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The Fate of Airborne Polycyclic Organic Matter

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Biological tests have shown that a significant part of the mutagenicity of organic extracts of collected airborne particulate matter is not due to polycyclic aromatic hydrocarbons (PAH). It is possible that part of these unknown compounds are transformation products of PAH. This survey focuses on the reaction of PAH in the atmosphere with other copollutants, such as nitrogen oxides, sulfur oxides, ozone and free radicals and their reaction products. Photochemically induced reactions of PAH are also included. The reactivity of particle-associated PAH is discussed in relation to the chemical composition and the physical properties of the carrier. Recommendations for future work are given.

Introduction

As early as the 1950s it was observed that a significant part of the carcinogenic compounds present in organic extracts of collected airborne particulate matter did not belong to the class of polycyclic aromatic hydrocarbons (PAH) (*1*). Several recent investigations seem to show that only a minor part of the mutagenic activity of organic extracts of environmental samples in Salmonella tests can be ascribed to the presence of PAH (*2-10*). Furthermore, laboratory experiments have shown that some PAH may react with copollutants to form compounds having mutagenic properties different from those of the parent PAHs (*11,12*). These transformation products therefore may be of considerable environmental interest.

In this survey we will discuss the possible transformation products formed by reaction of PAH with NO_x, SO_x, O_x and free radicals. The possible photochemically induced reactions of PAH are also treated.

The occurrence in the atmosphere of PAH and mutagenic particle-associated polycyclic organic matter (POM) shows seasonal variations (*4,7,8,13-16*). The potential transformation reactions may also show such variations. The main reactions of PAH and other POM in winter in the northern countries is presumed to be their reactions with nitrogen oxides, sulfur oxides and their corresponding acids. Photolytic reactions (*17-22*) and reactions with photochemical air pollutants, ozone, peroxyacetyl nitrate, hydroxyl and hydroperoxyl radicals (*11, 12,17,22-26*) may be important in summer in the northern countries.

Formation and Occurrence of Nitroarenes

Presence of Nitroarenes in Environmental Samples

The presence of PAH in exhaust gases, combustion emissions, and the atmosphere has been thoroughly investigated (*27-30*). However, several of the analytical techniques used for the fractionation and isolation of PAH in complex samples do not separate the PAH from the mononitro-PAH. Mononitro-PAH have been reported to be present in the PAH fraction in only a few cases, indicating that mononitro-PAH generally is not present in amounts comparable with those of the most common carcinogenic PAH in environmental samples.

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So far mononitro- and/or dinitro-PAH have been demonstrated to be compounds in samples from diesel exhaust (*10,31*), of airborne particulate matter (*31,32*) and of carbon black (*33-35*). Biological tests have confirmed that mutagenic complex nitroarenes are present in substantial amounts in polluted air in winter (*9,36,37*).

It seems plausible that the chemical structure of these compounds are more complicated than that of the simple nitro-PAH. Furthermore, the results attained by biological tests suggest that formation of mutagenic complex nitroarenes is possible in an atmosphere having a reducing character, and at low ambient temperatures. So far, most of the discussion concerning the formation of nitro-PAH in the atmosphere and during the collection of airborne particulate matter have been focused on an atmosphere containing high levels of photochemical oxidants, and at high ambient temperatures (*38*).

Most of the particle-adsorbed PAH is associated with the smaller-size particles (*39-41*). This has also been observed for the so-called directly acting mutagens (*42*). It appears reasonable, therefore, to assume that particle-bonded mutagenic complex nitroarenes will be associated mainly with respirable particles.

Formation of Nitroarenes by Radical Reactions

A substantial part of the low molecular weight PAH are present in vapor phase in the atmosphere (*15,43-46*). Subsequent reactions of vapor-phase PAH and other arenes with hydroxyl radicals and nitrogen dioxide may perhaps be a source for their transformation to nitro-derivatives under conditions of photochemical air pollution during the day. For toluene, it has been estimated (*47*), by means of the rate constants determined for the subsequent steps (*48,49*), that less than 5% of the toluene reacting with hydroxyl radicals will be transformed to nitrotoluene, even under circumstances of heavy pollution of nitrogen dioxide. It may, therefore, be possible that subsequent reactions of vapor phase arenes with hydroxyl radicals and nitrogen dioxide are not an important source for nitro derivatives.

The dominant reaction of nitrogen trioxide with phenols, and probably also with other hydroxyarenes, is hydrogen abstraction from the oxygen atom leading to nitric acid and phenoxy radicals (*50*). Concentrations of nitrogen trioxide exceeding 100 ppt have been observed in situations of low humidity (less than 60% RH), and with photochemical air pollution persisting during the night (*38,51* and U. Platt, personal communications, 1981). At a concentration of 10 ppt nitrogen trioxide, the half-life of phenol will be about 20 min. For the cresols the half-lives will be in the range 4-7 min (*50*). The main reactions of the phenoxyl radicals appear to be reactions with oxygen leading to quinones (*11, 52, 53*) and reactions with nitrogen dioxide to nitrohydroxy derivatives (*49*). In analogy to the latter reaction, nitrogen monoxide is able to transform the phenoxyl radical of 9-hydroxyanthracene to anthraquinone monooxime (tautomer to 9-hydroxy-10-nitrosoanthracene) (*52*). At ambient temperatures and a concentration of nitrogen dioxide of 25 ppb, the half-life for the transformation of the phenoxy radical of phenol to nitrophenols is about 0.07 sec (*49*). The reaction with nitrogen trioxide may therefore be a possible source for the formation of nitrohydroxy derivatives of the low molecular weight polycyclic organic matter in summer in situations with photochemical air pollution persisting during the night, even though the relative humidity may be higher than 60% most of the time.

Depending on the operating parameters of the combustion, the ratio of nitrogen dioxide to oxygen may be much higher in stack and exhaust gases than in the atmosphere. If so, this implies a higher probability for reactions of vapor-phase polycyclic organic matter with reactive radicals leading to nitro derivatives instead of oxidation products. High concentrations of hydroxyl radicals have been observed in post-combustion burned gases (*54,55*), but in cooled exhaust and stack gases the concentrations of hydroxyl radicals are probably low (*56*). Above 100-200°C the dominant reaction of benzene with hydroxyl radicals appears to be hydrogen abstraction from the aromatic system (*57,58*).

However, under the conditions pertaining to exhaust gases, the reaction pathways are poorly understood at present. Despite combination reactions of aryl radicals and nitrogen dioxide appear to be slow in solution experiments (*59*), hydrogen abstraction from PAH transforming these to aryl radicals and subsequently combination of aryl radicals with nitrogen dioxide could perhaps be a possible pathway for the formation of mononitro-PAH in stack and exhaust gases. At present, it is questionable whether mononitro-PAH are truly components of diesel exhaust gases or are formed as artifacts during the collection procedure (*60*).

Formation of Nitroarenes by Electrophilic Reactions

The reactions of particle-associated polycyclic organic matter (POM) may be a result of gas–solid, liquid–solid and combined gas–liquid and liquid–solid interactions. As soot particles (*61*) and probably also other types of airborne particulates are able to adsorb relatively large amounts of water and as the humidity appear to affect the adsorption of nitrogen dioxide (*62*), it is presumed in this survey that the most plausible nitration reactions of particle-associated POM in the atmosphere involve liquid–solid reaction step(s). If the presumption is correct, it is clear that qualitative aspects of studies of nitration reactions of PAH and other POM in polar solvents is of relevance for the evaluation of the atmospheric chemistry of particle-associated POM.

The radical cations of some PAHs, e.g., benzo(a)pyrene, are very stable (*63*), and the facile preparation of radical cations of reactive PAH having low oxidation and ionization potentials (*64-67*) have been utilized for preparing 1-nitropyrene and 3-nitroperylene (*68*). So far, there is spectroscopic evidence that radical cations are involved in the nitration reactions of some anilines (*69,70*). Whether or not nitrations of PAH involve radical cations is at present disputed (*71-73*). As discussed elsewhere (*47*), if reactive PAH are transformed to nitro-PAH via radical cations, it may be possible that one will observe high yields of nitro-PAH in simple model system and/or in systems using high concentrations of nitrous acid, nitrogen dioxide, and nitric acid (*11,24,74-77*). In the real world, however, an airborne particle of complex composition and in an atmosphere with relatively low concentrations of nitrogen dioxide, nitrous acid and nitric acid, the radical cations of the reactive PAH may be transformed to other species than nitro-PAH. Considering this, the importance of reactions of particle-associated PAH with nitrogen dioxide, nitrous acid and nitric acid in the atmosphere and during sampling of airborne particulate matter is a question of the transformation rates of the different PAH, and the identity of the transformation products.

Based on measurements of the decomposition rates of PAH in weekly acidic solutions containing relatively small concentrations of nitrate, nitrous acid and minute amounts of dinitrogen tetroxide, and on the correlations of the decomposition rate constants with, e.g., spectroscopical constants, a classification of the reactivity of PAH in electrophilic aromatic reactions has been proposed (*67*). This classification agrees reasonably well with the experimental results of others reports on the relative reactivities of adsorbed PAH (*24,78-80*). The PAHs have been divided into five groups. The most reactive ones are those in the group with the lowest number, and the most stable are in the group with the highest number. The classification is as follows: I, benzo(a)tetracene, pentacene, tetracene; II, anthanthrene, anthracene, benzo(a)pyrene, perylene; III, benz(a)anthracene, benzo(ghi)perylene, cyclopenteno(c,d)pyrene, pyrene; IV, benzo(c)phenanthrene, benzo(e)pyrene, chrysene, coronene, dibenzanthracenes; V, benzofluoranthenes, fluoranthene, indeno(1,2,3-c,d)pyrene, naphthalene, phenanthrene, triphenylene.

An investigation of the decomposition rates of substituted anthracenes shows that electron-donating substituents enhance the reactivity of a certain PAH, while it is reduced by electron-attracting substituents (*67*). Thus, hydroxy (if the compound is present as a phenol and not as the tautomer) (*65, 81*), alkoxy and alkyl substituents should generally be expected to promote the reactivity, and ammonium, carboxy, formyl, sulfo, keto and nitro groups should be expected to lower it (*82*).

Furan, pyrrole, and thiophene are far more reactive than benzene in electrophilic aromatic reactions (*82*). But in heteroaromatic compounds having two or more ring systems, the effect of the hetero atom is diluted (*83,84*), and an evaluation of the reactivity of oxa-, thia-, and azaarenes of the carbazol type would not be possible without thorough investigations. Pyridine, however, is less reactive than benzene (*82*).

Most of the azaarenes of the acridin-type are weak bases (pK_B = 8-11) (*85*). Electrophilic nitration reactions of aromatics are catalyzed by acids, and on most acidic particles it seems that pH in the water film on the particle may be below 3 (*86,87*). The protonation of the basic azaarenes is expected to reduce their reactivity, and it appears, therefore, to be a plausible hypothesis that under circumstances feasible for electrophilic aromatic nitration reactions the basic azaarenes will be less reactive than the corresponding PAH.

Stability of Nitro-PAHs

In general, knowledge of the chemistry of nitro derivatives of POM is rather limited. The most important transformation reaction of nitro-PAH is assumed to be photodegradation (*11,88*). Regarding PAH, photolytic reactions have been observed for PAH adsorbed on soot (*18-20,89,90*) and on airborne particulate matter (*21,22*). The latter is less conclusive, however, considering the adsorption techniques used. In contradiction to the results obtained with soot and airborne particles, PAH adsorbed on coal fly ash are highly resistant to photodegradation (*91,92*). The 1- and 3-nitrobenzo(a)pyrenes appear to be quite photostable (*88*), while photodegradation of 2,3-dimethyl-1-nitronaphthalene, 9-nitroanthracene and 6-nitrobenzo(a)pyrene have been observed in several cases (*11,52,53,93*). Some nitro-PAHs that are in the vapor phase or adsorbed on carbonaceous particles may, therefore, photodegrade. The photodegradation involves rearrangement of the nitro-PAH to the corresponding aryl nitrite and subsequent elimination of nitrogen monoxide to form the phenoxy radical (*53*). As discussed earlier, the main reactions of phenoxy radicals are their transformation to nitrohydroxy derivatives and quinones. Hydrogen abstraction of the phenoxyl radicals from alcohols, aldehydes and ketones may lead to the hydroxy derivatives (*94*). The aryl nitrites may also hydrolyze to the hydroxy derivatives and nitrous acid.

Looking at electrophilic aromatic reactions (*67*) and those with hydroxyl radicals (*95*), the transformation rate of nitro-PAH appears to be slower than that of the corresponding PAH. Reactions of nitro derivatives with hydroxyl radicals will probably not involve denitrations reactions (*96*).

Formation and Occurrence of PAH-SO_x Reaction Products

Laboratory Experiments

As a result of the sulfur content in various fuels such as oil and coal, sulfur oxides are formed by combustion. The original species formed are largely SO_2 and to a smaller extent SO_3. SO_2 adsorbed to particles are known to be oxidized to sulfate (*97*). The pH of small aerosol droplets has been shown to be less than 3 (*98*), indicating high concentrations of sulfuric acid.

Gaseous benzene reacts readily with gaseous SO_3 (*99*). Pyrene reacts at room temperature with concentrated H_2SO_4 to produce a mixture of disulfonic acids (*100*). Sulfinic acids may be formed through the reaction of PAH with SO_2 molecules activated by ultraviolet light (SO_2*). Apart from these substances, sulfones and sulfoxides may be formed via reaction with SO_3 and SO_2 or SO_2*, respectively. Of these derivatives, sulfinic acids and sulfoxides may further be oxidized to diaryldisulfoxides, disulfones and possibly even sulfonic acids by the catalytic action of the carrier.

Tebbens et al. (*18*) studied the degradation of benzo(a)pyrene (BaP) adsorbed to soot particles by various concentrations of SO_2. SO_2 concentrations of 50-80 ppm yielded approximately 50% degradation, whereas 8-10 ppm showed no degradation in the dark. In presence of light approximately 50% degradation was observed for both concentrations. No reaction products were identified.

Nagai et al. (*101*) observed the formation of anthracene-9-sulfonic acid by photocatalyzed reaction of anthracene and sulfur dioxide in various solvents at -25°C. A very high concentration (5-40%) of SO_2 was used.

Jäger and Rakovic (*102,103*) studied the reaction of pyrene and BaP, adsorbed on fly ash and alumina, with 10% sulfur dioxide in air, and isolated many sulfur-containing compounds, including pyrene-1-sulfonic acid, pyrenedisulfonic acid and BaP-sulfonic acid. However, under typical ambient conditions, no significant reaction of BaP exposed to 1 ppm in air was observed on a glass fiber filter.

Hughes et al. (*75*) exposed coal fly ash, enriched with PAH through vapor-phase adsorption (*104*), to gaseous concentrations of 100 ppm of SO_2 and SO_3. They observed no reaction with SO_2, while many reaction products were observed with SO_3. However, none of these were identified. The same reaction pattern also occurred on other substrates, such as alumina, silica and activated charcoal. Butler and Crossley (*79*) exposed PAH, naturally present on soot particles, to air containing 5 ppm SO_2 for 3 months without any significant loss.

The conclusion of these experiments is that PAH may react with SO_2 under special conditions and that PAHs do react with SO_3 in all experiments performed. Of the many theoretical reaction products, only some PAH-sulfonic acids have been identified in laboratory experiments. These products have never been identified in real samples as ambient air particles or fly ash. These acidic compounds are water soluble, and will probably not be extracted from particles with the usual solvents as cyclohexane and dichloromethane. They may therefore have been overlooked in previous studies of atmospheric POM.

Health Effects of PAH-Sulfonic Acids

Little work has been done to assess the possible health effects of PAH-sulfonic acids. In general the sulfo group appears to be strongly detoxifying. Even a highly toxic and carcinogenic compound such as 2-naphthylamine becomes nontoxic when sulfonic acid groups are introduced (*105*). Windaus and Rennbak reported in 1937 that BaP-monosulfonic acid was noncarcinogenic to mice (*106*). In a recent study, sulfone derivatives of pyrene showed little or no enhancement of the biological activity relative to the parent compound (*107*) in the Ames Salmonella test (*108*).

Transformation Reactions of PAH with Air, Ozone or Free Radicals

Air (Molecular Oxygen)

Gas-surface reactions in the dark between molecular oxygen and some PAHs (*91,109*) appear to be very slow, with a time scale of days or weeks. Hence, these reactions may not represent a significant degradation pathway for most PAH. Long-range transport of PAH reported both in Europe and the U.S. also indicates little degradation of some of the adsorbed PAH in air (*14,110-112*), particularly in absence of light or with low intensity light.

Ozone

Studies by Lane and Katz (*113*) have shown high reactivity of BaP on petri plates when it is exposed to sub-ppm levels of ozone in air. They reported a half-life of 0.6 hr for BaP at an ozone level of 190 ppb. In their experiments, irradiation did not seem to significantly affect the reactivity of the BaP-ozone system. They also observed that certain PAH containing five-membered rings such as benzo(k)-fluoranthene were far more resistant to oxidation than BaP. It is likely therefore that the reactivity varies strongly for different structures.

Experiments by Pitts and co-workers (*12*) have confirmed and extended the work of Lane and Katz. BaP-coated glass fiber filters were exposed to concentrations of 0.1-0.2 ppm ozone in air for periods varying from 5 min up to 4 hr. For 0.2 ppm O_3 conversion yields of 50% after 1 hr and 80% after 4 hr were observed (*12*). These data are in good agreement with the data of Lane and Katz (*113*).

Peters and Seifert (*22*) found in similar measurements that the BaP lifetime to be inversely correlated with the ambient ozone concentration. For irradiated BaP impregnated filters they observed decay curves similar to those obtained by Lane and Katz (*113*) and by Pitts et al. (*12*). Interestingly, however, they found a much more pronounced difference between the results of experiments carried out in the dark and those involving irradiation with a much slower decay observed for the dark samples. Also, they observed little difference between dust-free and dust-coated filters, suggesting that the presence of particulate matter is of minor importance for the stability of BaP on the filter (*22*).

Pitts and co-workers (*12,24,38*) isolated and identified the major reaction products from their ozone-BaP exposure experiments as ring-opened compounds, including dialdehydes, dicarboxylic acids and ketocarboxylic acids. The major skeleton remaining after the oxidation of BaP appears to be the benzanthrone structure, a compound that indeed has been detected in ambient particulates (*114*).

The reaction mixture from these experiments showed direct mutagenic activity in the Ames test. The major stable contributor to this direct activity has been identified (*12*) as BaP-4,5-oxide, a DNA-binding metabolite in biological systems, a powerful direct mutagen, and a weak carcinogen on mouse skin.

Free Radicals

Reactions of hydroxyl radicals with PAH have only been investigated in a few cases (*26,115*). By analogy to their reactivity in "simple" gas-phase systems (e.g., toluene) (*49,116*), addition of OH to the aromatic rings predominate. The radicals formed by initial attack of OH on PAH will presumably react further with O_2. Thus, as in the gas phase conversion of toluene to cresols, one might expect the formation of hydroxy derivatives of PAH and ring-opening oxidation products (*47,49*). The former could react further, for example, to quinones (*47,49,50,52,53,117*). The occurrence of hydroxyarenes in the atmosphere is poorly investigated, but a few hydroxy derivatives of benzene have been identified (*118*).

The average concentration of hydroxyl radical in the atmosphere at 60° N latitude is estimated to be about 1×10^6 molecule/cm^3 in summer (*119*). Taking into consideration the reaction with hydroxyl radicals alone, the half-life of benzene (*117,120*) will be about 6 days under these circumstances. The reactivities of alternant PAH such as pyrene towards radicals should be expected to be higher than that of benzene (*121-124*), but not by more than two orders of magnitude towards hydroxyl radicals (*26*). It is impossible to make any reliable predictions of the reactivities of nonalternant PAH, e.g., fluoranthene, as no investigation of radical reactions of these compounds seems to have been made so far. The reactions between hydroxyl radicals and hydroxyarenes seem to be faster than those between hydroxyl radicals and the parent arenes. Thus, at a hydroxyl radical concentration of 1×10^6 molecules/cm^3 and at 26°C the half-life of *o*-cresol (*50*) is 6 hr.

It has been observed that soot particles contain free organic radicals (*125,126*). Radical reactions of PAH and other POM adsorbed on particles may, therefore, be possible. Furthermore, gas-phase radicals in the atmosphere, e.g., hydroxyl radicals, may react with particle-associated POM. However, in experiments with pyrene adsorbed on soot, aluminum oxide, fly ash, and silica gel and exposed to nitrogen dioxide, the reactions of pyrene seemed to be independent of the irradiation parameters (*74*). This suggests, that reactions between gas-phase oxygen atoms [$O(^3P)$] or hydroxyl radicals (*127*) and the adsorbed pyrene were not important in these experiments.

Singlet Molecular Oxygen

The chemical reactions of singlet oxygen $O_2(^1\Delta_g)$ with PAH have not been studied in detail. However, reactions with gaseous olefins and cyclic ethers are reasonable well understood, yielding hydroperoxides and endoperoxides, respectively.

A photophysical mechanism for generating singlet oxygen from organics (e.g., in smog) has been postulated to involve a photosensitized reaction in which the organic pollutant absorbs light in the actinic ultraviolet region, crosses over to the triplet state, and then on quenching with oxygen, forms $O_2(^1\Delta_g)$ (*128*). Most PAHs satisfy this condition and can therefore be both sensitizer and reactant in the same reaction sequence.

PAH that have an anthracene skeleton in their structure, such as benz(a)anthracene should yield an endoperoxide intermediate similar to the cycloaddition of singlet oxygen to cyclohexadiene. Quinones are the ultimate product. Other PAH such as benzo(a)pyrene, however, cannot form this endoperoxide and probably yield a hydroperoxide (after rearrangement of the initially formed dioxetane) that can react further to give quinones.

McCoy and Rosenkranz (*129*) have reported the transformation of chrysene and 3-methylcholanthrene to direct mutagens by photodynamically generated singlet oxygen. They emphasized the importance of this potential mechanism of conversion of airborne PAH to mutagens and to potential "ultimate" (i.e., direct-acting) carcinogens.

Photochemically Induced Reactions of PAH

Several reaction pathways are possible when PAH are irradiated with ultraviolet light. These depend, of course, upon the size and structure of the PAH, and whether or not oxygen is present.

The relative efficiencies of photochemical changes of 15 PAHs during thin-layer chromatography has been studied (*130,131*). The PAHs were deposited on four different adsorbents (silica gel G, aluminum oxide G, cellulose powder and acetylated cellulose, 21%) and exposed to ultraviolet and room light. Phenanthrene, chrysene, triphenylene and picene did not react; however, on silica gel G and aluminum oxide G the other 11 PAHs including BaP, underwent pronounced changes. On less polar substrates, such as powdered cellulose or acetylated cellulose, the behavior of the 11 PAHs was similar, but the changes in appearance of fluorescence were much less extensive and occurred much more slowly. The reactions of these PAHs may be interpreted in terms of the formation of a PAH radical cation, leading to a phenoxyl radical by reaction with oxygen, as shown by Inomata and Nagata (*94*).

Geacintov (*132*) coated solid polystyrene fluffs with 20 PAHs and irradiated them in the presence of oxygen and nitric oxide. Interestingly, essentially no photoproducts were observed, but efficient energy transfer was observed from PAH to oxygen to form singlet molecular oxygen $O_2(^1\Delta_g)$, a well-known process in solution and in the gas phase.

The earliest study of PAH photochemical degradation was conducted by Falk and co-workers (*17*). A striking result is the higher reactivity, in light and air, for PAH in the pure form versus the same PAH adsorbed on soot. This was explained by the hypothesis that adsorption on a highly porous particle may provide some protection from photooxidation. The same pattern was not observed for exposure to smog; in this case the reactivity results were mixed for the pure versus adsorbed compound.

Tebbens et al. (*18*) studied the chemical modifications of BaP and perylene in smoke. They found that irradiation in a flow chamber caused disappearance of transformation of 35-65% of the original PAH content. Subsequently, Thomas et al. (*19*) employed a similar flow system to measure the reactions of BaP on soot at the entrance and exit of a chamber, and found a 58% decrease upon irradiation. However, some of these results are in variance with those of Falk et al. (*17*).

Natusch et al. (*91*) employed a model system in which individual PAHs were adsorbed onto the surface of fly ash collected from electrostatic precipitators of coal-fired power plants. None of the irradiated PAH showed a significant photodegradation. Such degradation occurred very rapidly and did not proceed further over time periods of up to 100 hr. On the other hand, a number of other compounds studied were observed to undergo quite extensive oxidation in the absence of light, and different fly ash substrates yielded different oxidation rates. Whether or not these results can be extrapolated to combustion-related POM is not clear since they observed that PAH adsorbed onto coal fly ash surfaces exhibit quite different chemical behavior (particularly photodecomposition) from PAH adsorbed onto other solid substrates such as alumina (*91*).

Fox and Olive (*21*) found that anthracene dispersed into atmospheric particulate matter is photooxidized to an array to products reminiscent of oxidation by singlet oxygen in solution phase. They also found that photooxidation is a more significant degradative pathway under ambient conditions than ozonation.

Effect of the Carrier on the Reactivity of PAH

The chemical reactivity of PAH adsorbed onto particles will be affected by two factors, one of which is physical, the other chemical in nature.

When a reactive compound is finely divided over a surface, its accessability for the gas molecules will depend on particle size, shape and specific surface area. While this physical parameter is probably more or less constant for glass fiber filters, it can vary immensely for reactions on particles. Dissolution of reactive gases in the liquid film on particles may be an additional factor affecting the sequence of reactions of adsorbed species.

The chemical structures of the adsorption sites of particle-associated PAH have so far been only partly unravelled (*19,61*). Some observations suggest that PAH are preferentially adsorbed on particles with a relative high content of carbon (*41,133*). Furthermore, the high extraction temperatures or the long extraction times needed to attain quantitative recoveries of PAH deposited on particles from diesel exhaust gases (*134*) and from some carbon black (*33,135,136*) confirm the high affinity (*137*) of PAH to graphitized soot (*138,139*). Increased concentrations of particles mainly consisting of lead halogenides and oxide appear to affect the distribution of PAH between being adsorbed on particles and being in vapor phase in diluted exhaust gas (*133,140*). This suggests, however, that particle-bonded PAH is not associated exclusively with carbonaceous particles. This point may perhaps be more important for the lower PAH (four rings) considering the difference in the particle-size distribution for the lower and higher PAH in diluted exhaust gas (*133*) and the substantial amount of the lower PAH in the atmosphere occurring in vapor phases (*15,43-46*).

Small changes in the solvent composition in solution experiments have a strong effect on the decomposition rate of anthracene in nitration reactions. It appears that the rate increases with increasing polarity and/or decreasing basicity of the solvent (*47*). Similar effects may be the reason that the formation rates of 1-nitropyrene and 6-nitrobenzo(a)pyrene were much slower, if pyrene and benzo(a)pyrene were adsorbed on carbonaceous deposits from the exhaust system of a four-stroke engine than if the carrier used was silica gel, neutral aluminum oxide, or fly ash from a power plant (*74*). Correspondingly, high transformation rates of benzo(a)pyrene and perylene adsorbed on glass fiber filters and exposed to nitrogen dioxide and nitric acid have been observed (*11,24*), while those of 10 PAHs adsorbed on soot (formed by incomplete combustion of ethylene) and exposed to nitrogen dioxide were relatively slow (*79*).

It should be stressed that further investigations are required, but the observations made so far indicate that most of the particle-bonded PAH is associated with carbonaceous particles. Transformation reactions of PAH on fresh carbonaceous particles appear to be relatively slow, but atmospheric oxidation processes change the chemical composition of these particles during their transport and may produce a surface containing higher amounts of hydrophilic sites and free acids (*19,141, 142*). Some evidence has been attained suggesting that the rates of the transformation processes of PAH with nitrogen dioxide on aged carbonaceous particles are higher than on freshly emitted particles. Dosage of nitrogen dioxide (mean 1 ppm) during 24 hr high-volume sampling on glass fiber filters of airborne particulate matter in the winter caused degradation of benzo(a)pyrene and other PAH. In the two worst cases, the degradation of benzo(a)pyrene was 70% and 90%. These cases coincided with long-range transport episodes of sulfur dioxide and sulfate (*80*). It appears reasonable to assume, therefore, that a substantial part of the PAH also originates from distant sources (*14*), and that these PAH have been associated with relatively aged aerosols.

It is difficult to make an exact evaluation of the rates of the transformation processes of PAH on fresh carbonaceous particles, as the experiments done so far appear to have been performed at a low humidity (*74,79*), the humidity may be an important parameter affecting the adsorption of nitrogen dioxide on the particles (*62*). In this connection, it may be important also that soot particles are able to adsorb relatively large amounts of water (*61*). Another point making it difficult to evaluate the rates of the transformation processes, is that the combined effects of different pollutants, nitrogen dioxide and nitric acid (*24,77*), nitrogen dioxide and sulfur dioxide (*77*), on the rates seem to be synergistic, that is, that the total effect is larger than the sum of the separate effects of these pollutants.

Reactions which involve irradiation are even more complex since PAH deposited inside porous particles or inner layers of PAH can easily be shielded from the incident light. At a given concentration, these parameters will determine the distribution of PAH into a monolayer or a multilayer. In heterogeneous reactions, the outer layer(s) is protected from further attack by the initially formed products.

A second factor affecting this reactivity is chemical in nature: the adsorption of organics onto the aerosol matrix can modify their reactivity through catalytic effects, induced by constituents of that matrix. Thus, the suppression of photochemistry of PAH, adsorbed onto coal fly ash might well be related to a stabilization of their ground electronic state.

Conclusions and Recommendations

Several experiments in the literature provide evidence for the high reactivity of various PAH in dark reactions with ozone and nitrogen dioxide as well as for photochemical degradation under simulated atmospheric conditions. Direct mutagens are formed in these laboratory experiments, which are likely to contribute also to the direct mutagenicity of ambient particulate matter.

Nitro-PAH have been identified in collected samples from diesel exhaust gases, but at present it is unknown whether they are truly components of diesel exhaust or instead are formed as artifacts during the sampling.

Biological tests have confirmed apparently unambiguously that mutagenic complex nitroarenes are present in substantial amounts in polluted air in winter or are formed during the collection of the samples. The lack of several observations on the presence of mononitro-PAH suggests that these compounds hardly make up a dominant contribution to the presence of mutagenic complex nitroarenes, unless most of the mononitro-PAH present should consist of supermutagenic species. Biological tests specific for nitroarenes combined with fractionation of the samples should be performed in order to gain more knowledge about the structure of the complex mutagenic nitroarenes. This should be combined with studies of artifact formation during the fractionation. Some nitro-PAH may photolyze in daylight. Quinones, hydroxy derivatives, nitrohydroxy derivatives and their tautomers are the most plausible products.

Very little is known about the presence of PAH-sulfonic acids and other reaction products from PAH and SO_x in environmental samples, and their possible health effects. If reactions occur, they are most likely under plume conditions. The PAH-sulfonic acids may have been overlooked in earlier studies due to the analytic procedures.

The limited data on health effects by these compounds indicate that the sulfonic acid group detoxify the molecule and could make them nonmutagenic in the Ames test. However, only a few substances have been tested, so no general conclusion can be drawn.

On days with photochemical air pollution the half-life of most of those PAH being in gas phase will be short, probably in the range of minutes to some hours. The most plausible transformation products appear to be hydroxy derivatives and other oxidation products, e.g., quinones.

Most of the particle-bonded PAH seems to be associated with carbonaceous particles. Some experiments suggest that the transformation reactions of PAH adsorbed on fresh soot particles and exposed to nitrogen dioxide, sulfur dioxide and ozone are relatively slow, but taking into consideration the experimental conditions, the possibility of synergistic effects of different pollutants on the transformation rates, and the possibility that chemical processes may change the nature of the particles during the transport in the atmosphere, it is difficult to make a reliable prediction of the rates in the atmosphere of, e.g., reactions between particle-associated benzo(a)pyrene and gaseous copollutants.

Despite the many experimental problems and the multitude of parameters involved, it is necessary to perform model studies using relevant particles and at atmospheric conditions as close as possible to ambient in order to gain information about the transformation rates.

Future work using simple model systems should focus on the unravelling of the effects of physical and chemical factors on the transformation rates and the product distribution. This work should not be limited to PAH, but also include other types of POM, e.g., oxa-, thia-, and azaarenes and derivatives of PAH. Mutagenicity studies of the reaction products should also be performed.

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