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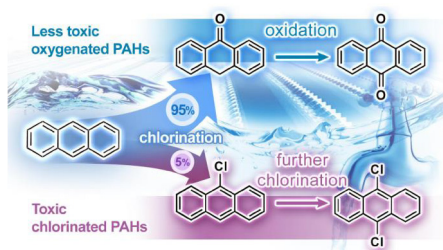
Kinetics and mechanisms of the formation of chlorinated and oxygenated polycyclic aromatic hydrocarbons during chlorination

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HIGHLIGHTS

- We investigated the reactivity and transformation product distribution of eight PAHs.
- Their reactivities were related to their chemical hardness.
- The byproducts were then quantitatively confirmed by the “tailor-made” references.
- We first presented observational evidence for a close mass balance of chlorination of anthracene.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) as disinfection products for source waters containing PAHs have raised environmental concern due to their dioxin-like toxicity and potential hazardous effect on human health. In this study, we investigated the reactivity and transformation product distribution of eight environmentally relevant PAHs, namely, naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flura) and pyrene (Py), during chlorination. Our results showed that Acy, Ant, Ace, and Py exhibited higher reactivity than Nap, Fl, Phe, and Flura, and their reactivities were reasonably related to their chemical hardness. Transformation products such as chlorinated and oxygenated PAHs were first predicted by electronic structure theory, then qualitatively identified by comprehensive two dimensional gas chromatography-quadrupole mass spectrometry technique, and finally quantitatively confirmed by the “tailor-made” reference compounds we synthesized. Ace and Py were found to be the major precursors of Cl-PAHs, and their chlorination mechanisms were elucidated based on the observational evidence for their mass balance. However, Acy and Ant mainly produced less toxic oxygenated PAHs. PAHs that tend to generate oxygenated transformation products seem to manifest higher reactivity than those form Cl-PAHs due to different reaction mechanisms: single electron transfer followed by a nucleophilic addition for oxygenation vs. electrophilic attack for chlorination. This study provides a fundamental mechanistic basis for

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better understanding of chlorination product formation process, and guides application of chlorination technology.

1. Introduction

Chlorination has long been used for microbial disinfection and removal of objectionable taste and odor during drinking water treatment processes [1]. However, this technology often produces unwanted disinfection products which are hazardous to human health [2,3]. For example, polycyclic aromatic hydrocarbons (PAHs), which are frequently detected in source waters in developing countries with total concentrations ranging from 10^2 to 10^3 ng L⁻¹ (e.g., China, see Text S1 and Table S1 in the Supporting Information SI) [4,5], are reported to generate chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) through aromatic electrophilic substitution reaction in chlorination systems [6,7]. Cl-PAHs structurally resemble polychlorinated dibenzodioxins (PCDDs) and polychlorinated biphenyls (PCBs). These chlorine substituted compounds exhibit mutagenic and aryl-hydrocarbon receptor mediated (AhR) activities [6], and their derivatives are even more harmful than the parent PAHs [8–10].

In the past decade, the discovery of widespread occurrence of Cl-PAHs in chlorination systems has attracted great scientific and public concern [7,11]. Previous studies reported the occurrence, formation kinetics, and toxicity of Cl-PAHs during water treatment processes, and indicated that formation of toxic Cl-PAHs even at low nanomolar concentration (10^{-2} – 10 ng L⁻¹) cannot be ignored in source waters containing PAHs [12,13]. Despite the potential health concern, fundamental questions regarding their formation mechanisms and potential reactivity still have not been completely elucidated. For example, which Cl-PAHs are most thermodynamically favorable and kinetically feasible to form? Are Cl-PAHs more readily generated than other transformation products such as oxygenated PAHs (O-PAHs)? What is the intrinsic nature that determines PAHs reactivity during chlorination? How does solution chemistry influence transformation product formation patterns?

Answering these fundamental questions is challenging due to two factors. First, the reactivity profile of parent PAHs during chlorination processes are not well established. To date, only a few studies compared the reactivities of limited numbers of PAHs during the aqueous chlorination process [13–15]. But little is known about other parent PAHs that are of more environmental relevance, especially PAHs with no more than four aromatic rings, which are more water soluble and more frequently detected in source waters [5]. Second, the transformation products of PAHs, Cl-PAHs in particular, were not well characterized, as they were challenging to synthesize in the laboratory [6,16]. Without relevant reference compounds, the transformation product identification relies on the experienced interpretation of mass spectrum [14,17], which is subjective. Specifically, ratio of transformed Cl- and O-PAHs is not clear due to lack of precise quantitation of transformation products with synthesized reference materials. Previous studies performed this ratio quantification by their abundance, which in fact was relatively inaccurate due to the mass response disparity of Cl- and O-PAHs [17,18].

However, it should be noted that Cl-PAHs transformation products formed during chlorination were expected to be extremely complex and cannot be quantitatively identified solely by mass spectroscopic technique, especially due to the presence of positional isomers. Therefore, a robust tool for predicting positional isomers of Cl-PAHs transformation products seems necessary. In previous studies, the Cl-PAHs isomers and congeners were successfully predicted by the Fukui index for electrophilic attack, $f^{-1}(r)$, which describes the reactivity of a specific site within a molecule [19,20]. Altarawneh and Dlugogorski discovered that the dominant halogenated carbazoles predicted by $f^{-1}(r)$ index

were consistent with the environmental profiles of the most prominent congeners of halogenated carbazoles [19]. Xu et al. also used $f^{-1}(r)$ to predict the structures of chlorinated carbazoles, and found that the predicted chlorinated carbazoles were consistent with the measured transformation products as well [20]. Thus, combining such modelling prediction with experimental analysis will be able to provide more accurate and in-depth mechanistic interpretation for the chlorination of PAHs with different structures and reactivities.

The objective of this study is to elucidate formation mechanisms of Cl- and O-PAHs during chlorination process by utilizing both experimental and computational approaches. We first investigated the formation kinetics and transformation product distribution of eight environmentally relevant PAHs, namely, naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flura), and pyrene (Py). In order to determine the intrinsic nature of PAHs reactivity during chlorination, we calculated a total of twelve geometrical, electrostatic, and quantum chemical descriptors using a density functional theory (DFT) approach [21,22], and conducted a correlation analysis between PAHs reactivity and these descriptors. In the following characterization of chlorination products, we first predicted Cl- and O-PAHs formation patterns with the electronic structure theory, and qualitatively confirmed the predicted isomers by a comprehensive two dimensional gas chromatography-quadrupole mass spectrometry (GC × GC-qMS). To improve the accuracy of the mass analysis, the identified transformation products were quantified with the “tailor-made” reference compounds that we synthesized. These experimental and computational results are central to propose full reaction schemes and present observational evidence for close mass balance of the PAHs that are reactive during chlorination.

2. Methods and materials

2.1. Chemical reagents

Parent PAHs, O-PAHs, Cl-PAHs, organic solvents, and NaClO were purchased and used without purification. The information of these chemicals such as abbreviations, purities, and manufacturers is tabulated in Table S2. The structures and relevant physicochemical properties of the eight parent PAHs are tabulated in Table S3.

Mono/di/tri/tetra chlorinated products (i.e., Cl-PAHs) that are commercially unavailable were synthesized. These chlorinated products include 5-chloroacenaphthene (5-Cl-Ace), 3-chloroacenaphthene (3-Cl-Ace), 5,6-dichloroacenaphthene (5,6-diCl-Ace), 3,6-dichloroacenaphthene (3,6-diCl-Ace), 3,5-dichloroacenaphthene (3,5-diCl-Ace), 9,10-dichlorophenanthrene (9,10-diCl-Phe), 3,5,6-trichloroacenaphthene (3,5,6-triCl-Ace), 3,5,8-trichloroacenaphthene (3,5,8-triCl-Ace), and 3,5,6,8-tetrachloroacenaphthene (3,5,6,8-tetraCl-Ace). Their molecular weights, purity, and identification methods were tabulated in Table S4. The quality of these synthesized chemicals was characterized by nuclear magnetic resonance (NMR) spectroscopy, and their spectra were illustrated in Figs. S1–S11.

2.2. Chlorination kinetics experiments

In order to compare reactivity of the eight PAHs in the presence of free chlorine, the degradation kinetics of the parent PAHs was conducted in batch mode under three conditions (Table S5) for different purposes. The stock solution of eight PAHs was prepared by mixing the PAHs standards in a volumetric flask. The concentration of the PAHs in

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