

Photooxidation of Anthracene on Atmospheric Particulate Matter

Abstract. Anthracene that has been dispersed into atmospheric particulate matter is photooxidized to an array of products reminiscent of oxidation by singlet oxygen in the solution phase. Photooxidation is a more important degradative pathway under ambient conditions than ozonation. Significant disappearance of anthracene also occurs by pathways not involving oxygenation.

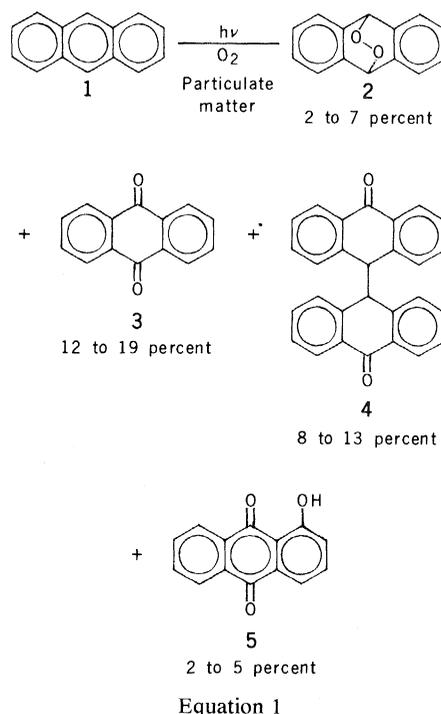
Although the nearly ubiquitous presence of polycyclic aromatic hydrocarbons (PAH) in atmospheric particulate matter is well established (1), the chemical details of their fate remain unknown. The reported sensitivity of organics in particulate samples to ultraviolet light (2) suggests that photooxidation may provide a significant decomposition pathway for such compounds. Oxygenated compounds have been shown, from solubility considerations, to account for major fractions (50 to 90 percent) of the total organics present in particulate matter (3), and these fractions have been shown to possess significant carcinogenicity in biological testing (4). Thus, if photooxidation can be shown to contribute significantly to the disappearance of PAH under conditions typically encountered by atmospheric particulate matter, then the common indices of potential danger (for example, the determination of PAH or benzo[a]pyrene concentrations in collected particulate) may seriously underestimate the potential carcinogenicity of such matter.

The complexity of the mixtures of compounds in neutral fractions (5) is multiplied when one analyzes the polar, oxygenated fractions. As a result, only a few oxygenated PAH derivatives have been identified (6). We felt that the best approach to characterizing possible photooxidation products in atmospheric samples would be to study the enrichment of a typical atmospheric sample with one or more PAH whose oxidative photochemistry is understood. Such enrichment would greatly simplify the determination of possible products formed under ambient photooxidative conditions. Accordingly, we have studied the photooxidation of anthracene (1) in enriched atmospheric particulate matter and have found that simple photooxidation is an important, but not exclusive, decomposition route.

Atmospheric particulate samples collected on glass-fiber filters from about 1500 m³ of air from two locations in Texas were enriched with anthracene by subliming a small sample (about 100 μ g) of anthracene onto the collected particulate matter. Anthracene, in the enriched samples, accounted for about 5 percent of the total benzene-soluble fraction. Each sample was divided into three

equal sections: the first section, the control, was stored in the dark at 0°C; the second, mounted in a secure support held approximately 3 m from ground level at a suburban location remote from heavy traffic or industry, was exposed to bright Texas sunshine for 4 days; and the third, similarly mounted, was shielded from light but exposed to atmospheric gases for the 4-day test period. The samples were extracted overnight with dry tetrahydrofuran and analyzed by reverse-phase, high-pressure liquid chromatography on μ Bondapak-C₁₈, as described elsewhere (5, 7). The effluent stream was simultaneously monitored at 280 and 340 nm by ultraviolet detectors and by a fluorescence detector (excitation at 290 nm; emission at 390 nm). The eluting peaks were identified by observing the relative absorption at the two ultraviolet monitoring wavelengths, by interrupting the column flow while a fraction was in the detector cell to quickly obtain a fluorescence spectrum or by coinjection of a standard sample of the suspected compound. Duplicate injections were reproducible to \pm 3 percent.

By comparison with the control sample, the samples exposed to the air but not to light remained essentially un-



changed over the test period. A trace peak corresponding in relative retention time to anthraquinone was discernible, but its small quantity precluded firm identification. The samples exposed to sunlight were dramatically altered. The anthracene peak was reduced to about 10 percent of its original (control) size. Nonenriched PAH also disappeared; that is, only about 15 percent of the original benz[a]pyrene peak remained after exposure to sunlight. The products in highest yield identified in the photooxidation extract are shown in Eq. 1, where the cited yields are based on the amounts of anthracene that disappeared. The listed ranges indicate fair reproducibility in the four samples examined. In addition, trace peaks corresponding in relative retention time to alizarin, anthrone, and bianthryl or the anthracene photodimer were detected but could not be unambiguously identified. At least four additional, unidentified (\geq 10 percent yield) products were also present.

Identification of products 2, 3, and 4 in the photooxidation mixture is suggestive of the participation of singlet oxygen in the photoconversion. Endoperoxide (2) has long been recognized as the product of solution-phase cycloaddition of 1 with singlet oxygen (8), and more detailed studies have shown that continued irradiation of 1 and 2 in solution ultimately leads to diones (3 and 4) (9). Although 3 can also be formed by ozonation of 1 (10), this dark reaction of anthracene is presumably a minor route to 3 under our atmospheric conditions since only a trace of 3 was detected in samples exposed to air but not to light. There is evidence for the formation of more highly oxidized anthraquinones by photooxidation (11), although 5 was not isolated in the earlier studies. Alternate photochemical routes to 2, 3, 4, and 5 are possible, the capture of triplet 1 by ground-state oxygen being an attractive one. Other mechanisms that use other oxidants are also conceivable routes to at least some of these photooxidized products. Pitts and his co-workers, for example, have shown that attack by NO₂ on 1 can lead to nitro derivatives (12), which can be photochemically converted to quinones (13).

Although mechanistic details are difficult to sort out in such a complex system, the adoption of PAH as potential sensitizers for singlet-oxygen formation is preceded (14), as is the possibility of heterogeneous, possibly catalyzed, gas-phase reactions and the sufficiency of ambient light interception in finely divided atmospheric particulates (15). Our results show that photooxidation of 1 can

occur on atmospheric particulate matter. The identified products, however, account for only about a third of the disappearance of 1. It is possible that, in addition to initiating oxidative paths, photochemical excitation can initiate polymerization pathways which lead to highly condensed systems (for example, soot), which are ultimately degraded by soil bacteria. We assume that, since other PAH can be oxidized by singlet oxygen (*I*6), photooxidative decomposition may possibly be general for at least some other PAH constituents of particulate matter. Since oxidation products can form in atmospheric samples, studies that evaluate carcinogenicity solely on the basis of PAH content will probably consistently underestimate carcinogenicity.

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References and Notes

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Atmospheric Burnup of the Cosmos-954 Reactor

Abstract. On 24 January 1978 the Russian satellite Cosmos-954 reentered the atmosphere over northern Canada. By use of high-altitude balloons, the atmosphere was sampled during 1978 up to an altitude of 39 kilometers to detect particulate debris from the reactor on board the satellite. Enriched uranium-bearing aerosols at concentrations and particle sizes compatible with partial burnup of the Cosmos-954 reactor were detected only in the high polar stratosphere.

The Russian satellite Cosmos-954 reentered the atmosphere at 55 to 67 km over northern Canada on 24 January 1978 (*1*). The reactor on board was assumed to be of the Romashka design—that is, a 40-kW (thermal) power plant containing as much as 50 kg of 90 percent enriched ²³⁵U (*2, 3*). Special flights in the High Altitude Balloon Sampling Program of the U.S. Department of Energy were made in 1978 up to 39 km to intercept any Cosmos-954 debris that might have ablated. On these flights and on routine flights, samples were collected on IPC-1478 filter papers. The identification and collection parameters of the filter papers from the special and selected routine flights are shown in Table 1.

Fractions of these filter papers with the scrim backing removed were analyzed for uranium isotopes by the Knolls Atomic Power Laboratory (KAPL) at the General Electric Company, Schenectady, New York (*4-7*); the results are reported in Table 2. The reported errors are estimates of analytical precision equivalent to 1 standard deviation (S.D.) of the total number of counts for each mass assignment or the deviation about the mean of duplicate measurements of a single solution as indicated. In 13 of 16 sets of duplicate isotopic measurements of identical solutions in this study, the duplicate analyses agreed with each other within 1 S.D. of the counting errors. The error of an isotopic analysis, determined with uranium standards provided by the National Bureau of Standards, is less than 1 percent.

The analytical precision of the measurement of the total uranium in a filter fraction is about ±0.5 percent. In correcting the fractional data to the value for the whole filter, a constant weight of the appropriate filter size was assumed; this could vary by about ±5 percent. Therefore, a ±5 percent error is applied to all results in the last column of Table 2, except when the standard deviation of duplicate analyses is larger.

The six blank filters in Table 2 exhibit an enrichment in ²³⁵U over natural uranium of 0.789 ± 0.070 percent (mean ± 1 S.D.). This enrichment probably occurred during the manufacture of the paper, possibly through use of a reagent such as HNO₃, which routinely shows

higher ²³⁵U atom percentages than natural uranium.

Considering the behavior of earlier radioactive tracers (*8, 9*), we believe that filters 3739, 3744, and 3763 sampled regions of the stratosphere where debris from a Cosmos-954 burnup should not have been present. As expected, these filters have ²³⁵U atom percentages similar to the mean for the blank filters. Therefore, in examining the exposed filters in this study for the presence of Cosmos-954 debris, we had only to consider the departures in their isotopic composition from that of the blank filters. Filter 3751 also fits this description, although before launch we were not sure whether it would intercept debris from a possible Cosmos-954 burnup.

Filters 3747 and 3765 were recovered from the region with the highest probability of containing particulates from such an event, and both exhibited a marked increase in ²³⁵U. We believe that interception of ablated particles from the reentry of Cosmos-954 is the only plausible cause of this increase.

To calculate the amount of Cosmos-954 uranium in these filters, we can write for each isotope an equation of the form

$$A_C x + A_B(N - x) = A_F N \quad (1)$$

where *A* is the atom percentage of that isotope; subscripts B, C, and F refer to background, Cosmos-954, and filter, respectively; *x* is the total number of uranium atoms from Cosmos-954 in the filter; and *N* is the total number of uranium atoms from all sources in the filter. Until mass isotopic data for the Cosmos-954 uranium are available, we must assume its composition in order to apply Eq. 1. It was assumed that the Cosmos-954 reactor was of the Romashka design and was fueled with 90 percent enriched ²³⁵U. We further assume that this uranium is similar in composition to the 90 percent enriched ²³⁵U available from the National Bureau of Standards (*10*). This assumed composition of the Cosmos-954 uranium, rounded off to the nearest 0.5 percent, is shown at the bottom of Table 2. The ²³⁵U and ²³⁸U percentages should be within 5 percent of the true values for Cosmos-954, but the ²³⁴U and ²³⁶U values may be in error by as much as a factor of 2.

Substituting the data in Table 2 into