

CHEMICAL REACTIVITY OF POLYCYCLIC AROMATIC COMPOUNDS  
VAPOR-ADSORBED ON COAL STACK ASH

A. A. Garrison, R. A. Yokley, R. J. Engelbach, E. L. Wehry, and G. Mamantov

Department of Chemistry, University of Tennessee,  
Knoxville, Tennessee 37996-1600

INTRODUCTION

Chemical reactions of polycyclic aromatic hydrocarbons (PAHs) under environmental conditions recently have received considerable attention (1-5), but much remains to be learned about the fate of PAHs in the atmosphere. Coal ash is a complex inhomogeneous mixture of many particle sizes, shapes and colors (6,7). It contains virtually every chemical element. The dominant elements are Si, Al, O, Fe, and C, along with significant concentrations of Ca, K, Mg, and Ti. The manner in which coal ash surfaces influence the chemistry of adsorbed PAHs undoubtedly represents a complex interplay of chemical and physical parameters. Their study is complicated by the heterogeneous, complex composition of coal ash and the extreme difficulty of detecting adsorbed organic compounds by optical or particle spectroscopic methods.

The chemical reactivities of five polycyclic aromatic hydrocarbons, as adsorbates on coal stack ash surfaces, have been examined. Each of the indicated compounds is deposited (from the vapor phase) on seven well-characterized coal stack ashes of diverse origins, physical properties, and chemical composition. A significant aspect of the research is the use of vapor-deposition techniques. PAHs were deposited from the vapor phase in a nitrogen atmosphere using diffusion cell and expanded adsorbent bed procedures described in detail elsewhere (8,9). This method was selected, as the photochemical behavior of PAHs adsorbed on coal fly ash may be significantly different from that of PAHs in liquid form, in the form of pure solids, or as adsorbates on alumina or silica (10-12).

The reactivity of adsorbed PAHs exposed to gaseous co-pollutants also is not well understood. For example, there appears to be a possibility that some nonphotochemical nitration reactions reported for adsorbed PAHs in the presence of NO<sub>2</sub> actually result from reactions with HNO<sub>3</sub> present as a contaminant in commercial NO<sub>2</sub> (13). The manner in which the reactivity of adsorbed PAHs with NO<sub>2</sub> is influenced by the nature of the adsorbate surface or the presence of light has not been established.

We have generally observed that coal stack ash surfaces stabilize polycyclic aromatic hydrocarbons with respect to both photochemical and nonphotochemical oxidative transformation processes. However, there are significant variations in the abilities of different ashes to exhibit such stabilizing effects. The chemical and physical characteristics of the various stack ashes which may play important roles in altering the chemical behavior of organic compounds adsorbed from the vapor phase are discussed below.

MATERIALS AND METHODS

Aromatic Hydrocarbons

Anthracene (hereafter abbreviated A), phenanthrene (Ph), pyrene (Py), benzo[a]pyrene (BaP), and benzo[a]anthracene (BaA) were obtained from commercial sources and, when necessary, purified by vacuum sublimation.

Adsorbents

Six ashes (from combustion of Eastern Appalachian (EA), East Tennessee (ET), Western Kentucky (WK), and Illinois (IL) bituminous coals; New Mexico (NM) subbituminous coal; and Texas (TX) lignite) were obtained from the Oak Ridge National Laboratory. All samples were obtained from power plant stack control devices; sampling and chemical analysis of these materials have been described (14). A seventh ash

used was an analytical standard (AR) obtained from Alpha Resources, Stevensville, Mich. An eighth ash, Kanab (KA), was a high carbon ash obtained from a stack collection device of a power plant experiencing operating difficulties at the time of collection. Elemental analyses of these ashes are listed in Table 1, as are pH values for aqueous extracts of the ashes.

Other adsorbents included alumina (neutral, Brockmann activity I); silica gel; controlled porosity glass (100 A average pore diameter, from Pierce Chemical Co., Rockford, Ill.); and flaked graphite (Southwestern Graphite Co. Burnet, Tex.). All adsorbents were sieved to pass a 45  $\mu$ m screen, stored in the dark, and degassed at elevated temperatures by passing high purity nitrogen over them in an expanded bed (8) immediately prior to use. Porosities and surface areas were measured by BET nitrogen adsorption. Diffuse reflectance spectra were measured using a Varian Cary 14L spectrophotometer.

TABLE 1

BULK ELEMENTAL COMPOSITION AND AQUEOUS EXTRACT pH VALUES FOR COAL STACK ASHES<sup>a,b,c</sup>

Element	EA	ET	WK	IL	NM	TX	AR	KA
Si	23.4	30.0	23.4	22.7	28.1	25.7	29.0	na
Al	13.6	15.5	10.1	9.1	13.1	7.5	11.4	na
Fe	10.9	1.7	16.9	16.5	2.5	3.4	4.0	na
Ca	1.0	0.2	1.3	2.4	4.2	14.5	2.9	na
Mg	0.8	1.8	0.4	0.6	0.7	1.9	0.8	na
Na	0.3	0.2	0.2	1.7	1.4	0.4	0.8	na
K	2.4	2.0	2.2	1.6	0.6	0.5	0.9	na
C	1.8	0.5	0.3	0.3	1.0	0.5	0.3	2.8
pH	8.2	4.7	4.4	3.3	11.9	10.8	11.4	6.4

a All analytical data as weight percentages of the elements.

b See preceding page for abbreviations.

c Data not available indicated by "na".

#### Adsorption Techniques

PAHs were deposited on the adsorbents from the vapor phase immediately after the degassing procedure. Design details for the diffusion cell and expanded adsorbent bed are discussed in the literature (8,9).

#### Photochemical Techniques

Two illumination cells were used: a rotatable quartz tube (11) and a fluidized-bed photoreactor similar to that described by Daisey, et al. (15). The source was a Cermox xenon illuminator (ILC Technology, Sunnyvale, Cal.) operated at 180-320 W and situated 34-38 cm from the photolysis cell. The spectrum of this lamp closely simulates the solar spectrum in the 300-700 nm wavelength range. To avoid thermolysis of samples under illumination, the near infrared output of the lamp was attenuated by passing the beam through 20 cm of water. A portion of each adsorbent sample was stored in the dark, to serve as a control.

#### Analytical Procedures

After illumination of a sample, it was subjected to micro-Soxhlet extraction for 24 hr in the dark with methanol or toluene. A portion of the same sample, not illuminated, was extracted identically. Because many PAHs cannot be extracted quantitatively from coal ash (16), samples were subdivided into four portions after illumination but before extraction, so that the PAH recovery for each sample could

be expressed as a 95% confidence interval for quadruplicate extractions. The resulting solutions were analyzed for their extractable PAH content by UV-visible absorption or fluorescence spectrometry. Decisions as to whether a given PAH exhibited degradation on a particular adsorbent were based on differences between the extraction recoveries (as 95% confidence intervals) for illuminated and unilluminated samples.

#### Studies with NO<sub>2</sub>

The photochemistry of adsorbed PAHs in the presence of NO<sub>2</sub> (12ppm in N<sub>2</sub>) was studied. To remove traces of HNO<sub>3</sub> from the NO<sub>2</sub>, the gas stream was passed through a 20 by 6.5 cm plastic tube packed tightly with nylon wool (17) and then through two 46-mm diameter nylon filters (18). Spectrophotometric analysis of the final nylon filter for nitrate (19) indicated that the system trapped all detectable quantities of HNO<sub>3</sub> present in the NO<sub>2</sub>.

#### RESULTS AND DISCUSSION

Photoreactivities of adsorbed PAHs were classified in the following categories, based on 24 hr illuminations:

- a) ++ : High reactivity (>50% loss of PAH)
  - b) + : Moderate reactivity (10-50% loss of PAH)
  - c) 0 : Little or no photochemical reactivity (0-10% loss of adsorbed PAH).
- Using these classifications, the results are summarized in Table 2.

TABLE 2

PHOTOREACTIVITY OF ADSORBED PAHs<sup>a,b</sup>

PAH	EA	ET	WK	IL	NM	TX	AR	KA	Silica	Alumina	Glass	Graphite
Py	0	0	0	0	0	++	++	0	++	++	++	0
BaP	0	0	0	0	0	++	+	0	++	++	++	0
A	0	+	+	0	+	++	+	0	++	++	++	0
BaA	na	+	na	0	na	++	na	0	++	++	++	na
Ph	na	0	0	0	0	+	na	0	++	++	++	na

a See "Materials and Methods" for abbreviations for PAHs and ashes.

b Data not available indicated by "na".

Major generalizations from these observations include the following.

- 1) Greater photochemical reactivity is observed for each PAH on alumina, silica gel, or controlled porosity glass than on any coal stack ash substrate.
- 2) For each PAH, greater photochemical reactivity is observed on Texas lignite (TX) ash than any other ash.
- 3) No photochemical reactivity is observed for any of the five PAHs on the high carbon Kanab (KA) ash. Also, pyrene, anthracene, and BaP fail to exhibit any measurable photoreactivity when adsorbed on graphite.
- 4) Of the five PAHs studied, anthracene is the most photoreactive on ET, WK, and NM ashes, but it appears less reactive than pyrene on the AR ash.
- 5) In contrast to the observations of Dlugi and Gusten (12), who examined the photochemistry of two PAHs on two ashes and reported much greater photoreactivity for both compounds on the more acidic ash (as estimated by the pH of aqueous extracts of the ashes), our two most "active" ashes (TX and AR) produce alkaline extracts. Several of the acidic ashes (IL,ET,WK) effectively suppress phototransformation of adsorbed PAHs. Likewise, one "alkaline" ash (NM) appears very effective at inhibiting the phototransformation of adsorbed PAHs. Hence, there does not appear to be an obvious relationship between ash surface acidity and the ability of that surface to suppress photodegradation of adsorbed PAHs.

6) A strong relationship is observed between the carbon content and the degree of inhibition of photochemical reactivity. A high iron content in the ash also appears to be related to suppression of phototransformation of adsorbed PAHs. Whether there is any relationship between these observations and the tendency for PAHs to be most strongly adsorbed on carbonaceous particles in stack ash (20) is not yet clear.

7) There is a pronounced general tendency for those ashes which are darkest in color (as noted visually and by uv-visible diffuse reflectance spectrometry) to be most effective in inhibiting photolysis of PAHs (see Figure 1). The lightest colored ashes (TX and AR) are those on which PAHs are photodecomposed most efficiently. The most deeply colored ashes (KA, EA, IL, and WK) effectively inhibit PAH phototransformation. Substrates which are virtually transparent throughout the 280-400 nm wavelength region, such as silica and alumina, show no inhibitive effect relative to solid or solution decomposition. Graphite, which absorbs strongly throughout this spectral region, appears to suppress photochemistry of adsorbed PAHs. In their earlier comparison of rates of photodegradation of anthracene and phenanthrene on two coal ashes, Długi and Gusten likewise noted that photodecomposition proceeded more rapidly on the lighter colored ash (12).

BET surface area and adsorption-desorption isotherm hysteresis measurements indicate that all adsorbents examined in this work possess pores of proper size to accommodate PAH molecules studied. The possibility exists, as earlier suggested by Nielsen, et al. (1), that PAHs "deposited inside porous particles... can easily be shielded from the incident light". It seems likely that such an "inner-filter effect" is a factor responsible for the variation in PAH photoreactivity between different ashes.

8) When pyrene or BaP is adsorbed on TX, ET, or IL ash or on silica gel, no detectable decomposition of either PAH is observed in the presence of NO<sub>2</sub> in the absence of light, provided that precautions are taken to remove the nitric acid impurity from the NO<sub>2</sub>.

In the presence of both NO<sub>2</sub> and light (but in the absence of HNO<sub>3</sub>), decomposition of pyrene and BaP is observed on silica gel and TX ash, but no evidence of nitro-substituted PAH is found.

These observations seem to corroborate the conclusions of Grosjean, et al. (18) that HNO<sub>3</sub>, but not NO<sub>2</sub>, effects nitration of adsorbed PAHs, irrespective of whether samples are illuminated or exposed to co-pollutants in the dark.

#### ACKNOWLEDGEMENTS

We thank D. A. Lee (Analytical Chemistry Division, Oak Ridge National Laboratory) for the surface area and porosity measurements. This work was supported by Contract ASO5-81ER60006 with the Office of Health and Environmental Research, U. S. Department of Energy.

#### REFERENCES

1. Nielsen, T.; Ramdahl, T.; Bjørseth, A. Environ. Health Perspect. **1983**, 47, 103-114.
2. Pitts, J. N., Jr. Environ. Health Perspect. **1983**, 47, 115-140.
3. Edwards, N. T. J. Environ. Quality **1983**, 12, 427-441.
4. Van Cauwenberghe, K.; VanVaeck, L. Mutat. Res. **1983**, 116, 1-20.
5. Nikolaou, K; Maslet, P.; and Mouvier, G. Sci. Total Environ. **1984**, 32, 103-132.
6. Fisher, G. L.; Natusch, D. F. S. in "Analytical Methods for Coal and Coal Products"; Karr, C., Ed. Academic Press: New York, 1979, pp. 489-541.
7. Hulett, L. D.; Weinberger, A. J. Environ. Sci. Technol. **1980**, 14, 965-970.
8. Miguel, A. H.; Korfmacher, W. A.; Wehry, E. L.; Mamantov, G.; Natusch, D. F. S. Environ. Sci. Technol. **1979**, 13, 1229-1232.
9. Korfmacher, W. A. Ph.D. Thesis, University of Illinois, Urbana, IL., 1978.
10. Korfmacher, W. A.; Natusch, D. F. S.; Taylor, D. A.; Mamantov, G.; Wehry, E. L. Science **1980**, 207, 763-765.

11. Korfmacher, W. A.; Wehry, E. L.; Mamantov G.; Natusch, D. F. S. Environ. Sci. Technol. 1980, 14, 1094-1099.
12. Dlügi, R.; Gusten, H. Atmos. Environ. 1983, 17, 1765-1771.
13. Pitts, J. N., Jr.; Van Cauwenberghe, K. A.; Grosjean D.; Schmid, J. P.; Fitz, D. R.; Belser, W. L., Jr.; Knudson, G. B.; Hynds, P. M. Science 1978, 202, 515-519.
14. Lauf, R. J. Application of Materials Characterization Techniques to Coal and Coal Wastes. ORNL/TM-7663, Oak Ridge National Laboratory, 1981.
15. Daisey, J. M.; Lewandowski, C. G.; Zorz, M. Environ. Sci. Technol. 1982, 16, 857-861.
16. Griest, W. H.; Caton, J. E. in "Handbook of Polycyclic Aromatic Hydrocarbons", Bjørseth, A., Ed. Marcel Decker: New York, 1983, pp 95-148.
17. Sanhueza. E.; Plum, C. N.; Pitts, J. N., Jr. Atmos. Environ. 1984, 18, 1029-1031.
18. Grosjean, D.; Fung, K.; Harrison, J. Environ. Sci. Technol. 1983, 17, 673-679.
19. Mullin, J. B.; Riley, J. P. Anal. Chim. Acta 1955, 12, 464-480.
20. Griest, W. H.; Tomkins, B. A. Sci. Total Environ. 1984, 36, 209-214.

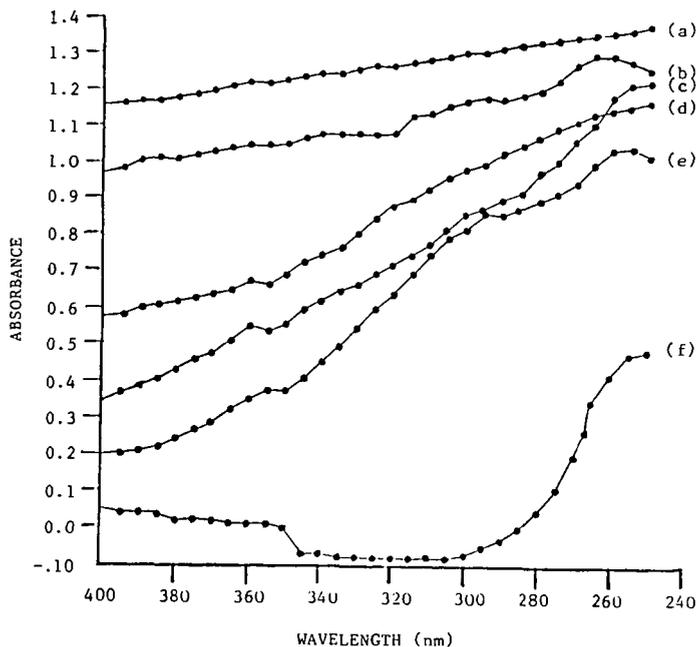


Figure 1. Graphical Representation of Data obtained from the Diffuse Reflectance Spectra of (a) Western Kentucky Bituminous, (b) Kaneb, (c) East Tennessee Bituminous, (d) New Mexico Subbituminous, and (e) Texas Lignite Coal Fly Ashes and, (f) Silica Gel.