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Thermal and Photochemical Decomposition of Particulate PAH

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ABSTRACT

Photochemical decomposition of several polycyclic aromatic hydrocarbons (including benzo[a]pyrene) proceeds much more slowly when the compounds are adsorbed on coal fly ash than in solution or when adsorbed on other solid surfaces. Certain other polycyclic hydrocarbons (fluorene, the benzofluorenes, 9,10-dimethylanthracene, and 9,10-dihydroanthracene) undergo rapid, non-photochemical, degradation when adsorbed onto fly ash surfaces; the extent of this decomposition depends upon the nature of the fly ash.

INTRODUCTION

Information about the fate of particulate polycyclic aromatic hydrocarbons (PAH) released to the atmosphere from combustion of carbonaceous fuels is presently fragmentary. It is often assumed, however, that photochemical oxidation processes play an important role since rapid photo-oxidation is known to occur for many PAHs in solution, in pure solid form, or when adsorbed onto certain solid substrates such as alumina (2,3). Consequently, it is widely accepted that the half-lives of particulate PAHs in the presence of sunlight may be of the order of only hours or, at most, a few days (2,4,9).

In order to test this supposition and to obtain quantitative data describing the rate and extent of photochemical decomposition of particulate PAH, a series of experiments were conducted in which individual PAHs were adsorbed onto coal fly ash particles and exposed to both real and simulated sunlight conditions.

EXPERIMENTAL

To simulate real plume samples, in which PAHs are adsorbed onto fly ash particles (8), a model system for adsorption of PAHs from the vapor phase onto fly ash was utilized. Samples of fly ash, collected from power-plant electrostatic precipitators, were size-separated and then placed into a vapor deposition apparatus similar to that described by Miguel (6). A simple diffusion cell (7) was used to prepare a known vapor-phase concentration of a particular PAH, and the expanded coal fly ash bed was exposed to this vapor for a known duration (typically 9 hr.).

To detect the occurrence of any non-photochemical decomposition of the vapor-adsorbed PAH which might occur, a portion of fly ash so prepared was immediately subjected to soxhlet extraction (benzene, cyclohexane, or methanol). The extract was then analyzed for the PAH and/or degradation products by liquid chromatography, UV absorption, or fluorescence spectrometry. The precision of these analyses was determined to be ±8% RSD. The remainder of the fly ash sample was subjected to irradiation, using any of several artificial light sources (150-W xenon lamp, 275-W sunlamp, or General Electric 500T3/Cl "quartzline" lamp; all unfiltered) or to outdoor sunlight. Extraction followed by analysis, as described above, was performed after cessation of illumination.

RESULTS

Rather unexpectedly, only modest (<20%) photodegradation was observed for the PAHs studied (Table I). Furthermore, no significant dependence upon irradiation time or illumination conditions was found. However, under similar illumination conditions, benzo[a]pyrene and anthracene photodecomposed to a much greater extent in solution or when adsorbed from methanolic solution onto alumina. To verify that the observed resistance to photodegradation of benzo[a]pyrene and anthracene was not artifactual, the compound of interest was adsorbed from methanolic solution onto commercial alumina thin-layer chromatography plates and prepared fly ash "thin-layer" plates. In a typical experiment, benzo[a]pyrene adsorbed onto alumina from solution underwent 50% photodecomposition upon 80-min exposure to an unfiltered 150-W xenon lamp; under identical conditions, benzo[a]pyrene adsorbed onto fly ash exhibited only 15% decomposition.

In addition to limited photochemical decomposition it was found that certain PAHs including fluorene, benzo[a]fluorene, benzo[b]fluorene, 9,10 dimethylanthracene, 9,10 dihydroanthracene and 4-azafluorene) underwent rapid, though not immediately complete, decomposition in the absence of light when adsorbed on fly ash. This process was studied most exhaustively for fluorene. The product of non-photochemical degradation of vapor-adsorbed fluorene is 9-fluorenone. The initial extent of reaction varies from 7% to 90% decomposition, depending upon the type of fly ash used as substrate. The reaction is not observed for solid fluorene, for fluorene vapor-adsorbed on several other solids (alumina, silica gel, Linde "Molecular Sieves", Rohm and Haas "Ambersorb XE-340"), or for fluorene dissolved in cyclohexane or methanol (the solvents used for soxhlet extraction of fluorene from fly ash). However, similar non-photochemical decomposition is observed for fluorene vapor-adsorbed on activated charcoal.

The non-photochemical degradation of PAHs adsorbed on fly ash is relatively rapid. For example, when fluorene was vapor-adsorbed on fly ash for a duration of only 0.5 hr, fluorene extracted from a portion of the sample 1.0 hr after adsorption had already decomposed to the extent of 35%. The decomposition process continues, albeit much more slowly, if the fly ash samples are "aged" in the dark after adsorption of the PAH has been completed. (Figure 1)

DISCUSSION

The foregoing results suggest that two types of chemical processes can operate in the oxidation of PAHs adsorbed onto solid substrates. First, it is apparent that PAHs adsorbed onto coal fly ash are general stabilized against photochemical oxidation by comparison with the same compounds present in solution, as the pure solid, or adsorbed onto substrates such as alumina or silica gel. On the other hand, a limited class of compounds is found to undergo spontaneous non-photochemical oxidation as a result of adsorption onto substrates such as coal fly ash and activated carbon.

The explanation of these findings is not presently clear. Based on the available evidence, however, it seems likely that energetic adsorption of PAH onto a highly active surface, such as that of coal fly ash or activated carbon, effectively stabilizes PAH against photo-oxidation which either increases the electronic excitation energy or decreases the lifetime of the excited state. The small amount of rapid photo-oxidation which is observed (Table I) could then be due to a fraction of the PAH which is not directly bonded to the active surface but rather to another PAH molecule (as in a multilayer configuration) or to a weakly adsorbing mineral impurity. The promotion of non-photochemical degradation could then, in turn, be due either to extensive molecular orbital rearrangement or simply to the ready availability of active oxygen on strongly adsorbing surfaces (1).

It is noteworthy that all of the compounds which undergo spontaneous oxidation as a result of adsorption onto coal fly ash (i.e. Fluorene, benzo[a]fluorene, benzo[b]fluorene, 9,10 dimethylanthracene, 9,10 dihydroanthracene, and 4-azafluorene) contain a benzylic carbon atom indicating that this structure is especially susceptible to non-photochemical oxidative attack.

From an environmental standpoint, the foregoing results have several important ramifications.

1. In general PAHs which would normally be expected to undergo photochemical decomposition are stabilized when adsorbed onto coal fly ash. This may result in effective retention of the carcinogenic potential of several compounds (e.g. Benzo[a]pyrene).

2. Certain compounds (e.g. those containing benzylic carbon atoms) are rapidly oxidized to the corresponding ketones or quinones as a result of adsorption onto coal fly ash. Whether such oxidation results in a net increase or decrease in the toxic potential of adsorbed PAHs is unknown, but it does suggest that specific concentrations (μg/g) of particulate PAHs in the plume from a coal fired power plant may differ substantially both between plants and with distance from a given plant stack.

3. Perhaps one of the more interesting ramifications of the non-photochemical process lies in the fact that certain highly carcinogenic PAHs (e.g. dimethylbenzanthracene) contain one or more benzylic carbon atoms and so would be expected to decompose quite rapidly following adsorption onto an active particulate substrate. This process may account for the facts that dimethylbenzanthracene has not been found either in atmospheric or emission source particulates and that fluorenone is normally present at much higher levels than fluorene in atmospheric aerosols (2,5).

CONCLUSION

While the results presented herein are not fully definitive, it would appear that particulate association of PAH does not generally promote photochemical decomposition as hitherto supposed (2). Nevertheless, some PAHs do undergo rapid oxidation as a result of adsorption onto active substrates such as these likely to be encountered in atmospheric aerosols.

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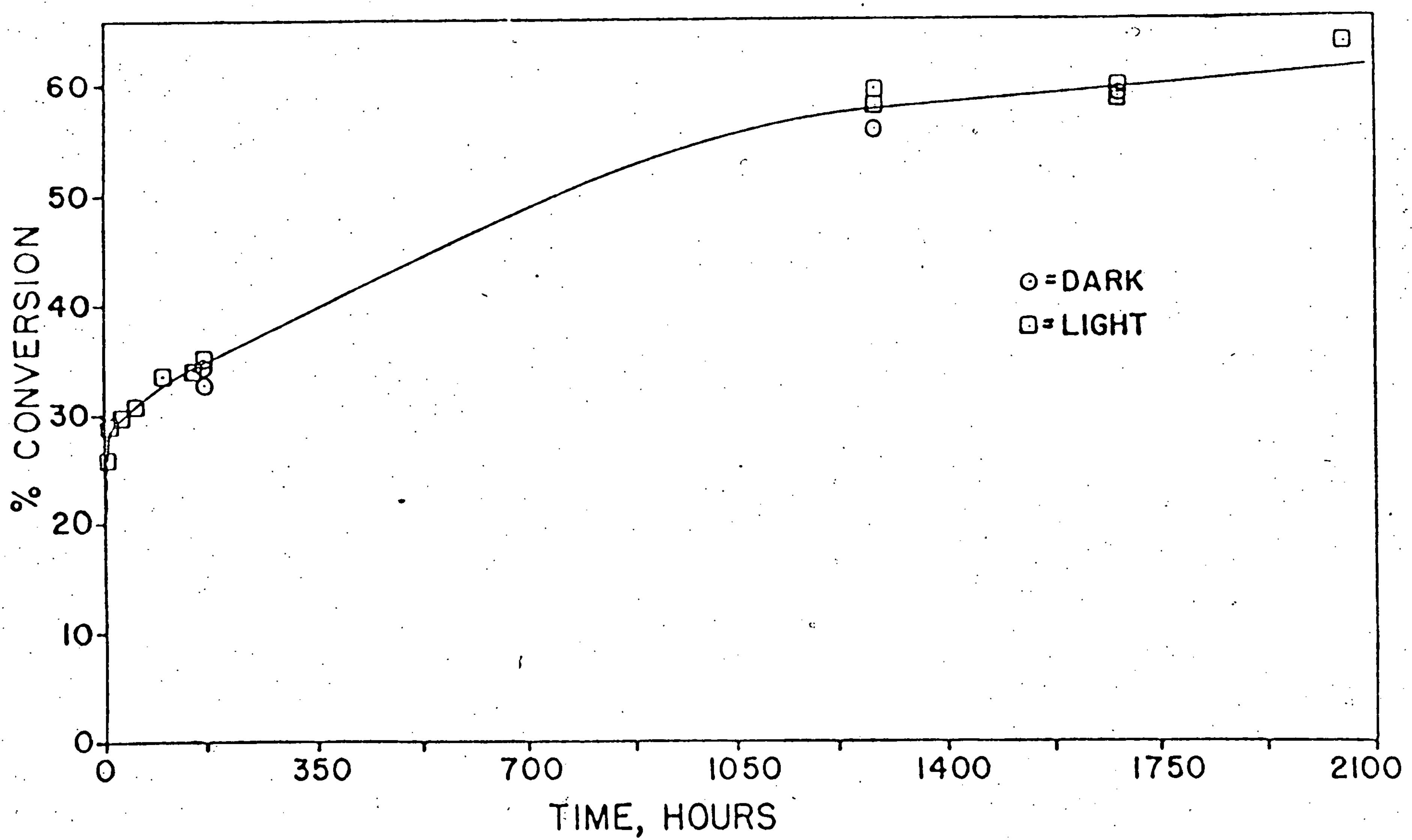
TABLE I

Typical Changes in Concentration of PAH Adsorbed onto Coal Fly Ash Following Irradiation.

PAH Adsorbed on fly ash	Light Source	Irradiation Time, hr.	Ave % Change
Pyrene	sun lamp	24.	-13
Phenanthrene	xenon arc	3.3	+ 7.5
Fluoranthene	xenon arc	14.2	- 9.
Anthracene	xenon arc	24.	-15.
Benzo(a) pyrene	xenon arc	21.	-16.
Benzo(a) pyrene	quartz line	8.7	- 8.

FIGURES

Figure1: Percentage Conversion of Fluorene Adsorbed onto Coal Fly Ash as a Function of Time Following Completion of Adsorption.



% CONVERSION
0
10
20
30
40
50
60
0
350
700
1050
1400
1750
2100
TIME, HOURS
⊙ = DARK
⊡ = LIGHT