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Barbara J. Finlayson-Pitts and James N. Pitts Jr.

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mass of the ITCZ,  $\Phi_{st}$  is the vertical mass flux per storm, and  $N_{st}$  is the number of active storms. [H. Riehl and J. M. Simpson, *Contrib. Atmos. Phys.* **52**, 287 (1979)].

9. D. Kley *et al.*, *Science* **274**, 230 (1996).
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11. A. R. Numaguti *et al.*, *J. Meteorol. Soc. Jpn.* **73**, 267 (1995); B. E. Mapes and P. Zuidema, *J. Atmos. Sci.* **53**, 620 (1996).
12. Potential temperature ( $\theta$ ) is defined as  $\theta = T$

$(1000/p)^\kappa$ , where  $T$  is the temperature,  $p$  is the pressure,  $\kappa = R/mc_p$ ,  $R$  is the gas constant,  $m$  is the molecular weight of dry air, and  $c_p$  is the heat capacity of air at constant pressure.  $\theta$  is the temperature that an air parcel would attain after adiabatic compression from given values of  $T$  and  $p$  to a pressure of 1000 hPa.

13. W. R. Stockwell and D. Kley, *Ber. Forschungszentrum, Jülich. Jül.*, 2868 (1994).
14. D. Brocco *et al.*, *Atm. Environ.* **31**, 557 (1997).

# Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles

Barbara J. Finlayson-Pitts and James N. Pitts Jr.

Tropospheric air pollution has impacts on scales ranging from local to global. Reactive intermediates in the oxidation of mixtures of volatile organic compounds (VOCs) and oxides of nitrogen ( $\text{NO}_x$ ) play central roles: the hydroxyl radical (OH), during the day; the nitrate radical ( $\text{NO}_3$ ), at night; and ozone ( $\text{O}_3$ ), which contributes during the day and night. Halogen atoms can also play a role during the day. Here the implications of the complex VOC- $\text{NO}_x$  chemistry for  $\text{O}_3$  control are discussed. In addition, OH,  $\text{NO}_3$ , and  $\text{O}_3$  are shown to play a central role in the formation and fate of airborne toxic chemicals, mutagenic polycyclic aromatic hydrocarbons, and fine particles.

Tropospheric air pollution has a long and storied history (1, 2). From at least the 13th century up to the mid-20th century, documented air pollution problems were primarily associated with high concentrations of sulfur dioxide ( $\text{SO}_2$ ) and soot particles. These problems are often dubbed “London Smog” because of a severe episode in that city in 1952. However, with the discovery of photochemical air pollution in the Los Angeles area in the mid-1940s, high concentrations of  $\text{O}_3$  and photochemical oxidants and their associated impacts on human health have become a major issue worldwide.

In this article we discuss recent research on air pollution on scales ranging from local to regional, although analogous chemistry occurs on a global scale, as discussed in the accompanying articles by Andreae and Crutzen (3) and Ravishankara (4). Thus, an increase in tropospheric  $\text{O}_3$  has been observed globally over the past century (5–11), an example of which is seen by comparison of  $\text{O}_3$  levels measured at Montsouris in France from 1876 to 1910 to those at a remote site on an island in the Baltic Sea (Arkona) from 1956 to 1983 (Fig. 1). Surface concentrations of  $\text{O}_3$  found in other

remote areas of the world now are similar, ~30 to 40 parts per billion (ppb) (1 ppb = 1 part in  $10^9$  by volume or moles), as compared with ~10 to 15 ppb in preindustrial times. This increase has been attributed to an increase in  $\text{NO}_x$  emissions associated with the switch to fossil fuels during the industrial period.

The potential effects of a global increase in  $\text{O}_3$  and other photochemical oxidants are far-ranging. Ozone is a source of the hydroxyl radical (OH) (see below), which reacts rapidly with most air pollutants and trace species found in the atmosphere. Hence, increased concentrations of  $\text{O}_3$  might be expected to lead to increased OH concentrations and decreased lifetimes of globally distributed compounds such as methane. Because both  $\text{O}_3$  and methane are greenhouse gases, this chemistry has implications for global climate change. In addition, because  $\text{O}_3$  absorbs light in the region from 290 to 320 nm, changes in  $\text{O}_3$  levels can affect the levels of ultraviolet radiation to which we are exposed.

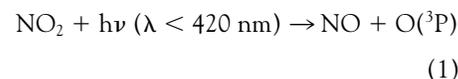
Inextricably intertwined with the formation and fate of  $\text{O}_3$  and photochemical oxidants in the troposphere are a number of closely related issues, such as the atmospheric formation, fate, and health impacts of airborne toxic chemicals and respirable particles. Understanding these issues is key

to the development of reliable scientific risk assessments (12, 13). In this context, we give an overview of the chemistry of tropospheric air pollution involving  $\text{O}_3$  and associated species and give examples of applications to strategies for control of  $\text{O}_3$ , airborne toxic chemicals, polycyclic aromatic hydrocarbons, and respirable particulate matter. We emphasize the key roles played by a remarkably few reactive species, such as OH. The chemistry of  $\text{SO}_2$  and acid deposition is closely linked with this chemistry, but that topic is beyond the scope of this article.

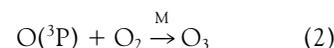
## Ozone and Other Photochemical Oxidants

The term “photochemical” air pollution reflects the essential role of solar radiation in driving the chemistry. At the Earth’s surface, radiation of wavelengths 290 nm and greater—the so-called actinic region—is available for inducing photochemical reactions. The complex chemistry involving volatile organic compounds (VOCs) and  $\text{NO}_x$  (where  $\text{NO}_x = \text{NO} + \text{NO}_2$ ) leads to the formation not only of  $\text{O}_3$ , but a variety of additional oxidizing species. These include, for example, peroxyacetyl nitrate (PAN) [ $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ]. Such oxidants are referred to as photochemical oxidants. We concentrate here on  $\text{O}_3$ , recognizing that a variety of other photochemical oxidants are associated with it.

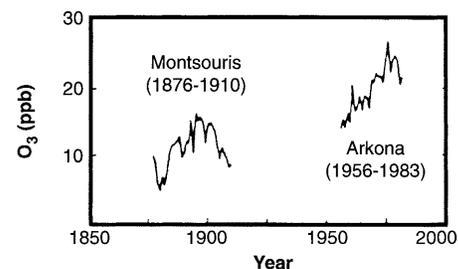
*Sources of  $\text{O}_3$ .* The sole known anthropogenic source of tropospheric ozone is the photolysis of  $\text{NO}_2$



followed by



(M in Eq. 2 is any third molecule that stabilizes the excited intermediate before it



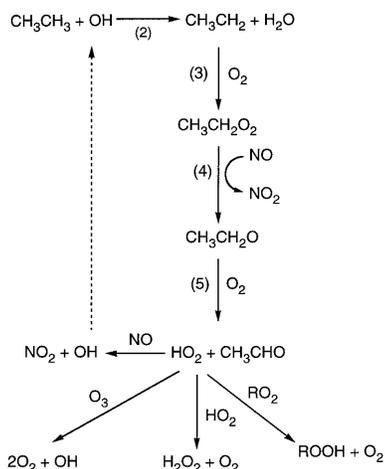
**Fig. 1.** Mean annual  $\text{O}_3$  concentrations in Montsouris (outside Paris) from 1876 to 1910 and at Arkona from 1956 to 1983, showing increasing  $\text{O}_3$  levels on a global scale [reprinted with permission from *Nature* (8), copyright 1988, Macmillan Magazines Ltd.].

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dissociates back into reactants). In addition, the influx of air containing natural O<sub>3</sub> from the stratosphere contributes to tropospheric ozone (11, 14).

Although some NO<sub>2</sub> is emitted directly into the atmosphere by combustion processes [see (15)], most is formed by the oxidation of NO (the major nitrogenous byproduct of combustion) after dilution in air. This conversion of NO to NO<sub>2</sub> occurs as part of the oxidation of organic compounds, initiated by reactive species such as the OH radical. Figure 2 illustrates this chemistry, using ethane as the simplest example. Alkyl peroxy (RO<sub>2</sub>) and hydroperoxy (HO<sub>2</sub>) free radicals are generated (steps 3 and 5), which oxidize NO to NO<sub>2</sub>, and a substantial fraction of the time the OH is regenerated to continue the reaction.

Once NO is converted to NO<sub>2</sub>, a variety of potential reaction paths are available (Fig. 3). These include photolysis to form ground-state oxygen atoms—O(<sup>3</sup>P)—which generate O<sub>3</sub>, as well as reaction with OH to form nitric acid. When there are sufficient concentrations of both NO<sub>2</sub> and O<sub>3</sub>, the nitrate radical (NO<sub>3</sub>) and dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) are formed. Like OH, NO<sub>3</sub> reacts with organics to initiate their oxidation. NO<sub>3</sub> chemistry is important only at night because it photolyzes rapidly during the day. NO<sub>3</sub> has been detected in both polluted and remote regions (16–19) and is believed to be the driving force in the chemistry at night when the photolytic production of OH (see below) shuts down. As discussed by Andreae and Crutzen (3) and Ravishankara (4), the formation and subsequent hydrolysis of N<sub>2</sub>O<sub>5</sub> on wet surfaces, including those of aerosol particles, is believed to be a significant contributor to the formation of nitric acid in the atmosphere on both local and global scales (20, 21).

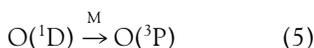
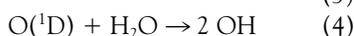
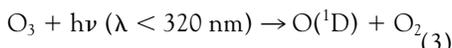


**Fig. 2.** Example of the role of organic compounds in the conversion of NO to NO<sub>2</sub>.

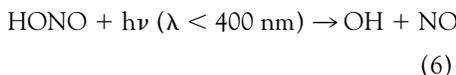
The chemistry in remote regions differs from that in polluted areas primarily in the fate of RO<sub>2</sub> and HO<sub>2</sub>. In polluted areas, sufficient NO is present [more than ~10 parts per thousand (ppt) (where 1 ppt = 1 part in 10<sup>12</sup> by volume or moles)] that HO<sub>2</sub> formed during the oxidation of VOCs (Fig. 2) converts NO to NO<sub>2</sub>, which then forms O<sub>3</sub>, at least in part. However, remote regions are characterized by small concentrations of NO, so that the self-reaction of HO<sub>2</sub> and its reactions with RO<sub>2</sub> and O<sub>3</sub> become competitive with, or exceed, that with NO.

In short, whether or not O<sub>3</sub> is formed by VOC-NO<sub>x</sub> reactions in air depends critically on the NO concentration. This notion is consistent with the association of the global increase in O<sub>3</sub> with increased oxides of nitrogen.

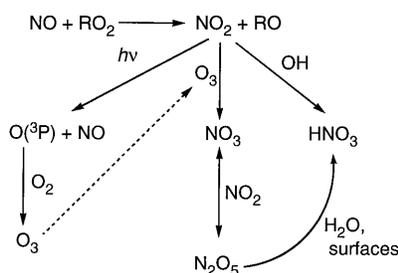
*Sources of OH.* The hydroxyl radical plays a central role in atmospheric chemistry because of its high reactivity with organic compounds as well as inorganic compounds. A major source of OH is the photolysis of O<sub>3</sub> to form electronically excited O(<sup>1</sup>D) atoms, which react with H<sub>2</sub>O in competition with deactivation to ground-state O(<sup>3</sup>P):



The photolysis of nitrous acid is also believed to be a significant source of OH in polluted atmospheres (22, 23):



However, sources and ambient concentrations of HONO are not well known. It has been measured in the exhaust of automobiles that do not have catalysts (24, 25), inside automobiles during operation (26), and indoors from the emissions of gas stoves (27–32). There are also heterogeneous sources of HONO (33–39), in particular the complex reaction shown in Eq. 7.



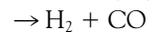
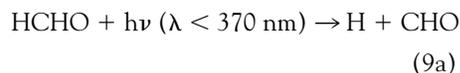
**Fig. 3.** Summary of the major reaction paths for NO<sub>x</sub> in air.



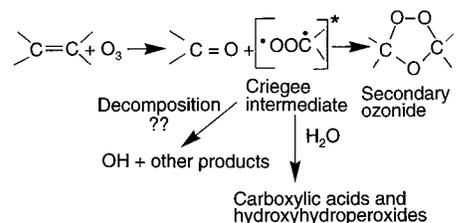
Through the HO<sub>2</sub> + NO reaction



sources of HO<sub>2</sub> are also potential sources of OH. Hence, the photolysis of such organic compounds as formaldehyde serves ultimately as a source of OH.



Finally, the O<sub>3</sub>-alkene reaction is also a source of OH (40–42). In the gas phase, the initial O<sub>3</sub> reaction produces a carbonyl compound and a Criegee intermediate (commonly described as a biradical, as opposed to a zwitterion as in solution).



**Scheme 1**

A portion of the Criegee intermediates has sufficient energy (denoted by the asterisk) to decompose to free radicals; and depending on the structure of the reacting olefin, one of these can be the OH radical. These reactions may be significant sources of OH and HO<sub>2</sub> in urban areas during the day and evening (43). However, neither the detailed mechanisms leading to free-radical production nor the reactions of the stabilized Criegee intermediate are well understood.

## Halogen Atom Chemistry in the Troposphere

It has been increasingly recognized that halogen atoms may play a role in tropospheric chemistry (44, 45). A ubiquitous source of tropospheric halogens is sea salt aerosol (46–48). Chlorine atoms (Cl) liberated from these particles, for example, in the reaction in Eq. 12, (44, 45, 49, 50)



may also play a role in VOC-NO<sub>x</sub> chemistry, in much the same manner as OH. The rate constants for Cl atom reactions with most organic compounds are an order of magnitude faster than for the reaction with

O<sub>3</sub> (51); given that the tropospheric concentrations of biogenics are of the same order of magnitude as O<sub>3</sub>, the reaction with organics



is expected to predominate in the loss of atomic Cl. Thus, Cl atoms in polluted coastal regions may initiate organic oxidation in a manner analogous to that of OH (Fig. 2), accelerating the formation of O<sub>3</sub>.

Excellent evidence for the oxidation of organics by Cl atoms was found in the Arctic troposphere during the spring when surface-level O<sub>3</sub> fell to near zero (52). Although the loss of O<sub>3</sub> appears to be related to bromine chemistry (3, 52–60), Cl chemistry occurs simultaneously (Fig. 4). The rate constants for the reactions of Cl atoms with *i*-butane and propane are similar ( $1.4$  and  $1.2 \times 10^{-10}$  cm<sup>3</sup> per molecule s<sup>-1</sup>, respectively), whereas those for reaction with OH differ ( $2.3$  and  $1.2 \times 10^{-12}$  cm<sup>3</sup> per molecule s<sup>-1</sup>). Thus, *i*-butane and propane should decay at similar rates in the absence of fresh emissions, dilution, and so on (61) if Cl atoms are the oxidant, and the ratio of their concentrations should follow the vertical line in Fig. 4. A similar argument follows for OH and *i*-butane and *n*-butane, where the OH rate constants are  $2.3$  and  $2.5 \times 10^{-12}$  cm<sup>3</sup> per molecule s<sup>-1</sup>, respectively, but for Cl atoms are  $1.4$  and  $2.1 \times 10^{-10}$  cm<sup>3</sup> per molecule s<sup>-1</sup>. The data in Fig. 4 illustrate that atomic Cl is indeed the predominant oxidant under low O<sub>3</sub> conditions in the Arctic.

Although the evidence for the contribution of Cl atom chemistry is compelling in this particular case, Cl chemistry may contribute to a lesser degree in other tropospheric situations. For example, Wingenter *et al.* (62) and Singh *et al.* (63) used the differences in concentrations of selected organic compounds from night to day over the Atlantic and Pacific oceans to estimate Cl atom concentrations at dawn of  $\sim 10^4$  to  $10^5$  cm<sup>-3</sup>. On the other hand, Singh *et al.* (64) and

Rudolph *et al.* (65) have used tetrachloroethene measurements and emissions estimates, combined with the known OH reaction kinetics, to show that oxidation by Cl does not appear to be important on a global scale. However, the effects of Cl atom production on organic compounds such as dimethylsulfide emitted by the ocean into the marine boundary layer may still be important (66), as may their contribution to chemistry in polluted coastal regions.

At coastal sites, Cl-containing species other than HCl have been identified at concentrations up to  $\sim 250$  ppt (67, 68) and Cl<sub>2</sub> has been identified (69). However, the sources of such halogen atom precursors remain elusive, despite numerous studies of the reactions of NaCl and sea salt particles, which one might expect to have relatively simple chemistry. For example, it has recently been shown that small amounts of water strongly adsorbed to the salt surface—probably at defects, steps, and edges—controls the uptake of HNO<sub>3</sub> (70). Furthermore, it appears that NaCl may not control the reactivity of sea salt and that crystalline hydrates in the mixture may be important (71). Finally, once the salt surface has reacted to form surface nitrate, the interaction of water with this metastable layer of nitrate generates some interesting morphological and chemical changes (72, 73) producing, for example, hydroxide ions on the surface (74).

Thus, although there are some intriguing hints about the importance of halogen chemistry in the troposphere, more research is needed to define the contribution of halogen chemistry to remote and polluted coastal regions. A top priority is the development and application of specific, sensitive, and artifact-free analytical techniques for some of the potential gaseous halogen precursors, including ClNO<sub>2</sub>, Cl<sub>2</sub>, ClONO<sub>2</sub>, and HOCl, as well as their bromine analogs and mixed compounds such as BrCl.

### Tropospheric Chemistry and Ozone Control Strategy Issues

**VOC and NO<sub>x</sub> controls.** Given the complexity of the chemistry as well as the meteorology, it is perhaps not surprising that quantitatively linking emissions of VOCs and NO<sub>x</sub> to the concentrations of O<sub>3</sub> and other photochemical oxidants and trace species at a particular location and time is not straightforward. Particularly controversial for at least three decades has been the issue of control of VOCs versus NO<sub>x</sub>.

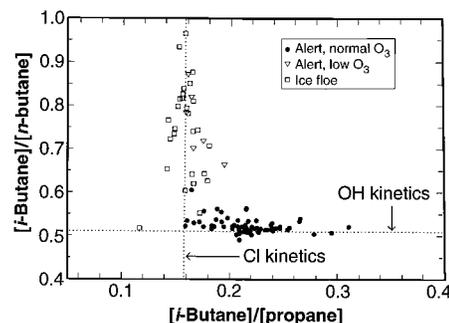
High concentrations of NO and O<sub>3</sub> are not observed simultaneously because of their rapid reaction to form NO<sub>2</sub>. In addition, high NO<sub>2</sub> concentrations divert OH from the oxidation of VOCs by forming HNO<sub>3</sub> (Fig. 3), which also effectively short-

circuits the formation of O<sub>3</sub>. Because of these reactions, decreasing NO<sub>x</sub> can actually lead to an increase in O<sub>3</sub> at high NO<sub>x</sub>/VOC ratios; in this VOC-limited regime, control of organic compounds is most effective. However, these locations tend not to be the ones experiencing the highest peak O<sub>3</sub> concentrations in an air basin. Furthermore, NO<sub>2</sub> has documented health effects for which air quality standards are set.

On the other hand, at high VOC/NO<sub>x</sub> ratios, the chemistry becomes NO<sub>x</sub>-limited; in essence, one can only form as much O<sub>3</sub> as there is NO to be oxidized to NO<sub>2</sub> and subsequently photolyzed to O(<sup>3</sup>P). The issues are even more complicated, because the chemical mix of pollutants tends to change from a VOC-limited regime to a NO<sub>x</sub>-limited regime as an air mass moves downwind from an urban center. This is because there are larger sources of NO<sub>x</sub>, such as automobiles and power plants, in the urban areas. NO<sub>x</sub> is oxidized to HNO<sub>3</sub> (Fig. 3), which has a large deposition velocity, and hence is removed from the air mass as it travels downwind. VOCs do not decrease as rapidly because of widespread emissions of biogenics as well as less efficient deposition of many organic compounds. It is apparent that reliance on either VOC or NO<sub>x</sub> control alone will be insufficient on regional scales; control of both is needed (75–77).

**Control of VOCs and O<sub>3</sub> forming potentials.** Shortly after the demonstration in the early 1950s that VOCs and NO<sub>x</sub> were the key ingredients in photochemical air pollution. Haagen-Smit and Fox (78) reported that various hydrocarbons had different O<sub>3</sub>-generating capacities. That is, when mixed with NO<sub>x</sub> and irradiated in air, different amounts of O<sub>3</sub> were formed, depending on the structure of the organic compound. The chemical basis for these differences is now reasonably well understood (79–88) and has been applied in the promulgation of a new set of regulations in California for exhaust emission standards for passenger cars and light-duty trucks. The intent is to regulate on the basis of the O<sub>3</sub>-forming potentials of the VOC emissions, rather than simply on their total mass.

The number of grams of O<sub>3</sub> formed in air per gram of total VOC exhaust emissions is defined as specific reactivity. Determination of the specific reactivity of the exhaust emissions for a given vehicle/fuel combination requires accurate knowledge of the identities and amounts of all compounds emitted, as well as how much each contributes to O<sub>3</sub> formation. The latter factor, the O<sub>3</sub>-forming potential, is treated in terms of its incremental reactivity (IR): the number of molecules of O<sub>3</sub> formed per VOC carbon atom added to an initial “surrogate” reac-



**Fig. 4.** Relative concentrations of some organics used to probe OH and Cl atom chemistry in the Arctic troposphere at Alert, Canada, and on an ice floe 150 km north of Alert [from (60)].

tion mixture of VOC and NO<sub>x</sub>.

The differences in IRs are greatest at the lower VOC/NO<sub>x</sub> ratios. At higher ratios such as >12 ppm C/ppm NO<sub>x</sub>, the system tends to become NO<sub>x</sub>-limited, and the peak O<sub>3</sub> is not very sensitive to either the concentrations of the VOCs present or to the composition of the VOC mixture. The peak value of the IR, which generally occurs at a VOC/NO<sub>x</sub> ratio of ~6, is known as the maximum incremental reactivity (MIR) (Fig. 5). As expected on the basis of its chemistry, methane has a very small MIR. On the other hand, highly reactive alkenes, for example, have relatively high MIRs. Because the tail-pipe emissions of vehicles fueled on compressed natural gas (CNG) contain very low concentrations of organic compounds with high MIR values, CNG is an attractive alternate fuel.

Because the amount of O<sub>3</sub> formed depends on the VOC/NO<sub>x</sub> ratio of the air mass into which the organic species is emitted and is greatest at smaller VOC/NO<sub>x</sub> ratios, this focus on VOC reactivity is appropriate primarily for the high NO<sub>x</sub> conditions found in the most polluted urban centers. For effective O<sub>3</sub> control throughout an air basin or region, from urban city cores to the downwind suburban and rural areas, it must be used in conjunction with a stringent NO<sub>x</sub> control policy.

### Tropospheric Chemistry and Risk Assessment

Clearly, if risk management decisions and regulations are to be both health-protective and cost-effective, the atmospheric chemistry input into the exposure portion of the risk assessments must be reliable (89). In the United States, the Clean Air Act Amendments of 1990 specified 189 chemicals as hazardous air pollutants (HAPs) (90). HAPs include a wide range of industrial and agricultural chemicals, as well as complex mixtures of polycyclic organic matter. Although there are emissions sources of these HAPs, some are also formed at least in part by

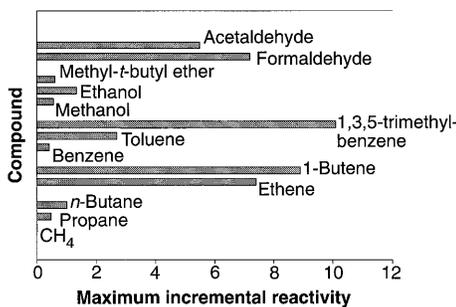


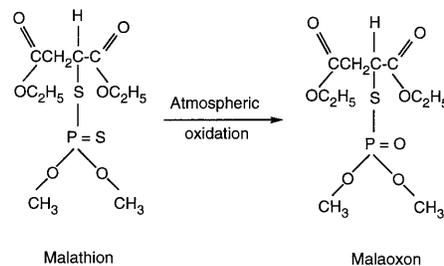
Fig. 5. Maximum incremental reactivities of some typical organics in grams of O<sub>3</sub> formed per gram of each organic emitted [data from (84)].

chemical transformations in air (acetaldehyde and formaldehyde produced in VOC-NO<sub>x</sub> oxidations, for instance) (91–93).

HAPs are often activated into more toxic compounds, or deactivated into less toxic species, by reactions after they are released into the atmosphere (12, 13). Classic examples of such atmospheric activation and deactivation are found in the area of pesticides (94, 95). An example of atmospheric deactivation is found in the use of 1,3-dichloropropene, where a mixture of the cis and trans isomers is the active ingredient in some soil fumigants (such as Telone, used in the control of nematodes). Because this HAP is an alkene, it reacts rapidly with OH. Rate constants for the reaction of the cis and trans isomers with OH are 0.77 and  $1.3 \times 10^{-11}$  cm<sup>3</sup> per molecule s<sup>-1</sup>, respectively (96). At an OH concentration of  $1 \times 10^6$  radicals cm<sup>-3</sup>, the lifetimes ( $\tau$ ) of the cis and trans isomers are calculated to be  $\tau = (k[\text{OH}])^{-1}$  ~36 and 21 hours, respectively, where  $k$  is the appropriate rate constant. Their reactions with O<sub>3</sub> are much slower, and lifetimes at an O<sub>3</sub> concentration of 70 ppb are 45 days and 10 days for these two isomers.

Thus, although 1,3-dichloropropene is a HAP, it is destroyed relatively rapidly by reaction with key atmospheric oxidants. Hence, long-range transport and persistence in the environment are not as important as for some other pesticides such as the halogenated alkane dibromochloropropane. However, the products of the OH oxidation of 1,3-dichloropropene include formyl chloride [HC(O)Cl] and chloroacetaldehyde (ClCH<sub>2</sub>CHO). It is not clear whether these present potential health risks at the concentrations at which they are formed in ambient air.

An example of atmospheric activation is the atmospheric oxidation of organophosphorus insecticides, such as the extremely toxic ethyl parathion, which has been banned in the United States, and malathion, which has widespread commercial and domestic uses. In ambient air, both are rapidly activated, in part by reaction with OH radicals (97); and the P=S bond is oxidized to the P=O oxone form (94, 95).



Scheme 2

The importance of this transformation was established in a definitive study involving aerial spraying of a populated area in

southern California to combat an invasion of the Mediterranean fruit fly (98). A key finding was that although malaoxon was initially present as an impurity in the malathion, its concentration relative to malathion measured at several ground locations increased dramatically after the application, to as much as a factor of 2 greater than that of the parent pesticide 2 to 3 days after spraying. One concern is that the oral toxicity of malaoxon in rats is much greater than that of the parent malathion (98).

### Respirable Mutagens and Carcinogens in Ambient Air: Atmospheric Transformations of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in our air environment (99–103), being present as volatile, semivolatile, and particulate pollutants (104–106) that are the result of incomplete combustion. Emissions sources are mobile [such as diesel and gasoline engine exhausts (107–114)], stationary (such as coal-fired, electricity-generating power plants), domestic [such as environmental tobacco smoke (115) and residential wood or coal combustion (116, 117)], and area sources (such as forest fires and agricultural burning).

The importance of PAHs to air pollution chemistry and public health was recognized in 1942 with the discovery that organic extracts of particles collected from ambient air produced cancer in experimental animals (118). Some three decades later, in 1972, a National Academy of Sciences panel reported that, in addition to the already well-known carcinogenic PAHs such as benzo[a]pyrene (BaP) (119), other as yet unidentified carcinogenic species must also be present (99). Since then, chemical and toxicological research has continued not only on BaP and associated PAHs (99–103, 114), as reflected in recent risk assessments for Copenhagen (120) and the state of California (121), but increasingly on these unknown carcinogens.

In 1977, a breakthrough occurred with the discovery that organic extracts of particles collected in the United States (122, 123), Japan (124), Germany (125), and subsequently in Scandinavia (126–128) contained genotoxic compounds that showed strong frame-shift-type mutagenic activity on strain TA98 in the Ames *Salmonella typhimurium* bacterial assay (129–132). Most important, metabolic activation was not required. Therefore, the particles must contain not only promutagens already known to be present, such as BaP, but also hitherto unknown, powerful, direct mutagens. A key question then became: Could some of these direct mutagens also be the unknown carcinogens?

Today this phenomenon of direct bacterial mutagenicity in *Salmonella* assays is recognized as being characteristic of respirable particles collected in polluted air sheds throughout the world, such as Finland (133), Mexico City (134), Athens (135), Rio de Janeiro (136), and a number of Italian towns (137). This is the case not only for studies employing the Ames reversion assay but also those using the *S. typhimurium* TM677 forward mutation assay (138–140). In addition, particles collected at several selected sites in southern California were shown to contain human cell mutagens (141).

Establishing the chemical natures, abundance in air, sources, reactions, and sinks—of these gaseous and particle-bound genotoxic air pollutants is an essential element in risk assessments of combustion-generated pollutants. We focus here on one important aspect of such evaluations: the formation of directly mutagenic nitro-PAH derivatives [for reviews, see (16) and (146–150)].

An important aspect of this research area is the use of bioassay-directed fractionation (151). In this novel approach, the various chemical constituents are separated by high-performance liquid chromatography (HPLC), and the mutagenicity of each fraction is then determined by the Ames *Salmonella* assay (129, 130), generally with the microsuspension modification, which greatly increases its sensitivity (152). The mutagenic activity for each HPLC fraction is plotted in a manner analogous to a conventional chromatogram and is referred to as a mutagram [see, for example, (149, 153)].

Many directly mutagenic mono- and dinitro-PAH derivatives have been identified in extracts of primary combustion-generated particles collected from diesel soot (108–112, 151), automobile exhaust (154), coal fly ash (155), and wood smoke (116, 127, 128), and in respirable particles collected from polluted ambient air (126, 128, 147, 149, 150, 156–159). Certain of these, such as 1-nitropyrene and 3-nitrofluoranthene and several dinitropyrenes, are strong direct mutagens [for reviews see (107, 148–150, 157–161)].

However, the distribution of the nitro-PAH isomers in the direct emissions is generally significantly different from that in extracts of particles actually collected from ambient air (150, 162). For example, 2-nitrofluoranthene and 2-nitropyrene, both strong direct mutagens in the Ames assay, are ubiquitous components of particulate matter in areas ranging from Scandinavia to California, even though they are not directly emitted from almost any combustion sources (163–166). Indeed, they have been

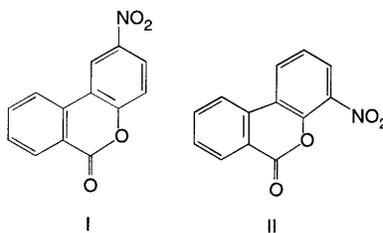
found in different types of air sheds throughout the world (167).

The key to understanding the ubiquitous occurrence of these 2-nitro derivatives was the observation that they form rapidly in homogeneous reactions of gaseous pyrene and fluoranthene in irradiated  $\text{NO}_x$ -air mixtures (168). The mechanism involves OH radical attack on the gaseous PAH, followed by  $\text{NO}_2$  addition at the free radical site (Fig. 6), which occurs in competition with the reaction with  $\text{O}_2$ . The kinetics of the competing reactions of such radicals with  $\text{O}_2$  and  $\text{NO}_2$  are uncertain (169, 170). However, in the presence of sufficient  $\text{NO}_2$ , the nitro-PAH products are formed and may then condense out on particle surfaces (150, 163, 165, 168).

This OH-radical initiated mechanism also explains the presence in ambient air, and the formation in irradiated PAH- $\text{NO}_x$ -air mixtures, of volatile nitroarenes from gaseous naphthalene and the methyl naphthalenes, such as 1- and 2-nitronaphthalenes (171) and 1- and 2-methylnitronaphthalene isomers (172), respectively. These nitroarenes are also formed in the dark by the gas-phase attack of nitrate radicals on the parent PAHs in  $\text{N}_2\text{O}_5$ - $\text{NO}_3$ - $\text{NO}_2$ -air mixtures (150, 171, 173).

Although 2-nitrofluoranthene and 2-nitropyrene are powerful direct mutagens found in ambient particles throughout the world, in southern California air they contribute only ~5 to 10% of the total direct mutagenicity (150). Recently, however, the isolation and quantification of two isomers of nitrodibenzopyranone—2- and 4-nitro-6H-dibenzo[*b,d*]pyran-6-one (Scheme 3)—from both the gas and particle phases in ambient air have helped to make up this deficit in ambient samples assayed with the microsuspension modification of the Ames assay (149, 150, 174–176).

These nitrolactones are also formed in



Scheme 3

irradiated phenanthrene- $\text{NO}_x$ -air mixtures in laboratory systems through OH radical-initiated reactions (149, 150, 176). Of interest to toxicologists as well as atmospheric chemists, the 2-nitro isomer (I in Scheme 3) makes a major contribution to the total direct mutagenicity of ambient air (150).

A recent report (177) showed that in ambient air, nitronaphthalenes and meth-

ylnitronaphthalenes contribute significantly not only to the daytime gas-phase mutagenicity but also, to an even larger extent, to the nighttime mutagenicity of the gaseous phase of ambient air collected in Redlands, California, approximately 60 miles east (downwind) of Los Angeles. This was attributed to  $\text{NO}_3$  radical-initiated attack on naphthalene and methylnaphthalene.

In summary, gas-phase daytime OH and nighttime  $\text{NO}_3$  radical-initiated reactions of simple volatile and semivolatile PAHs to form nitro-PAH derivatives appear to be responsible for a substantial portion of the total direct mutagenic activity of respirable airborne particles—as much as 50% in southern California (150). Furthermore, the total vapor-phase direct mutagenicity of ambient air, at least in that region, is approximately equal to that of the particle phase (149, 150, 178). The remaining mutagenic activity of both phases appears to be the result of more polar, complex PAH derivatives that have not as yet been characterized (149, 150, 179). Heterogeneous reactions of gases with particle-bound PAHs are also important but are beyond the scope of this article [see (16, 146, 180–184) and references therein].

Clearly, reliable risk assessments of PAHs will require a great deal of new toxicological and chemical research on the atmospheric formation, fates, and health effects of these respirable airborne mutagens.

## PM10 and PM2.5

Particulate matter less than 10  $\mu\text{m}$  in diameter, known as PM10, has come under detailed scrutiny as a result of recent epidemiological studies (185–187) that suggest that an increase in the concentration of inhaled particles of 10  $\mu\text{g m}^{-3}$  is associated with a 1% increase in premature mortality. Because it is the smaller particles that reach the deep lung (188), a PM2.5 standard is under consideration in the United States.

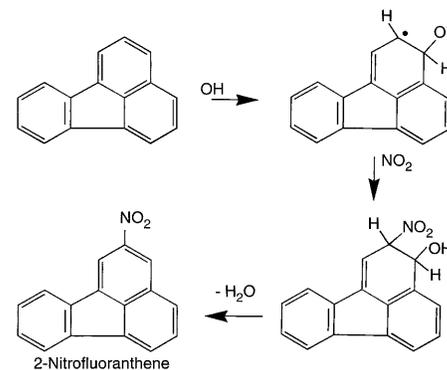


Fig. 6. Mechanism of formation of 2-nitrofluoranthene in air.

What is particularly interesting from a chemical point of view is that this relation between mortality and PM10 has been reported to hold regardless of the area in which the studies have been carried out, varying from cities with major SO<sub>2</sub> and particle sources to those with much lower direct emissions of these pollutants but with substantial formation of photochemical oxidants. This pattern suggests either that there is a general inflammatory response to inhalation of such particles and that the specific chemical composition is not important or that there are common reactive intermediates that are found in most particles (189).

The smallest particles (Fig. 7) tend to be those formed by combustion processes and by gas-to-particle conversions. As a result, their composition is complex and generally includes sulfates, nitrates, and organics, particularly polar oxidized organics (190–192). In areas such as Los Angeles, as much as 50% of the organics in aerosols does not originate from direct emission (that is, as primary pollutants) but are formed in VOC-NO<sub>x</sub> oxidations (that is, they are secondary pollutants) (190–192). Hence, the formation and fate of such particles is intimately associated with the formation of O<sub>3</sub> and other photochemical oxidants. Whether there is enough chemistry and photochemistry in such particles to generate reactive species that might be associated with the reported health effects is not known.

Particularly interesting are results from a recent laboratory study dealing with the effects of changes in diesel engine designs on the size distributions of exhaust particles. Emissions of particles in the accumulation mode (0.046 to 1.0 μm), as well as the total

particulate mass, from a 1991 heavy-duty engine running on a low-sulfur fuel (0.01 weight % S) were much lower than from a less sophisticated 1988 model operating on the same fuel. Both were running under steady-state conditions. However, there was a 30-fold or greater increase in the number of ultrafine particles (0.0075 to 0.046 μm) emitted by the 1991 engine with its newer technology (113).

Clearly, understanding the chemistry of aerosol particles in the troposphere is critical to quantifying the relation between emissions of VOCs and NO<sub>x</sub> and the formation and fate of photochemical oxidants, as well as elucidating relations between the chemical composition and sizes of these aerosol particles and their health effects. This issue has attracted national and international public attention because of its potential impacts.

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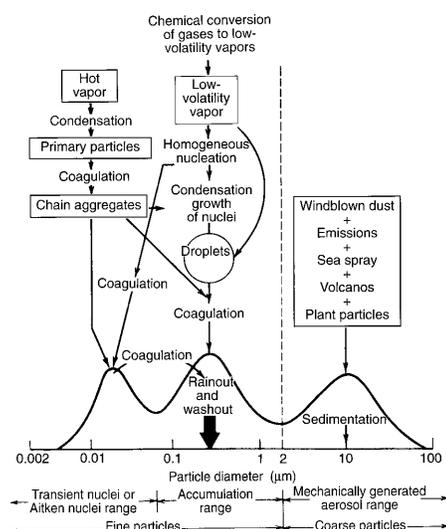


Fig. 7. Schematic sources of atmospheric aerosols in different size ranges [from (193)].

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Laboratory investigations have shown that reaction 1 can occur in a spin-forbidden mode at wavelengths between 310 and 325 nm (9), and even up to 410 nm (10). In the latter case, calculated O(<sup>1</sup>D) and OH formation at low-sun conditions at mid-latitudes will increase by more than a factor of 5 compared with earlier estimates (8). Globally and diurnally averaged, the tropospheric concentration of OH radicals is about 10<sup>6</sup> cm<sup>-3</sup>, corresponding to a tropospheric mixing ratio of only about 4 × 10<sup>-14</sup> (11). Reaction with OH is the major atmospheric sink for most trace gases, and therefore their residence times and spatial distributions are largely determined by their reactivity with OH and by its spatiotemporal distribution. Among these gases, methane (CH<sub>4</sub>) reacts rather slowly with OH, resulting in an average residence time of about 8 years and a relatively even tropospheric distribution. The residence times of other hydrocarbons are shorter, as short as about an hour in the case of isoprene (C<sub>5</sub>H<sub>8</sub>) and the terpenes (C<sub>10</sub>H<sub>16</sub>), and consequently, their distributions are highly variable in space and time.

Reliable techniques to measure OH and other trace gases important in OH chemistry have recently been developed and are being used in field campaigns, mainly to test photochemical theory (12). However, because of their complexity they cannot be used to establish the highly variable temporal and spatial distribution of OH. For this purpose, we have to rely on model calculations, which in turn must be validated by testing of their ability to correctly predict the distributions of industrially produced chemical tracers that are emitted into the atmosphere in known quantities and removed by reaction with OH (such as CH<sub>3</sub>CCl<sub>3</sub> and other halogenated hydrocarbons) (13). Distributions of OH derived in this way (Fig. 1) can be used to estimate the removal rates and distributions of various important atmospheric trace gases, such as CO, CH<sub>4</sub>, NMHCs, and halogenated hydrocarbons. In the tropics, high concentrations of water vapor and solar UV radiation combine to produce the highest OH concentrations worldwide, making this area the photochemically most active region of the atmosphere and a high priority for future research.

Especially because of its role in producing OH, ozone (O<sub>3</sub>) is of central importance in atmospheric chemistry. Large amounts of ozone are destroyed and produced by chemical reactions in the troposphere, particularly the CO, CH<sub>4</sub>, and NMHC oxidation cycles, with OH, HO<sub>2</sub>, NO, and NO<sub>2</sub> acting as catalysts. Because emissions of NO, CO, CH<sub>4</sub>, and NMHC

# Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry

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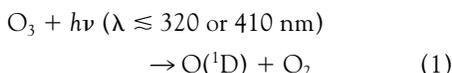
Atmospheric aerosols play important roles in climate and atmospheric chemistry: They scatter sunlight, provide condensation nuclei for cloud droplets, and participate in heterogeneous chemical reactions. Two important aerosol species, sulfate and organic particles, have large natural biogenic sources that depend in a highly complex fashion on environmental and ecological parameters and therefore are prone to influence by global change. Reactions in and on sea-salt aerosol particles may have a strong influence on oxidation processes in the marine boundary layer through the production of halogen radicals, and reactions on mineral aerosols may significantly affect the cycles of nitrogen, sulfur, and atmospheric oxidants.

Over the past decade, there has been intense interest concerning the role of aerosols in climate and atmospheric chemistry. The climatic effects of aerosols had already been recognized in the early to mid-1970s [for a review, see (1)], but the focus of scientific attention shifted during the 1980s to the impact of the growing atmospheric concentrations of CO<sub>2</sub> and other "greenhouse" gases. Scientific interest in the climatic role of aerosols was rekindled after the proposal of a link between marine biogenic aerosols and global climate (2). This proposal, which was originally limited to the effects of natural sulfate aerosols, triggered a discussion about the role of anthropogenic aerosols in climate change (3), which led to the suggestion that they may exert a climate forcing comparable in magnitude, but opposite in sign, to that of the greenhouse gases (1, 4).

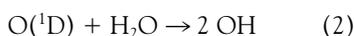
The main sources of biogenic aerosols are the emission of dimethyl sulfide (DMS) from the oceans and of nonmethane hydrocarbons (NMHCs) from terrestrial vegetation, followed by their oxidation in the troposphere (1). Carbonyl sulfide (COS), which has a variety of natural and anthropogenic sources, is an important source for stratospheric sulfate aerosol (5) and therefore indirectly plays an important role in stratospheric ozone chemistry (6). These sources are susceptible to changes in physical and chemical climate: The marine production of DMS is dependent

on plankton dynamics, which is influenced by climate and oceanic circulation, and the photoproduction of COS is a function of the intensity of ultraviolet-B (UV-B) radiation. Air-sea transfer of DMS changes with wind speed and with the temperature difference between ocean and atmosphere. The amount and composition of terpenes and other biogenic hydrocarbons depend on climatic parameters, for example, temperature and solar radiation, and would change radically as a result of changes in the plant cover due to land use or climate change. Finally, the production of aerosols from gaseous precursors depends on the oxidants present in the atmosphere, and their removal is influenced by cloud and precipitation dynamics. Consequently, the fundamental oxidation chemistry of the atmosphere is an important factor in the production of atmospheric aerosols. In turn, aerosols may also play a significant role in atmospheric oxidation processes.

The oxidation efficiency of the atmosphere is primarily determined by OH radicals (7, 8), which are formed through photodissociation of ozone by solar UV radiation, producing electronically excited O(<sup>1</sup>D) atoms by way of



where  $h\nu$  is a photon of wavelength  $\lambda$ , and by



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