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Sonolytic reactions of phenanthrene in organic extraction solutions

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Abstract

Ultrasonic extraction is a common method used to extract semi-volatile and nonvolatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs) from solid matrices. However, ultrasonic energy has been suspected to lead to undesired reactions of the solute and thus affect qualitative and quantitative results. In this paper, sonolytic reactions of phenanthrene in common organic extraction solutions were examined using a 20 kHz ultrasonic probe under conditions commonly used for ultrasonic extraction. Extraction parameters including phenanthrene concentration, solvent type, pulse length, and sonication time were investigated. Hexane:acetone (1:1 V/V) resulted in less phenanthrene degradation than dichloromethane (DCM):acetone (1:1 V/V). Initial solute concentration, length of sonication time, and solvent type affected the degradation of phenanthrene. Reaction byproducts including methylphenanthrene and methylnaphthalene detected after sonication indicate that phenanthrene reacts by both direct pyrolysis and reaction with methyl or ethyl radicals formed from solvent pyrolysis.

Keywords: Ultrasonic extraction; PAHs; Sonolytic reaction

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds found throughout the environment in the air, water, and soil, and persist in the environment for months to years (Wild et al., 1990). A common analysis procedure for PAHs on a solid matrix is extraction followed by gas chromatography/mass spectrometry (GC/MS) analysis. Previous studies indicate that PAHs are tightly bound to solids because of their strong hydrophobicity; hence, the type of extraction procedure used will strongly influence the quantitative data obtained (Noordkamp et al., 1997; Jonker and Koelmans, 2002). Ultrasonic extraction can reduce the extraction time from 16 to 18 h used in Soxhlet extraction to a few minutes. This method has been specified as US EPA standard method 3550B and has been widely used for extracting nonvolatile and semi-volatile organic compounds from solid matrices such as soils, sludges and solid wastes (US EPA, 1996).

The reduced times of ultrasonic extraction are attributed to the chemical and physical effects of ultrasound which are the result of the formation and collapse of cavitation bubbles in solution (Hromadkova et al., 1999). For example, high pressure generated upon bubble collapse enhances penetration of the solvent and transfer of the adsorbed solutes from the solid matrix (Margulies and Schwarz, 1985). High temperature improves solubility and diffusivity of solute. Moreover, when cavitation bubbles collapse, shock waves and shear forces are produced that create microscopic turbulence within interfacial films surrounding nearby solid particles (Doktycz and Suslick, 1990). This phenomenon increases mass transfer across the film, thus increasing the intrinsic mass–transfer coefficient (Wilhelm et al., 1993). When cavitation bubbles collapse near a solid surface several orders of magnitude larger than the cavitation bubbles, collapses occur asymmetrically. This asymmetric collapse results in a fast moving stream of liquid

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passing through the cavity and impacting the surface of the solid at high velocity. This phenomenon is called a microjet (Suslick, 1990). Microjets of solvent are formed perpendicular to the solid surface, and lead to pitting and erosion of the surface, reducing the path length for diffusion from the solid to the solvent (Suslick and Doktycz, 1990).

Either an ultrasonic cleaning bath or probe has been commonly used to conduct ultrasonic extractions. Solid samples have been sonicated in a glass beaker or flask for times ranging from minutes to hours (Griest et al., 1988; Sun et al., 1998; Mitra et al., 1999; Ghosh et al., 2000; Mastral et al., 2001; Mecozzi et al., 2002). Although ultrasonic extraction is widely accepted as a valid extraction method, the ultrasonic energy has been suspected to lead to undesired reactions of the solute and thus affect quantitation (Burford et al., 1993; Song et al., 2002). Previous research on the sonochemical decomposition of solutes has been conducted predominately in aqueous solution (Leonhardt and Stahl, 1998; Cataldo, 2000; Little et al., 2002); thus, the sonochemistry of solutes dissolved in organic solvents remains largely unexplored. Therefore, an investigation on the possible decomposition of PAHs in organic solution is necessary to elucidate the effect of ultrasound on PAHs during extraction.

In this research, we examined the sonolytic reactions of phenanthrene in two common organic extraction solutions without the presence of solid particles with a particular focus on the solvent effect, solute concentration, pulse time, sonication time and formation of reaction byproducts.

2. Materials and methods

2.1. Chemicals

Phenanthrene was used as a model PAH. It was purchased from Sigma–Aldrich with a purity of 99+% and was used without further purification. A standard containing 16 different PAHs (2000 mg l^{-1} each) and a deuterated internal standard including a mixture of acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, napththalene-d_8, perylene-d_{12} and phenanthrene-d_{10} (2000 mg l^{-1} each) were purchased from Ultra-Scientific. Hexane, acetone, dichloromethane (DCM), purchased from Fisher Scientific, were of HPLC grade and used as received. Working solutions (2000 mg l^{-1}) of phenanthrene were prepared by dissolving the precisely weighed compound in DCM in a sealed volumetric flask. Different concentrations (0.1–10 mg l^{-1}) of working solution were prepared by diluting the stock solution using either pure hexane or DCM.

2.2. Sonication experiments

Standard ultrasonic extraction conditions recommended in method 3550B (US EPA, 1996) were followed to test the reactions of phenanthrene under sonication. An ultrasonic probe system with a 1.90 cm diameter titanium tip (Sonic Dismembrator 550, Fisher Scientific), operating at 20 kHz, was used to conduct experiments. The ultrasonic probe was properly tuned before each experiment. In all experiments, 1 ml of phenanthrene stock solution at various concentrations was added directly to a 100 ml solvent mixture of hexane:acetone 1:1 V/V or DCM:acetone 1:1 V/V and followed by 3 min sonication with output control knob set at 10 (full power) and pulse mode (energy on 50% of time and off 50% of time). Thus, the total ultrasonic irradiation time was 1.5 min. The solution was sonicated in a 400 ml glass beaker (Pyrex). The end of the probe tip was located 1.3 cm (1/2 in.) below the surface of the liquid. After sonication, the solution was decanted and collected in a flask. The extracts were condensed using a Kuderna–Danish (K–D) concentrator to less than 10 ml. High purity nitrogen gas (Praxair) was used to further blowdown the extract to 1 ml.

The percent remaining of phenanthrene after sonication was defined as the following equation:

$$\text{Percent remaining (\%)} = \frac{\text{Measured phenanthrene after sonication} - \text{Phenanthrene in blank}}{\text{Added phenanthrene before sonication}} \times 100\% \qquad (1)$$

where added phenanthrene before sonication is the known amount of phenanthrene added into organic solvent before sonication, measured phenanthrene after sonication is the amount of phenanthrene after sonication. Phenanthrene blank is the amount of phenanthrene measured in the pure solvent mixture after sonication.

Unless stated otherwise, experiments were conducted in triplicate to ensure reproducibility. Selected experiments were conducted on different days to verify temporal reproducibility.

2.3. Control experiments

Control experiments were conducted to determine if volatilization of phenanthrene led to its loss during sonication. Solutions of phenanthrene (100 μg l^{-1}) in hexane/acetone and DCM/acetone were continuously stirred while the temperature was increased 20 °C (e.g., from 17 °C to 37 °C) to mimic conditions of ultrasonic extraction. Solutions were then condensed and analyzed for phenanthrene. In addition, a 10 ml solution of phenanthrene (200 μg l^{-1}) in hexane/acetone mixture was put into a 20 ml sealed glass vial and sonicated using an ultrasonic bath (Branson, model 2210) for 30 min. Gas phase samples were withdrawn using a gas tight syringe and analyzed for phenanthrene and byproducts by GC/MS.

Sonication of solvents was carried out to test if PAHs in background air could dissolve into the solvent during sonication. The formation of byproducts from sonicating pure solvents was also tested.

2.4. Instrumental analysis

Quantitative analysis of PAHs was determined using a gas chromatograph with ion trap mass spectrometer