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Oxidative Transformations of Polycyclic Aromatic Hydrocarbons Adsorbed on Coal Fly Ash

Abstract. *Polycyclic aromatic hydrocarbons adsorbed onto coal fly ash were found to be stabilized against photochemical decomposition. However, a number of adsorbed polycyclic aromatic hydrocarbons will spontaneously oxidize in the absence of light, with those compounds containing a benzylic carbon being particularly susceptible. The decomposition rate appears to be fly ash–dependent.*

Recently it has been reported (*1*) that fly ash emitted from coal-fired power plants contains compounds that are mutagenic as indicated by the Ames test (*2*). Although the identities of these compounds have not been firmly established, present indications (*1, 3*) are that most are either polycyclic aromatic hydrocarbons (PAH's) or derivations and heteroatom analogs thereof. Such compounds are known to be adsorbed onto the surface of emitted fly ash (*4, 5*), and several have been shown to be both mutagenic and carcinogenic (*3, 6, 7*). Since emitted fly ash may contribute significantly to the atmospheric aerosol, it is important to establish the ways in which associated toxic and carcinogenic compounds may change prior to inhalation by human beings.

Information about the fate of particulate PAH's released to the atmosphere is at present fragmentary and unclear. It is generally assumed, however, that photochemical oxidation processes play an important role (*3*). There is ample evidence that most PAH's will undergo photooxidation in solution, as the pure solid, and when adsorbed onto certain solid substrates such as alumina (*3*). It has been inferred that similar processes take place when the compounds are adsorbed on airborne particulates (*3, 8*). Indeed, it has been suggested that the half-lives of such PAH's in the presence of sunlight may be "only hours or days" (*3*, p. 60).

Contrary to this expectation, we now report that the rate and extent of photodecomposition of PAH's may be decreased substantially by adsorption onto coal fly ash particles. Certain PAH's, however, undergo rapid oxidation in the dark when adsorbed onto fly ash.

In our studies we used a model system in which individual PAH's were adsorbed onto the surface of fly ash collected from the electrostatic precipitators of several coal-fired power plants. Known gas-phase concentrations of individual PAH's were generated in either pure air or pure nitrogen by use of a simple diffusion cell (*5, 9*) and passed through an expanded bed (*5, 10*) of fly ash. By regulating the bed temperature and the time of exposure, we were able to control the amount of a PAH adsorbed. All fly ash samples were size-fractionated by sieving; we used particles in the size range from 44 to 74 μm on the assumption that the surface chemistry of particles in this size range is similar to that of the small fly ash particles (< 5 μm) likely to be emitted to the atmosphere. This assumption is supported by the results of extensive surface analyses of several fly ashes (*11*). Exhaustive preextraction with several solvents (cyclohexane, benzene, and methanol) showed that none of the fly ashes used contained more than 50 ng per gram of total PAH. The PAH's were thereafter adsorbed onto raw unextracted fly ash to avoid the possibility that the preextraction procedure might modify the fly ash surface.

We believe that this model system for adsorbed PAH on fly ash is closely reminiscent of the real situation, that is, fly ash collected from within the power plant stack system is used as an adsorbent just as occurs in practice. On the other hand, aged fly ash has different amounts of carbonates, hydroxides, and hydration water from freshly generated fly ash, and so the model system we used could conceivably exhibit different surface chemical behavior and extraction characteristics. No indications of such differences have been observed.

We carried out the sample irradiation in both pure air and pure nitrogen, using outdoor sunlight and several artificial light sources [150-W xenon arc lamp, 275-W commercial sunlamp, and "quartz line" lamps (General Electric model 5-OT3/Cl), all unfiltered]. The fly ash was revolved slowly in a quartz container to provide equal exposure of all surfaces, and radiant fluxes were estimated to be equal to or greater than that of midday summer sunlight (45°N) over the wavelength range 300 to 800 nm. Selected fly ashes were analyzed by electron spectroscopy for chemical analysis

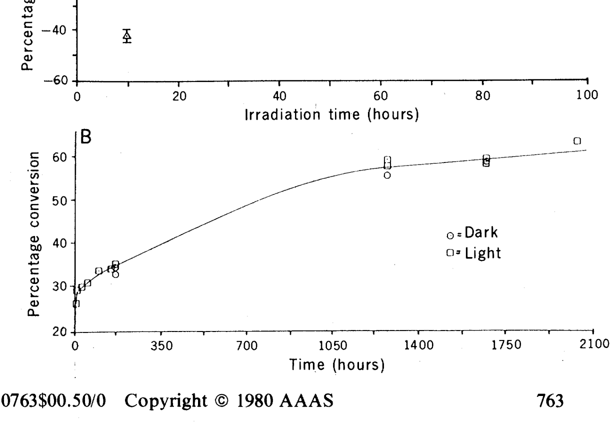

Fig. 1. (A) Percentage conversion of benzo[*a*]pyrene adsorbed onto coal fly ash. Each point surrounded by a circle represents a different fly ash sample, and several light sources are also represented. The point surrounded by a triangle indicates the percent decomposition of benzo[*a*]pyrene dissolved directly in methanol. (B) Percentage conversion of fluorene adsorbed on coal fly ash as a function of time.

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Table 1. Decomposition of irradiated polycyclic aromatic hydrocarbons (PAH's) adsorbed on coal fly ash.

Compound	Irradiation time (hours)	PAH adsorbed (μg/g)	Samples (No.)	Average change (%)
Pyrene	5 to 126	67 to 291	19	− 6.3(± 14.7)
Phenanthrene	2 to 113	129 to 186	5	+10 (± 12.3)
Fluoranthene	2.5 to 18	49 to 115	2	− 7.2(± 2.0)
Anthracene	3 to 24	300	3	−11.0(± 7.0)
Benzo[*a*]pyrene*	2.5 to 36.5	44 to 110	5	− 8 (± 8)
Benzo[*a*]pyrene†	21 to 100	15 to 44	4	−14 (± 7)

*Quartz line lamp. †Xenon arc lamp.

before and after irradiation; no change was observed in the spectral peaks of the surface constituents as a result of this treatment.

Portions of each fly ash sample were exhaustively extracted immediately after exposure to gaseous PAH and then after irradiation or dark storage. In the analyses for the original PAH and for degradation products, we used high performance liquid chromatography (ultraviolet absorbance detection) and ultraviolet absorption and fluorescence spectrometry. The extent of decomposition was normally determined either from the disappearance of the original PAH or from the appearance of its reaction products. (The reproducibility of multiple analyses was established to be ± 8 percent relative standard deviation, and the extraction efficiencies were shown to be > 94 percent of the PAH originally adsorbed.) Individual experiments were conducted to determine the influence of PAH type and concentration, irradiation time, intensity, wavelength distribution, dark stability, and the nature of the adsorbing substrate on the rate and extent of PAH decomposition.

None of the PAH's that were irradiated after adsorption onto fly ash exhibited appreciable photodegradation (Table 1). Such degradation as did occur took place very rapidly and did not proceed thereafter over time periods up to 100 hours (Fig. 1A). Furthermore, no significant dependence on irradiation intensity or amount of PAH adsorbed was observed. Under similar illumination conditions, however, extensive photodecomposition was observed for all PAH's irradiated in solution (Fig. 1A) and for both anthracene and benzo[*a*]pyrene adsorbed onto alumina from methanolic solution. We obtained additional evidence for the apparent influence of adsorbent substrate on photodecomposition by adsorbing anthracene and benzo[*a*]pyrene vapors onto both fly ash and alumina coated on thin-layer chromatographic plates which were then exposed to identical irradiation. In a typical experiment of this type benzo[*a*]pyrene present on the alumina surface underwent 50 percent decomposition upon exposure for 80 minutes to an unfiltered 150-W xenon arc lamp; by contrast, only 15 percent decomposition was observed for the benzo[*a*]pyrene adsorbed on fly ash.

Although the extent of photodegradation of PAH's adsorbed on fly ash is apparently small, a number of the compounds studied (Table 2) were found to undergo quite extensive oxidation in the absence of light. In particular, different fly ashes were found to give different oxidation rates. The oxidation products were not always the same as obtained from the photooxidation process, but a ketone or quinone was generally present. Considerable conversion occurs during the actual PAH adsorption for fluorene, which oxidizes to 9-fluorenone (Fig. 1B), but subsequent irradiation has no effect upon the rate or extent of further reaction. The extent of the initial reaction, which occurs at the elevated adsorption temperature, varies from 7 to 90 percent decomposition depending on the type of fly ash used as the adsorbent substrate and is not due simply to passage of a PAH through the adsorption apparatus. The nature of the adsorbent is thus an important factor determining the rate of this dark reaction. This observation is borne out by the findings that nonphotochemical conversion does not occur for solid fluorene, for fluorene dissolved in methanol or cyclohexane, or for fluorene adsorbed onto alumina, silica gel, 13× molecular sieve (Linde), glass, or adsorbent resin (Ambersorb XE-340). However, fluorene adsorbed onto activated carbon or graphite decomposed in a manner similar to that of fluorene adsorbed on coal fly ash.

Table 2. Decomposition of nonirradiated polycyclic aromatic hydrocarbons (PAH's) adsorbed on coal fly ash.

Compound	Change
Acenaphthene	None
7,12-Dimethylbenz[*a*] anthracene	None
Carbazole	None
Acridine	None
Phenazine	None
Fluoranthene	None
Phenanthrene	None
Benzo[*a*]pyrene	Very slow and minimal decomposition
Anthracene	
Fluorene	Decomposed
Benzo[*b*]fluorene	Decomposed
Benzo[*a*]fluorene	Decomposed
9,10-Dimethyl-anthracene	Decomposed
9,10-Dihydro-anthracene	Decomposed
4-Azafluorene	Decomposed

Most of the compounds that undergo spontaneous oxidation as a result of adsorption onto coal fly ash (Table 2) contain a single-bonded carbon atom attached to an aromatic ring; this linkage is thus especially susceptible to nonphotochemical oxidative attack. Possible exceptions to this rule are anthracene and benzo[*a*]pyrene which do not contain a benzylic carbon atom but which exhibit very slow nonphotochemical oxidation when adsorbed onto fly ash. Also, 7,12-dimethylbenz[*a*]anthracene contains two benzylic carbon atoms but shows no tendency to decompose when adsorbed.

It is apparent from the foregoing results that PAH's adsorbed onto the surface of coal fly ash exhibit quite different chemical behavior from PAH's adsorbed onto other solid substrates, or present either as the pure solid or in solution. The net result is stabilization of PAH against photochemical oxidation on the one hand but promotion of spontaneous nonphotochemical oxidation for a limited class of compounds on the other.

These findings are of considerable importance for an environmental standpoint because they show the following:

1) The adsorptive association of PAH's with coal fly ash stabilizes these compounds against photochemical degradation, thereby preserving their potentially carcinogenic properties. However, a limited number of PAH's are quite rapidly converted to their corresponding ketones or quinones, whose toxic and carcinogenic potential is largely unknown (*6*, *7*). Fluorenone is normally encountered at much higher atmospheric concentrations than fluorene (*12*).

2) On the basis of the evidence presented herein, one would not expect to find diurnal variations in the concentration of PAH's present in the plume emitted from a coal-fired power plant. One would, however, expect significant differences in concentrations with distance from the point of emission and between PAH transformation rates in plumes derived from different power plants.

3) If, in fact, all PAH's containing a benzylic carbon atom are susceptible to nonphotochemical oxidation, as suggested herein, then the probable oxidative behavior of a large number of PAH's can be predicted (*6, 10*). For example, one would expect strongly carcinogenic compounds such as 9,10-dimethylbenz[*a*]anthracene and 3-methylchloranthene (*3*) to be rapidly oxidized and thus detoxified. Possible evidence in support of this prediction is afforded by the fact that these compounds, if found at all in atmospheric particles, are present at barely detectable levels.

The widespread belief that particulate association of PAH's will promote their photochemical conversion is not substantiated by experiment. Nevertheless, substantial nonphotochemical conversion of PAH's adsorbed on coal fly ash can occur and may result in significant detoxification of several particulate PAH's.

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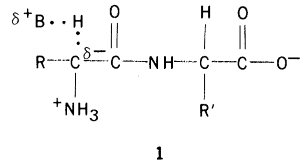
Racemization of Amino Acids in Dipeptides Shows COOH > NH_2 for Non-Sterically Hindered Residues

Abstract. *The relative rates of racemization for amino acid residues at the NH_2 and COOH ends of 37 different dipeptides were determined. In nine dipeptides containing alanine, leucine, phenylalanine, aspartic acid, and methionine, the amino acid residue racemized faster at the COOH-terminal position than at the NH_2-terminal position (COOH > NH_2). The sterically hindered amino acids isoleucine and valine showed NH_2 > COOH. Six proline dipeptides showed NH_2 > COOH. Intramolecular effects have been invoked to explain these surprising results.*

The significance of amino acid racemization and epimerization in biogeochemistry (geochronology and geothermometry) and paleobiology, as well as in peptide synthesis and the study of natural products, has been recognized in recent years. Several review articles have appeared (*1-5*). In polypeptides, racemization rates are reported to be altered by hydrolysis (*6*), which competes with racemization, complicating the study of racemization rates in peptides compared with those in free amino acids.

By employing optically active phases on a capillary gas chromatography column, we studied the racemization rates of eight amino acids, including isoleucine, in 37 different dipeptides. Unexpectedly, the dipeptides of alanine, leucine, phenylalanine, aspartic acid, and methionine, whether attached to a hindered or a nonhindered amino acid (valine and glycine, respectively), showed the COOH-terminal amino acid residues racemizing faster than the NH_2-terminal amino acid residues (Table 1). Emphasis is given these results because simple electrostatic theory predicts NH_2 > COOH. In nonproline dipeptides, only the sterically hindered amino acids isoleucine, valine, and serine showed NH_2 > COOH (Table 2). Proline, apparently, has a special effect. With proline dipeptides all amino acid residues showed NH_2 > COOH (Table 2), and the rates were faster at both ends with non-sterically hindered amino acids. All NH_2-terminal amino acid residues, including isoleucine and valine, racemized very rapidly in X-Pro dipeptides (33 to 53 percent D, Table 2). However, the sterically hindered amino acids isoleucine and valine racemized very slowly at the COOH-terminal position, particularly in Pro-X (~ 1 percent D, Table 2). Therefore, rate enhancement at NH_2 and rate retardation at COOH result in very high NH_2/COOH values for these sterically hindered amino acids. These data clearly show that position in the peptide, as well as amino acid structure, has a major effect on racemization and that steric hindrance affects racemization more at the COOH position than at the NH_2 position. Our results for isoleucine confirm those published recently by Kriausakul and Mitterer (*7*), who reported NH_2 > COOH in the epimerization of isoleucine in dipeptides of glycine, alanine, valine, tyrosine, and phenylalanine (Table 2). Because more of the amino acids racemize faster at the COOH position, the result NH_2 > COOH appears to be the exception rather than the rule. Serine falls in a class by itself. Its racemization was very fast at both positions, but its NH_2/COOH value was only slightly greater than 1.0 (1.2).

Racemization is generally considered to proceed through the removal of the α-methine hydrogen by base. Applying Neuberger's (*8*) mechanism, the transition state leading to the carbanion is an incipient carbanion (**1**) with varying C-H bond polarization. Stabilization of this incipient carbanion transition state controls the rate of racemization, and factors that alter the entropy or enthalpy of transition, $\Delta S^\ddagger$ or $\Delta H^\ddagger$, or both, affect the rate. At *p*H 7.6, at which this study was carried out, the dipeptide is principally in its zwitterion form. The $-{}^+NH_3$ group, through its electrostatic effect, would stabilize an adjacent incipient carbanion, while the $-CO_2{}^-$ group, through its inductive and field effects, would destabilize an incipient methine carbanion formed at the COOH-terminal position. Simple electrostatic theory predicts that



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