filter out high-energy UV bands ($\lambda < 290$ nm). Although this setup does not duplicate the spectral distribution of the actinic flux, it does reproduce the wavelengths normally encountered in the atmosphere. The photoreactor was positioned in a water bath with constant water circulation and the temperature in the bath was maintained at 25($\pm$1) °C. The solutions were irradiated in 13 mm × 100 mm quartz reaction tubes.

The quantum yields (ϕ) for each ClPAH and PAH photolysis was determined as follows. The photolysis quantum yield ϕ_{λ_i} for a certain wavelength λ_i (nm) is defined as:

$$\phi_{\lambda_i} = \mathrm{Rate}_{\lambda_i}(I^{\mathrm{abs}}_{\lambda_i})^{-1} \tag{1}$$

where $\mathrm{Rate}_{\lambda_i}$ (mol l^{-1} s^{-1}) would be the degradation rate of the compound accounted for by the direct photolysis induced by the λ_i emission line only, and $I^{\mathrm{abs}}_{\lambda_i}$ is the intensity of radiation absorption by the compound on irradiation at

9-chlorophenanthrene (#2)   3,9-dichlorophenanthrene (#3)   9,10-dichlorophenanthrene (#4)   3,910-trichlorophenanthrene (#5)

3-chlorofluoranthene (#7)   8-chlorofluoranthene (#8)   3,4-dichlorofluoranthene (#9)   3,8-dichlorofluoranthene (#10)

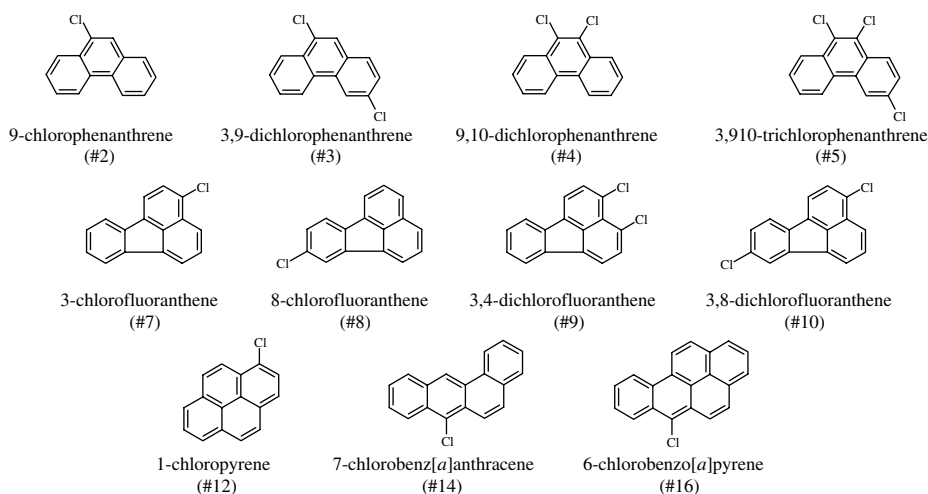1-chloropyrene (#12)   7-chlorobenz[*a*]anthracene (#14)   6-chlorobenzo[*a*]pyrene (#16)

Fig. 1. Chemical structures of the chlorinated polycyclic aromatic hydrocarbons tested (the numbers correspond to those in Table 1).