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厦门大学

硕 士 学 位 论 文

天然光敏剂对蒽和苯并[a]蒽光解动力学的影响研究

Effect of Photosensitizers in Atmospheric Aerosol on Photodegradation of Anthracene and Benzo[a]anthracene

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摘要

多环芳烃（Polycyclic Aromatic Hydrocarbons, 简称 PAHs）是一类半挥发性有毒有机物，一旦排放进入大气，就会在气相和颗粒相之间进行分配，其中高分子量 PAHs 主要以颗粒相形式存在，低分子量 PAHs 则主要以气相形式存在。吸附于气溶胶上的 PAHs 在大气迁移过程中，可由干湿沉降和光降解从大气中清除，其中 PAHs 的光降解速率受 PAHs 本身的性质及颗粒基质组成所影响。气溶胶颗粒中存在的光敏剂如 4-甲基邻苯二酚、愈创木酚（又称 2-甲氧基酚）、紫丁香醇（又称 2, 6-二甲氧基苯酚）可在一定程度上改变 PAHs 的光解速率，进而影响 PAHs 的大气停留时间和迁移距离。

本研究以蒽（Anthracene，简称 Ant）和苯并[a]蒽（Benzo[a]anthracene, 简称 BaA）两个受光解影响显著的化合物为代表，研究在正己烷相、甲醇相和水相体系中上述 3 种光敏剂对 Ant 和 BaA 光降解速率的影响，获得如下结果：

1. 在紫外辐射条件下，Ant 和 BaA 均发生直接光降解，且均是在水相中光解速率最大，其次是甲醇相，在正己烷相中光解速率最小。

2. 光敏剂本身在紫外辐射的条件下，也具有光降解性。

3. 当溶剂体系为甲醇时，同一浓度的光敏剂，其浓度越高，越促进 Ant 和 BaA 的光解；当溶剂体系为正己烷时，4-甲基邻苯二酚和愈创木酚促进 Ant 和 BaA 的光解，紫丁香醇抑制 Ant 和 BaA 的光解；当溶剂体系为水相时，同一浓度的光敏剂，其浓度越低，反而越促进 Ant 和 BaA 的光解。

4. 当同一光敏剂浓度一定时，Ant 和 BaA 的光解速率在正己烷相、甲醇相和水相体系中差异性明显，不同溶剂中 Ant 和 BaA 的光解速率大小顺序是水相>甲醇相>正己烷相。

5. 相同溶剂中，不同光敏剂对 Ant 和 BaA 的光降解速率影响也是呈现差异性。在正己烷相中，愈创木酚对 Ant 的光解促进作用最大，4-甲基邻苯二酚和紫丁香醇促进作用相当；光敏剂对提高 BaA 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚 > 紫丁香醇。甲醇相中 3 种光敏剂对提高 Ant 的光降解速率影响大小顺序是 4-甲基邻苯二酚>愈创木酚 > 紫丁香醇；光敏剂对提高

BaA 的光降解速率影响大小顺序是 4-甲基邻苯二酚 > 紫丁香醇 > 愈创木酚。在水相中，3 种光敏剂对提高 Ant 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚>紫丁香醇；光敏剂对提高 BaA 的光降解速率影响大小顺序是愈创木酚 > 4-甲基邻苯二酚≈紫丁香醇。

6. 根据本实验室的模拟研究，推测在气溶胶由非极性变为极性老化过程（包含吸附的水分）中，Ant 和 BaA 的光解速率逐渐提高。在不考虑外界来源输入的前提下，当气溶胶老化到最终阶段时，Ant 和 BaA 的光解速率最大。

关键词：光敏剂；气溶胶老化；蒽；苯并[a]蒽；光降解

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are identified to be one of the major toxic air pollutants in urban. When PAHs enter into aerosol, it will be distributed between gas phase and particles phase. PAHs mainly exist in the particle phase with high molecular weight, while exist in the gas phase with low molecular weight. When PAHs are absorbed in aerosol, they will be cleared from the atmosphere by dry/wet deposition and photodegradation in atmospheric migration. The photochemical behavior of PAHs can be influenced by organic matter and properties of PAHs. There are large amounts of photosensitizers in wood smoke particles, such as 4-methylcatechol, guaiacol and 2,6-dimethoxyphenol, they can change the photodegradation dynamics of anthracene and benzo[a]anthracene under stimulated sunshine, which both effect residence time and migration distance of PAHs in air.

This study choose anthracene (Ant) and benzo[a]anthracene (BaA) as representative PAHs, to better understand the effect of aerosol polarity and concentrations of photosensitizers to photodegradation dynamics of anthracene and benzo[a]anthracene when the aerosol is aging. The results are as follows:

1. Photodegradation experiments of anthracene and benzo[a]anthracene show that they could photodegrade under stimulated sunlight. The photolysis rates of anthracene and benzo[a]anthracene in methanol, hexane and water decrease as this order: water > methanol > hexane. Much faster decay of anthracene and benzo[a]anthracene are observed in water.

2. Photosensitizers can also photolysis under stimulated sunlight.

3. Photodegradation experiments of effect of photosensitizers to anthracene and benzo[a]anthracene in different solvents show that faster decay of anthracene and benzo[a]anthracene in methanol composed of high concentration of photosensitizers. The photodegradation rates of anthracene and benzo[a]anthracene are increased in hexane composed of 4-methylcatechol and guaiacol, while photodegradation rates are decreased in hexane composed of 2,6-dimethoxyphenol. The photodegradation

rates of anthracene and benzo[a]anthracene are decreased in water composed of photosensitizers, the lower concentration of photosensitizers, the faster decay of anthracene and benzo[a]anthracene.

4. Photodegradation experiments of effect of solvents to anthracene and benzo[a]anthracene in different photosensitizers show that the photolysis rates of anthracene and benzo[a]anthracene as this order: pure water > methanol > hexane.

5. When the solvent is same, the effect of photosensitizers to the photodegradation of anthracene and benzo[a]anthracene are also different. The photolysis rates of anthracene in methanol decrease as this order: 4-methylcatechol > guaiacol > 2, 6-dimethoxyphenol. The photolysis rates of benzo[a]anthracene in methanol decrease as this order: 4-methylcatechol > 2, 6-dimethoxyphenol > guaiacol. The effect of guaiacol to the photodegradation of anthracene in hexane is larger than 4-methylcatechol and 2, 6-dimethoxyphenol. The effect of 4-methylcatechol and 2, 6-dimethoxyphenol to the photodegradation of anthracene is almost same. The photolysis rates of benzo[a]anthracene in hexane decrease as this order: guaiacol > 4-methylcatechol > 2, 6-dimethoxyphenol. The photolysis rates of anthracene in pure water decrease as this order: guaiacol > 4-methylcatechol > 2, 6-dimethoxyphenol. The photolysis rates of benzo[a]anthracene in hexane decrease as this order: guaiacol > 4-methylcatechol≈2, 6-dimethoxyphenol.

6. According to the results of this study, we can indicate that when the aerosol is aging, polarity of aerosol become stronger and aerosol contains much of water in the end, the photolysis rates of anthracene and benzo[a]anthracene increase, and photolysis quickly when the ratio of water is increasing.

The photodegradation products of anthracene and benzo[a]anthracene with photosensitizer under stimulated sunshine are also preliminary discussed in this study. The main photodegradation products of anthracene and benzo[a]anthracene contain benzy alcohol, 2-methyl-phenol, 3-methyl-phenol, 2-benzyltoluene, 4-methyl-phenol, 2-methoxy-phenol, 3, 3’-dimethylbiphenyl, mequinol and so on. Different products are produced in different solvents with different photosensitizers.

Key words: Photosensitizers; Aerosol aging; Anthracene; Benzo[a]anthracene; Photolysis