

# Effect of phenolic compounds on photodegradation of anthracene and benzo[*a*]anthracene in media of different polarity



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## ABSTRACT

The photodegradation of anthracene (Ant) and benz[*a*]anthracene (BaA) were studied in air-equilibrated hexane, methanol and pure water solutions in the absence and presence of phenolic compounds (4-methylcatechol, guaiacol and syringol). In the absence of phenolic compound, the pseudo first-order degradation rate constants of Ant and BaA increased with the polarity of solvent, demonstrating the influence of solvent effects on the photoreactivity. The differences can be attributed to factors such as the proton donating potential of the solvent, and the formation potentials of PAH radical cation and hydroxyl radical in solvent. In the presence of phenolic compound, Ant and BaA photodegradation rates were accelerated in hexane and methanol while inhibited in water solutions. Photodegradation kinetics of the phenolic compounds were also measured; and visible colored products were observed in all three solvents. The observed accelerations of Ant and BaA photodegradation in the presence of the phenolic compounds can be explained by energy transfer from the phenolic compound to PAH, phenolic hydrogen abstraction by excited PAH and more reactive radical formation from the phenolic compound. However, the inhibition effects of Ant and BaA photodegradation in water were more influenced by the quenching of photo-produced reactive oxygen species (ROS) by the phenolic compound and/or its photoproducts. The results indicate that the photodegradation of PAHs will be highly dependent on the aerosol water content, i.e., the chemical composition of the environmental aerosols.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of atmospheric pollutants, which are released into the atmosphere mainly by the incomplete combustion of fossil and biogenic fuels [1]. PAHs have been extensively investigated due to their potentially carcinogenic and direct mutagenic activities. PAHs are semi-volatile and most have appreciable fractions in both gaseous and condensed phases under typical ambient conditions [2,3]. It has been demonstrated that, in addition to being removed from atmosphere by deposition, photochemical degradation is an important removal process of airborne PAHs [4,5]. Absorption of light energy can alter the toxicity of PAHs through photosensitization and photomodification, and the photoproducts of PAHs are in many cases more toxic than the parent compounds [6,7].

Recently, both atmospheric measurement and numerical modeling work has shown that the long-range transport potential of PAHs associated with aerosols were significantly higher than that of PAHs in the gaseous phase [8,9]. It has also been reported that carbonaceous materials such as soot, carbon black and fly ash can act as shields against PAHs photodegradation [10,11] while methoxyphenols, anthraquinones and benzophenone-like compounds on carbonaceous aerosol can act as atmospheric photosensitizers and greatly enhance the photodegradation of PAHs [12–17]. The atmospheric impact of methoxyphenol-enhanced photodegradation of PAHs associated with particles is potentially important because wood smoke as well as urban atmospheric aerosols are enriched in methoxyphenols and PAHs [18–24].

PAH photodegradation rates in methoxyphenol mixtures with a water content of 10% were observed to be higher than that of mixtures which did not contain water and several possible explanations including oxygen solubility increase and more stable polar reaction intermediates were proposed [25]. Aqueous photodegradation mechanisms of PAHs in air equilibrated solutions were thought to proceed through reactions of O<sub>2</sub> with the excited PAHs

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to generate singlet oxygen which then adds to ground-state PAHs forming the endoperoxide [7,26]. Higher solubility of O<sub>2</sub> in nonpolar solvents compared to polar ones has been used to explain the higher photodegradation rates of fluorene and nitro-PAHs observed in nonpolar solvents compared to polar solvents [27,28]. Fasnacht and Bolugh [29] found that quantum yields of some PAH photodegradation increased with increasing O<sub>2</sub> concentration. However, much higher photodegradation rate constants were observed in methanol than in hexane—even though O<sub>2</sub> usually has higher solubility in hexane than in methanol [30]. An earlier study observed minor or inconsistent effects of O<sub>2</sub> concentration upon the photodegradation of PAHs in dilute solutions [31]. The electron-accepting potential of the solvent molecules has been proposed as the primary influence on the photodegradation rate constants of PAHs [30]. Librando et al. [32] found that photodegradation rates in the polar media were faster than those in the nonpolar media and quantum yields were found to increase with increasing polarity of the medium.

The photodegradation rates of benz[a]anthracene (BaA) were found to increase with increasing methoxyphenol concentration (0.01–50% by mass) in toluene solutions [13]. Similarly, the observed pseudo-first rate constants of BaA were a linear function of the concentrations of vanillin and a second-order reaction rate constant of  $81.17 \pm 3.19 \text{ M}^{-1} \text{ h}^{-1}$  was calculated when vanillin concentration was relatively constant over the course of the experiment [12]. If the decay of methoxyphenols or production of quinones and aromatic carbonyls derived from PAH photooxidation is significant during the atmospheric process, the estimation of photodegradation rates of PAHs associated with wood smoke will be complicated and variable [4,13,14]. Wood smoke and diesel soot are generally thought to consist an elemental carbon core surrounded by a liquid organic layer [5,13,33]. McDow et al. [13] studied PAH photodegradation in methoxyphenols and hexadecane, which were chosen to be representative of aliphatic hydrocarbons abundant in diesel soot and automobile exhaust. Several polycyclic aromatic ketones and quinones were selected as representative compounds in the photodegradation experiments of BaA [14]. Feilberg and Nielsen [34] investigated the photodegradation of four ring nitro-PAHs in a chemical model system simulating the liquid film on particles from diesel exhaust and wood stove stack gases. Similarly, the photodegradation of PAHs in

homogeneous solutions under laboratory conditions could roughly simulate the direct photolytic process of PAHs dissolved in an organic or aqueous layer surrounding the particle core. Understanding the atmospheric fate of PAHs upon exposure to UV light is an important component in the prediction of the chemical and physical properties of biomass burning aerosol.

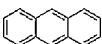
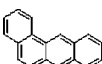
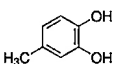
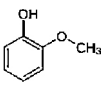
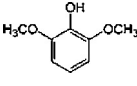
Because both anthracene (Ant) and benz[a]anthracene (BaA) have two most reactive positions in the molecule: 9 and 10 positions in Ant and 7 and 12 positions in BaA, the two PAH compounds are often used to investigate PAH's photodegradation [12–17,25–29]. Upon UV irradiation, both Ant and BaA react with oxygen to form endoperoxides followed by the formation of quinones through rearrangement and oxidation. 4-methylcatechol (4-MC), guaiacol (2-methoxyphenol, 2-MP) and syringol (2,6-dimethoxyphenol, 2,6-DMP) – all of which are common phenolic compounds observed in wood smoke [19,21] and can act as photosensitizers to accelerate the rate of PAH's photodegradation [13,14] – were selected as representative photosensitizers to investigate their effects on Ant and BaA photodegradation. Three media from apolar (hexane) to weak polar (methanol) to polar (water) were chosen to be representative of organic aerosol ranging from hydrophobic (less aged) to hydrophilic (more photochemically aged) in the atmosphere. Prior to the photosensitization experiments, the effect of solvent polarity on direct photolysis of the photosensitizers was investigated. The aim of the present study is to investigate the influence of media on the rate of PAH's photodegradation in the absence and presence of phenolic compounds.

## 2. Materials and methods

### 2.1. Chemicals and sample preparation

Anthracene (99%), benzo[a]anthracene (99%), 4-methylcatechol (98%), 2-methoxyphenol (99%) and 2,6-dimethoxyphenol (99%) were supplied by AccuStandard Inc. (J&K Scientific Ltd., China) and used without additional purification. Physicochemical properties of these compounds are listed in Table 1. Hexane (99.9%) and methanol (99.9%) were obtained from Merck (Darmstadt, Germany). Pure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, USA). A PAH standard mix

**Table 1**  
Chemical structure of PAHs and phenolic compounds.

Compound/abbr.	Molecular	Formula	MW (g/mol)	B.P. (°C)	Solubility (mg/L)
Anthracene/Ant	C <sub>16</sub> H <sub>10</sub>		178.2	394	$6.6 \times 10^{-2}$
Benzo[a]anthracene/BaA	C <sub>18</sub> H <sub>12</sub>		228.3	481	$1.1 \times 10^{-2}$
4-Methylcatechol/4-MC	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>		124.1	251	Soluble
2-Methoxyphenol/2-MP	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>		124.1	205	$1.7 \times 10^4$
2,6-Dimethoxyphenol/2,6-DMP	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>		154.1	262	$2.0 \times 10^4$

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