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Atmospheric Photochemistry

The photochemistry of the lower atmosphere is dominated by atoms, molecules, and free radicals.

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The chemistry of the atmosphere above an altitude of about 80 kilometers is dominated by ions and electrons; that below this altitude is concerned largely with neutral molecules, free radicals, and atoms. The composition and reactions of the former region, the ionosphere, were recently reviewed by Donahue (*1*). Therefore, we shall restrict ourselves to a discussion of the photochemistry of the lower part of the atmosphere.

There are many reasons for interest in the chemistry of the lower atmosphere. One of these, of course, is strictly academic: we would like to satisfy our curiosity as to this aspect of the way our universe behaves and the way our atmosphere evolved. Another is that the concentrations of many minor constituents vary considerably from one atmospheric region to another and thus can be used to follow atmospheric motions. Chemical reactions are often responsible for the formation and removal of such constituents (ozone, O_3, for example), and a knowledge of the photochemistry involved is essential to the correct interpretation of concentration measurements. Studies of this sort have provided much information concerning large-scale atmospheric motions, information which may eventually aid in the development of numerical methods for long-range weather forecasting.

A third reason relates to air pollution. A prevalent type of pollution ("photochemical smog") has very unpleasant properties that are largely the result of substances produced by photochemical reactions involving the contaminants. Preventing the emission of all such contaminants into the atmosphere is impractical at present, and an understanding of the chemical reactions that produce the unpleasant substances is essential to the effective selection of pollutants on which to concentrate the greatest control efforts. Also important is a knowledge of the ultimate fate of pollutants since this affects pollution on a worldwide basis. This fate is often that the pollutants undergo further photochemical reactions.

The chemical and dynamic behavior of the atmosphere is markedly influenced by its temperature structure which is often used to establish atmospheric regions lying one above another (Fig. 1). The lowest region of the atmosphere is the troposphere, which extends from the earth's surface up through the region of generally decreasing temperature to the tropopause, the boundary between the troposphere and the stratosphere. The tropopause decreases in altitude with increasing latitude but at mid-latitudes is at about 12 kilometers. The troposphere, as we all know, is a region of storms and turbulence and receives most of its heat from the ground rather than directly from the sun. The stratosphere is a region of nearly constant or of increasing temperature with increasing altitude, which extends upward to about 50 kilometers. Above the stratosphere, starting at the stratopause, is the mesosphere in which the temperature falls until an altitude of 80 to 85 kilometers is reached. Farther out is the thermosphere, a region of rising temperature to at least 200 to 300 kilometers that is often considered to blend with the solar corona. Thus our discussion is restricted to the chemistry of the troposphere, stratosphere, and mesosphere.

Photochemical reactions can be defined as those in which the initiating step is the absorption of a photon by an atom, molecule, free radical, or ion. This absorption can produce excited species, decomposition (photolysis), or ionization. A minimum photon energy (frequency) is required for each process and each species. The initial effect of photon absorption can be considered to be the primary photochemical reaction. Subsequent reactions initiated by primary products are called secondary photochemical reactions, and almost all atmospheric reactions involve both types of reaction.

A large assortment of techniques is used to study the chemistry of the atmosphere, but in general these can be classified into three types. One involves the qualitative and quantitative determination of the composition of atmospheric samples. Near the ground, fairly conventional chemical and instrumental analytical techniques can usually be applied, although special methods are sometimes required where the concentrations are very low, for example, in the range of parts of constituent per billion parts of air by volume (ppb). Samples at higher altitudes are collected from balloons, aircraft, or rockets. A recent development at the National Center for Atmospheric Research (NCAR) is the rocket-borne "cryogenic sampler" which collects a sample of air between 40 and 60 kilometers altitude (Fig. 2). With liquid hydrogen

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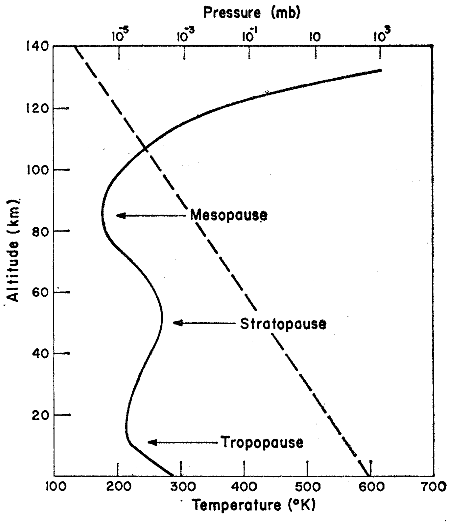


Fig. 1. Schematic diagram of air temperature (solid line) and pressure (dashed line) as a function of height (*36*).

used as the coolant, most of the sample is condensed as it is rammed into the device during passage through the atmosphere. The second class of techniques involves indirect methods of analysis. For example, the absorption or scattering of solar ultraviolet radiation by ozone can be used to determine ozone concentrations at various altitudes. The third class consists of laboratory studies of reactions believed to occur in the atmosphere. Some of these involve attempts to reproduce the atmosphere in the laboratory. Such attempts have often been successful, especially in air pollution research. Other laboratory studies have been designed to obtain fundamental quantitative information on the individual reactions which can be applied to the atmosphere.

The Troposphere

The chemistry of the troposphere is mainly that of a large number of minor atmospheric constituents and of their reactions with molecular oxygen. The photochemical behavior is dominated by the fact that essentially no solar radiation of wavelength less than 2900 angstroms reaches the tropopause, radiation of the shorter wavelengths having been removed largely by reaction with ozone in the stratosphere and with molecular oxygen. Above 3300 angstroms, however, the solar spectral intensity distribution is similar to that at the top of the atmosphere for a sun directly overhead. At large zenith angles, that is, with the sun near the horizon, attenuation is observed over all wavelengths as a result of scattering, diffusion, and the increased path length for ozone in the atmosphere. Typical curves for the distribution of solar spectral intensity are shown in Fig. 3 for $z = 0°$ and $z = 80°$, at ground level in mid-latitudes. Nitrogen does not absorb radiation that reaches the troposphere, and molecular oxygen absorbs only very weakly in the red end of the visible spectrum. Thus the primary photochemical processes in the troposphere are almost entirely restricted to minor constituents.

The atmospheric chemistry of sulfur compounds has been studied extensively because they are unpleasant constituents of smog and pollute the atmosphere worldwide. Also, their variation in concentration has posed some challenging questions with regard to large-scale motions. For example, it is not at all clear why the relative concentrations of airborne sulfate particles are exceptionally high in polar regions (*2*). The sources of such compounds include domestic and industrial fuel consumption, volcanoes, forest fires, and bacterial action (*3*). The oceans also may be an important source of sulfur dioxide. The most abundant of these substances are hydrogen sulfide, sulfur dioxide, sulfuric acid, and various sulfates. The concentrations are extremely variable but are as much as several parts per million (ppm) in severe smog.

Hydrogen sulfide and sulfur dioxide undergo a number of oxidation reactions. Ozone is produced in photochemical smog, and some also mixes into the troposphere from the stratosphere where it is a natural constituent. Hydrogen sulfide reacts with ozone to form mainly sulfur dioxide and water but at rates probably too slow, at least in the gas phase, to be important (*4*). Hydrogen sulfide has a bond energy of 81.1 kilocalories per mole per H–S bond, corresponding to a wavelength (λ) of 3510 angstroms. However, it does not appreciably absorb radiation of wavelength greater than about 2700 angstroms; thus it does not undergo photolysis or react photochemically with molecular oxygen. Hydrogen sulfide, ozone, and molecular oxygen are all soluble in water. The rate of oxidation of hydrogen sulfide by these oxidants in solution, for example, in fog or cloud droplets, may be very fast, but these reactions have not been studied. Atomic oxygen, produced largely by the photolysis of ozone and of nitrogen dioxide, is present in extremely small amounts in the troposphere. In spite of the low concentrations, atomic oxygen reactions almost certainly occur to an appreciable extent, especially in some polluted atmospheres. The reaction of atomic oxygen with hydrogen sulfide (*5*) can be represented by the equation

$$H_2S + O \rightarrow OH + HS \qquad (1)$$

and

$$-d[H_2S]/dt = k[H_2S][O]$$

where k, "the rate constant," equals 4×10^{-14} cubic centimeters per molecule per second. The brackets refer to concentrations expressed in numbers of molecules or atoms per cubic centimeter, and time is in seconds (*6*). Reaction 1 is followed by a chain reaction leading to products such as SO_2, SO_3, H_2SO_4, H_2, and H_2O.

Sulfur dioxide in its electronic ground state does not react with ozone in the gas phase either in the presence or in the absence of water vapor (*7*). The energy for the dissociation of SO_2 into SO and O is about 135 kilocalories per mole ($\lambda < 2100$ angstroms). However, SO_2 absorbs strongly in the near-ultraviolet region to form electronically excited SO_2 which may react with ozone. This reaction has not been studied. Similarly, ground state SO_2 does not react with O_2 in the gas phase. However, excited sulfur dioxide does react, and several laboratory studies have been made of this reaction (*8*). The rate at which such a reaction occurs in the atmosphere can be estimated from the photochemical yield Φ (the ratio of molecules of product formed per photon absorbed), the absorption coefficient of the primary reactant, the intensity of solar radiation, and the concentration of the reactants. Integration is necessary over the wavelength range in which absorption occurs. Unfortunately, a very wide range of values for Φ has been obtained. Recent results obtained in our laboratory indicate that Φ is about 1.7×10^{-2} at 3130 angstroms, but over the wavelength range from 2800 to 4200 angstroms, Φ is about 2×10^{-3}. This difference may partially explain the previous discrepancies. The latter value corresponds to an atmospheric reaction rate of about one SO_2 molecule per thousand oxidized per hour.

Two nonphotochemical means of oxidation of SO_2 by O_2 are of possible importance. Urone *et al.* (*9*) have found that in the presence of powdered oxides of aluminum, calcium, chromium, iron, lead, and vanadium sulfur dioxide in air is oxidized very rapidly without sunlight. Airborne dust particles may have a similar effect. Sulfur dioxide dissolved in fog or cloud droplets is oxidized by O_2 much more rapidly than by the gas-phase photochemical reaction, especially when certain metal salts are present (*10*).

Sulfur dioxide undergoes a three-body reaction with atomic oxygen (*11*):

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (2)$$

where M is a molecule of O_2 or N_2, and $k = 1.3 \times 10^{-32}$ cm^6 molecule^{-2} sec^{-1}. This reaction is more important in stratospheric and in polluted air than in the "natural" troposphere. The sulfur trioxide formed almost immediately reacts with water vapor to form sulfuric acid, which in turn will rapidly react mainly with any ammonia present to form ammonium sulfate or ammonium bisulfate (*12*). Thus sulfur trioxide never exists to an appreciable extent in the open atmosphere.

Nitrogen compounds, such as ammonia, nitrous oxide, nitric oxide, nitrogen dioxide, and nitric acid vapor, are interesting minor constituents of the atmosphere. Several of these undergo oxidation and hydrolysis, the end products being nitric acid and nitrates. Ammonia is liberated from the soil and the sea and is probably removed from air, where it exists both as the gas and as ammonium salts, mainly as a result of the scrubbing action of rainfall. Except for reaction with acids, ammonia is chemically quite stable in the natural troposphere. The reaction with ozone has not been studied but is probably very slow. Ammonia does not absorb visible or ultraviolet radiation of wavelengths exceeding 2200 angstroms and thus does not undergo excitation or photolysis below the ionosphere. It does react with atomic oxygen (*13*)

$$NH_3 + O \rightarrow NH_2 + OH \qquad (3)$$

where $k = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}.

Nitrous oxide (N_2O) is the prevalent oxide of nitrogen in the atmosphere, occurring throughout the lower atmosphere at about 0.3 to 0.5 ppm. The main source of nitrous oxide seems to be soil bacteria, since reactions of ground state or excited O, O_2, or O_3 with N_2 cannot account for it (*11, 14*). In the lower atmosphere N_2O is chemically quite inert.

Nitric oxide (NO) is the main oxide of nitrogen produced by combustion of organic material in air (by "nitrogen fixation"), and combustion is probably the chief source below the ionosphere. Its concentration in the troposphere away from major sources is probably of the order of 10^{-2} ppm. It is very slowly oxidized by O_2 but rapidly by O_3 (*15*):

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

where $k = 5 \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}. Nitric oxide does not absorb solar radiation that reaches the troposphere. Atmospheric NO_2 is produced mainly by the oxidation of NO. Little is known concerning its concentration in unpolluted air, although Lodge and Pate (*16*) found comparable concentrations of NO and NO_2 in the tropics.

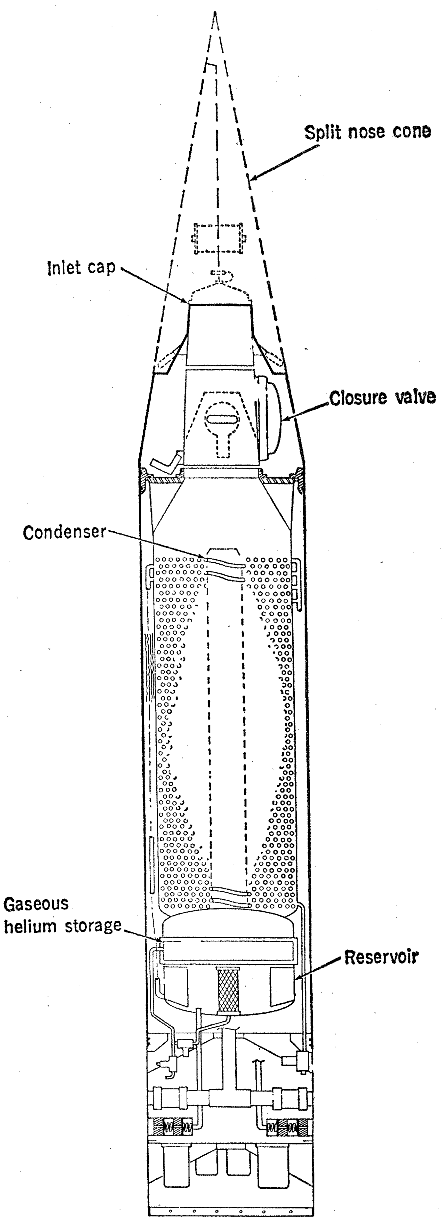


Fig. 2. National Center for Atmospheric Research cryogenic sampler. The cooling agent is liquid hydrogen pressurized with helium.

When nitrogen dioxide is irradiated with near-ultraviolet radiation, O_2 and NO are formed (*17*):

$$NO_2 + h\nu \rightarrow NO + O \qquad (5)$$

$$NO_2 + O + M \rightarrow NO + O_2 + M \qquad (6)$$

where $k = 4.2 \times 10^{-31}$ cm^6 molecule^{-2} sec^{-1}, and $h\nu$ represents a photon of light. However, in air containing less than 1 ppm of NO_2 and 21 percent O_2, the following reaction will be faster than reaction 6 (*18*):

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

where $k = 7.5 \times 10^{-34}$ cm^6 molecule^{-2} sec^{-1}. Since reaction 7 is followed by reaction 4, steady-state concentrations of NO_2 and O_3 may be maintained at times, although these are usually disturbed by transport of ozone from the stratosphere and from photochemical smog formed as discussed below.

Ozone also reacts with NO_2, although not so rapidly as with NO. The reaction occurs in two steps:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (8)$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \qquad (9)$$

The rate is controlled by the slower reaction, reaction 8. The rate constant for this reaction was found by Ford *et al.* (*19*) to be 3.3×10^{-17} cm^3 molecule^{-1} sec^{-1}. The N_2O_5 reacts very rapidly with water vapor to form nitric acid vapor, HNO_3.

Nitrogen dioxide hydrolyzes in the gas phase:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO \qquad (10)$$

This reaction has been investigated by McHaney (*20*) who found the following equilibrium constant:

$$K = \frac{[HNO_3]^2[NO]}{[NO_2]^3[H_2O]} = 0.004/\text{atm} \qquad (11)$$

at 300°K. The equilibrium lies far to the left, but in air, with its high concentration of water vapor, about 5 percent of the NO_2 is converted to HNO_3 at room temperature.

Various organic compounds are present in the natural troposphere, the most abundant being methane. Concentrations of methane, butane, acetone, *n*-butanol, and carbon monoxide were found to be 1.6 ppm, 0.06 ppb, 1.0 ppb, 190 ppb, and 90 ppb, respectively, in uncontaminated arctic air masses at Point Barrow, Alaska (*21*). Many plants evolve organic vapors such as hydrocarbons, esters, aldehydes, and ketones.

Methane in the atmosphere is of considerable interest chemically. It is evolved by the natural and polluted environment. Natural sources include anaerobic decay of vegetation in the biosphere and natural gas seepage. Atmospheric concentrations away from sources of pollution average about 1.5 ppm. Methane does not absorb solar radiation above a wavelength of 1600 angstroms and is chemically quite inert in the troposphere. Considerable evidence exists that some of the other organic compounds undergo photochemical reactions similar to those occurring in smog which are described below. Such reactions may be responsible for the formation of the haze often observed over forests.

Table 1. Typical concentrations of trace constituents in photochemical smog; parts of constituent per hundred million parts of air by volume, pphm.

Constituent	Concentration (pphm)
Oxides of nitrogen	20
NH$_3$	2
H$_2$	50
H$_2$O	2×10^6
CO	4×10^3
CO$_2$	4×10^4
O$_3$	50
CH$_4$	250
Higher paraffins	25
C$_2$H$_4$	50
Higher olefins	25
C$_2$H$_2$	25
C$_6$H$_6$	10
Aldehydes	60
SO$_2$	20

The Polluted Atmosphere

It is difficult to divorce a discussion of chemical reactions occurring in a localized polluted environment from tropospheric chemistry as a whole. The difference is mainly a matter of concentration. Unfortunately, it takes exposure to severe local pollution and observation of the accompanying unpleasant effects, such as eye irritation, odor, plant damage, and reduced visibility, to make us acutely aware of the profuse contamination of the atmosphere. We should, however, also be aware that, when conditions are not conducive to the maintenance of a stagnant atmospheric layer, the same contaminants are pumped at the same rate into the troposphere but, fortunately, are diluted by diffusion and mixing into a considerably larger volume.

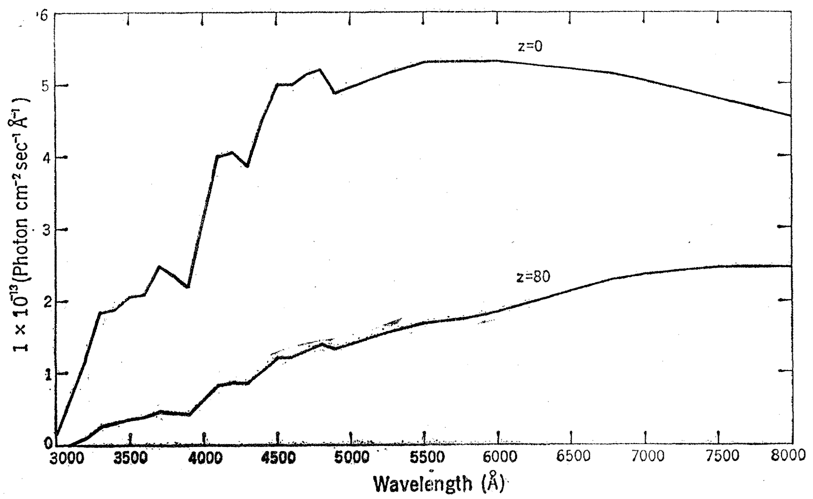
Although several types and combinations of pollution are observed, we shall confine our discussion to pollution of the type first recognized in the Los Angeles basin and often called photochemical smog. We now know that the unpleasant properties of the smog over practically all cities are caused at least in part by compounds produced by photochemical reactions.

It is well established that the main contaminants in photochemical smog originate from automobile exhaust, although certainly there is a contribution from industrial activity and the incineration of wastes (Table 1). The exhaust gases consist primarily of nitrogen oxides, nitrogen, uncombusted and partially combusted hydrocarbons from the fuel, oxides of carbon, and water vapor. Carbon oxides and water vapor are relatively inert to solar radiation at the ground and therefore are not involved in the primary photochemical processes, but they may play a role in secondary reactions (*22*). For a detailed review of the data available prior to 1961, the reader is referred to the excellent treatise by Leighton (*23*). The limitations on the size of this article preclude more than a general description of the major processes involved. Obviously, the interactions are numerous and complex, and the problem is compounded by the large variety of reactants.

Variation in the concentration of major reactive species with time of day during a typical smoggy day in Los Angeles is shown in Fig. 4. The sequence of formation, destruction, and dispersion is easily observed. The rate of emission of pollutants into the atmosphere varies throughout the day and peaks around midmorning and late afternoon. The solar radiation intensity also varies continuously, increasing in the morning and decreasing in the afternoon.

During the daylight hours, the nitric oxide is rapidly converted to nitrogen dioxide. The mechanism of this rapid conversion and that of the production of ozone (Fig. 4) are two of the major problems in understanding the development of smog. Oxidation of the nitric oxide directly by O$_2$ is much too slow a reaction to account for the conversion, and, as pointed out above, nitric oxide does not absorb solar radiation in the troposphere.

Laboratory experiments suggest that the most important primary photochemical reaction in smog may be the photolysis of nitrogen dioxide (reac-



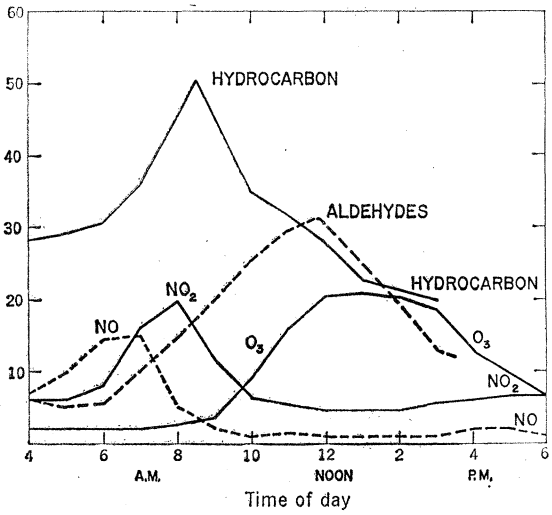
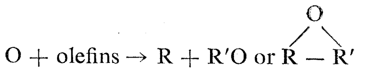


Fig. 3 (left). Estimated solar spectral intensity distribution at ground level and mid-latitudes for zenith angles 0° and 80° (*23, 37*). Fig. 4 (right). Typical variation of components in photochemical smog for a day of intense smog (*23*); *pphm*, parts of constituent per hundred million parts of air by volume.

tion 5), which is always formed to a slight extent by the direct reaction with O_2. Most of the oxygen atoms produced ($>$ 99 percent) react with molecular oxygen (reaction 7) to produce ozone, but this is followed by the very rapid reaction 4 which leads to the regeneration of NO_2. The result, if these were the only reactions occurring, would be a steady-state concentration of ozone much lower than that observed in smog (*24*). However, a small part of the atomic oxygen reacts with the hydrocarbons and other organic compounds to produce a wide variety of organic and inorganic free radicals, for example:



$$\mathrm{O + olefins \rightarrow R + R'O \text{ or } \overset{O}{\widehat{R - R'}}} \qquad (12)$$

where $k = 1.7$ to 8.0×10^{-12} cm^3 molecule^{-1} sec^{-1}, and R and R′ are organic radicals. The ozone also reacts with various organic compounds, especially olefins, to form a multitude of compounds, including free radicals:

$$\mathrm{O_3 + olefins \rightarrow products} \qquad (13)$$

where $k = 3$ to 30×10^{-18} cm^3 molecule^{-1} sec^{-1}.

The organic free radicals react rapidly with O_2 to form peroxy free radicals (*23*):

$$\mathrm{R + O_2 \rightarrow RO_2} \qquad (14)$$

where k is approximately equal to 10^{-14} cm^3 molecule^{-1} sec^{-1}. These are capable of oxidizing NO to NO_2 and may be responsible for most of the conversion of NO to NO_2 in smog.

Aldehydes are products of the reaction of both ozone and atomic oxygen with olefins. They can react with ozone and atomic oxygen, which initiates new chain reactions. Generally, ozone reacts with aldehydes to produce peroxy acids. Atomic oxygen, on the other hand, abstracts hydrogen to produce a hydroxyl and an acyl radical.

The reaction of oxygen atoms with acetaldehyde has been studied in this laboratory (*25*):

$$\mathrm{O + CH_3CHO \rightarrow CH_3CO + OH} \qquad (15)$$

where $k = 4.5 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. Both of these products are capable of reacting further and maintaining a reaction chain. For example, the hydroxyl radical may react with the relatively inert carbon monoxide (*26*) by way of the reaction

$$\mathrm{OH + CO \rightarrow CO_2 + H} \qquad (16)$$

where $k = 1.7 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. The hydrogen atoms thus produced will react almost exclusively with oxygen to form hydroperoxy radicals (*27*) by way of the reaction

$$\mathrm{H + O_2 + M \rightarrow HO_2 + M} \qquad (17)$$

where $k = 3 \times 10^{-32}$ cm^6 molecule^{-2} sec^{-1}, and the hydroperoxy radicals are capable of oxidizing nitric oxide to nitrogen dioxide. Also, the acyl radicals will probably react with oxygen to produce acylperoxy radicals which are capable of oxidizing nitric oxide.

Finally, it has been suggested that excited molecular oxygen may be produced by energy transfer from photoexcited hydrocarbons (*28*). This oxygen may then react with nitric oxide, olefins, or aldehydes to produce nitrogen dioxide directly or indirectly.

The ozone in smog may be produced largely by the reaction of peroxy radicals with O_2 (*24*):

$$\mathrm{RO_2 + O_2 \rightarrow RO + O_3} \qquad (18)$$

Many other components absorb solar radiation at the wavelengths we have considered, for example, nitric acid, nitrates, nitrites, nitro compounds, aldehydes, ketones, peroxides, acyl nitrates, and particles. All that can be said at this time is that the absorption of solar radiation by these compounds will contribute to the production of free radicals which in turn will produce new compounds.

The products that are particularly noxious to plant and animal life are reasonably well understood. Formaldehyde, peroxyacyl nitrate, and acrolein are probably the main components responsible for eye irritation. Formaldehyde is a product of the reaction of ozone or atomic oxygen with terminal olefins; so, for that matter, is acrolein. Peroxyacyl nitrate, on the other hand, is the termination product of a reaction chain and requires the addition of nitrogen dioxide to a peroxyacyl radical.

The photooxidation of sulfur dioxide occurs by way of processes mentioned in the section dealing with the chemistry of the natural troposphere.

The Stratosphere and Mesosphere

The photochemistry of the stratosphere and mesosphere differs considerably from that of the troposphere largely because of the presence of shorter-wavelength, more energetic, solar radiation (down to about 2000 angstroms at the top of the mesosphere, although there is a small amount below 2000 angstroms, for example, the so-called Lyman α band at 1216 angstroms).

The chemical reactions in the stratosphere and mesosphere are largely the result of the photolysis of O_2 to form atomic oxygen. This photolysis is produced by absorption in the strong Schumann-Runge bands in the wavelength range from 1760 to 2030 angstroms and the weaker absorption extending to wavelengths of about 2450 angstroms:

$$\mathrm{O_2 + h\nu \rightarrow O + O} \qquad (19)$$

The following reaction sequence then occurs, leading to the formation and destruction of ozone (*29*):

$$\mathrm{O + O + M \rightarrow O_2 + M} \qquad (20)$$

where $k = 2.8 \times 10^{-33}$ cm^6 molecule^{-2} sec^{-1}; atomic oxygen reacts with molecular oxygen to form ozone (reaction 7);

$$\mathrm{O + O_3 \rightarrow 2O_2} \qquad (21)$$

where $k = 1.9 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}; and

$$\mathrm{O_3 + h\nu\ (\lambda < 11{,}400\ \text{Å}) \rightarrow O_2 + O} \qquad (22)$$

Reactions 7 and 21 constitute the principal mode of recombination of O atoms in this region. Numerous investigations have been made of the rate constants and photochemical yields of these reactions. These and the absorption coefficients for ozone and oxygen have formed the basis for numerous calculations of concentrations of atomic oxygen and of ozone as a function of altitude in the stratosphere and mesosphere. Perhaps the greatest uncertainties in these calculations, other than atmospheric transport effects, are the activation energy for reaction 21 and the extent to which the absorption of ultraviolet radiation by O_2 and O_3 obeys the Beer-Lambert law.

Calculations should probably also include reactions involving hydrogen compounds and free radicals. Unfortunately, the chemistry then becomes extremely complicated. Photochemical dissociation of water vapor in the mesosphere, oxidation of methane and other hydrocarbons in the stratosphere, and reactions of electronically excited O from ozone photolysis in the ultraviolet are eventual sources of hydrogen atoms which may react by at least 30 processes; the two most important processes in the stratosphere are reactions 17 and 23 (*27, 30*):

$$\mathrm{H + O_3 \rightarrow OH + O_2} \qquad (23)$$

where $k = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. The process represented by reaction 23 has been suggested as being responsible for the airglow emission by the hydroxyl radical. Two other processes of particular importance are (*13*):

$$OH + O \rightarrow H + O_2 \qquad (24)$$

where $k = 5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}, and

$$HO_2 + O \rightarrow OH + O_2 \qquad (25)$$

where k is greater than or equal to 10^{-11} cm^3 molecule^{-1} sec^{-1}. These reactions are of some importance in the mesosphere where atomic oxygen concentrations are not less than 10^{10} per cubic centimeter during the day. Generally, in the mesosphere the atomic oxygen concentration exceeds that of ozone during the day; the reverse is true in the stratosphere.

A considerable number of secondary processes, incorporating the destruction of atomic hydrogen, hydroxyl, and perhydroxyl, occur in the mesosphere. Incorporation of all possible reactions into a complete scheme to describe the mesosphere would be a monumental task and could only be attempted by the use of a high-speed computer. The complexity of this region is demonstrated by Fig. 5, which indicates the concentrations of some of the constituents as a function of altitude.

The photolysis of ozone produces electronically excited O_2, at least for $\lambda < 2500$ angstroms. The role that such oxygen plays in the chemistry of the stratosphere and mesosphere is unknown.

Numerous comparisons have been made of the calculated and measured concentrations of ozone. The differences have provided much useful information concerning atmospheric motion.

Little direct information exists concerning nitrogen compounds (other than N_2) in the stratosphere and mesosphere. Ammonium compounds have been detected in the particulate material collected from the lower stratosphere, for example, by Cadle *et al.* (*32*). These were probably formed by the reaction of ammonia with droplets of sulfuric acid produced as described below. Nitrous oxide is chemically stable throughout this region. Nitric oxide, which enters the stratosphere from below, is rapidly oxidized by ozone to NO_2, which in turn is oxidized to N_2O_5. The end product of these reactions (reactions 4, 8, 9, and the reaction of N_2O_5 with water vapor) is nitric acid vapor, which has been detected spectroscopically in the stratosphere.

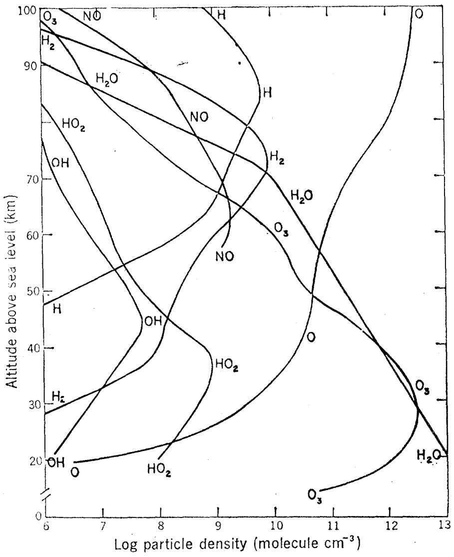


Fig. 5. Daytime equilibrium profiles for a hydrogen-oxygen atmosphere. A composite of experimental data from the *Handbook of Geophysics* (Macmillan, New York, 1961) and the theoretical estimates of Hunt (*38*). The nitric oxide profile was measured by Pearce (*39*).

Small amounts of H_2S and SO_2 must reach the stratosphere from the troposphere and be oxidized, largely by reaction with atomic oxygen (reactions 1 and 2). However, the only sulfur compounds that have been detected in this region are particulate sulfates and persulfates. Some of these particles are produced in the troposphere or at the earth's surface, but most are probably formed in the stratosphere by chemical reactions, such as reactions 1 and 2 followed by reaction of the SO_3 with water vapor and ammonia to form ammonium sulfate (*3*, pp. 111–208; *11*). Cadle *et al.* (*32*) showed that the concentration of sulfate immediately above the tropopause is considerably greater than that just below it. A very interesting feature of the stratosphere is the existence of a worldwide layer containing an especially large concentration of such particles at an altitude of about 18 kilometers (*3*, pp. 111–208). The concentration seems to be markedly increased after major volcanic eruptions, presumably as a result of the emission of large amounts of sulfur compounds into the atmosphere.

The main carbon compounds in the stratosphere and mesosphere are carbon monoxide, carbon dioxide, and methane. The chief source of carbon monoxide is the combustion of organic material, especially by the internal combustion engine. Carbon monoxide is relatively inert in the troposphere, but in the stratosphere it is removed by reaction with O and OH, especially the latter (reaction 16) (*26*). Although numerous studies have been made of the reaction of O with CO, there is considerable uncertainty concerning the kinetics of this reaction.

Carbon dioxide is both created and destroyed at ground level, the main source being the combustion of fossil fuels. Scavenging is accomplished mainly by the action of plants, bacteriological action, and solution in the sea. Carbon dioxide is transported vertically by mixing processes and presumably is destroyed above the mesopause by photochemical decomposition, which requires radiation of shorter wavelength than 1650 angstroms.

Present estimates of CO_2 concentrations near ground level average about 330 ppm. Although there is some evidence that it decreases by about 5 ppm above the tropopause, recent measurements made by Scholz *et al.* (*33*) in the vicinity of the stratopause indicate a CO_2 concentration of about 320 ppm. This value was obtained for a sample of air collected with the cryogenic sampler between 45 and 62 kilometers. Concern has been expressed over several decades about the CO_2 abundance, which apparently is increasing at the rate of 0.7 to 1 ppm per year. The strong influence of CO_2 on the stratospheric radiation budget suggests that increased heating will cause major climatological changes to occur at the earth's surface. Fortunately or unfortunately, this seems to have been offset or even reversed by a cooling effect due to the accumulation of particulate matter in the atmosphere.

A limited number of vertical profiles of methane have been obtained by Bainbridge and Heidt (*34*). They found a nearly constant mixing ratio (the concentration relative to O_2 and N_2) below the tropopause, which decreased at and above the tropopause. These results were extended by Kyle *et al.* (*35*). Scholz *et al.* estimated that there was less than 0.1 ppm of CH_4 in a sample of air collected with the cryogenic sampler. Cadle and Powers (*11*) suggested that the primary process responsible for removal of the methane was reaction with stratospheric atomic oxygen:

$$O + CH_4 \rightarrow CH_3 + OH \qquad (26)$$

where $k = 5.5 \times 10^{-15}$ cm^3 molecule^{-1} sec^{-1}. In this way, all hydrocarbons that reach stratospheric levels would be eventually oxidized to CO_2 and water. Furthermore, this reaction may be an important source of OH.

Summary

Photochemical reactions in the troposphere, stratosphere, and mesosphere are, to a large extent, reactions among minor constituents of the atmosphere. The chemistry is markedly limited by the minimum wavelength of the solar radiation which penetrates to a given atmospheric level. It is useful to differentiate between the chemistry of city smog and that of the ambient atmosphere, but the entire atmosphere is being polluted and the difference is one of degree.

Both laboratory and field studies are contributing to our knowledge of atmospheric photochemistry, and the most convincing conclusions have been obtained by combining the results of the two methods of investigation.

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The Genetics of Schizophrenic and Schizoid Disease

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The contribution of genetic factors to the etiology of schizophrenia has been confirmed decisively. Because the investigations that have led to this result have uncovered questions cutting across several fields of inquiry, a fresh look at some central aspects of the schizophrenia problem is warranted. These questions and the factual background underlying them are the main concerns of this article. Because emphasis is placed on formulating testable hypotheses, the evidence is organized in support of a particular genetic theory.

The Basic Evidence

During the first half of this century, systematic family studies demonstrated that the distribution of schizophrenia is that of a genetic disease. Relatives of schizophrenics were found to be afflicted with the illness much more frequently than members of the general population. The child of a schizophrenic parent, for example, was found to have a risk of schizophrenia about 15 times that of a member of the population at large. It was found that, among all classes of relatives, the closer the genetic relationship to a schizophrenic proband (or index case) is, the greater is the likelihood of schizophrenia in the relative. Finally, and most telling of all, monozygotic twins were found to be concordant with respect to schizophrenia about four times as often as dizygotic twins. Several authorities have critically reviewed these basic data (*1*, *2*). But, despite the supporting evidence, a genetic etiology for schizophrenia was not widely accepted, especially in this country. It was pointed out that the investigators did not pay enough attention to important procedural matters, such as providing sampling safeguards and insuring against bias on the part of the investigator. But the paramount objection to a genetic interpretation of the evidence was the objection that the whole research strategy was faulty. The results of these studies, it was held, were just as compatible with transmission of schizophrenia through the social environment as with transmission through genes. The closer the

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