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Products of Benz[*a*]anthracene Photodegradation in the Presence of Known Organic Constituents of Atmospheric Aerosols

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Little is known about atmospheric reaction mechanisms or products of polycyclic aromatic hydrocarbons associated with aerosol particles. Products of benz[*a*]anthracene photodegradation were determined after irradiation of benz[*a*]anthracene in the presence of three common constituents of atmospheric aerosols previously found to accelerate benz[*a*]anthracene photodegradation; 9,10-anthraquinone, 9-xanthone, and vanillin. Irradiation was carried out in toluene, benzene, and benzene-d_6, and products were analyzed by GCMS, FTIR, and NMR. Among the major tentatively identified products were benz[*a*]anthracene-7,12-dione, phthalic acid, phthalic anhydride, and 1,2-benzenedicarboxaldehyde. Evidence for production of polycyclic dicarboxylic acids and dialdehydes was also obtained. Product distribution was strongly influenced by solvent effects and dissolved aerosol constituents. The results suggest that products of PAH photodegradation in atmospheric aerosols are likely to be quite complex and strongly influenced by the organic composition of PAH-containing aerosol particles.

Introduction

Results from outdoor chamber studies indicate that under appropriate conditions PAHs associated with combustion aerosols from a variety of sources decay rapidly in sunlight (*1*). Laboratory studies have suggested that PAH photodegradation rate is likely to be strongly influenced by the organic composition of the aerosol (*2*) and that the mechanism of PAH photodegradation in the presence of methoxyphenols, abundant wood smoke constituents, may involve a phenoxy radical intermediate (*3*). In a previous paper, we described the photodegradation of benz[*a*]anthracene in the presence of 15 different organic compounds identified in atmospheric particulate matter or combustion sources (*4*). Decay of benz[*a*]anthracene was accelerated by certain methoxyphenols, polycyclic aromatic ketones and quinones, substituted furans, and substituted benzaldehydes. The results suggested that in some cases singlet oxygen and in other cases free radicals might be involved as reaction intermediates, but that further study was required to understand the reaction mechanisms. In this paper, we extend that work to identification of reaction products by reporting the determination of photodecay products of benz[*a*]anthracene in the presence of vanillin, 9-xanthone, and 9,10-anthraquinone, three of the constituents previously observed to accelerate the photodegradation.

TABLE 1. Elution Volumes and Solvent Ratios in Column Separation

	solvent ratio			
fraction	hexane	$MeCl_2$	acetone	elution vol (mL)
1	1.0	0	0	30
2	0.75	0.25	0	30
3	0.5	0.5	0	30
4	0.25	0.75	0	30
5	0	1.0	0	30
6	0	0.75	0.25	30
7	0	0.5	0	30
8	0	0	1.0	30

Experimental Section

Irradiation Experiments. The photodegradation experiments were carried out in a photochemical turntable reactor (Ace Glassware, Vineland, NJ) equipped with a 450-W medium-pressure mercury arc lamp in a borosilicate immersion well (*3, 4*). Although this system does not exactly emulate the solar irradiation spectrum, it does filter out high-energy UV bands not encountered in the troposphere with a cutoff greater than 300 nm. The entire apparatus was submerged in a 70-L water bath, and the temperature was maintained at 16 °C by pumping the water through an ice bath at 75 mL/min. Samples were irradiated in 13 mm × 100 mm fused quartz test tubes (Ace Glassware). The concentration of benz[*a*]anthracene and co-solutes was 1×10^{-3} M. Each solution was irradiated for 5 h.

Benz[*a*]anthracene (99% Aldrich) was irradiated using vanillin (99%, Aldrich), 9,10-anthraquinone (97%, Aldrich), and 9-xanthone (99%, Aldrich) as co-solutes as well as in the absence of a co-solute. Each of these solutions was irradiated in three different solvents, optima grade toluene (Fisher T291-4), benzene (EM Science BX0220-5), and benzene-d_6 (Aldrich, 99.5 atom % D).

Product Analysis. After completion of the irradiation experiments, solutions were concentrated under a stream of nitrogen, and each solution was fractionated on a silica gel column (1.5 cm i.d., $l = 30$ cm, BIO-SIL A, 100−200 mesh, supplied by Bio-Rad, activated at 140 °C for 24 h). The elution solvent was changed progressively from *n*-hexane through methylene chloride to acetone. Table 1 shows the solvent ratios and elution volumes of the sequential fractions eluted. After fractionation, the collected fractions were evaporated under a stream of nitrogen and refrigerated until analysis.

Irradiation products were analyzed by gas chromatography/mass spectrometry using a Hewlett-Packard 5890 gas chromatograph interfaced to a Hewlett-Packard 5971A mass selective detector. Chromatography was carried out on a J&W, 30 m, 0.32 mm i.d., DB-5 column with a 0.25-μm film thickness. A Hewlett-Packard 7673 autoinjector was used for all injections. The temperature program was 120 °C for 2 min, 120 to 250 °C at 15 °C/min, 250 to 300 °C at 8 °C/min and hold for 3 min at 300 °C. Mass spectra were obtained by scanning from 50 to 550 amu at 1.5 scans/s.

NMR spectra were obtained with a Varian XL-400 NMR spectrometer using $CDCl_3$ as the solvent. Chemical shifts were referenced directly to tetramethylsilane as an internal standard. One-dimensional proton spectra were obtained with a pulse width of 30 deg and a line width of 5299 Hz at ambient temperature. $^{1}H-^{13}C$ two-dimensional NMR spectra were obtained at 90 deg with a spectral width of 2541.9 Hz. An acquisition time of 0.118 s and a relaxation delay of 1.0 s were used. Infrared spectra were obtained using absorbance

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TABLE 2. Tentative Product Identifications

I	7,12-benz[*a*]anthracenedione
II	phthalic acid
III	phthalic anhydride
IV	1,2-benzenedicarboxaldehyde
V	2,3-napththalenedicarboxylic acid/anhydride
VI	phenanthrene/anthracene dicarboxaldehyde
VII	dialdehyde derivative
VIII	7,12-dihydrobenz[*a*]anthracene
IX	unknown
X	10-benzyl-10-hydroxyanthracen-9-one
XI	bibenzyl
XII	benzyl alcohol
XIII	1,2-diphenylethanol

mode with a Mattson Polaris TM infrared spectrometer, and samples were prepared in KBr pellets.

Results

After irradiation, a yellowish-orange precipitate was found whenever benzene and benzene-d_6 were used as solvents. No precipitate formed after irradiation of toluene solutions. The solid product would not dissolve in a small amount of methylene chloride used for injection onto the fractionation column, but it was possible to dissolve it in acetone for that purpose. This suggests that the precipitate may consist of highly oxidized compounds such as aromatic ketones, acids, and anhydrides.

Tentative identifications of irradiation products are listed in Table 2. Product I was tentatively identified as 7,12-benz[*a*]anthracenedione by matching its mass spectrum to the NIST library spectrum. Other tentatively identified products included a number of oxygenated monocyclic (II−IV) and polycyclic (V−VII) aromatic compounds, dihydrobenz[*a*]anthracene (VIII), one unidentified product (IX), and several compounds that are most likely solvent irradiation products (X−XIII). Their structures are shown in Figure 1, and the distribution of products among the irradiated solutions are presented in Table 3. For compounds V and VI, other structures are likely, and alternatives V′ and VI′ are also shown in Figure 1.

7,12-Benz[*a*]anthracenedione (I) was the only product identified in all 12 of the solutions irradiated. It was generally found in the fourth, fifth, or sixth fraction of Table 1. Its mass, FTIR, and NMR spectra are given in Figure 2. The mass spectrum matches that of the NIST library spectrum of 7,12-benz[*a*]anthracenedione with a 98% fit. The base peak at 258 amu corresponds to the molecular weight of a benz[*a*]anthracenedione. A prominent molecular ion peak is also characteristic of aromatic ketones. Other prominent peaks at 230 and 202 amu correspond to the loss of one and two carbonyl groups, respectively. The most reactive sites of benz[*a*]anthracene are the 7 and 12 positions, so the reaction product is most likely 7,12-benz[*a*]anthracenedione.

The NMR spectrum exhibits a complex splitting pattern characteristic of protons on substituted aromatic hydrocarbons, with a number of peaks between 7.7 and 8.5 ppm. The doublet between 9.7 and 9.8 ppm probably corresponds to the proton at the 1 position, which is shifted downfield due to its proximity to the carbonyl oxygen at the 12 position.

The FTIR spectrum also supports the identification of compound I as a 7,12-benz[*a*]anthracenedione. The absorption bands at 1460 and 1589 cm^{-1} are typical of aromatic C−C ring stretch. The absorption band at 1666 cm^{-1} is consistent with the carbonyl stretching for a quinone. The absorption bands at 1278 and 1309 cm^{-1} are probably due to bending vibration of carbon−carbon bonds between the carbonyl carbon and adjacent carbon atoms. The small band at 1774 cm^{-1} is probably an anhydride impurity.

Oxygenated aromatic compounds (II−VII) were found in several of the irradiated solutions. Typical examples of mass spectra of compounds III, IV, V, and VII are presented in Figure 3. It was not possible to distinguish between phthalic acid (II) and phthalic anhydride (III) by GCMS using the splitless injector because phthalic acid is converted to phthalic anhydride under the conditions used. Consequently, a mass spectrum of phthalic acid was not obtained. However, both compounds were identified as products after irradiation by their NMR spectra. In Table 3, the identification of phthalic acid and phthalic anhydride as products is based on their NMR spectra.

At least one of these two compounds was found after irradiation in all benz[*a*]anthracene solutions in benzene or benzene-d_6. Concentrations were highest in benzene-d_6. However, they were found in toluene solutions only when vanillin was present and only at low concentrations. Compound III eluted between the fourth and sixth fractions, and compound II eluted between the sixth and eighth fractions. This is consistent with expected elution order for an anhydride and a dicarboxylic acid.

Typical NMR and FTIR spectra of compounds II and III are provided in Figure 4. In this case, both spectra were obtained after irradiation of benz[*a*]anthracene in the presence of 9-xanthone in deuterated benzene. In the NMR spectra, both compounds are present as relatively minor impurities in the presence of high concentrations of 9-xanthone. Only the aromatic region of each spectrum is shown, and the phthalic acid and phthalic anhydride spectra each appear as small clusters of peaks between much larger peaks corresponding to 9-xanthone. In each spectrum, characteristics of a complex disubstituted monoaromatic compound can be observed, with aromatic protons between 7.9 and 8.1 ppm for compound II and between 7.6 and 8.0 ppm for compound III.

In the FTIR spectrum of compound III, the absorption bands at 1774 and 1851 cm^{-1} are consistent with symmetric and asymmetric C=O stretch for a conjugated anhydride. Bands also appear at 1147, 1240, and 1346 cm^{-1}, corresponding to C−O stretch, and at 1600−1450 cm^{-1}, corresponding to aromatic C=C stretch.

Compound IV was found when benz[*a*]anthracene was irradiated in the presence of 9,10-anthraquinone or 9-xanthone with either benzene or benzene-d_6 as a solvent. It was not detected after irradiation of benz[*a*]anthracene in any of the toluene solutions nor in the presence of vanillin in any of the solvents used. It was detected when benz[*a*]anthracene was irradiated without a co-solute in benzene, but not in benzene-d_6 or toluene.

Compound IV is tentatively identified as a 1,2-benzenedicarboxaldehyde, based on a molecular ion peak at 134 amu,

TABLE 3. Products Identified in Each Irradiation

	solvent		
co-solute	benzene-d_6	benzene	toluene
no co-solute	I, II, III, V	I, III, IV, IX	I, IX, XII
9,10-anthraquinone	I, II, III, IV	I, II, III, IV	I, X, XI, XII
9-xanthone	I, II, III, IV, VII, IX	I, III, IV, VII, IX	I, IX, XI, XII, XIII
vanillin	I, II, III, VI, VII, VIII	I, III, VI, VII, VIII, IX	I, III, VII, VIII, IX, XI, XII

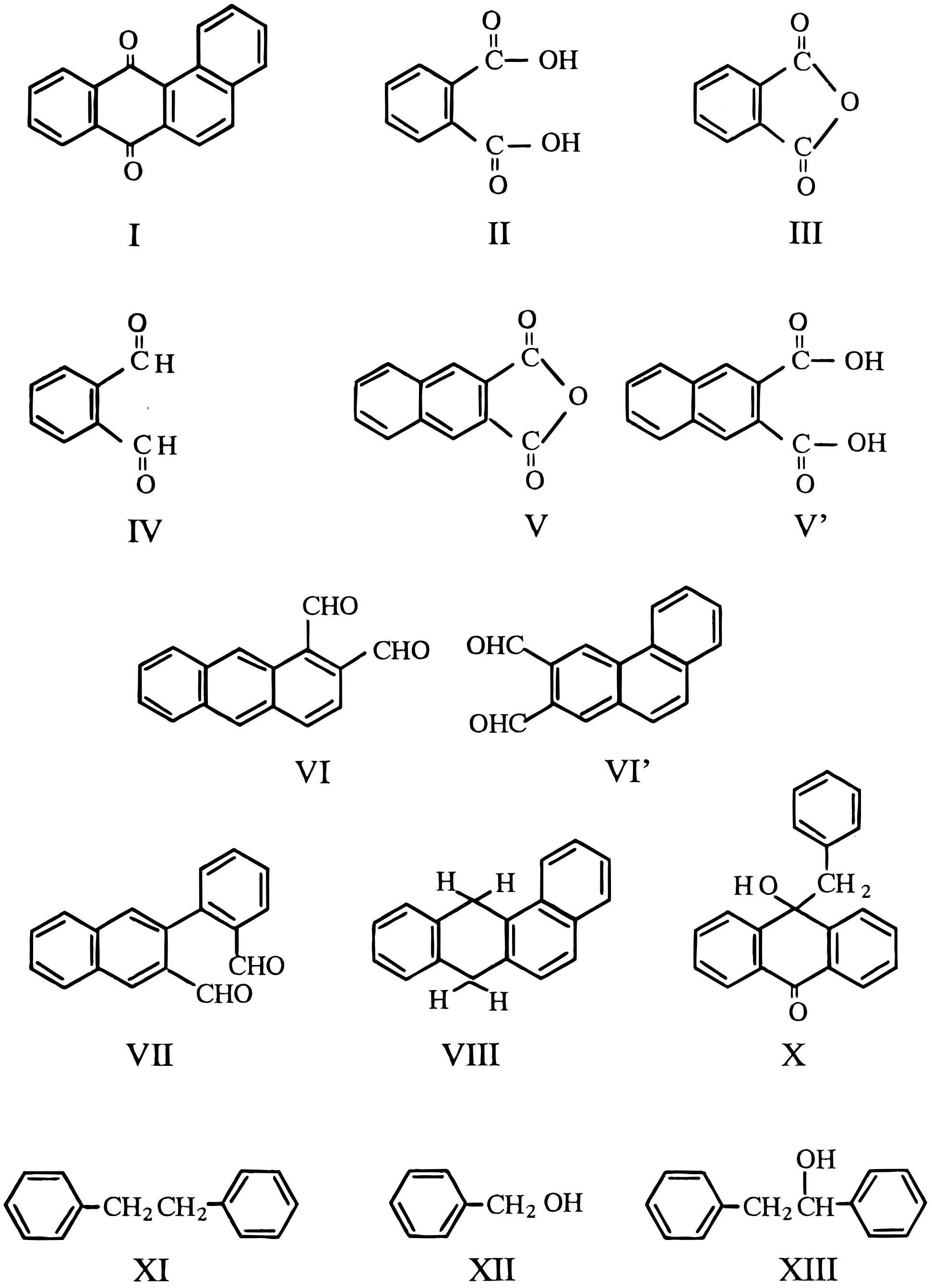

FIGURE 1. Structures of tentatively identified products.

a base peak at 105 amu corresponding to the loss of one aldehyde group, and prominent peaks at 77 and 51 amu corresponding to the phenyl ion and $C_4H_3^+$, both diagnostic of aromatic systems. A 92% fit was observed for comparison to the NIST library. It was not observed as a product in toluene solutions or in the presence of vanillin, probably because of its rapid photoreaction when a hydrogen source is present.

Compound V was only observed before elution over silica gel and apparently did not survive the fractionation procedure. It was only observed with certainty after irradiation of benz[*a*]anthracene only in benzene-d_6. However, analysis before fractionation was not generally carried out, so it may have also been produced under other conditions. In this case, it appeared to be present at much lower levels than phthalic acid. Based on its base peak of $m/e = 126$, molecular ion peak at $m/e = 198$, and a prominent peak at $m/e = 154$, it is tentatively identified as 1,2-naphthalic anhydride.

Compound VI was only produced when benz[*a*]anthracene was irradiated in the presence of vanillin in either benzene or benzene-d_6. A complete mass spectrum of compound VI could not be obtained because it appeared as only a trace constituent in an unresolved portion of the total ion chromatogram. Its tentative identification is based on a well-defined peak on the ion chromatogram at $m/e = 234$, which corresponds to the molecular weight of phenanthrene- or anthracenedicarboxyaldehyde, both of which are possible products of benz[*a*]anthracene decay.

Compound VII was found after irradiation of benz[*a*]anthracene in all solutions that contained vanillin as a cosolvent and in the presence of 9-xanthone in benzene and benzene-d_6. A molecular ion peak of 260 amu in Figure 3D corresponds to that expected for the ring-opening dialdehyde product of benz[*a*]anthracene. A base peak at 231 amu and another prominent peak at 202 amu corresponding to loss of one and two aldehyde groups, respectively, further support this interpretation. It can be concluded that irradiation of benz[*a*]anthracene under these conditions appears to produce several oxygenated ring-opening products.

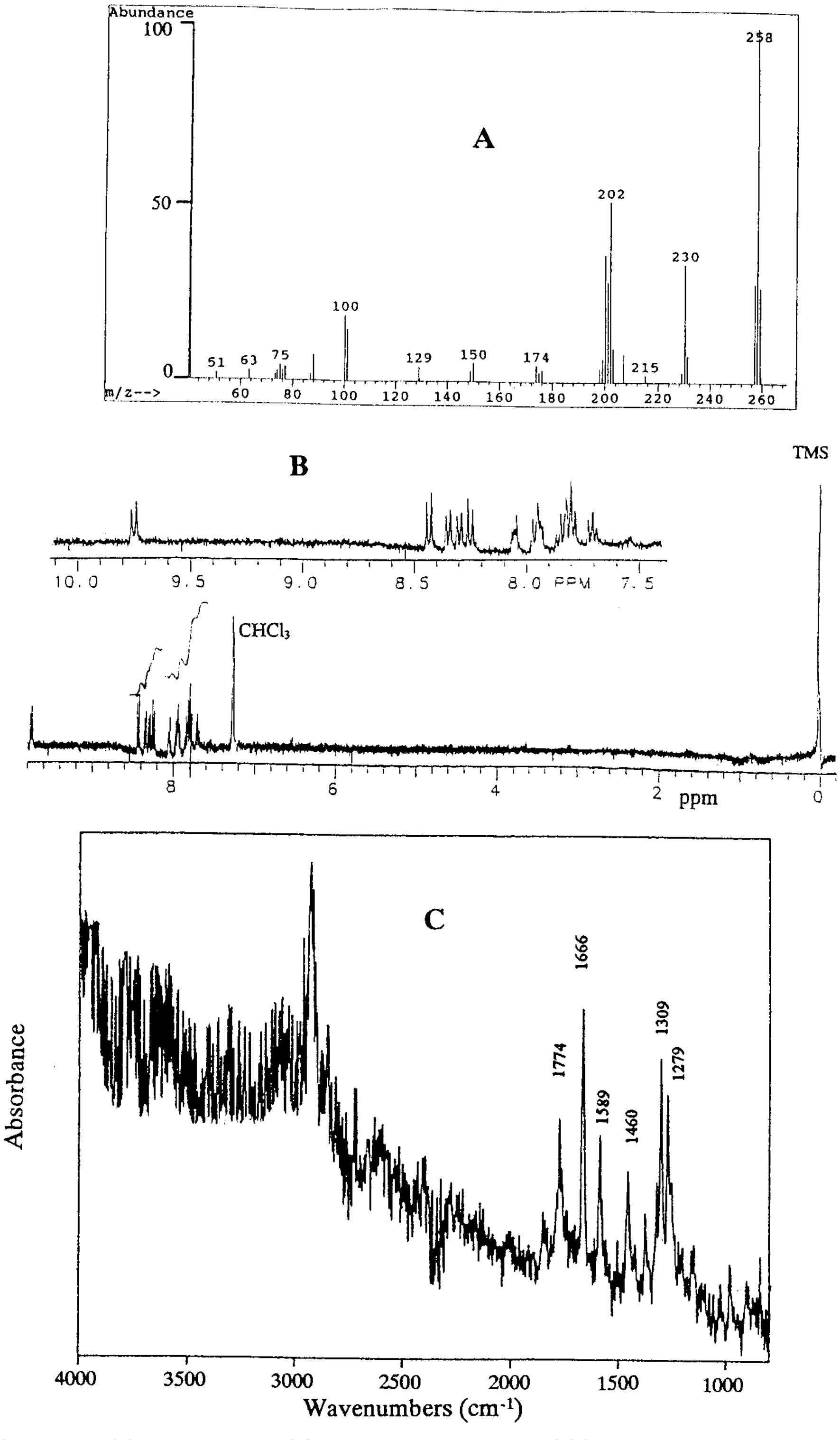

FIGURE 2. Compound I spectra: (A) mass spectrum, (B) proton NMR spectrum, and (C) FTIR spectrum.

A variety of additional products were also identified. Compound VIII was produced after irradiation of benz[*a*]anthracene in the presence of vanillin in each of the solvents used, but only in amounts barely above the noise level. It was not detected in any of the solutions that did not contain vanillin. It was generally found in the first fraction of Table 1, making it the least polar product identified. It also eluted earlier in the gas chromatogram than benz[*a*]anthracene. The mass spectrum is relatively simple, with a molecular ion peak at 230 amu and prominent M − 1 and M − 2 peaks. On the basis of this mass spectrum and the GC and silica column elution characteristics, compound VIII is tentatively identified as 7,12-dihydrobenz[*a*]anthracene.

Compound IX generally appeared as a product of benz[*a*]anthracene irradiation in benzene and toluene except in the presence of 9,10-anthraquinone. It was also detected after benz[*a*]anthracene irradiation in the presence of 9-xanthone in benzene-d_6. It eluted in the sixth fraction of Table 1. From its NMR spectrum, a complex splitting pattern was observed between 6.8 and 7.8 ppm, indicating that compound IX is a substituted aromatic compound. The only other spectral features were two singlets at about 5 ppm, which may indicate an olefinic or disubstituted aliphatic substituent. No acid or hydroxyl functionality were indicated in the FTIR spectrum, but from the band at 1737 cm^{-1} a carbonyl group is evident. Compound IX appears to be a carbonyl-substituted

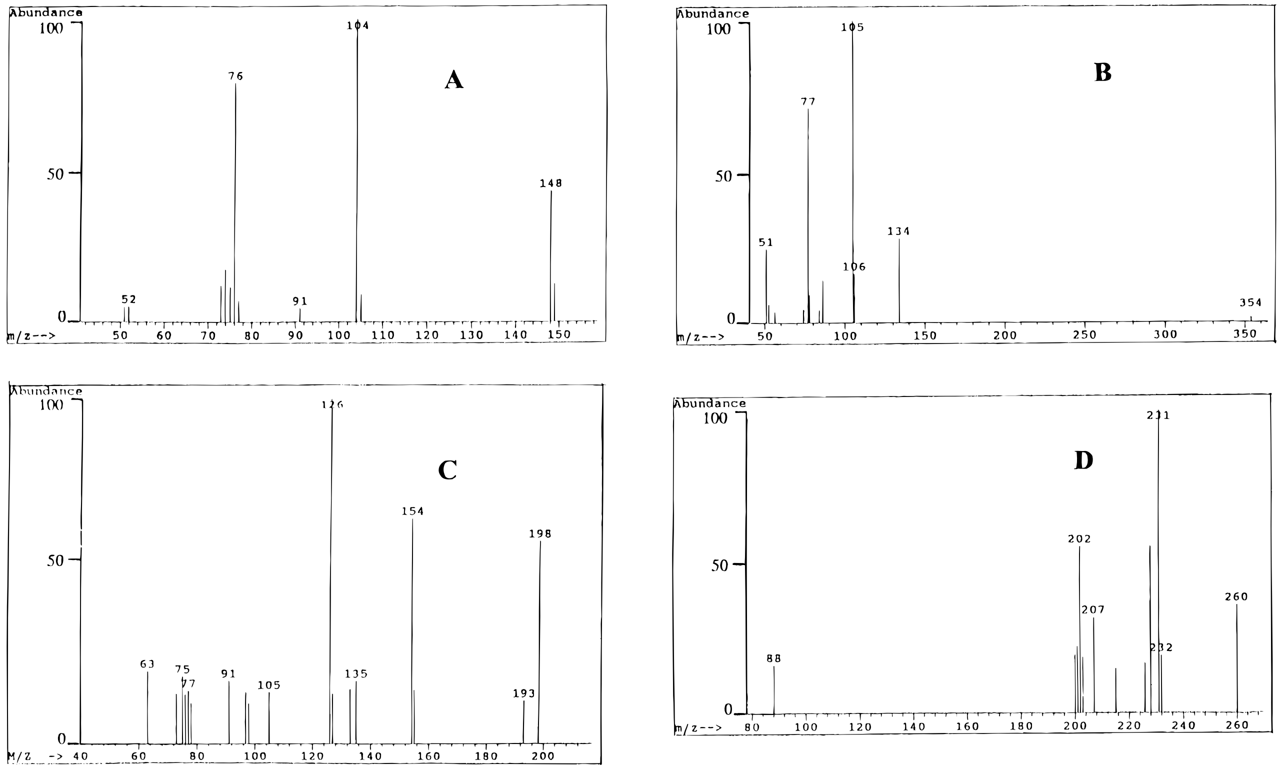

FIGURE 3. Mass spectra: (A) compound III, (B) compound IV, (C) compound V, and (D) compound VII.

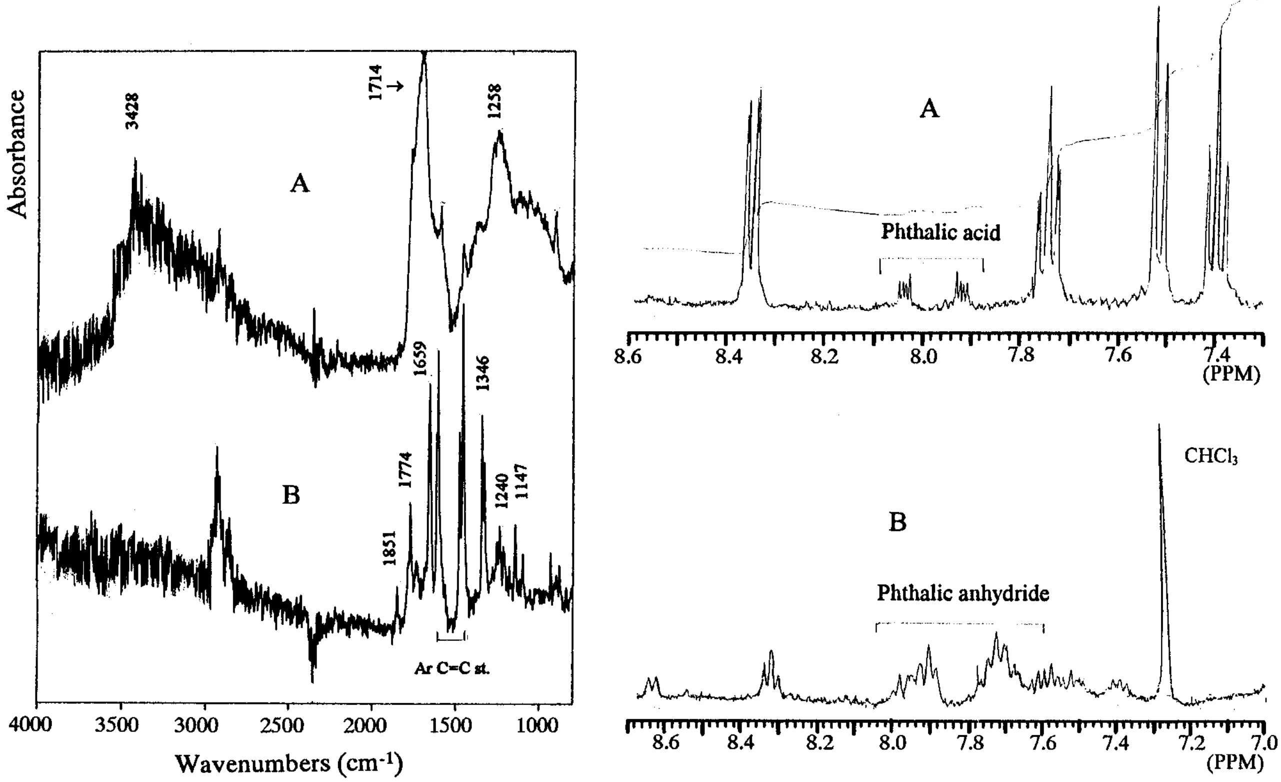

FIGURE 4. Proton NMR and FTIR spectra of (A) compound II and (B) compound III.

aromatic compound with a molecular weight greater than 259, but little more can be concluded.

The remaining products from Table 2 are most likely formed from solvent reactions rather than from benz[*a*]anthracene decay. Although they would not be expected to form in atmospheric aerosols, they provide insight into the benz[*a*]anthracene decay mechanism in the presence of other aerosol constituents. The most interesting of these is compound X, which was observed only after irradiation of the toluene solution containing benz[*a*]anthracene and 9,-10-anthraquinone. Its mass spectrum showed a molecular ion peak at m/e = 300, with a base peak at m/e = 209 corresponding to the loss of the benzyl radical.

One- and two-dimensional NMR spectra of compound X are shown in Figure 5. In the one dimensional NMR of Figure 5A, a complex aromatic splitting pattern between 6.8 and 8.1

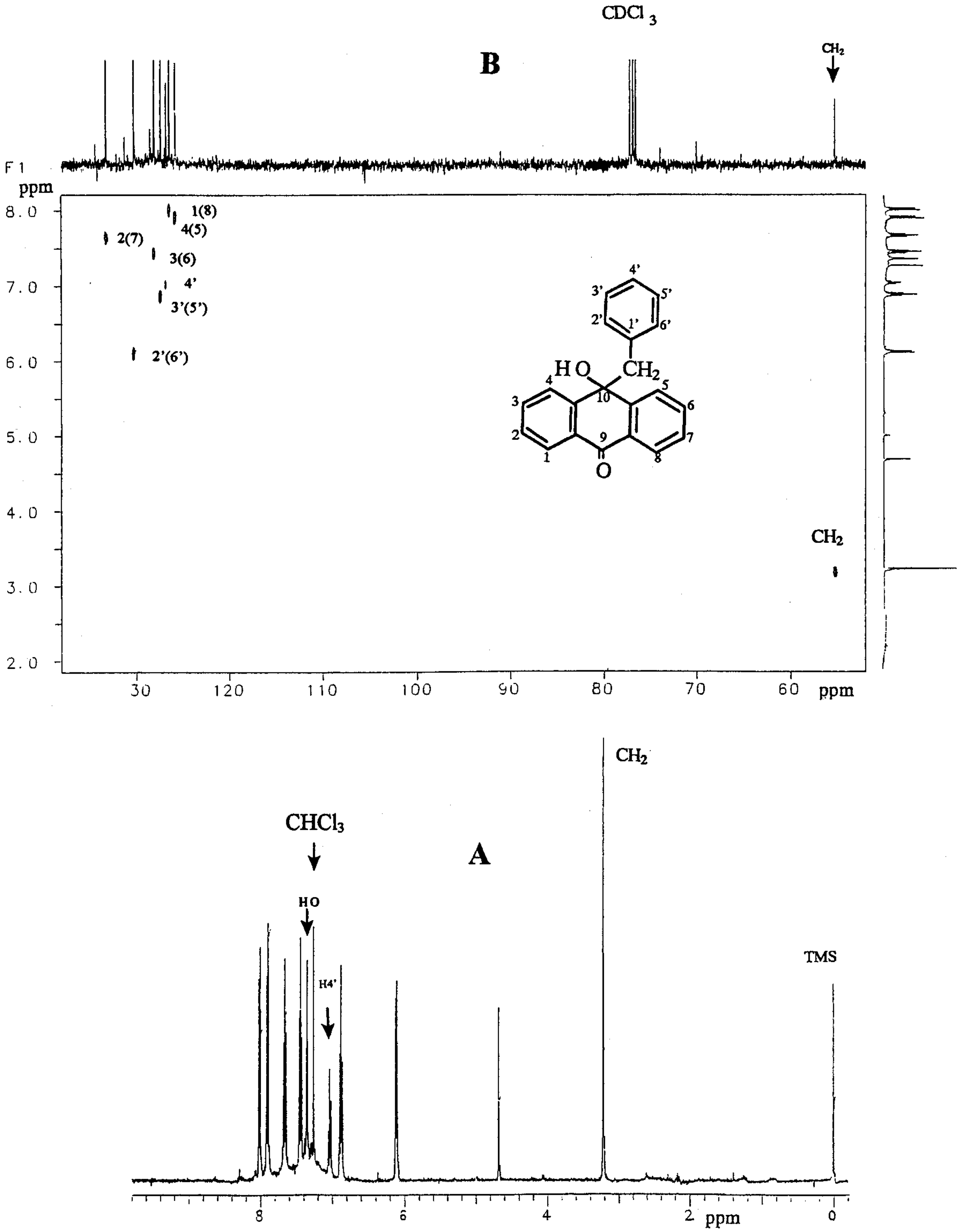

FIGURE 5. Compound X NMR spectra: (A) one-dimensional proton NMR spectrum and (B) high field two-dimensional COSY NMR spectrum based on $^{1}H-^{13}C$ hetero nuclei correlation.

ppm and a singlet at 3.2 ppm corresponding to the methylene hydrogens are observed. The peak at 6.1 ppm corresponds to carbon 2′(6′), and the peak at 4.6 ppm is apparently an impurity. Assignments for the two-dimensional NMR are given in Figure 5B. Based on these spectra, compound X is tentatively identified as 10-benzyl-10-hydroxyanthracen-9-one. This structure is also supported by the FTIR spectrum, which exhibits bands at 3600−3000 cm^{-1}, corresponding to O−H stretch and at 1660 cm^{-1} corresponding to C=O stretch.

Compound XI generally eluted in the second fraction of Table 1, indicating that it was less polar than most of the other products. It was tentatively identified as bibenzyl because of its molecular ion peak at 182 amu, base peak at 91 amu corresponding to cleavage of the aliphatic C−C bond, and prominent peak at 77 amu corresponding to the phenyl ion. It matched the NIST library spectrum of bibenzyl with a fit of 83%. Compound XII eluted in the fifth or sixth fraction of Table 1, indicating that it was more polar than compound XI. It was tentatively identified as benzyl alcohol because of its molecular ion peak at 108 amu, phenyl ion peak at 77 amu corresponding to cleavage of the C−C bond next to the oxygen atom, and a prominent peak at 51 amu. Its mass spectrum matched that of the NIST library spectrum for benzyl alcohol with a 92% fit. Compound XIII was tentatively identified as 1,2-diphenylethanol, in agreement with an 80% fit when matched to the NIST library spectrum of this compound.

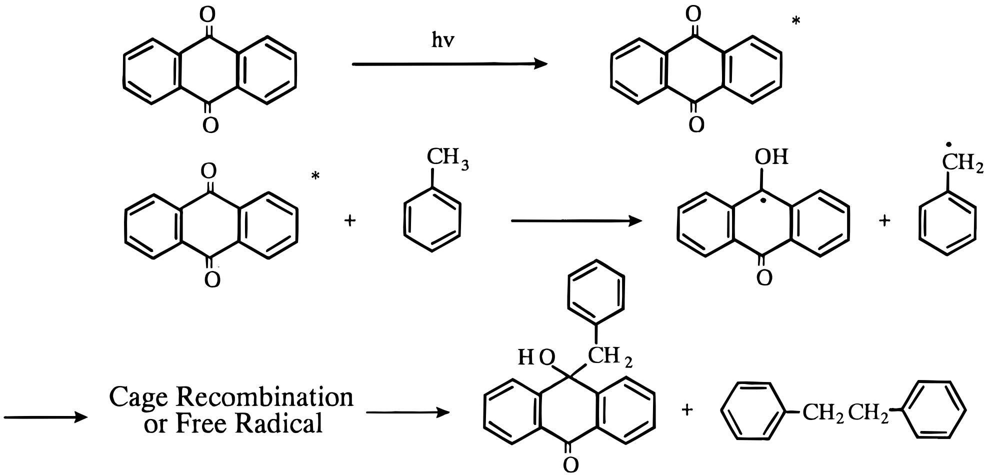

FIGURE 6. Photoreduction of 9,10-anthraquinone in toluene.

This compound exhibited a very small molecular ion peak at 198 amu and cleavage of the C−C bond next to oxygen, leading to benzyl and hydroxybenzyl fragments.

Discussion

In spite of significant research efforts in the study of atmospheric decay of PAHs, little is known concerning their atmospheric decay products with the exception of a few mutagenic nitro-subsitituted (*5*−*10*) and oxygenated (*11*−*13*) PAHs produced in relatively low yield. It has proved difficult to account for the bulk of benz[*a*]anthracene loss after irradiation by UV light in laboratory experiments or by sunlight in smog chamber studies. This is probably due at least in part to difficulties in using GCMS to analyze highly oxygenated or polymeric products likely to be produced by photodegradation of PAHs.

Of the products observed in this work, 7,12-benz[*a*]anthracenedione stands out as a ubiquitous product of benz[*a*]anthracene photodegradation detected under all irradiation conditions investigated. Previous smog chamber studies suggest that significant decay of benz[*a*]anthracene in sunlight can occur under typical atmospheric conditions (*13*). 7,12-Benz[*a*]anthracenedione has also been found in particulate matter under photochemical smog conditions (*14*). Compound IX, another carbonyl-containing compound, was also detected in many of the experiments. Formation of ketones and quinones from irradiation of anthracene associated with atmospheric particulate matter has been observed (*11*).

The tentative identification of phthalic acid, phthalic anhydride, and 1,2-benzenedicarboxaldehyde are important indications of benz[*a*]anthracene ring cleavage products. There are many known examples of aromatic ring cleavage involving free radical or singlet oxygen intermediates. It is well known that radical addition to atmospheric monocyclic aromatic compounds leads to ring-opening products, and a variety of ring-opening mechanisms based on hydroxyl radical addition have been proposed (*15*−*20*).

PAHs are also known to undergo aromatic ring cleavage when exposed to ozone (*21, 22*), irradiated on silica surfaces (*23*), exposed to singlet oxygen (*24*), and exposed to hydrogen peroxide and UV light in advanced oxidation processes for water treatment (*25*). Thus, the observation of ring cleavage products observed in this work is consistent with this free radical or singlet oxygen attack suggested by the reaction kinetics described in a previous work (*4*).

Phthalic acid has also been observed in atmospheric samples (*14, 26, 27*), and it has been suggested that the samples are formed from atmospheric reactions of PAHs and ozone (*26*). Photochemical formation of phthalic acid from naphthalene and substituted naphthalenes has also been observed on silica surfaces (*23*) and in water in the presence of hydrogen peroxide (*25*). Phthalic acid, phthalic anhydride, and 1,2-benzenedicarboxyaldehyde have been observed as products of the reaction of ozone with naphthalene or alkylnaphthalenes in solution (*28*−*30*). The observation of phthalic acid and related compounds from benz[*a*]anthracene photodegradation in the presence of organic aerosol constituents suggests that other mechanisms besides ozone attack can also lead to the production of phthalic acid and related compounds from benz[*a*]anthracene and possibly from other PAHs. Polycyclic aromatic dicarboxylic acids have also been found in atmospheric particulate matter (*27*).

Hydro-substituted PAHs, including 7,12-dihydrobenz[*a*]anthracene, have previously been identified in ambient air. Lao et al. were the first to identify them and noted that they accounted for approximately 15% of their total measured PAH fraction (*31*). Cautreels and Van Cauwenberghe (*27*) also identified several hydro-PAH derivatives in ambient air, including dihydro derivatives of benzo[*c*]fluorene and benzo[*c*]phenanthrene, and reported a chromatographic peak corresponding to a mixture of 7,12-dihydrobenz[*a*]anthracene and dihydrochrysene.

The assignment of compound X as 10-benzyl-10-hydroxyanthracen-9-one can be made with more confidence than assignments for any of the other products. It is most likely the asymmetric radical recombination product of the reaction scheme in Figure 6. A symmetric recombination product, bibenzyl, was also tentatively assigned to compound XI, as indicated in Table 3. The other symmetric product is unlikely to form because of steric hindrance. These products are consistent with a free radical reaction initiated by hydrogen abstraction from the solvent by excited state 9,10-anthraquinone.

Compounds XI, XII, and XIII in Table 1 are solvent reaction products that are most likely produced by hydrogen transfer from toluene solvent to excited state triplet carbonyl compounds. As described earlier, compound XI was tentatively identified as bibenzyl. This was found in toluene in all cases when a co-solute was present, but was not observed as a reaction product when benz[*a*]anthracene was irradiated in toluene in the absence of a co-solute. Since bibenzyl is indicative of a hydrogen transfer reaction, the results suggest that 9,10-anthraquinone, 9-xanthone, and vanillin all initiate a hydrogen transfer reaction in toluene, which results in the formation of bibenzyl. Bibenzyl formation was also observed after irradiation in toluene of several other compounds that appeared to accelerate benz[*a*]anthracene photodegradation (*4*). Compound XII, benzyl alcohol, appeared to be produced in the greatest abundance in the presence of 9-xanthone in toluene. Its formation also probably involves hydrogen abstraction from toluene to produce the benzyl radical. It is possible that oxygen then reacts with the benzyl radical to form benzyl alcohol. Compound XIII, tentatively identified as 1,2-diphenylethanol, is probably formed through a similar process.

At least two mechanisms appear to be operative in these irradiation experiments. The first mechanism apparently results in the production of phthalic acid (II) and other ring-opening products (III-VII). At least some of these products were observed whenever benzene or benzene-d_6 was used as the solvent, and their concentrations were highest in benzene-d_6. None of these products were observed in toluene solutions, except in the presence of vanillin. It is possible that this mechanism involves singlet oxygen addition to the aromatic ring. This is a reasonable ring-opening reaction process for unsubstituted aromatic compounds like benz[*a*]anthracene. Also singlet oxygen has a longer lifetime in benzene-d_6, and the singlet oxygen reaction is not expected to be competitive in toluene because toluene is a strong hydrogen donor. Similar products have been observed for phenanthrene, anthracene, acenaphthylene, and 1-methoxynaphthalene photodegradation in experiments in which singlet oxygen was directly observed (*32*−*35*).

In the second mechanism, several solvent products (X−XIII) containing a benzyl moiety are formed. At least one of these products was observed whenever toluene was used as the solvent. The mechanism probably involves hydrogen abstraction from the solvent by carbonyl-substituted aromatic compounds, leading to radical formation. It has been shown that the benz[*a*]anthracene decay rate is related to bibenzyl formation rate (*4*), but it is not clear whether benz[*a*]anthracene then decays by subsequent radical addition or some other process. In any case, its decay does not appear to lead to ring-opening products.

Apparently, the first mechanism is most important in benzene and benzene-d_6, and the second mechanism is most important in toluene. The observation of a precipate after all irradiations in the presence of each of the co-solutes in benzene-d_6 and benzene but not in toluene also suggests that different mechanisms are responsible for benz[*a*]anthracene decay in the different solvents.

Previous results from kinetic experiments in toluene were also consistent with a mechanism involving hydrogen abstraction from the solvent (*4*). However, on the basis of those experiments it was less certain whether singlet oxygen was involved in the reaction mechanism. Since singlet oxygen seems the most likely explanation for the ring-opening products observed, the possibility of a singlet oxygen intermediate in benzene and benzene-d_6 should still be considered.

We previously concluded that aerosol organic composition may strongly influence PAH photodegradation rates in atmospheric particulate matter and that the mechanism of decay apparently depends on the composition of light-absorbing compounds present (*2*). The product results here support these conclusions and further suggest that atmospheric PAH decay processes may also depend on such properties as hydrogen-donating facility and singlet oxygen solubility, which are also likely to depend on aerosol organic composition. Both hydrogen abstraction-initiated radical reactions and singlet oxygen attack are possible mechanisms of benz[*a*]anthracene decay in atmospheric particulate matter.

The model systems used in this work were useful for determining possible reaction mechanisms that should be explored in organic aerosol photochemistry. In real atmospheric particles, the compounds investigated in this study are minor components of a complex, largely unknown organic mixture. The relative importance of the proposed mechanisms depends on such properties as oxygen solubility and singlet oxygen lifetime in the aerosol particle, hydrogen-donating properties of its organic components, and light-absorbing species present, all of which are difficult to determine. Because the composition of the organic fraction in most organic aerosols is incompletely understood, it is possible that other mechanisms may be more important. However, it can be concluded that the organic composition is likely to play an important role in influencing the reaction mechanisms and products of PAH photodegradation in atmospheric aerosol particles.

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