consideration, and then analyzed 529 of those that we (and 140 consultants) considered to be essential for the clinical advances.

Our analysis showed the following. (i) Of 529 key articles, 41 percent of all work judged to be essential for later clinical advance was not clinically oriented at the time it was done; the scientists responsible for these key articles sought knowledge for the sake of knowledge. (ii) Of the 529 articles, 61.7 percent described basic research (defined as research to determine mechanisms by which living organisms—including humans—function, or mechanisms by which drugs act); 21.2 percent reported other types of research; 15.3 percent were concerned with development of new apparatus, techniques, operations, or procedures; and 1.8 percent were review articles or reported synthesis of the data of others. Our data show that clinical advance requires different types of research and development and not one to the exclusion of another. Thus the problem is not either-or, but a question of how much support to one type and how much to another. Our data compel us to conclude (i) that a generous portion of the nation's biomedical research dollars should be used to identify and then to provide long-term support for creative scientists whose main goal is to learn how living organisms function, without regard to the immediate relation of their research to specific human diseases, and (ii) that basic research, as we have defined it, pays off in terms of key discoveries almost twice as handsomely as other types of research and development combined.

We believe that much more research needs to be done on the nature of research and its application so that data from objective studies can be applied to all aspects of biomedical research. Because the very nature of research on research, particularly if it is prospective rather than retrospective, requires long periods of time, we recommend that an independent, highly competent group be established with ample, long-term support to conduct and support retrospective and prospective research on the nature of scientific discovery, to analyze the causes of long and short lags between discovery and clinical application and to suggest and test means of decreasing long lags, and to evaluate present and proposed mechanisms for the support of biomedical research and development.

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3. Of these, 70 were clinicians, 37 were basic medical scientists, and 33 were engineers, science administrators (in industry, government, or universities), or science writers.
4. Some consultants did not designate such contributions as key articles. We did, however, because we knew of a number of instances in which the final step was "inevitable" but no one seemed willing to take it (for example, vascular surgery was inevitable by 1910 but was not applied until 1939).
5. Bias could also enter into our selection of reviewers of tables. Thirty-two reviewers were physicians, surgeons, or medical or surgical specialists; 10 were basic medical scientists. All were highly knowledgeable in the field that they reviewed.
6. Supported by contract 1-HO-1-2327 from the National Heart and Lung Institute and grants from the Commonwealth Fund and The Burroughs Wellcome Fund.

Photochemistry of the Polluted Troposphere

SO_x is now included with NO_x and HC in homogeneous and heterogeneous atmospheric chemistry.

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

Photochemical smog was only recognized about three decades ago in Los Angeles, although "London-type" sulfurous smog has been known for at least eight centuries. However, air pollution is not a new phenomenon in southern California. In 1542, heavy haze caused Juan Rodriquez Cabrillo to name San Pedro Bay the "Bay of Smokes," and, as early as 1868, eye irritation was recorded in Los Angeles (*1*).

Since the first recognition that photochemical oxidant (Ox) (*2*) is produced by action of solar ultraviolet (UV) [290 ≤ wavelength (λ) ≤ 430 nm] light on mixtures of reactive hydrocarbons (HC) and oxides of nitrogen (NO_x) (*3*)

$$NO_x + HC + \text{solar UV} \rightarrow O_3 + CH_3C(O)OONO_2\ (PAN) + NO_2 + \ldots \quad (1)$$

where PAN is peroxyacetyl nitrate, its frequency and global distribution have increased dramatically. Thus, under appropriate conditions of emissions, meteorology, and topography, it constitutes a serious problem in many major urban areas of the world; furthermore, its impact can extend hundreds of kilometers downwind.

One goal of current air pollution research is the generation of accurate urban airshed models capable of predicting the impact on air quality of spatial and temporal changes in the quantity and composition of primary pollutants (*4*) under various meteorological conditions. Such models, although complex, are essential for the evaluation of cost-effective pollutant control strategies and transportation, land-use, and growth alternatives. They are also of increasing importance in the development of efficient energy options that minimize adverse effects on public health, as in the allocation of natural gas and low-sulfur fuels, the location of coal-fired power plants, or the use of alternate fuels such as methanol.

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Until recently, sulfurous and photochemical air pollution were treated independently, in part because the conditions favoring their formation—smoke, fog, and low temperatures compared to hot, initially clear days—differ markedly. This differentiation was reflected not only in the chemical literature, but also in reports on health effects and visibility.

Today, however, physical, chemical, and physiological interactions between sulfurous and photochemical smog are reported with increasing frequency. Consequently, SO_x and particulate chemistry must be included in models of photochemical smog, especially in sunny urban regions where high-sulfur fuels have been introduced because of the energy shortage.

With these considerations in mind, we shall discuss selected aspects of the submodel for chemical transformations involving NO_x, HC, Ox, and SO_x, an area in which many uncertainties still exist. Because of the necessary brevity of treatment, many fascinating and important aspects of the formation of photochemical air pollution cannot be included here; for further details, the reader is referred to several reviews (*5–7*).

Real and Simulated Atmospheres

The diurnal variations of some major and minor gaseous pollutants in a severe photochemical air pollution episode are shown in Fig. 1 (*8*). Significant concentrations of other hydrocarbons and primary and secondary aerosols (*9*) were also present. The latter are primarily responsible for the degradation of visibility associated with photochemical smog and may affect human health (*10*). Thus gas-to-particle conversions must be included in any comprehensive mechanism for photochemical smog.

Three questions basic to the chemistry of photochemical smog formation are suggested by Fig. 1: (i) How is the NO converted to NO_2 prior to the formation of O_3? (ii) What are the overall reactions and reaction intermediates that consume the hydrocarbon? and (iii) How are minor, but significant, contaminants such as formic acid formed?

Answering these questions requires laboratory studies carried out under carefully controlled conditions where meteorological effects have been removed. Ideally, they should cover a wide range in temperature, relative humidity, solar flux (including both intensity and spectral distribution in the UV), and variations in mixtures and concentrations of primary pollutants that, insofar as possible, duplicate "real world" polluted atmospheres. Such experiments have been carried out since the 1950's in large environmental reaction cells commonly referred to as "smog chambers"; a diagram of a recently constructed smog chamber is shown in Fig. 2. Primary pollutants are injected into these chambers, and the reactant and product concentrations are followed while the system is irradiated with light in the actinic UV ($\lambda \gtrsim 290$ nm). Figure 3 shows the results of a typical experiment in which NO_x and propylene are irradiated in the evacuable smog chamber with a 25-kw xenon lamp as the source in a solar simulator (*11*).

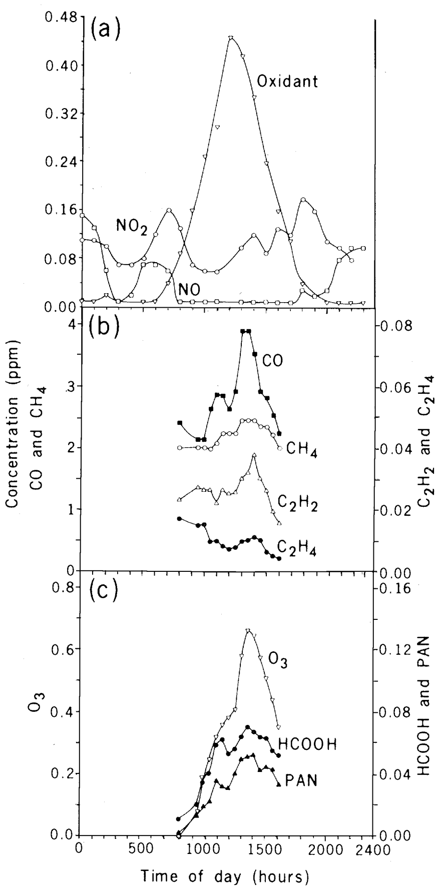


Fig. 1. Diurnal variation of some primary and secondary pollutants in Pasadena, California, on 25 July 1973 (*8*). The O_3 concentrations in (c) should be multiplied by 0.88 to correct for the effect of resolution on the absolute absorptivity of O_3 at 9.48 μm [see (*7*)].

Until recently, a major problem has been the lack of well-characterized chambers and light sources and detailed concentration-time profiles for all significant reactants and products, including labile and trace species (*12, 13*). Consequently, mathematical modeling studies (*12, 13*) of these systems have generally tended to focus on the profiles of only the major reactants (HC and NO_x) and products (O_3 and PAN). However, since significant discrepancies between theory and experiment may become evident only when minor secondary pollutants such as H_2O_2, HNO_3, or HONO are examined, such species must be included to completely validate any proposed mechanism. Clearly, the utilization of well-characterized chamber facilities and the development of more accurate analytical procedures for trace and labile compounds are urgently needed.

Important Intermediate Species

Historically, concentration-time profiles, such as those in Figs. 1 and 3, were explained in terms of a series of reactions initiated by the photodissociation of NO_2 in the actinic UV, to produce NO and ground state oxygen atoms, $O(^3P)$

$$NO_2 + h\nu \xrightarrow{\lambda < 430\text{ nm}} NO + O(^3P) \quad (2)$$

Subsequently, two very important inorganic reactions occur

$$O + O_2 + M \rightarrow O_3 + M \quad (3)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

Reaction 3 is the only known source of O_3 in urban air, while the rapid rate of reaction 4 explains why the concentration of O_3 does not rise significantly until that of NO has fallen to low values. The quenching of O_3 by reaction 4 also explains why atmospheric O_3 levels are generally lower in regions of high NO emissions—for example, in central city areas or immediately adjacent to freeways.

The mechanism of photooxidation of hydrocarbons was then treated primarily in terms of reactions with O_3 and $O(^3P)$. The $O(^3P)$ reacts rapidly with olefins, aromatics, and alkanes, but its estimated concentrations in smog were so low [$\sim 10^{-8}$ part per million (ppm)] (*5*) that it was understood that they could be responsible for only a small fraction of the hydrocarbon loss. Ozone, on the other hand, was known to be present at much higher levels (up to $\sim$0.6 ppm in heavy smog) (*14*), and although its rate constant for reaction with olefins is only moderate ($k \sim 10^3$ to 10^5 liter $mole^{-1}$ sec^{-1}), O_3 attack was believed to be their major loss process; aromatics and alkanes, on the other hand, were known to react slowly with O_3.

The combined rates of decay of the hydrocarbons from attack by O_3 and $O(^3P)$, however, fell far short of the observed loss in chamber studies. Thus, free radicals, such as hydroxyl (OH) and hydroperoxyl (HO_2), were considered as additional oxidizing species, but rate constants of their reactions with virtually any of the organic or inorganic pollutants were unknown before the mid-1960's.

With the first reliable determinations of the rate constants for the reactions of OH with CO and with a series of alkanes (*15*) came the realization that OH was an important intermediate, not only in hydrocarbon oxidation, but also in the oxidation of NO to NO_2 (*16*) through such chains as

$$OH + CO \rightarrow CO_2 + H \quad (5)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (7)$$

Subsequently, the rates of reaction of OH with a wide variety of hydrocarbons and oxygenates to form organic free radicals ($RH + OH \rightarrow R + H_2O$) were shown to be very fast, and these organics are now believed to play a major role in the oxidation of NO (see below). In fact, the role of CO in the conversion of NO to NO_2 in ambient air is likely to be minor compared to that of the organics.

Today OH is believed to be the major oxidizing species in the early stages of photochemical smog formation. Figure 4 shows the theoretical rate of removal of *trans*-2-butene by OH, O_3, HO_2, and $O(^3P)$ as a function of time in an irradiated mixture containing NO_x, CO, and CH_4 (*12*). At short reaction times, the rate of attack of OH exceeds that of any other species by more than an order of magnitude. However, after irradiation for 30 minutes, O_3 and, to a lesser extent, HO_2 contribute significantly; after 2 hours hydrocarbon consumption by O_3 and HO_2 is comparable to that by OH. The $O(^3P)$ participates to a minor extent throughout; details of the kinetics and mechanisms of its reaction with hydrocarbons are in the literature (*7*) and will not be considered further here.

The various classes of hydrocarbons (and other organics such as aldehydes and halogenated solvents), and indeed compounds within a class, react at different rates in photochemical smog. A variety of criteria have been employed to categorize their "reactivity"; these include maximum oxidant (or O_3) level formed, rate of hydrocarbon decay, rate of conversion of NO to NO_2, eye irritation, and so forth (*6*).

The earlier hydrocarbon reactivity scales focused primarily on olefins and aromatics (and specific solvents) and were established on the basis of relatively short (2 to 6 hour) chamber irradiations. In 1966, for example, they formed the basis of a well-known rule ("Rule 66") set by Los Angeles County to restrict the use of highly reactive hydrocarbons in commercial solvents, paints, and other products. However, it has become well established since then that given enough irradiation time and intensity, alkanes can also produce high ozone levels (*17*). Such long hours of bright sunlight are available in summer months; in addition, transport conditions, especially during severe episodes, are frequently such that a particular air parcel can be continuously irradiated for at least 9 to 12 hours. Under these conditions, the higher alkanes—indeed all but methane—must be considered reactive, and previous reactivity scales revised accordingly. One recently proposed reactivity scale has a range from 1 to 10^4, and a particular hydrocarbon or oxygenate falls into one of five categories, depending on the absolute rate constant of its reaction with OH radicals (*18*).

In short, reactive intermediates such as OH and HO_2, in addition to O_3, are important in atmospheric hydrocarbon consumption. Furthermore, OH, HO_2, and RO_2 (peroxyalkyl) are essential to the chain oxidation of NO to NO_2 prior to O_3 formation. We will first examine possible sources of OH and HO_2 in the polluted troposphere and then discuss how these and other species participate in the oxidation of both inorganics and organics.

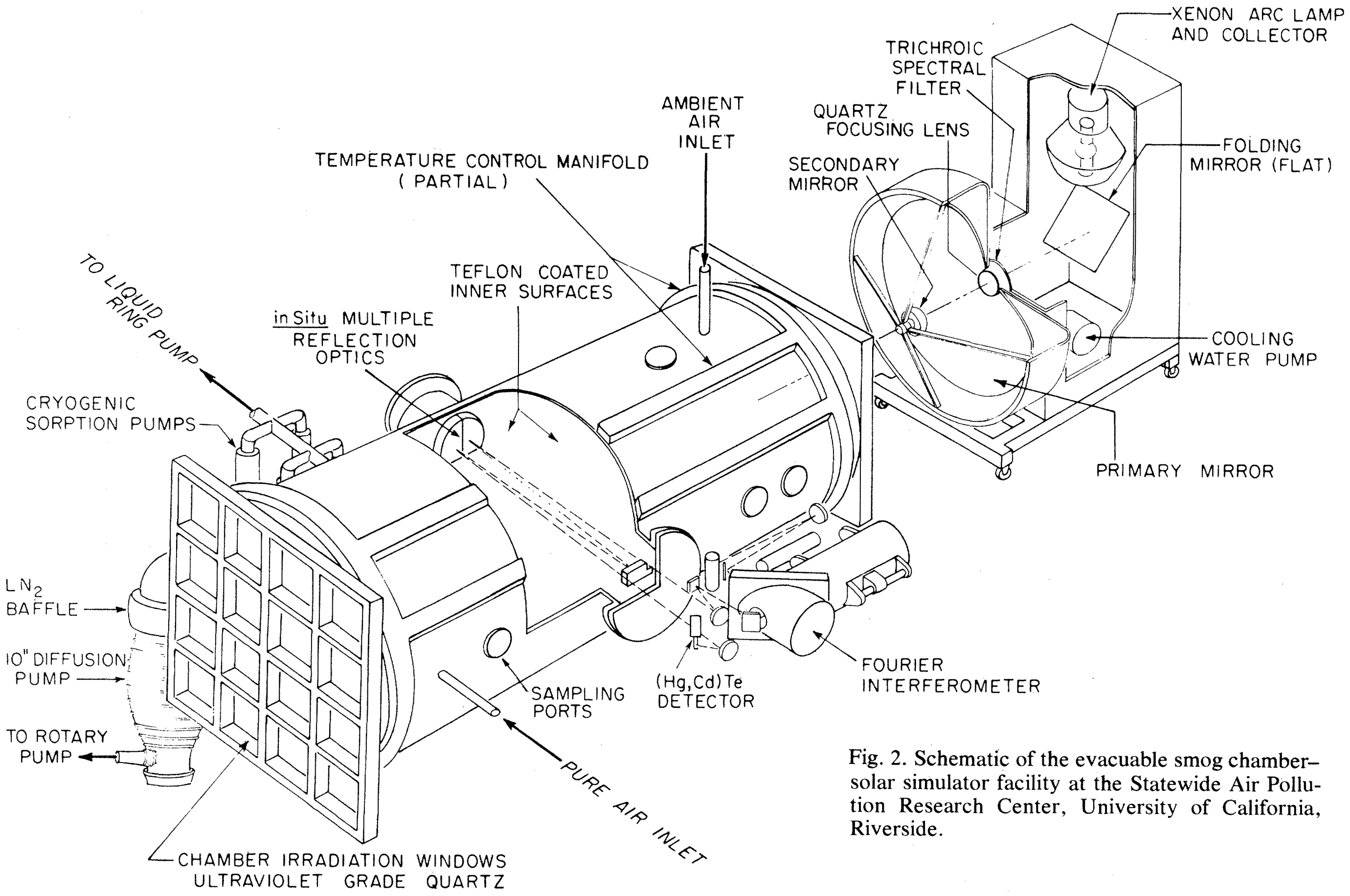


Fig. 2. Schematic of the evacuable smog chamber–solar simulator facility at the Statewide Air Pollution Research Center, University of California, Riverside.

Sources of Intermediate Radicals

The hydroxyl radical. In an important experiment, OH was recently detected (*19*) in ambient air in Dearborn, Michigan, at peak concentrations exceeding 10^7 radicals per cubic centimeter; the source of the OH was suggested to be photolysis of nitrous acid (HONO), which photodissociates at $\lambda \lesssim 400$ nm (*20*).

The labile HONO has been recorded in smog chamber experiments with fairly high concentrations of propylene (7.8 ppm), NO (6.2 ppm), and NO_2 (3.8 ppm) in moist air (*21*); there is also one report of its detection in ambient air (*22*). It is probably formed in reaction 8, 9, or 10 (*20, 23*)

$$OH + NO \xrightarrow{M} HONO \qquad (8)$$

$$HO_2 + NO_2 \rightarrow HONO + O_2 \qquad (9)$$

$$NO_2 + NO + H_2O \rightleftharpoons 2HONO \qquad (10)$$

Photodissociation of hydrogen peroxide (H_2O_2) at $\lambda \leq 370$ nm also gives OH (*5, 24*), although its extinction coefficient is low in the actinic UV. Hydrogen peroxide was detected once in heavy smog at concentrations up to 180 parts per billion (ppb) (*25*) by a wet chemical method. Analysis of ambient air during a severe smog episode by Fourier transform long-path infrared spectroscopy indicated, although not conclusively, an H_2O_2 concentration of ~ 70 ppb (*8*).

A third source of OH is the photolysis of O_3 to produce $O(^1D)$ (*26*)

$$O_3 + h\nu \xrightarrow{\lambda < 319 \text{ nm}} O(^1D) + O_2(^1\Delta_g) \qquad (11)$$

which may then be quenched to $O(^3P)$ or react with water (*27*)

$$O(^1D) + H_2O \rightarrow 2OH \qquad (12)$$

Electronically excited singlet molecular oxygen, $O_2(^1\Delta_g)$, which is produced simultaneously in reaction 11 and is present in the atmosphere, is also of interest because of its chemical and physiological effects (*7*).

Finally, an important source of OH in smog is reaction 7 of NO with HO_2.

Sources of HO_2. The species HO_2 may be produced by three-body recombination of H atoms with O_2 (reaction 6). Hydrogen atoms are produced in the photolysis of formaldehyde (HCHO), which occurs at $\lambda < 370$ nm (*24*) and may be formed in a variety of other processes. Formaldehyde is emitted directly into the air—for example, from automobile exhaust—and is also formed during hydrocarbon oxidation in the atmosphere. It may account for as much as 40 percent of total ambient aldehydes (*28*), although there is a lack of published data on the concentrations of these and other oxidized hydrocarbons.

A second source of HO_2 is hydrogen atom abstraction from alkoxy radicals (*29*)

$$RCH_2O + O_2 \rightarrow RCHO + HO_2 \qquad (13)$$

Alternatively, the formyl radical (HCO), which may be formed, for example, by abstraction from formaldehyde or photodissociation of formaldehyde and the aliphatic aldehydes (*24*), may act as the precursor to HO_2 through reaction 14a

$$HCO + O_2 \begin{cases} \xrightarrow{(a)} HO_2 + CO \\ \xrightarrow{(b)} HCO_3 \end{cases} \qquad (14)$$

The relative rates of reactions 14a and 14b at atmospheric pressure are not known; thus while peroxyformyl nitrate, $HC(O)OONO_2$, was observed as a product of photolysis of NO_2-HCHO-Cl_2-air mixtures (*30*), which suggests the formation of the peroxyformyl radical, HC(O)OO was not observed in spectroscopic studies of the H-CO-O_2 system (*31*).

Free Radical Chain Oxidation of NO

The free radical species, OH and HO_2, are not only important in hydrocarbon oxidation, they are essential to the conversion of NO to NO_2. Thus, NO is oxidized to NO_2 to a large extent by HO_2 (reaction 7) as well as by RO_2

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (15)$$

where RO_2 may be a simple species like CH_3O_2 or a more complex one such as HC(O)OO. These free radicals are then regenerated in a chain reaction through the important intermediary OH—for example, by abstraction followed by the addition of O_2

$$OH + RH \rightarrow H_2O + R \xrightarrow{O_2} RO_2 \qquad (16)$$

Mechanisms of Hydrocarbon Oxidation

While the rates of reaction of OH with alkanes, alkenes, and aromatics and of O_3 with olefins have now been established fairly reliably (*7*), much less is known about the mechanisms of these reactions (including, by definition, products and intermediates). In addition, little is known about the kinetics or mechanisms of the reactions of HO_2.

The mechanisms of oxidation of aromatics remain a mystery, even though these hydrocarbons constitute a signifi-

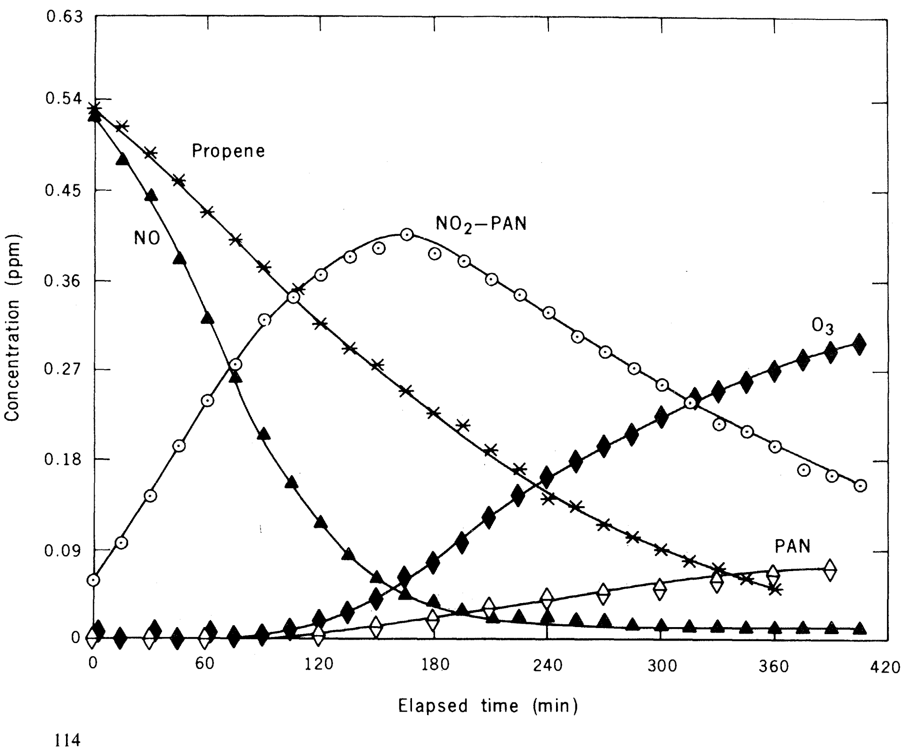


Fig. 3. Concentration-time profiles of the major primary and secondary pollutants during irradiation of propylene (0.53 ppm) and NO_x (0.59 ppm) in an evacuable smog chamber in 1 atmosphere of purified air (*11*).

cant fraction of the total ambient hydrocarbons (*32*). Indeed, we do not know in detail the products of the reaction of even one aromatic hydrocarbon with any one of these important species. Consequently, aromatics have usually been omitted entirely from computer simulations of photochemical smog formation. As one group of modelers recently stated (*12*), "We will not consider the effects of the addition of the aromatic hydrocarbons since the authors are not aware of meaningful experimental evidence relating to their decay paths."

Reactions of OH with Organics

The OH radical reacts rapidly with olefins at rates ($k \sim 10^9$ to 10^{11} liter mole^{-1} sec^{-1}) approaching those of diffusion-controlled processes (*33–37*). These rate constants first led to the observation that hydrocarbon reactivities determined in smog chamber experiments showed a better correlation with rates of reaction with OH than with other species such as $O(^3P)$ (*34*). Thus, the original hypothesis that OH is important in hydrocarbon consumption and reactivity was placed on a firmer base.

At least a portion of the total reaction involves addition of OH to the double bond. This is indicated by (i) the pressure dependence of the OH-ethylene rate constant from 3 to 300 torr in helium (*35*), (ii) the increase in rate constant with increasing substitution on the double bond (*33, 34*), and (iii) mass spectral observation of a peak corresponding to the OH-olefin adduct in the ethylene and propylene reactions, the intensity of which increased as the pressure increased from 1 to 4 torr (*36*).

It has been proposed, on the basis of kinetic (*37*) and mass spectrometric (*38*) data, that a significant fraction of the reaction proceeds by abstraction of the allyl hydrogen atom. However, since the mass spectrometric studies (*38*) were carried out at very low pressures ($\sim 10^{-2}$ to 10^{-3} torr), the observed intermediates and products likely resulted from the decomposition of the excited adduct. Data from recent product studies at higher total pressures (*39*) indicate that addition is the predominant route at atmospheric pressure.

There have been very few product studies, but major stable products in the torr pressure range are the corresponding aldehydes and ketones—that is, CH_3CHO and $C_2H_5CHO + CH_3COCH_3$ from the C_2H_4 and C_3H_6 reactions, respectively (*36, 40*). However, their mechanism of formation (as well as that of the entire oxidation) is not known.

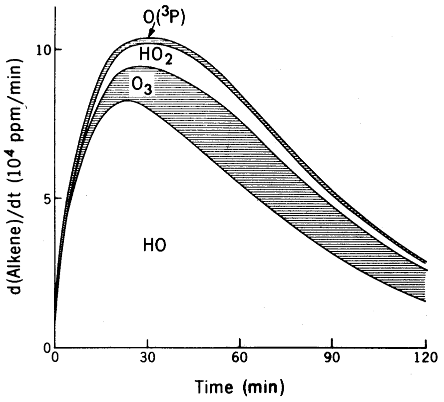


Fig. 4. Theoretical rates of reaction of various reactive species with *trans*-2-butene in a computer-simulated, sunlight-irradiated atmosphere (solar zenith angle, 40°) containing *trans*-2-C_4H_8 (0.10 ppm), NO (0.025 ppm), NO_2 (0.075 ppm), CO (10 ppm), and CH_4 (1.5 ppm) at 5 percent relative humidity (*12*).

Some information is just now becoming available on the reactions of aromatics with OH. Recent measurements of absolute and relative rate constants for the reactions of OH with a series of simple aromatics indicate that they are fast ($k \sim 10^9$ to 10^{10} liter mole^{-1} sec^{-1}) and increase with increasing alkyl substitution; for example, the xylenes react with OH about as rapidly as propylene.

It is interesting that the initial rates of disappearance of aromatics in smog chamber experiments on the HC-NO_x-air system can be explained by assuming that they react solely with OH (*41*). Thus, absolute rate constants have been derived for OH-aromatic reactions by measuring the relative rates of disappearance of the aromatics and *n*-butane in an all-Pyrex, 6000-liter environmental chamber and normalizing them to published values for the absolute rate constant of the OH–*n*-butane reaction (*41*); the values obtained are in good agreement with those determined on an absolute basis by using the flash photolysis–resonance fluorescence technique (*42*). Such experimental results support the hypothesis that OH plays a large role in hydrocarbon consumption in the early stages of photochemical smog formation (Fig. 4) and form the basis of the reactivity scale cited earlier (*18*).

Of considerable interest is the mode of attack of OH radicals on aromatics—that is, addition to the ring versus hydrogen atom abstraction. The pressure dependence of the absolute rate constants for benzene and toluene (*42*) indicates that the majority of OH radicals add to the ring, even for toluene, with its readily abstractable methyl group hydrogen atoms. However, the presence of benzaldehyde as a minor product in smog chamber experiments on the toluene-NO_x-air system suggests that some abstraction by OH also occurs (*43*). These results are consistent with studies of the liquid phase, in which addition of OH to the ring was observed (*44*).

The products of OH attack on aromatic rings are interesting because they may include long-chain oxygenated compounds, which may be involved in aerosol formation (see below). Alternatively, the products of these reactions may produce additional free radicals capable of initiating and maintaining the chain oxidation processes characteristic of photochemical smog (*43*).

The reactions of OH with alkanes, and probably with aldehydes, proceed by abstraction (*33*) to produce alkyl (R) and carbonyl (RCO) radicals which, after further reaction with ground state molecular oxygen, form RO_2 and RCO_3. These radicals may then oxidize NO to NO_2 (see above). In addition, RCO_3 may act as a precursor to the formation of PAN's, which are eye irritants, are highly toxic, and produce severe plant damage (*45*)

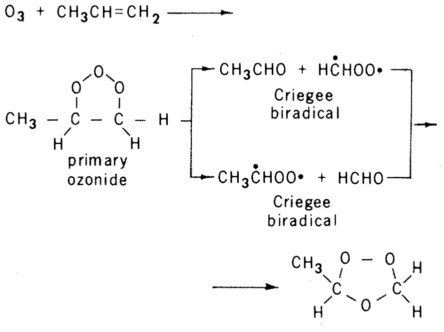
$$CH_3CO_3 + NO_2 \rightarrow CH_3C(O)OONO_2 \qquad (17)$$

Reactions of O_3 with Hydrocarbons

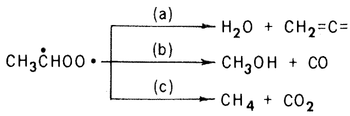
In the gas phase, O_3 reacts at a moderate rate with olefins ($k \sim 10^3$ to 10^5 liter mole^{-1} sec^{-1}), only slowly with alkanes and aldehydes ($k < 25$ liter mole^{-1} sec^{-1}), and, with the exception of NO and NO_2, very slowly with most inorganics such as CO and SO_2 (*46*). Ozone also reacts slowly with aromatic hydrocarbons, but ring opening occurs and the products may be significant. Hence, we shall consider here only the O_3-olefin and O_3-aromatic systems.

An understanding of the kinetics and mechanisms of the reactions of ozone with simple olefins is important because the latter constitute a significant fraction of the total hydrocarbons in urban atmospheres (*32*), and their reactions are important in photochemical smog formation. Unfortunately, detailed mechanisms remain unclear, despite extensive experimental (*5–7*) and theoretical (*47, 48*) studies.

The initial product of the attack of O_3 on an olefinic double bond is believed to be a highly unstable primary ozonide (or molozonide), which may decompose to a carbonyl compound and Criegee biradical ($R_1R_2COO\cdot$). The biradical may decompose, rearrange, or undergo further reactions (*49*)—for example, reactions 18 and 19



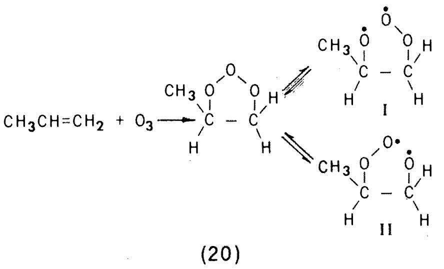
(18)



(19)

However, the observation of chemiluminescence in O_3-olefin reactions (*50*) and the detection by photoionization mass spectrometry of radicals, such as OH and HO_2, in addition to a variety of stable products (*50*), are not easily rationalized in terms of this classical mechanism alone (*7*).

Several attempts have been made to explain these more recent data theoretically in terms of a unified mechanism of gas phase ozonolysis. Thus, on the basis of extensive thermochemical kinetic calculations, it was proposed (*47*) that the primary ozonide could undergo internal hydrogen abstractions in addition to the Criegee split, as in the propylene-ozone system



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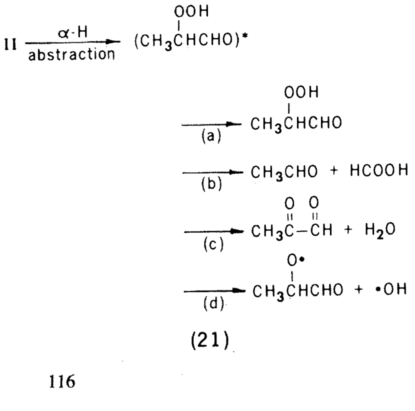


$$II \xrightarrow[\text{abstraction}]{\alpha\text{-H}} (CH_3\overset{OOH}{C}HCHO)^*$$

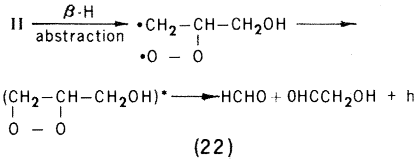
$$\xrightarrow[(a)]{} CH_3\overset{OOH}{C}HCHO$$

$$\xrightarrow[(b)]{} CH_3CHO + HCOOH$$

$$\xrightarrow[(c)]{} CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}H + H_2O$$

$$\xrightarrow[(d)]{} CH_3\overset{O\cdot}{C}HCHO + \cdot OH$$

(21)



$$II \xrightarrow[\text{abstraction}]{\beta\text{-H}} \cdot CH_2-\underset{\cdot O - O}{CH}-CH_2OH \longrightarrow$$

$$(\underset{O\;-}{CH_2}-\underset{O}{C}H-CH_2OH)^* \longrightarrow HCHO + OHCCH_2OH + h\nu$$

(22)

The primary ozonide **I** is proposed to undergo an analogous reaction sequence.

The predictions of a second major theoretical study (*48*) of ozone-olefin reactions, based on generalized valence bond and configuration interaction calculations for methylene peroxide, $H\dot{C}HOO\cdot$ (the Criegee biradical anticipated from the reactions of olefins containing a terminal double bond), are generally in agreement with the thermochemical proposals (*47*).

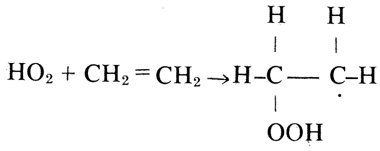
Much further experimental work is needed to establish the intermediates and products (and their time variations) over a wide range of reactant and oxygen concentrations and total pressures. Pressure is particularly important, since the relative rates of the various reaction paths predicted theoretically (*47, 48*) should be a function of total pressure as well as of the size of the olefin. However, it appears that the primary role of ozone-olefin reactions is the production of free radicals, such as R, HO_2, and HCO, which carry on the chain oxidations. These reactions may also produce species harmful to plants, animals, and humans (*7*). Finally, as discussed below, intermediates produced in O_3-olefin reactions appear to rapidly oxidize ambient SO_2 to particulate sulfate, a process of concern if high-sulfur fuels are used in areas of severe photochemical smog.

Very few investigations of ozone–aromatic hydrocarbon reactions have been reported. It appears, however, that α-dicarbonyl compounds are the major products (*51, 52*); for example, benzene yields glyoxal (OHCCHO), *p*-xylene gives glyoxal and methyl glyoxal (CH_3COCHO), and *o*-xylene gives glyoxal, methyl glyoxal, and biacetyl ($CH_3COCOCH_3$) (*51*). Such ring-opening oxidative processes may explain the presence of α-dicarbonyls, such as biacetyl (*53*), in polluted urban air and may also act as an additional source of free radicals through photolysis of the product species.

Reactions of HO_2 with Hydrocarbons

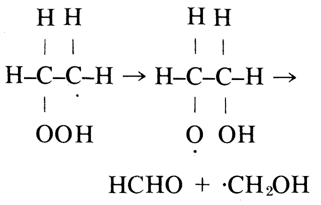
Studies of the kinetics and mechanisms of the reactions of HO_2 have been severely hampered by the lack of a clean source of HO_2 that is free from other highly reactive species such as OH (*54*). The rates of the reactions of HO_2 with olefins, which fall in the range 10^4 to 10^5 liter $mole^{-1}$ sec^{-1} (*54*), are not known to better than an order of magnitude. Thus, there is considerable uncertainty associated with the calculated contribution of HO_2 to hydrocarbon consumption. Reactions of HO_2 with aldehydes and alkanes, which proceed by abstraction to form H_2O_2, are slower than those with olefins by approximately two and five orders of magnitude, respectively (*54*).

The mechanisms of the reactions of HO_2 with olefins appear to involve an initial addition of the radical to the olefinic double bond (*54, 55*)



$$HO_2 + CH_2{=}CH_2 \rightarrow H-\underset{OOH}{\overset{H}{C}}-\underset{\cdot}{\overset{H}{C}}-H \quad (23)$$

Subsequent isomerization and decomposition of the adduct may lead to the observed products, HCHO and HO_2



$$H-\underset{OOH}{\overset{H}{C}}-\underset{\cdot}{\overset{H}{C}}-H \rightarrow H-\underset{\dot{O}}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \rightarrow$$

$$HCHO + \cdot CH_2OH \quad (24)$$

$$\cdot CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (25)$$

However, experimental confirmation of this mechanism seems necessary since oxygen atoms, and perhaps OH (*54*), were present, and hence the observed products may not be wholly attributable to reactions of HO_2.

Reactions of HO_2 with inorganic molecules, such as NO, are of great importance; they are discussed where appropriate throughout the text and will not be treated separately here.

Secondary Aerosol Formation

The chemical composition of particulates in photochemical smog is complex. Thus, a variety of trace metals (for example, Pb, Na, Mg, Al, V, and Zn), inorganics (for example, sulfates, water, nitrates, and ammonium), and organic materials (*56, 57*) are commonly found in ambient particulate matter. Trace metals generally come from primary emissions from both natural and anthropogenic sources, while the inorganics commonly arise from gas phase precursors. Organic aerosols may be predominantly primary or secondary, depending on the nature of the emissions and on the atmospheric conditions; under some circumstances secondary aerosol formation from gas-to-particle conversions may equal or exceed that due to direct emissions (*56, 58*).

While we will focus our discussion on the chemical characteristics of aerosols, their physical properties are also very important (*56, 57, 59*). For example, they can be useful for identifying the particulate source. In addition, the size distribution is a critical parameter in determining health and visibility effects, as particles in the range of approximately 0.1 to 2 μm are most effective for penetrating deep into the lungs (*10, 56*) and also cause maximum light-scattering and visibility reduction (*57*). The U.S. Primary Federal Air Quality Standard for particulates, however, is written in terms of total mass concentration only (annual average 75 $\mu g/m^3$ or 24-hour average 260 $\mu g/m^3$, not to be exceeded more than once per year). Hence, an air parcel containing relatively few large particles may exceed the Primary Federal Air Quality Standard for particulates, while being less harmful in terms of health and visibility than one containing many smaller particles. It would be prudent to define an air quality standard in terms of "respirable" particulates.

Formation of Sulfate from SO_2

In areas of severe photochemical smog, particulate sulfate arises primarily from the oxidation of gaseous SO_2. (We shall not consider here sulfuric acid or sulfate production from catalyst-equipped motor vehicles or geogenic sources such as the oxidation of H_2S.) The rates and mechanisms of this gas-to-particle conversion are of special interest, since it has been stated that adverse health effects may be associated with sulfates (*10*). Furthermore, the sulfate content of aerosols strongly influences their light-scattering characteristics and hence visibility degradation (*56, 58*).

In a "clean" atmosphere, the dark reaction of SO_2 with O_2 is negligible; even the photooxidation of SO_2 in pure air is a relatively slow process, typically less than 0.1 percent per hour (*57, 60*). This conversion is thought to occur through photooxidation of SO_2 to SO_3, which then reacts with water to form H_2SO_4.

In the presence of hydrocarbons and NO_x, the photooxidation of SO_2 speeds up dramatically (*5, 60*). Thus, SO_2 conversion rates in ambient air in the Los Angeles area may be as high as ~ 5 to 10 percent per hour (*56*). In other areas, for example central Europe, the conversion rate is much lower ($\lesssim$ 0.25 percent per hour) (*61*).

Recent investigations (*62*) have shown that an unidentified intermediate in ozone-olefin reactions oxidizes SO_2 to sulfuric acid aerosol and, in ambient air, could account for a conversion rate of approximately 3 percent per hour.

Possible alternate homogeneous photooxidation paths for SO_2 in such atmospheres have recently been proposed (*12*) and include, in addition to the processes discussed above, the reactions of SO_2 with OH, HO_2, $O(^3P)$, O_3, NO_3, N_2O_5 (*63*), RO_2, and RO.

Present uncertainties in the rate constants and in many of the products of these reactions preclude a quantitative assessment of their importance, although OH is probably important. For example, the reactions of SO_2 with HO_2 and RO_2 may proceed either by an oxygen atom transfer or by addition; nothing is known about the relative rates of these two processes or, in fact, about their absolute rates, except when R = H. However, organic sulfur compounds observed in the O_3-olefin-SO_2 system (*64*) may arise from addition reactions, such as those with RO_2 or RO.

The radical addition products of SO_2 have been postulated to undergo a complex series of reactions in the atmosphere (*12*). For example, that from the reaction of OH with SO_2 (*65*) to form $HOSO_2$ may oxidize NO to NO_2 (*12, 60, 65*)

$$HOSO_2 + O_2 \rightarrow HOSO_2O_2 \overset{NO}{\rightarrow} HOSO_2O + NO_2 \qquad (26)$$

as well as form a wide variety of sulfur and nitrogen compounds (*12*).

Computer simulations of SO_2-NO_x-hydrocarbon mixtures suggest that such homogeneous processes can account for a maximum SO_2 removal rate of ~ 5 percent per hour (*12*). Where higher conversion rates have been observed, heterogeneous processes have been invoked. Unfortunately, relatively little is known about the absolute contribution of such reactions in oxidizing atmospheres.

Other sulfur-containing compounds, such as H_2S, are also oxidized in the atmosphere, eventually forming sulfate. For example, OH reacts rapidly with H_2S ($k = 3.15 \times 10^9$ liter mole^{-1} sec^{-1}) (*66*), so that at typical atmospheric levels of OH (3×10^6 radicals per cubic centimeter) (*19*) the half-life of H_2S is short, of the order of half a day. In heavy smog, where the levels of OH are substantially higher (*19*), the lifetime of H_2S is even shorter.

Nitrates in Aerosols

Nitrogen dioxide is oxidized to gaseous nitric acid, which then forms particulate nitrate—for example, by reaction with NH_3 to form ammonium nitrate. The initial oxidation to the acid may involve a three-body reaction with OH, particularly in the early stages of the reaction (*67*)

$$OH + NO_2 \overset{M}{\rightarrow} HNO_3 \qquad (27)$$

Later the reaction with O_3 (*68*) may be important

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (28)$$

$$NO_3 \xrightarrow{NO_2,\ M} N_2O_5 \overset{H_2O}{\rightarrow} 2HNO_3$$

The reaction of N_2O_5 with H_2O appears to occur slowly in the gas phase, but a more rapid heterogeneous reaction can occur on surfaces (*69*). Hence, one role of ambient particulates may be catalysis of such reactions.

Finally, it has been suggested that the reaction of HO_2 with NO produces not only NO_2 but also, to a lesser extent, nitric acid, although the relative rates of these reactions are not clear (*20, 70*). Alternatively, particulate nitrate may arise from heterogeneous processes—for example, absorption of NO_x into the aerosol droplet, followed by its oxidation to nitrate (*56*).

Organic Aerosol Component

Under conditions of severe photochemical smog, carbon may account for as much as 45 percent of the average aerosol mass (*57, 58*), and as much as 95 percent of the organic fraction of the aerosol may be of secondary origin. Organic nitrates, carboxylic acids and their esters, carbonyl compounds, alcohols, and polymeric peroxidic material have all been identified in particulate matter (*56–58, 71–73*). Long-chain alkanes and alkenes, as well as several of the dicarboxylic and fatty acids, have also been identified (*72*).

The hydrocarbon precursors of the dicarboxylic acids have been suggested (*72*) to be diolefins or cyclic olefins. Cyclopentene, for example, has been observed in ambient air (*32, 74*) at concentrations that could produce significant quantities of glutaric acid [$HOOC(CH_2)_3COOH$] (*72*). However, whether there are sufficient ambient concentrations of the other precursor hydrocarbons is not clear. We feel that an additional path for the formation of the observed multifunctional compounds might be the oxidation of aromatic compounds by such species as OH, HO_2, O_3, and O(^3P); this is consistent with the identification of significant amounts of unsaturated organics in particulate matter (*58*).

Recently, laboratory investigations of model aerosol systems have been undertaken in the hope of identifying compounds whose presence might then be sought in atmospheric samples. For example, studies (*75*) of the aerosol formed during irradiation of mixtures of NO_x (~ 0.1 to 2 ppm) and hydrocarbons (~ 0.25 to 10 ppm) in air, using infrared analysis and paper chromatography, have established that simple olefins and diolefins are precursors of substituted monocarboxylic acids, dicarboxylic acids, and organic nitrates in the condensed phase.

Similar studies have been carried out for mixtures of NO_x (2 to 5 ppm) with 10 ppm of toluene, cyclohexene, and α-pinene, chosen as being representative of ambient hydrocarbons observed in urban or forested rural areas (*76*). A variety of products were identified in the least polar portions of the aerosol extracts, including multifunctional compounds containing two or more of the carbonyl, alcohol, carboxylic acid, and nitrate functions. The 5-nitratopentanoic acid, $HOOC(CH_2)_3CH_2ONO_2$, observed in the cyclohexene reaction, and pinonic acid, observed in the α-pinene reaction, were subsequently found in atmospheric aerosols (*72, 76*).

Thus, the organic composition of even these relatively simple model systems is enormously complex, and a complete and accurate analysis of aerosols is a difficult but worthwhile research goal.

Inhibition of Photochemical Smog

The use of inhibitors to prevent or delay smog formation by trapping radical intermediates in the chain process was first considered almost two decades ago. Recently, studies have been made of the effect of various "inhibitors" on the percentage conversion of NO to NO_2 as a function of time, the maximum NO_2, O_3, and PAN levels reached, or the irradiation time required to reach the NO_2 and O_3 maximums (*77, 78*). Aniline (*77, 78*) and diethylhydroxylamine (DEHA) (*77*) caused a significant delay in the conversion of NO to NO_2 in irradiated NO_x-hydrocarbon mixtures, while aniline, and to a lesser extent benzaldehyde and naphthalene, decreased the maximum O_3 concentration formed (*78*). However, at least aniline, benzaldehyde, and naphthalene lead to significant aerosol formation in the light-scattering size range (*78*).

We believe that the use of such inhibitors as DEHA is fraught with potential problems and urge the utmost caution in considering their introduction into real atmospheres. Extrapolation of the results of these experiments to real urban atmospheres is questionable. For example, a delay in photochemical smog formation may merely transfer the problem downwind. More importantly, the effects of DEHA and its oxidation products on humans are not known in detail. Thus, DEHA is at least structurally similar to the notorious carcinogen diethylnitrosamine. Prudence dictates that very detailed studies of the effects of DEHA and its oxidation products be conducted before direct exposure of the general public is seriously considered.

Summary

Historically, the reactions of O_3 and O(^3P) in photochemical smog formation have received major attention; however, during the last 5 years, the great importance of other species, such as OH and HO_2, has been established. Indeed, the hydroxyl radical has now been measured directly in urban air. Determination of the concentration-time profiles of OH under a variety of conditions in simulated and real atmospheres will most certainly greatly enhance our understanding of photooxidation processes occurring in these complex mixtures. Development of sufficiently sensitive detection techniques for other free radical species such as HO_2 (*79*) will also prove of great value.

Detailed quantitative data on the irradiation of simulated and real polluted atmospheres (even on the stable products) remain sparse; this is especially true for reactions of aromatic hydrocarbons. Furthermore, virtually no quantitative information, necessary for the validation of computer models, is available on the yields of such minor but mechanistically important species as HONO and H_2O_2.

The complex chemistry of photochemical smog must include heterogeneous as well as homogeneous reactions. In addition, studies of physical and chemical synergisms arising from the introduction of SO_2 into the HC-NO_x-Ox-UV system are of top priority, since the rate of photooxidation of gaseous SO_2 to particulate sulfate is greatly enhanced in ambient photochemical smog. Synergisms in these systems may also have important biological consequences.

Finally, physical and chemical transformations occurring in the HC-NO_x-Ox-UV system must be far better understood, because such knowledge is a cornerstone of rational, cost-effective air pollution control strategies. However, while this overall research goal is being pursued, we must utilize our existing knowledge and continue to press for an acceptable balance among our needs in energy, economics, and air quality.

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3. Oxides of nitrogen include NO, NO_2, and other nitrogenous compounds such as PAN and HNO_3; most of the NO_x is emitted directly as NO, which is oxidized in the atmosphere to NO_2 (see text). The other compounds (PAN, HNO_3, and so forth) are commonly present in much lower concentrations than NO and NO_2.
4. Primary pollutants are those emitted directly into the atmosphere; secondary pollutants are those formed by the atmospheric reactions of the primary pollutants.
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