Articles

Urban Air Pollution: State of the Science

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Urban air pollution is comprised of a highly complex mixture of gaseous and particulate components. Much progress has been made in our understanding of the detailed chemistry and physics of air pollution, but important areas of uncertainty still remain.

THE URBAN ATMOSPHERE IS A GIANT CHEMICAL REACTOR IN which pollutant gases such as hydrocarbons and oxides of nitrogen and sulfur react under the influence of sunlight to create a variety of products, including ozone and submicrometer aerosols. The National Ambient Air Quality Standard for ozone allows no more than one exceedance per year (on average over 3 years) of a daily maximum 1-hour average ozone concentration of 0.12 parts per million (ppm) by volume. Although substantial progress has been made in reducing airborne levels of sulfur dioxide and carbon monoxide in U.S. cities, the standard for ozone was exceeded during 1983–1985 in 76 urban areas of the United States (*1*). Of the six "criteria" pollutants for which air quality standards have been established, ozone remains the most resistant to efforts at abatement.

Ozone

The only significant chemical reaction producing ozone in the atmosphere is that between atomic and molecular oxygen:

$$O + O_2 + M \rightarrow O_3 + M \qquad (1)$$

where M is any third body, such as N_2 or O_2, that removes the energy of the reaction and stabilizes O_3. At high altitudes (above 20 km) the oxygen atoms are produced by photodissociation of molecular oxygen by radiation in the deep ultraviolet. At lower altitudes, where only radiation with wavelengths greater than 280 nm is present, the only significant oxygen atom production is from photodissociation of nitrogen dioxide:

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

where the photon $h\nu$ has a wavelength between 280 and 430 nm. The nitric oxide produced in this reaction reacts rapidly with ozone to regenerate NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

The above three reactions occur rapidly, establishing a steady-state ozone concentration given by the so-called photostationary state relation,

$$[O_3] = \frac{J[NO_2]}{k[NO]} \qquad (4)$$

where k is the rate constant for reaction 3 and $J[NO_2]$ is the photolysis rate of NO_2. At a ratio of $[NO_2]/[NO] = 1$, $[O_3]$ predicted by the photostationary state at solar noon in U.S. latitudes is about 20 parts per billion (ppb) by volume. While ozone concentrations in unpolluted tropospheric air vary between 20 and 50 ppb, levels as high as 400 ppb are obtained in polluted urban areas.

In reaction 3, one ozone molecule is required to regenerate NO_2 from NO. A reaction path that converts NO to NO_2 without consuming a molecule of ozone circumvents reaction 3 and allows ozone to accumulate. Such a path is provided by the presence of hydrocarbons (*2*). In particular, peroxy radicals (RO_2 where R is an alkyl group) produced in the oxidation of hydrocarbon molecules react with NO to form NO_2, thereby shifting the photostationary state in favor of ozone production. The net process is:

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (5)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (6)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (7)$$

$$\text{Net:} \quad RO_2 + O_2 + h\nu \rightarrow RO + O_3 \qquad (8)$$

The rate of ozone generation is related closely to the rate of RO_2 production. Generation of the organic peroxy radicals RO_2 occurs largely by the attack of the hydroxyl radical (OH) on hydrocarbons. Interestingly, OH attack, which ultimately scavenges hydrocarbons from the atmosphere, is also that which, through oxidation of NO to NO_2, produces ozone. The chemical structure of the hydrocarbon determines the number and form of peroxy radicals and hence the number of NO to NO_2 conversions that occur as the hydrocarbon is oxidized.

There are three principal sources of hydroxyl radicals in the sunlit urban atmosphere: (i) photochemical dissociation of ozone, (ii) photochemical dissociation of carbonyl compounds, and (iii) photochemical dissociation of nitrous acid. Photochemical dissociation of ozone leads to the formation of excited oxygen atoms, $O(^1D)$, that react with water vapor to form hydroxyl radicals:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (9)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (10)$$

where the photon has a wavelength between 280 and 310 nm. Photochemical dissociation of aldehydes (RCHO) leads to the formation of radicals that through a rapid series of reactions lead ultimately to the formation of OH:

$$RCHO + h\nu \rightarrow R + HCO \qquad (11)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (12)$$

$$HO_2 + NO \rightarrow NO_2 + OH \qquad (13)$$

where the photon has a wavelength between 280 and 360 nm. An important source of OH radicals is also nitrous acid (HONO). Nitrous acid achieves concentrations in polluted urban air of 1 to 10

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ppb, with maximum levels occurring just before sunrise. In the presence of sunlight, HONO has a photolysis lifetime of about 15 minutes, and its photolysis

$$HONO + h\nu \rightarrow OH + NO \qquad (14)$$

provides an early morning source of OH. Its nighttime formation route is thought to involve a heterogeneous hydrolysis of NO_2.

The primary OH removal process is the reaction with NO_2 to form gaseous nitric acid:

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (15)$$

(Reaction with hydrocarbons is not actually a sink for OH since subsequent reactions of the OH-hydrocarbon reaction products, most of the time, result in regeneration of OH.) Nitric acid is also a major sink for nitrogen oxides through the above reaction.

One important free radical removal process for the organic peroxy radicals involves the peroxyacetyl radical reaction with NO_2 to produce peroxyacetylnitrate, denoted PAN:

$$CH_3C(O)O_2 + NO_2 \rightleftarrows CH_3C(O)O_2NO_2 \qquad (16)$$

The formation reaction is reversible as the PAN molecule can decompose thermally with a lifetime at 298 K of about 45 minutes. The PAN molecule serves as a temporary reservoir for both the peroxyacetyl radical and NO_2, with its concentration dependent on temperature and on the ratio of NO to NO_2 concentrations (because the peroxyacetyl radical also reacts with NO to form NO_2). PAN concentrations peak in late afternoon and early evening; levels of 5 to 10 ppb are measured in Los Angeles.

Because the formation of ozone and other secondary species is not instantaneous following emission of hydrocarbons and nitrogen oxides, significant transport and mixing occur simultaneously with chemical reaction. The complex interplay between atmospheric chemistry and transport processes can be visualized by considering a column of air of arbitrary cross section that extends from the surface to the top of the boundary layer. The height of the daytime boundary layer is usually constrained by an elevated temperature inversion (that is, warm air over cold) at about 1 to 2 km, the so-called mixing height. Turbulent convection in the boundary layer ensures rapid vertical mixing in the layer.

Table 1. Ambient air hydrocarbons in 39 U.S. cities—the 25 most abundant compounds based on median concentration (*66, 67*).

Compound	Concentration (ppbC)	
	Median	Maximum
Isopentane	45.3	3393
n-Butane	40.3	5448
Toluene	33.8	1299
Propane	23.5	393
Ethane	23.3	475
n-Pentane	22.0	1450
Ethylene	21.4	1001
m-Xylene, *p*-xylene	18.1	338
2-Methylpentane	14.9	647
Isobutane	14.8	1433
Acetylene	12.9	114
Benzene	12.6	273
n-Hexane, 2-ethyl-1-butene	11.0	601
3-Methylpentane	10.7	351
1,2,4-Trimethylbenzene	10.6	81
Propylene	7.7	455
2-Methylhexane	7.3	173
o-Xylene	7.2	79
2,2,4-Trimethylpentane	6.8	106
Methylcyclopentane	6.4	293
3-Methylhexane	5.9	168
2-Methylpropene, 1-butene	5.9	365
Ethylbenzene	5.9	159
m-Ethyltoluene	5.3	83
n-Heptane	4.7	233

The air parcel can be thought to follow a trajectory through the region as determined by the horizontal wind components. If the air parcel starts upwind of the urban core, the relatively clean parcel picks up hydrocarbon and NO_x emissions as it is carried over the source-rich areas. Over a time scale of about 1 hour, hydroxyl radical attack on the hydrocarbons commences. As the air parcel moves out of the urban core, the emission density decreases. Concentrations of precursor hydrocarbon and nitrogen oxides (NO_x) peak and start to decline with downwind distance as a result of the effects of chemical reaction and mixing. Ozone in the parcel continues to increase as the array of hydrocarbons is photooxidized. The increase in O_3 level is sustained over a 1- to 5-hour period as the more reactive olefins and aromatics are consumed. After 5 to 10 hours of travel, medium reactivity hydrocarbons contribute to net ozone production. The ozone level in the air parcel ultimately begins to decrease reflecting the effects of dilution, conversion of NO_2 to nitric acid, and removal at the surface. At sunset, all photochemical ozone production ceases. At night when the regeneration of ozone by means of NO_2 photolysis does not occur, the overall effect of the ozone reactions with NO and NO_2 is to provide a route for converting the nitrogen oxides to nitric acid. (We will discuss nighttime chemistry shortly.) During nighttime, radiative cooling at the ground usually leads to the establishment of a ground-based inversion layer with a height of several tens to hundreds of meters inhibiting ground-based emissions from reaching any ozone stored aloft. The following sunrise, the inversion is rapidly eroded, bringing ozone and other products from the previous day stored aloft down to mix with the fresh emissions and to feed the second day's photochemistry.

This concept of an "air parcel" traveling downwind from the point of maximum emission density, that is, the urban core, to the location of peak ozone concentration is the central idea behind the U.S. Environmental Protection Agency's Empirical Kinetic Modeling Approach (EKMA) used to relate hydrocarbon and NO_x emissions changes to changes in maximum ozone concentrations for a particular urban area (*3*).

Hydrocarbon Chemistry

The feature that distinguishes the chemistry of the urban atmosphere from that of the natural troposphere is the relatively high concentrations of a great number of anthropogenic hydrocarbons (Table 1).

Alkanes. Alkanes constitute a major class of anthropogenic hydrocarbon emissions (see Table 1). Under urban conditions alkanes react with OH radicals during daylight hours and with the NO_3 radicals at night, with the latter process being of minor (<10%) importance to total alkane consumption (*4–6*). Both reactions proceed by H-atom abstraction from C–H bonds. The resulting alkyl (R) radical reacts rapidly, and exclusively, with O_2 to yield an alkyl peroxy radical (RO_2). Under tropospheric conditions, these alkyl peroxy radicals react with NO by two pathways

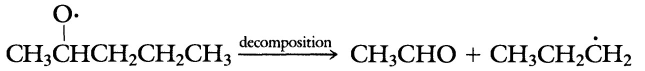
$$RO_2 + NO \rightarrow NO_2 + RO \qquad (17)$$

$$\xrightarrow{M} RONO_2 \qquad (18)$$

with HO_2 radicals

$$RO_2 + HO_2 \rightarrow RO_2H + O_2 \qquad (19)$$

or with other RO_2 radicals. At NO concentrations above about 30 parts per trillion (ppt), reaction with NO is the dominant reaction pathway for RO_2 radicals. The yield of the alkyl nitrate ($RONO_2$) increases with the number of carbon atoms in RO_2, for example, from <0.014 for a C_2 alkane up to about 0.33 for a C_8 alkane. The alkoxy (RO) radicals react by unimolecular decomposition, unimolecular isomerization, or with O_2. For the 2-pentoxy radical, for example,



$$CH_3\overset{O\cdot}{\overset{|}{C}}HCH_2CH_2CH_3 \xrightarrow{\text{decomposition}} CH_3CHO + CH_3CH_2\dot{C}H_2 \quad (20)$$

$$\xrightarrow{\text{isomerization}} CH_3CHOHCH_2CH_2\dot{C}H_2 \quad (21)$$

$$\xrightarrow{O_2} CH_3COCH_2CH_2CH_3 + HO_2 \quad (22)$$

The isomerization reactions occur mainly by a 1,5 shift of hydrogen, so they require a four-carbon chain; where this is available, these reactions are expected to dominate over decomposition or reaction with O_2. The reactions occurring after alkoxy radical isomerization have not been experimentally established, although many routes have been postulated.

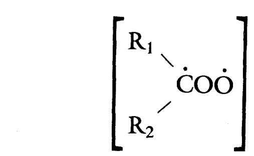
For alkanes, the expected products of photooxidation include aldehydes, ketones, alkyl nitrates, and bifunctional compounds including keto-alcohols and aldehyde-alcohols. It is likely that these intermediate products continue to react with other species present. Although it is predicted that, for alkanes with four or more carbons, δ-bifunctional compounds of the general form $RCOCH_2CH_2CHOR'$ would be formed, at present no definitive evidence for the formation of these compounds exists. Also, our present understanding suggests the possibility of formation of δ-hydroxynitrate alkanes, for example, $RCHOHCH_2CH_2CH(ONO_2)R'$. Investigations are needed to determine whether such compounds are formed in the photooxidation of alkanes with five or more carbons.

In summary, the chemistry of C_2 to C_4 alkanes is reasonably well understood. For C_5 and larger alkanes, the fate of the corresponding alkoxy radicals is not well established, and the role of $RO + NO_2 \rightarrow RONO_2$ for such species as an NO_x sink is not fully known. The chemistry of cycloalkanes is essentially unknown.

Alkenes. The rates of reaction of alkenes with OH radicals are significantly higher than those of the corresponding alkanes. Alkenes also react with NO_3 and O_3. Alkene reactions tend to dominate product generation shortly after the emission of a hydrocarbon mixture into the atmosphere. All of the OH-radical–alkene reactions proceed by OH addition to the double bond followed by rapid addition of O_2 to yield the corresponding hydroxyalkyl peroxy radical. Subsequent reaction of the hydroxyalkyl peroxy radical with NO yields the β-hydroxyalkoxy radical. (The hydroxynitrate path accounts for only about 1% and can be neglected.) While the β-hydroxyalkoxy radicals can react with O_2 or undergo unimolecular decomposition or isomerization, available data indicate that at room temperature isomerization does not compete with decomposition (*6*). Furthermore, only for ethene does reaction with O_2 compete with decomposition. Thus, for alkenes with more than three carbons, OH radical reaction leads, by cleavage of the C=C double bond, to the formation of aldehydes or ketones or both.

NO_3 reacts with alkenes by addition to the alkene double bond. The adduct is expected to react first with O_2 and then NO, leading to aldehydes, ketones, or dinitrates (*7*, *8*). Because of the reported high toxicity of the dinitrates, further research is needed to better define their yields. Furthermore, the reaction sequences occurring in the absence of NO, as typically occurs at night when NO_3 radical reactions are of importance, are not presently known.

The O_3-alkene reaction proceeds by addition of O_3 across the olefinic double bond followed by rapid decomposition of the resulting molozonide. The major uncertainty associated with this reaction concerns the fate of the initially energy-rich biradical



(23)

which can be collisionally stabilized or undergo unimolecular decomposition (*9*). The thermalized biradicals can react with a number of species, including H_2O, NO, NO_2, SO_2, CO, and aldehydes, while the decomposition products have not been fully established.

Carbonyls. Aldehydes undergo photolysis and reaction with OH and NO_3 radicals, the first two being the major loss processes. The formaldehyde-OH reaction yields the formyl (HCO) radical which subsequently reacts with O_2 to form HO_2 and CO:

$$\begin{array}{l} OH + HCHO \rightarrow H_2O + HCO \\ \qquad\qquad\qquad\qquad\qquad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\quad HO_2 + CO \end{array} \quad (24)$$

For the higher aldehydes, the acyl (RCO) radical initially formed rapidly adds O_2 to yield a peroxyacyl radical [$RC(O)OO\cdot$]. As noted earlier, the peroxyacyl radical can react with NO or NO_2, the latter reaction leading to the peroxyacylnitrates (PANs). It is estimated that 80 to 90% of the formaldehyde in the urban atmosphere results from the photooxidation of other organics and only about 10 to 20% from direct emission.

Ketones are exemplified by acetone and its higher homologues. Photolysis and OH reaction are the major atmospheric loss processes, although, with the exception of acetone, photolysis is probably of minor importance. The major reaction products from the atmospheric reactions of ketones are aldehydes and PAN precursors, and bifunctional oxygen-containing compounds may be formed in small yield.

The most important uncertainties in carbonyl chemistry involve photolysis rates and quantum yields (for example, formaldehyde is known only to ±30%), the fate of hydroxycarbonyls (OH-olefin adducts and RO isomerization products), and the existence of nitrate carbonyls resulting from higher alkanes. Because carbonyl photolysis is such an important source of free radicals, uncertainties in photolysis rates translate into uncertainties in ozone formation rates.

Alcohols. The atmospheric reaction of the simple aliphatic alcohols involves OH attack, for example, for methanol:

$$OH + CH_3OH \xrightarrow{a} \dot{C}H_2OH + H_2O \quad (25)$$

$$\xrightarrow{b} CH_3O\cdot + H_2O \quad (26)$$

with path (a) accounting for about 85% of the overall reaction pathway at 298 K. Both the $\dot{C}H_2OH$ and $CH_3O\cdot$ radicals react with O_2 to give formaldehyde and HO_2. Thus, the overall methanol-OH reaction can be written as:

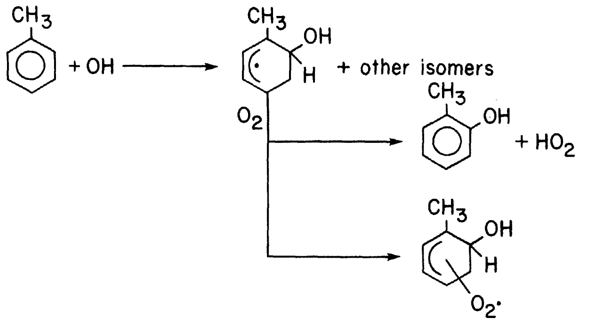
$$CH_3OH + OH \xrightarrow{O_2} H_2O + HO_2 + HCHO \quad (27)$$

Carboxylic acids. Carboxylic acids, such as formic and acetic acid, react with the OH radical through the formation of an addition complex, for example, for formic acid

$$\begin{array}{l} OH + HCOOH \rightarrow H_2O + COOH \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow O_2 \\ \qquad\qquad\qquad\qquad\quad CO_2 + HO_2 \end{array} \quad (28)$$

Products formed from the reactions of OH with higher carboxylic acids have not been established.

Aromatics. Aromatic hydrocarbons are a major class of organics associated with the urban environment (Table 1). The monocyclic aromatic hydrocarbons react solely with the OH radical, a reaction that can proceed by two pathways: (i) H-atom abstraction of alkyl H-atoms for alkyl-substituted aromatics from the alkyl-substituent groups and (ii) OH radical addition to the aromatic ring (*10*). The H-atom abstraction path leads mainly to the formation of aromatic aldehydes, such as benzaldehyde, with subsequent reactions of these aldehydes leading to the production of peroxyacylnitrates and nitrophenols. This H-atom abstraction path accounts for less than 10% of the overall OH radical reaction for benzene and the alkyl-substituted aromatic hydrocarbons. For toluene, for example, the OH-addition path is assumed to proceed by two routes:



The H-atom abstraction by O_2 from the OH-aromatic adduct to yield phenolic compounds has been shown to be relatively minor, accounting for about 16% of the overall OH radical products of toluene. The major reaction pathway is thought to be that involving ring cleavage of the OH-aromatic-O_2 adduct. The α-dicarbonyls, glyoxal, methylglyoxal, and biacetyl, which have been identified as products from benzene and the methyl-substituted benzenes, are indications of ring cleavage (*11–14*). In laboratory studies of the ring-fragmentation process, however, the total yield of products as a percentage of the parent aromatic is only about 30% for the toluene-OH reaction and approximately 50% for the *m*-xylene reaction (*11–16*). The remaining carbon-containing products have not been identified.

The uncertainties in atmospheric aromatic chemistry are major: (i) ring-opening versus ring-conserving pathways; (ii) the nature and yield of all products in ring-opening; and (iii) the phenol distribution and subsequent reactions of ring-conserving paths. These uncertainties have been well known to atmospheric chemists for 10 years; progress in reducing them requires development of new analytical techniques for large (more than six carbons) molecules at very low concentrations. Because aromatics constitute probably the most important class of reactive organics in the urban atmosphere, determining the detailed reaction pathways of these compounds constitutes one of the greatest needs in air pollution chemistry.

Nighttime Chemistry

The key difference between day and night chemistry, aside from the absence of photolytic reactions, is the accumulation at night of the nitrate free radical, NO_3, which is rapidly photolyzed during the day so that its daytime concentration is negligible. During the night, NO_3 is produced by

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (30)$$

which is followed by

$$NO_2 + NO_3 \underset{M}{\overset{M}{\rightleftarrows}} N_2O_5 \qquad (31)$$

where M is a third body. As noted earlier, NO and O_3 can scavenge each other by

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (32)$$

and NO_3 can be reconverted to NO_2 by

$$NO + NO_3 \rightarrow 2NO_2 \qquad (33)$$

or thermally decompose:

$$NO_3 \rightarrow NO + O_2 \qquad (34)$$

Finally, N_2O_5 is irreversibly converted to nitric acid in the presence of water:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (35)$$

The main importance of the nighttime chemistry is the conversion of NO_x into nitric acid by a route not involving OH radicals. The relative importance of different pathways leading to the formation of HNO_3 at night, namely the N_2O_5-H_2O reaction and NO_3 reactions with organic species, needs to be elucidated. The origin and fate of nitrous acid (HONO) at night also must be understood because of its role as an early morning OH source.

Since the NO_3 radical is the key to nighttime chemistry, comparison of predicted (by means of the above mechanism plus a number of other, less important reactions) and observed NO_3 concentrations provides a test of the degree of understanding of this chemistry (*17–21*). Predicted NO_3 concentrations have somewhat exceeded those measured, although the temperature-dependent cross section of NO_3 (*22*) has yet to be employed to relate its concentration to its absorption spectrum. Further comparisons of measurements and predictions for nighttime urban conditions are needed.

Chemical Reaction Mechanisms for Urban Air Pollution

Air pollution chemistry is studied experimentally at two levels: laboratory studies of the kinetics and mechanisms of individual reactions, and smog chamber experiments, in which single organics or mixtures of organics are photooxidized in the presence of NO_x. The main function of smog chambers is to provide data to test our degree of understanding of air pollution chemistry. Because the photodegradation of a hydrocarbon can involve 100 or more individual reactions, for even one organic molecule one must infer many of the chemical details from the relatively few species that can be measured in such chambers. Smog chambers are not a perfect simulation of atmospheric chemistry. For example, the light flux may not be the same as the solar flux, and, to facilitate measurement, organic concentration levels in chambers are usually about ten times those in the atmosphere. The most important problem relating to the use of smog chambers, however, is that the walls generally influence the chemistry occurring. Typically, the release of species absorbed on the walls may contribute 10% of the total free radicals in the chamber. Although empirical models of the wall radical source have been proposed (*23*), a fundamental understanding of the processes occurring at chamber walls is lacking. Elucidation of these heterogeneous processes involving NO_x is the most pressing need associated with evaluating smog chamber experiments.

About 500 smog chamber experiments have been carried out in both indoor and outdoor chambers over the past 15 years. Current chemical reaction mechanisms have been evaluated against a large fraction of these data and generally simulate peak ozone concentrations to within ±30%. It is generally agreed that an acceptable chemical mechanism must simulate this large body of smog chamber data at least as accurately as mechanisms it is proposed to replace. Because of a lack of measurements of many intermediate species and products, fitting of the chamber data for O_3, NO_x, PAN, and the starting organics provides only a global evaluation of a mechanism. It is possible that compensating errors in the mechanism may yield reasonable O_3 predictions.

Because it is not practical to use a mechanism that includes the detailed, specific chemistry of each organic compound present in the atmosphere (for example, for each of the compounds in Table 1), "lumping" procedures are required to limit both the number of species and the number of reactions included in chemical reaction mechanisms. Two general lumping approaches have emerged: (i) the "lumped molecule" approach in which a particular organic molecule, or a generalized organic species, is used to represent similar organics, and (ii) the "lumped structure" approach in which organics are grouped according to the type and number of carbon bonds in each compound.

Three mechanisms that are based on the most recent kinetic and mechanistic information are: (i) the Carbon Bond Mechanism—Version IV (CB4) (*24*), a lumped structure mechanism; (ii) the Carter-Atkinson-Lurmann (CAL) mechanism (*25*); and (iii) the Regional Acid Deposition Model (RADM) mechanism (*26*), the latter two being lumped molecule mechanisms. Although each of these mechanisms is based on the same body of available kinetic data, important uncertainties in those data have led to somewhat different treatments in the mechanisms of those areas where uncertainties exist.

Inorganic chemistry in all mechanisms is very similar, and thus discrepancies in predictions among them are the result of differing treatments of organic chemistry. There are three major differences in the representation of the organic chemistry in the above three mechanisms. As noted earlier, the mechanism of ring fragmentation in the aromatic-OH reaction has not yet been identified. The RADM mechanism uses dicarbonyls as surrogates for all the unidentified products, and, consequently, dicarbonyl yields in the RADM mechanism are approximately a factor of 2 higher than those in CB4 and CAL. The second major difference in the mechanisms concerns the treatment of PAN chemistry. The CB4 assumes a different temperature dependency than the other two mechanisms for the reaction of peroxyacetyl radicals with NO_2. The large negative activation energy used in the CB4 causes PAN formation to increase significantly as temperature decreases, while PAN formation in the CAL and RADM mechanisms is relatively insensitive to temperature changes. The third major difference among the mechanisms concerns the reactions of organic peroxy radicals with other radicals, which can lead to substantial differences in H_2O_2 predictions. Dodge (*27*) has reported extensive simulations with the three mechanisms. While the three mechanisms were found to predict nearly identical levels of ozone under most conditions, differences in predictions were noted with (i) high NO_x levels, (ii) high levels of aromatics, and (iii) low temperatures.

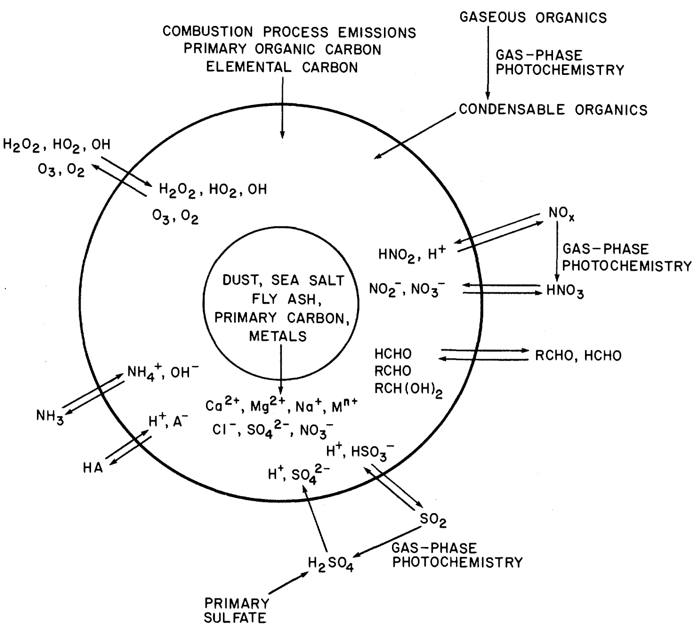


Fig. 1. Processes influencing the composition of a typical urban aerosol particle.

Inorganic atmospheric NO_x chemistry is well established. There exist, however, significant areas of organic chemistry where only the initial reaction and the first-generation products are known. A key question is whether resolving the uncertainties in the detailed chemistry will substantially change our understanding of the overall features of hydrocarbon/NO_x chemistry. Our current ability to simulate reasonably well the global behavior of the large body of smog chamber data would suggest not, although a more definitive resolution awaits the simulation of ambient data, particularly for intermediate species such as formaldehyde, hydrogen peroxide, PAN, and nitric acid. The 1987 Southern California Air Quality Study (SCAQS) offers promise in this regard (*28*).

Urban Aerosol

Particles of sizes below about 2-μm diameter are largely responsible for the severe visibility deterioration observed in areas like Los Angeles. Such particles are also easily respirable and may contain toxic or mutagenic components. Control of the fine particle component of the urban aerosol is a particularly important problem facing air pollution control agencies.

The atmospheric aerosol is a highly complex entity, representing a mixture of primary emissions, such as soot and fly ash, and secondary species that are the "sink" of many atmospheric chemical processes. Because of the role of the aerosol as an end product, knowledge of its chemical composition is essential to a full understanding of the chemical processes that preceded its formation. Prevalent compounds of urban aerosols are sulfates, nitrates, ammonium, trace metals, carbonaceous material, and water (Fig. 1).

Our detailed knowledge of the size-composition distribution of the urban aerosol is limited (*29–32*). Primary particles, once emitted, undergo chemical and physical processes that result in a continually changing chemical composition and particle size distribution. Particles of a single substance emitted from a specific source, for example, soot or sea salt, may react with the products of gas-phase reactions such as H_2SO_4 produced from the oxidation of SO_2. Also, the products of gas-phase reactions may themselves homogeneously nucleate to form new particles.

The gas-to-particle conversion process includes (i) homogeneous, homomolecular nucleation, that is, the formation of a new, stable particle from a single vapor species; (ii) homogeneous, heteromolecular nucleation, that is, the formation of a new particle involving two or more vapor species—usually one of the vapor species is water; and (iii) heterogeneous condensation, the transfer of vapor molecules to preexisting particles (*33*). Gas-phase chemical reactions generate products, some of which have a low vapor pressure. As these low-volatility products are formed, the atmosphere becomes supersaturated with respect to these species. The degree of supersaturation will determine the competition between new particle formation by nucleation and existing particle growth by condensation.

Aerosol sulfate forms from the gas-phase oxidation of SO_2 to H_2SO_4 followed by H_2SO_4 nucleation or condensation or from the oxidation of SO_2 in the aqueous phase of aerosols and water droplets. Sulfuric acid will also react with ammonia to form salts such as ammonium bisulfate (NH_4HSO_4), ammonium sulfate [$(NH_4)_2SO_4$], letovicite [$(NH_4)_3H(SO_4)_2$], or mixed salts with ammonium nitrate (*34, 35*). Catalytic oxidation of SO_2 may occur on soot aerosol surfaces (*36*).

Aerosol nitrate exists primarily as nitrate salts, principally ammonium nitrate, but also others such as sodium nitrate. The oxidation of NO_x to nitrate occurs primarily through the NO_2-OH reaction during the daytime and through the N_2O_5 hydrolysis route at night. Unlike sulfuric acid, nitric acid has a high vapor pressure and does not readily condense on aerosols. The formation of aerosol nitrate requires the presence of NH_3, or other alkaline species, to form salts such as NH_4NO_3. An equilibrium is presumed to exist among NH_3, HNO_3, and NH_4NO_3:

$$NH_3 + HNO_3 \rightleftarrows NH_4NO_3 \qquad (36)$$

This equilibrium is strongly influenced by temperature, relative humidity, and pH (*37, 38*), and favors the formation of NH_4NO_3 at low temperature, high humidity, and low pH.

Stelson *et al.* (*37, 38*) and others (*34, 35, 39, 40*) have postulated that the sulfate-nitrate-ammonium aerosol constituents should be in thermodynamic equilibrium with the local gas phase. Ambient measurements have generally confirmed the equilibrium relationship among these species (*41, 42*).

Carbonaceous aerosol generally accounts for a significant fraction of the fine urban particulate matter; in Los Angeles, for example, aerosol carbon alone accounts for about 40% of the total fine particle mass (*43*). Black graphitic (elemental) carbon particles are the predominant light-absorbing particulate matter in the atmosphere (*44*). The carbonaceous fraction of the urban aerosol consists of both primary (elemental and organic) and secondary components. The elemental carbon, nonvolatile and inert, is from sources of primary emissions. Organic carbon may be emitted as primary aerosol from sources or formed in the atmosphere from the low vapor pressure products of reactions involving hydrocarbons containing approximately seven or more carbon atoms (*45–50*). Organic aerosol components present in motor vehicle exhaust (*51*) and in ambient samples (*52*) have been found to be mutagenic in the Ames test, and soots have been shown to be carcinogenic in animal studies (*53*).

Aerosol carbon is not routinely monitored, and emissions data on carbonaceous particles are scarce. Cass *et al.* (*54*) carried out an inventory of organic and elemental carbon particle emissions in the Los Angeles area for 1980, which should be typical of most large urban areas. One-quarter of the total came from gasoline-powered vehicle exhaust, one-fourth from diesel engine exhaust, and the remainder from a large variety of stationary fuel burning, industrial, and distributed sources. Black elemental carbon emissions were dominated by diesel exhaust. The ratio of total carbon to elemental carbon in primary aerosol emissions was estimated to be about 3.2:1. Enhancement of this ratio in ambient samples relative to source emissions gives an indication of the extent of enrichment in organic aerosol attributable to secondary aerosol formation. Field measurements carried out in 1982 in Los Angeles showed little seasonal dependence in the ratio of total to elemental carbon (*43*), although some individual days at inland sites did show large levels of organic carbon enrichment. An enrichment of up to 0.54 parts organic carbon added to the 2.43:1 ratio observed at Lennox, a coastal site, represented a 22% increase in total carbon relative to elemental carbon from one end of the South Coast Air Basin to the other. On average over long periods of time, it was estimated that approximately 75% of Los Angeles fine aerosol carbon concentrations are attributable to primary source emissions, with the remainder caused by secondary aerosol formation.

Acid Deposition and Acidic Fogs

The importance of acid fog as a component of the general acidic deposition phenomenon has recently been recognized. Hoffmann and co-workers have reported pH values of fogs in southern California as low as 1.69 (*55*). These fogs were much more acidic, and concentrations of anions and cations such as SO_4^{2-}, NO_3^-, and NH_4^+ were higher by one to two orders of magnitude than in precipitation in the same areas. The physicochemical processes leading to acid fog have yet to be fully elucidated.

An acid fog encompasses virtually the entire range of atmospheric chemical phenomena: gas-phase chemistry to produce HNO_3 and H_2SO_4 vapors, aerosol formation, cooling of moist air followed by condensation of water vapor on the aerosol particles that serve as condensation nuclei, scavenging of gaseous species by the droplets, followed by ionization and aqueous-phase reactions. Gravitational settling delivers the acidic fog contents to the ground.

Several differences exist between a fog and a cloud environment. Urban radiation fogs typically develop under stable meteorological conditions resulting in weak mixing and significant vertical gradients of species like H_2O_2, NH_3, and HNO_3 (*56*). The deposition process during a dense radiation fog leads to rapid removal from the atmosphere of the major ionic species. Because of the proximity of the fog to sources of pollutants like SO_2 and NO_x, gas-phase pollutant concentrations in the fog can reach much higher levels than in a cloud. In such a case, pathways for aqueous sulfate formation that are of secondary importance in a cloud may become significant in a fog.

Polycyclic Aromatic Hydrocarbons

A large number of polycyclic aromatic hydrocarbons (PAH), ranging from naphthalene ($C_{10}H_8$) to 5- and 6-ring and higher PAH, their alkyl substituted analogues, and their oxygen- and nitrogen-containing derivatives, are emitted from motor vehicle sources. In addition, heterocyclic analogues containing ring O-, S-, and N-atoms are possible combustion source emissions. The PAH, their analogues and derivatives, demonstrated in many cases to be mutagenic or carcinogenic or both, have relatively low vapor pressures and are distributed between gas and particulate phases (*57*). In temperate climates, the 2- to 4-ring PAH are found primarily in the gas phase; under mid-continental wintertime temperatures, the distribution shifts markedly toward the particulate phase.

Atmospheric transformations of PAH depend dramatically on the phase with which they are associated. For PAH present in the gas phase, reaction with the OH radical and, to a lesser extent, N_2O_5 leads to atmospheric PAH lifetimes of a few hours or less. Many studies of the chemistry of PAH adsorbed on different substrates have been carried out. Data obtained indicate that reactions occurring, including photolysis, are strongly dependent on the nature of the adsorbent species (*58*). Photolysis and reaction with O_3, NO_2, HNO_3, and N_2O_5 have been shown to lead to loss of PAH and their derivatives on several substrates, although because of the substrate dependence of these adsorbed-phase reactions, complete conclusions concerning the full spectrum of possible consumption reactions and the products of those reactions are not yet available.

Recent ambient data from Norway, Denmark, and the United States have shown that 2-nitrofluoranthene and 2-nitropyrene, nitro-PAH not observed directly from combustion sources, are the major nitro-PAH of ambient particulate matter (*59*). Since no formation pathway for these two nitro-PAH can be identified during sampling, it appears that they must be formed in the atmosphere by gas-phase reactions involving other PAH.

Comprehensive, systematic investigations of the gas- and adsorbed-phase reactions of PAH are needed to assess the atmospheric fate of these species.

Some Critical Policy Issues in Urban Air Pollution

Effect of precursors on ozone. Despite large efforts and expenditures to control emissions of hydrocarbons and nitrogen oxides, decreases in ozone concentrations nationwide have been modest, approximately 10% between 1979 and 1985 (*60*). The effect of precursor emission controls on ozone concentrations is complex, depending on meteorological conditions, the absolute and relative amounts of volatile organic compounds (VOCs) and NO_x, and the background concentrations of ozone and its precursors (Fig. 2).

There is general agreement that reductions in hydrocarbon emissions will lead to ozone decreases (except at very high VOC/NO_x ratios where ozone levels will remain unchanged). The role of NO_x in ozone formation, however, depends on the level of organics. When organics are abundant relative to NO_x (VOC/NO_x ratios of order 20 ppmC/ppm, where ppmC is parts per million by volume of carbon atoms), there is a shortage of NO that can be oxidized by peroxy radicals. Ozone formation is controlled primarily in that case by the amount of NO_x available and decreasing NO_x decreases ozone formation. At low VOC/NO_x ratios, the order of 5 ppmC/ppm, ozone formation is limited by the amount of organics available since O_3 scavenging by the NO-O_3 reaction is more effective than the peroxy radical oxidation of NO to NO_2. Furthermore, the NO_2-OH reaction forming nitric acid effectively competes with organics for OH, thereby inhibiting the formation of peroxy radicals. Decreasing NO_x under these conditions leads to an increase in ozone formation since it favors the peroxy radical–NO reaction channel. As NO_x emissions are reduced, the rate of formation of ozone increases and ozone levels close to the NO_x source region will increase. Ozone levels downwind can then be expected to decrease, although the actual amount must be assessed by computer simulation (*61*). As overall emissions levels in a region are decreased, the importance of natural sources and of material flowing in across the region's boundaries increases. Uncertainties in concentration levels aloft and at region boundaries and in emissions inventories themselves must be explicitly accounted for and propagated through computer simulations when determining emissions control strategies.

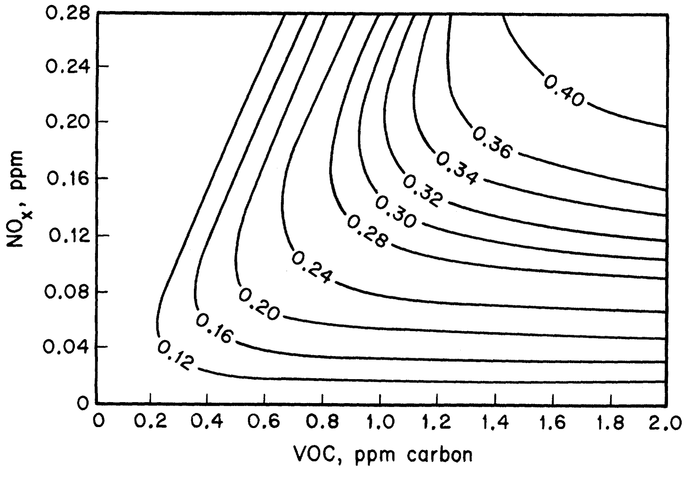


Fig. 2. Peak ozone concentrations in parts per million (labeled on the contour lines) as a function of initial organic (VOC) and NO_x levels. This plot was generated using EPA's EKMA method under standard default conditions. It is useful to envision long-term control strategies for ozone reduction on this diagram. Strategies that follow the ridge toward the origin will be less effective in reducing ozone than those favoring steeper descents from the ridge. Strategies favoring reductions of the limiting precursor descend more steeply; those favoring reductions of the nonlimiting precursor ascend, cross the ridge, and then descend. To judge whether to favor a VOC or an NO_x strategy for reducing ozone, one must know on which side of the ridge and how far from the ridge line the region is located. Ozone, of course, is not the only secondary pollutant of concern. The benefits of reducing the atmospheric concentrations of nitrogen-bearing species through NO_x emissions reductions and of secondary organic aerosol through VOC reductions must be factored into the analysis. Also, the positions of the ozone isopleths in a plot such as that above will vary with location in a large urban area, so the use of a single plot to define control strategies for a large urban area is an oversimplification.

The U.S. Environmental Protection Agency (EPA) has historically encouraged exclusive reliance on VOC controls for ozone abatement because VOC controls have been assumed to be cheaper and more readily available than those for NO_x and because simultaneous VOC and NO_x reductions frequently are not predicted to be as effective for ozone control as VOC reductions alone. The critical policy issue at this point is, to what extent should NO_x controls be invoked for further ozone abatement, in view of the fact that VOC controls alone do not seem to have been as effective in ozone reduction as predicted? In this regard, there is mounting evidence that hydrocarbon emissions inventories in urban areas may be seriously underestimated (*62*) and that, therefore, ozone reductions are less than originally anticipated. Emission factors for mobile sources must be verified, for example, by comprehensive monitoring in highway tunnels. Models for the spatial and temporal distribution of traffic must also be verified in field programs. Reconciliation of inconsistencies between estimated historical hydrocarbon emissions and ozone trends must be attempted.

Role of biogenic hydrocarbons in urban air pollution. Hydrocarbons emitted by vegetation are primarily photochemically reactive cyclic and other olefins with internal double bonds. In the United States, trees are the principal emitters of such hydrocarbons, with isoprene and α-pinene being the primary species emitted. Isoprene and the other naturally emitted olefins are highly reactive, but the atmospheric degradation pathways of these compounds are not well known. For example, only about 50% of the degradation pathways of isoprene have been identified, and those for α-pinene are even less well known. The ozone-forming potential of biogenic hydrocarbons, under urban VOC/NO_x conditions, is roughly equivalent, on a molecule-for-molecule basis, to that of the anthropogenic hydrocarbon mix. At high VOC/NO_x ratios, however, characteristic of rural conditions, the natural hydrocarbons, which react with ozone, become a net destroyer of ozone and form aerosol.

The extent of involvement of biogenic hydrocarbons in urban photochemical smog has generally been assumed to be small. Computer simulations of ozone levels in Atlanta, however, including estimates of biogenic hydrocarbon emissions and their chemistry, indicate that anthropogenic hydrocarbon emissions reductions needed to reduce ozone concentrations could become much more stringent if biogenic hydrocarbon emissions occur at the level assumed in the study and if their chemistry occurs as presumed (*63*). These results point to the need to better define biogenic hydrocarbon emissions inventories and to clearly establish the role of these hydrocarbons in photochemical smog chemistry in urban areas where such emissions are likely to be important.

Methanol-fueled vehicles. Methanol has been proposed as a replacement for gasoline and diesel fuels. Unlike gasoline-fueled vehicles, methanol-fueled vehicles emit only a few compounds, primarily unburned methanol and formaldehyde (a product of incomplete combustion). The principal benefit of replacing gasoline with methanol is that the unburned methanol, which is 90 to 95% of the organic emissions, is less photochemically reactive, as an ozone former, than the organics in gasoline-fueled vehicle exhaust. For conditions favorable to ozone formation over a 1-day period, computer simulations of incremental reactivity that incorporate chemical reaction mechanisms indicate that methanol alone will form approximately 20 to 33% as much ozone per unit of emission (on a mass basis) as the current on-road emissions. The benefits in ozone reduction appear to diminish in successive days of a typical, severe multiday episode. Formaldehyde, on the other hand, is very reactive and is emitted by methanol-fueled vehicles at rates greater than those by gasoline-fueled vehicles. It is also a suspected carcinogen. Formaldehyde and methanol emissions are generally correlated; the exhaust formaldehyde is a certain mass fraction of the methanol content.

The benefits of methanol as a fuel are greatly dependent on the level of formaldehyde emissions that can be achieved. Computer simulations have shown that, as formaldehyde emissions from methanol-fueled vehicles increase, a crossover point is reached where the photochemical ozone-forming capability of the emissions is equal to that of conventional gasoline-fueled exhaust (*64, 65*). While significant progress has been made in developing methanol vehicle technology, only a relatively small number of vehicles have been emissions tested, and therefore emission levels are still uncertain. Also, little information exists on evaporative emissions from methanol-fueled vehicles. Use of methanol in light- and heavy-duty diesel vehicles would lead to a dramatic reduction in fine particles emitted. Effects of methanol emissions on atmospheric cloud chemistry and aerosol formation are at this time unknown.

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