

3

Tropospheric Ozone and Its Precursors

3.1 Introduction

Ozone (O_3) and other oxidants found in ambient air, such as peroxyacyl nitrates (PANs) and hydrogen peroxide (H_2O_2), are formed as the result of atmospheric physical and chemical processes involving two classes of precursor pollutants, volatile organic compounds (VOCs) and nitrogen oxides (NO_x). The formation of O_3 and other oxidants from these precursors is a complex, nonlinear function of many factors, including temperature, the intensity and spectral distribution of sunlight, atmospheric mixing and related meteorological conditions, the concentrations of the precursors in ambient air and the ratio between VOC and NO_x , and the reactivity of the organic precursors.

An understanding of the atmospheric chemistry and meteorological parameters and processes responsible for the formation and occurrence of elevated concentrations of O_3 in ambient air is basic to the formulation of strategies and techniques for its abatement. Such an understanding is required for representing those parameters and processes adequately in predictive models used to determine the emission reductions needed for complying with the National Ambient Air Quality Standards (NAAQS) for O_3 . In addition, the identification and quantification of O_3 precursors in ambient air are essential, along with emission inventories or emission models, for the development, verification, and refinement of photochemical air quality models and for comparisons of ambient concentrations with emission inventories (source reconciliation), as a check on the accuracy of measurements and of inventories.

Product identification and quantification of yields, in both chambers and ambient air, are helpful in the verification of photochemical air quality models and in testing theoretical chemical mechanisms. Likewise, product identification and quantification are useful in determining the need for research on the potential effects of the simultaneous or sequential co-occurrence with O_3 and related oxidants of multiple air pollutants.

The ability to measure O_3 and its precursors, its reaction products, and the products of the atmospheric reactions of its respective precursors is essential for understanding the atmospheric chemistry of O_3 formation, verifying chemical mechanisms and models, quantifying emission rates, and adequately characterizing exposure-response factors for both biological and nonbiological receptors.

For these reasons, this chapter presents information on a broad range of topics. The chapter describes the chemical processes by which O_3 and other photochemical oxidants are formed in ambient air (Section 3.2). The chapter also characterizes the nature of the precursors in terms of their sources and emissions into the atmosphere and their

concentrations in ambient air (Section 3.4), as well as the methods by which their concentrations in ambient air are measured (Section 3.5).

In addition to information on the chemistry of oxidants and their precursors, this chapter includes a discussion of meteorological processes (Section 3.3) that contribute to the formation of O₃ and other oxidants and govern their transport and dispersion. Finally, an overview is given (Section 3.6) of models of the relationships between precursor emissions and O₃ formation in the atmosphere.

Readers are referred to other sources (e.g., Finlayson-Pitts and Pitts, 1986; Seinfeld, 1986; the U.S. Environmental Protection Agency, 1986a; National Research Council, 1991) for additional information on the chemical and physical aspects of photochemical air pollution.

3.2 Tropospheric Ozone Chemistry

3.2.1 Background Information

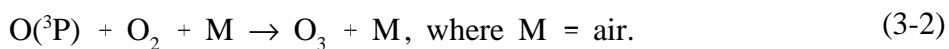
Ozone is formed photochemically in the stratosphere and transported downward, resulting in the presence of O₃ in the natural or "clean" troposphere. The presence of O₃ in the clean troposphere, in the absence of perturbations caused by human activities, is highly important because O₃ is a precursor to the hydroxyl (OH) radical, the key intermediate species in the tropospheric degradation of VOCs emitted into the atmosphere. Although O₃ at relatively low concentrations is an integral part of the clean troposphere, its presence at higher concentrations is detrimental.

The chemical processes occurring in the atmosphere that lead to the formation of O₃ and other photochemical air pollutants are complex. Tropospheric O₃ is formed as a result of (1) the emissions of NO_x and VOCs into the atmosphere from anthropogenic and natural sources, (2) the transport of these emissions and their reaction products, and (3) chemical reactions occurring in the atmosphere concurrent with transport and dispersion of the emissions. These processes lead to the formation of O₃ and other photochemical oxidants, such as peroxyacetyl nitrate (PAN), nitric acid (HNO₃), and sulfuric acid (H₂SO₄), and to other compounds, such as particulate matter and formaldehyde (HCHO) and other carbonyl compounds. Additionally, deposition of gases and particles along the trajectory of an air parcel occurs, reducing the concentrations of precursors and products in the atmosphere, but possibly leading to adverse impacts on the earth's environment.

The basic process leading to the photochemical formation of O₃ in the troposphere involves the photolysis of nitrogen dioxide (NO₂) to yield nitric oxide (NO) and a ground-state oxygen atom, O(³P),



which then reacts with molecular oxygen to form O₃:



The NO and O₃ react to reform NO₂:



The presence of reactive VOCs leads to the conversion of NO to NO₂ without the intermediary of O₃ (Reaction 3-3), and the photolysis of NO₂ then leads to the formation of elevated levels of O₃:



The photochemical cycles leading to O₃ production are best understood through a knowledge of the chemistry of the atmospheric oxidation of methane (CH₄), which can be viewed as being the chemistry of the clean or unpolluted troposphere (although this is a simplification because vegetation releases large quantities of complex VOCs into the atmosphere). Although the chemistry of the VOCs emitted from anthropogenic and biogenic sources in polluted urban and rural areas is more complex, a knowledge of the CH₄ oxidation reactions aids in understanding the chemical processes occurring in the polluted atmosphere because the underlying chemical principles are the same.

This section first describes the structure of the atmosphere, followed by discussions of the formation of the OH radical and of tropospheric NO_x chemistry. The photochemical formation of tropospheric O₃ from the oxidation of CH₄ then is discussed in some detail because the CH₄ oxidation cycle serves as a model for the photochemical formation of O₃. In Section 3.2.4, the chemistry of the major classes of nonmethane VOCs and the formation of O₃ from these VOCs are discussed. Finally, in Section 3.2.5, a brief account of the photochemical formation of aerosols is given because the same processes that lead to the formation of elevated levels of O₃ result in the formation of both particulate matter (leading to visibility degradation) and atmospheric acidity.

3.2.2 Structure of the Atmosphere

Earth's atmosphere is composed of a number of layers (McIlveen, 1992). For the purposes of this chapter, those of concern are the troposphere and the stratosphere, and the boundary between them, the tropopause.

The troposphere extends from the earth's surface to the tropopause (≈10 to 18 km altitude, depending on latitude and season). The altitude of the tropopause is greatest in the tropics and lowest in the wintertime polar regions, with an average altitude of ≈14 km. The temperature in the troposphere decreases with increasing altitude from an average of 290 K at the earth's surface to ≈210 to 220 K at the tropopause, and the pressure decreases from ≈760 torr at the earth's surface to ≈100 torr at the tropopause.

The stratosphere extends from the tropopause to an altitude of ≈50 km. In the stratosphere, the temperature increases with increasing altitude from ≈210 to 220 K at the tropopause to ≈270 K at the top of the stratosphere. The pressure in the stratosphere decreases with increasing altitude from ≈100 torr at the tropopause to ≈1 torr at the top of the stratosphere.

3.2.2.1 Vertical and Horizontal Mixing in the Atmosphere

In the troposphere, temperature generally decreases with increasing altitude. As will be discussed in Section 3.3, the lowest 1 to 2 km of the troposphere is influenced by the planetary boundary layer (PBL) and, in certain locales, by inversion layers. These boundary and inversion layers inhibit the vertical movement of pollutants into the free troposphere. Above inversion and boundary layers, vertical mixing in the "free" troposphere has a time scale of ≈ 10 to 30 days (Langner et al., 1990; World Meteorological Organization, 1990a).

Because temperature increases with increasing altitude in the stratosphere, vertical mixing in the stratosphere is slow, with a time scale of months to a few years.

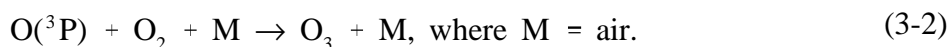
Horizontal mixing in the troposphere occurs both within and between the hemispheres. The time scale for mixing between the Northern and Southern Hemispheres is ≈ 1 year (Cicerone, 1989; Singh and Kanakidou, 1993). Transport within a hemisphere is more rapid (Graedel et al., 1986a), and local, regional, and global transport distances of <100 km, 100 to 1,000 km, and $>1,000$ km, respectively, are observed. For a wind speed of 15 km h^{-1} ($\approx 4 \text{ m s}^{-1}$), transport times over these local, regional, and global distances are a few hours, a few hours to a few days, and ≥ 10 days, respectively.

3.2.2.2 Formation of Stratospheric Ozone

At altitudes between approximately 20 and 35 km, the stratosphere has a layer of air containing O_3 at mixing ratios up to approximately 10 ppm. The sun emits radiation >170 nm, and this radiation impacts the upper levels of the atmosphere. The bulk composition of the atmosphere (78.1% nitrogen [N_2], 21.0% molecular oxygen [O_2], 0.9% argon [Ar], 0.03% carbon dioxide [CO_2], with variable trace gas concentrations) is invariant up to at least 50 km (McIlveen, 1992). The shorter wavelength radiation (175 to 240 nm) is absorbed by O_2 in the stratosphere, leading to dissociation into two ground-state oxygen atoms, $\text{O}(^3\text{P})$,



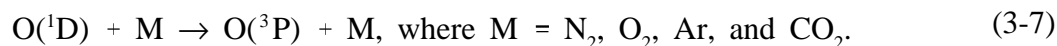
followed by the reaction of $\text{O}(^3\text{P})$ atoms with O_2 in the presence of a third body, M, to form O_3 :



Ozone also photolyzes, at wavelengths <360 nm (DeMore et al., 1992),



where the oxygen atom produced can be in the ground state, $\text{O}(^3\text{P})$, or electronically excited state, $\text{O}(^1\text{D})$. The $\text{O}(^1\text{D})$ atoms produced are deactivated to the ground-state $\text{O}(^3\text{P})$ atom by N_2 , O_2 , CO_2 , and Ar:



The reaction of $\text{O}(^3\text{P})$ atoms with O_3 is the termination step of this reaction sequence,



These reactions, called the Chapman reactions (Chapman, 1930), are responsible for the layer of O_3 found in the stratosphere. Because the stratospheric O_3 layer absorbs the sun's radiation below ≈ 290 nm, only radiation of wavelengths > 290 nm can penetrate into the troposphere and impact the earth's surface. Any depletion of the stratospheric O_3 layer allows shorter wavelength ultraviolet radiation (< 320 nm) to be transmitted through the stratosphere and into the troposphere.

In addition to the biological effects expected from increased ultraviolet B (UV-B) radiation (290 to 320 nm), increased penetration of UV-B into the troposphere can lead to changes in tropospheric O_3 . Model calculations indicate that O_3 in the troposphere could increase with increasing UV-B in urban and rural areas impacted by anthropogenic NO_x emissions (Gery et al., 1988; Liu and Trainer, 1988; Thompson et al., 1989; Thompson, 1992) but could decrease with increasing UV-B in remote tropospheric areas characterized by low NO_x levels (Liu and Trainer, 1988; Thompson et al., 1989). Besides the implications of long-term trends in stratospheric O_3 concentrations leading to corresponding changes in the intensity of UV-B radiation impacting the troposphere, short-term changes (including daily changes) in stratospheric O_3 levels lead to short-term changes in the rates of photolysis of several important species. These include the photolysis of formaldehyde to produce radicals and of O_3 to form the OH radical. These changes in photolysis rates affect the formation rates and ambient concentrations of key radical intermediates, specifically of the OH radical, in the troposphere. Information concerning such short-term changes in stratospheric O_3 concentrations is needed as input to urban and regional airshed computer models of photochemical air pollution formation.

In the clean atmosphere, stratospheric O_3 also is influenced by the emission of nitrous oxide (N_2O) from soils and oceans (World Meteorological Organization, 1992). Because N_2O is chemically inert in the troposphere and does not photolyze (Prinn et al., 1990), it therefore is transported into the stratosphere, where it undergoes photolysis and also reacts with $\text{O}(^1\text{D})$ atoms (DeMore et al., 1992; Atkinson et al., 1992a). The reaction of N_2O with the $\text{O}(^1\text{D})$ atom is the major source of stratospheric NO, which then participates in a series of reactions known as the NO_x catalytic cycle (Crutzen, 1970; Johnston, 1971).



The Chapman reactions and the NO_x catalytic cycle reactions control the O_3 concentrations in the lower clean stratosphere.

Additional reaction sequences leading to the removal of stratospheric O_3 arise from the ClO_x and BrO_x catalytic cycles, which result when chlorine (Cl)- and bromine



(Br)-containing organic compounds are emitted into the atmosphere. These O₃-depleting compounds include the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), carbon tetrachloride (CCl₄), methyl chloroform, halons, and methyl bromide (Anderson et al., 1991; Rowland, 1990, 1991; World Meteorological Organization, 1992). Analogous to N₂O, the CFCs, CCl₄, and certain halons (CF₃Br and CF₂ClBr) are inert in the troposphere and are transported into the stratosphere, where they photolyze to generate Cl or Br atoms (World Meteorological Organization, 1992). Methyl bromide and the HCFCs react to a large extent in the troposphere, so that only a fraction of these Cl- and Br-containing species that are emitted into the troposphere are transported into the stratosphere (World Meteorological Organization, 1990b, 1992).

3.2.3 Background Ozone in the Troposphere

As noted in Section 3.2.1, O₃ is present in the troposphere even in the absence of human activities. Although this "natural" O₃ has received widely varying estimates in the literature, there has not been an attempt to standardize the definition because natural background O₃ is a multidimensional and complex concept. Concentrations of background O₃ can vary with temperature; wind speed and direction; vertical motion; geographical location, including latitude and altitude; and season of the year. Because of the decrease of total pressure with increasing altitude, the O₃ concentration in the clean troposphere may be taken to be reasonably independent of altitude at $\approx 7 \times 10^{11}$ molecules cm⁻³.

For purposes of this document, the primary focus is on the background O₃ concentration near the surface over the United States during the O₃ season. However, the length of the O₃ season varies from state-to-state, depending predominantly on latitude (see Chapter 4). These variations in O₃ season affect the determination of which seasonal averaging period to apply when estimating O₃ concentrations. Based on available assessments of O₃ monitoring measurements, a daytime, 7-h (0900 to 1559 hours), seasonal (April to October) average O₃ concentration of 25 to 45 ppb can be assumed (Altshuller and Lefohn, 1996) as an estimated background concentration (see Chapter 4). Although one component of this background is of natural origin, the other can be attributed to anthropogenic contributions associated with long-range transport of O₃. This assumption is consistent with the relatively long lifetime of O₃ in the troposphere, which can be as long as 30 to 60 days.

The background of O₃ can be attributed to the following sources: downward transport of stratospheric O₃ through the free troposphere to near ground level, in situ O₃ production from methane emitted from swamps and wetlands reacting with natural NO_x emitted from soils and lightning strikes and from the downward transport of NO from the stratosphere into the troposphere, and in situ production of O₃ from the reactions of biogenic VOCs with natural NO_x (National Research Council, 1991). Another source to be considered is the long-range transport of O₃ from distant pollutant sources.

It is important to appreciate that NO_x has a limited lifetime, often estimated to be as short as 6 h in plumes (Altshuller, 1986) and possibly up to 1 to 2 days under less polluted conditions. Because of this relatively short lifetime, the NO_x emitted from cultivated areas in

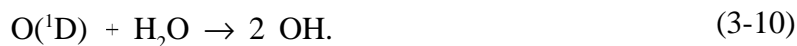
the United States as a result of agricultural practices may not survive long enough to interact with substantial emissions of biogenic VOCs in distant forested areas. There also is no direct way to distinguish natural NO_x from anthropogenic NO_x in a rural or remote location.

3.2.3.1 Tropospheric Hydroxyl Radicals

It is now recognized that the key reactive species in the troposphere is the OH radical, which is responsible for initiating the degradation reactions of almost all VOCs. In the presence of NO, these OH radical reactions with VOCs lead to the formation of O₃ and, hence, to O₃ concentrations above those encountered in the clean troposphere. The OH radical is produced from the ultraviolet (UV) photolysis of O₃. Ozone photolyzes in the UV radiation at wavelengths <320 nm to generate the electronically excited O(¹D) atom (DeMore et al., 1992; Atkinson et al., 1992a),



The O(¹D) atoms either are deactivated to the ground state O(³P) atom by Reaction 3-7 or they react with water vapor to form the OH radical:



The O(³P) atoms formed directly in the photolysis of O₃ or formed from deactivation of O(¹D) atoms (Reaction 3-7) reform O₃ through Reaction 3-2. At room temperature and 50% relative humidity, 0.2 OH radicals are formed per O(¹D) atom generated from the photolysis of O₃. Hydroxyl radical production from Reactions 3-6a and 3-10 is balanced by reaction of the OH radical with carbon monoxide (CO) and CH₄. Because the water vapor mixing ratio decreases with increasing altitude in the troposphere (Logan et al., 1981; World Meteorological Organization, 1992) and the O₃ mixing ratio generally increases with increasing altitude, the OH radical concentration is expected to be reasonably independent of altitude (Dentener and Crutzen, 1993).

A knowledge of ambient tropospheric OH radical concentrations is needed for an understanding of tropospheric chemistry and to reliably calculate the lifetimes of chemical compounds. Because OH and hydroperoxyl (HO₂) radicals are interrelated through a series of reactions (Section 3.2.3.3), concurrent measurements of OH and HO₂ radical concentrations improve the knowledge of tropospheric chemistry. Only in the past few years have measurements been made of lower tropospheric OH radical concentrations (see, for example, Felton et al., 1990; Hofzumahaus et al., 1991; Eisele and Tanner, 1991; Mount and Eisele, 1992; Comes et al., 1992; Hard et al., 1992). The limited data available show that, as expected, the OH radical concentrations exhibit a diurnal profile, with daytime maximum concentrations of several times 10⁶ molecules cm⁻³. A global, annually, seasonally, and diurnally averaged tropospheric OH radical concentration also can be derived from the estimated emissions and measured atmospheric concentrations of methylchloroform (CH₃CCl₃) and the rate constant for the reaction of the OH radical with CH₃CCl₃ (its major tropospheric loss process). Using this method, Prinn et al. (1992) have derived a 24-h average OH radical concentration of 8 × 10⁵ molecules cm⁻³ (equivalent to a 12-h daytime average of 1.6 × 10⁶ molecules cm⁻³ [≈0.1 ppt]). Ambient air measurements of the decay of nonmethane

hydrocarbons in urban plumes (Blake et al., 1993) give OH radical concentrations of similar magnitude to those derived from direct tropospheric measurements and globally averaged estimates.

3.2.3.2 Tropospheric Nitrogen Oxides Chemistry

The presence of NO_x is necessary for the formation of O₃ from the oxidation of CH₄ and other VOCs. Sources of tropospheric NO_x include downward transport from the stratosphere, in situ formation from lightning (National Research Council, 1991; World Meteorological Organization, 1992) (see Section 3.4.1.2), and emission from soils (National Research Council, 1991; World Meteorological Organization, 1992). Recent measurements show that the NO_x concentrations over maritime areas increase slightly with increasing altitude, from ≈15 ppt in the marine boundary layer (Carroll et al., 1990) to ≈30 to 40 ppt at 3 to 7 km altitude (Ridley et al., 1989; Carroll et al., 1990). Significantly higher NO_x concentrations (≈100 ppt) have been observed in the boundary layer over relatively unpolluted continental areas (Carroll et al., 1990), with the NO_x concentrations decreasing with increasing altitude to ≈50 ppt at 3 to 7 km (Ridley et al., 1989; Carroll et al., 1990).

In the troposphere, NO, NO₂, and O₃ are interrelated by the following reactions:



Because Reaction 3-2 is fast (the lifetime of an O(^3P) atom at 298 K and 760 torr of air is ≈10⁻⁵ s), the O₃ concentration at photoequilibrium is given by

$$[\text{O}_3] = J_1[\text{NO}_2]/k_3[\text{NO}], \quad (3-11)$$

where J₁ and k₃ are the photolysis rate of NO₂ (≈0.5 min⁻¹ for an overhead sun) and the rate constant for the reaction of NO with O₃, respectively.

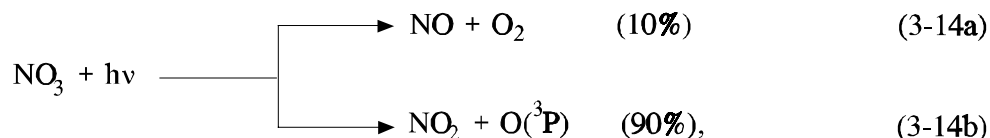
There are other important reactions involving NO_x. The reaction of NO₂ with O₃ leads to the formation of the nitrate (NO₃) radical,



which in the lower troposphere is nearly in equilibrium with dinitrogen pentoxide (N₂O₅):



However, because the NO_3 radical photolyzes rapidly (with a lifetime of ≈ 5 s for an overhead sun [Atkinson et al., 1992a]),



its concentration remains low during daylight hours, but can increase after sunset to nighttime concentrations of $< 5 \times 10^7$ to 1×10^{10} molecules cm^{-3} (< 2 to 430 ppt) over continental areas influenced by anthropogenic emissions of NO_x (Atkinson et al., 1986). Nitrate radical concentrations over marine areas are low because NO_x concentrations are low over lower tropospheric marine areas (Noxon, 1983), and an NO_3 radical mixing ratio of 0.25 ppt has been measured at 3 km altitude in Hawaii (Noxon, 1983). Atkinson (1991) has suggested the use of a 12-h nighttime average NO_3 radical concentration of 5×10^8 molecules cm^{-3} in the lower troposphere over continental areas, with an uncertainty of a factor of ≈ 10 .

The tropospheric chemical removal processes for NO_x involve the daytime reaction of NO_2 with the OH radical and the nighttime wet and dry deposition of N_2O_5 to produce HNO_3 .



The gas-phase reaction of the OH radical with NO_2 is the major and ultimate removal process for NO_x in the troposphere. This reaction removes radicals (OH and NO_2) and competes with the reaction of the OH radical with VOCs. Gaseous HNO_3 formed from Reaction 3-15 undergoes wet and dry deposition, including combination with gaseous ammonia (NH_3) to form particulate phase ammonium nitrate ($\text{N}_2\text{H}_4\text{O}_3$). The tropospheric lifetime of NO_x due to chemical reaction (mainly Reaction 3-15) is ≈ 1 to 2 days. The tropospheric NO_x reactions are shown schematically in Figure 3-1. It should be noted that OH radicals also can react with NO to produce nitrous acid (HNO_2):



In urban areas, HNO_2 also can be formed during nighttime hours (Harris et al., 1982; Pitts et al., 1984a; Rodgers and Davis, 1989), apparently from the heterogeneous hydrolysis of NO_2 or NO_x , or both (Sakamaki et al., 1983; Pitts et al., 1984b; Svensson et al., 1987;

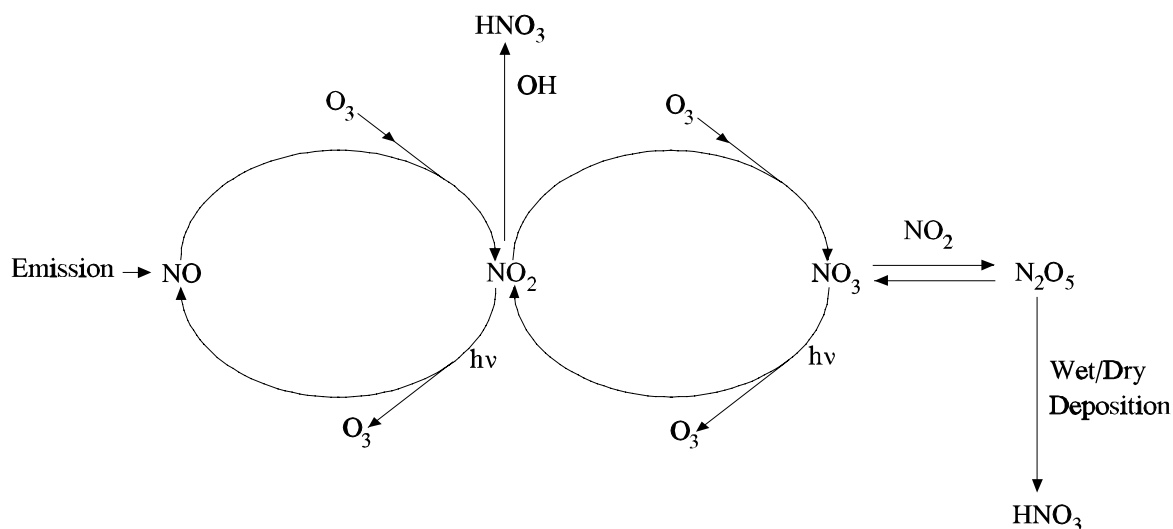


Figure 3-1. The cyclic reactions of tropospheric nitrogen oxides.

Jenkin et al., 1988; Lammel and Perner, 1988; Notholt et al., 1992a,b). The photolysis of HNO_2 during the early morning hours,



thus can become an important source of OH radicals, leading to the rapid initiation of photochemical activity (Harris et al., 1982).

In the troposphere, the initially emitted NO is converted to NO_x ($\text{NO} + \text{NO}_2$), then to reservoir and termination species (PAN and its homologues, organic nitrates, HNO_3 , and particulate nitrate). These reservoir and termination species are referred to as NO_z . The term " NO_y " refers to the total amount of nitrogen, with $\text{NO}_y = (\text{NO}_x + \text{NO}_z)$. Parrish et al. (1993) have investigated the partitioning between the individual nitrogen-containing species at several rural sites in the eastern United States, and Trainer et al. (1993) and Olszyna et al. (1994) have shown that, in rural areas in the eastern United States, there is a good correlation between the O_3 levels and NO_y . Trainer et al. (1993) further showed that O_3 levels correlate even better with NO_z than with NO_y , as may be expected because NO_z quantifies the amount of initially emitted NO that has been processed photochemically, forming O_3 in the process.

3.2.3.3 The Methane Oxidation Cycle

Methane is emitted into the atmosphere from swamps and wetlands, as well as from ruminants (Fung et al., 1991a; World Meteorological Organization, 1992). The major tropospheric removal process for CH_4 is by reaction with the OH radical, with the CH_4 lifetime equal to

$$(k_{21} [\text{OH}])^{-1}, \quad (3-19)$$

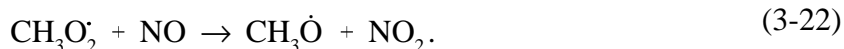
where k_{21} is the rate constant for Reaction 3-21, and $[\text{OH}]$ is the (variable) atmospheric OH radical concentration. The calculated lifetime of CH_4 in the troposphere is ≈ 10 to 12 years. As for other saturated organic compounds, the OH radical reaction with CH_4 proceeds by hydrogen (H)-atom abstraction from the carbon (C)-H bonds to form the methyl (CH_3) radical:



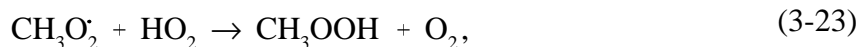
In the troposphere, the methyl radical reacts solely with O_2 to yield the methyl peroxy (CH_3O_2) radical (Atkinson et al., 1992a):



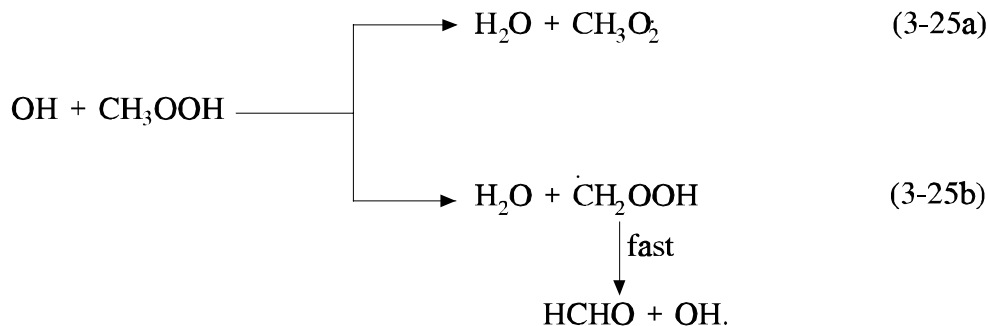
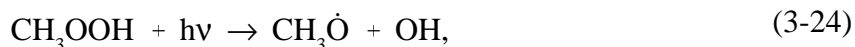
In the troposphere, the methyl peroxy radical can react with NO, NO_2 , HO_2 radicals, and other organic peroxy (RO_2) radicals, with the reactions with NO and HO_2 radicals being the most important (see, for example, World Meteorological Organization, 1990b). The reaction with NO leads to the formation of the methoxy ($\text{CH}_3\dot{\text{O}}$) radical,



The reaction with the HO_2 radical leads to the formation of methyl hydroperoxide (CH_3OOH),



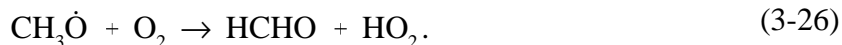
which can photolyze or react with the OH radical (Atkinson et al., 1992a):



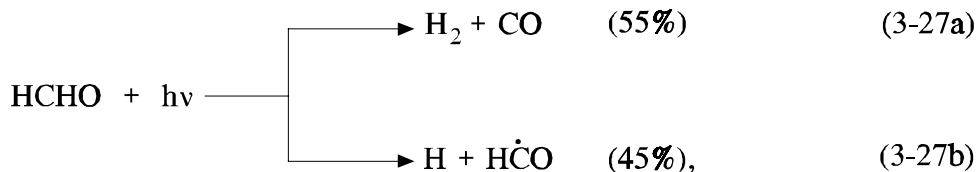
Methyl hydroperoxide also undergoes wet and dry deposition or incorporation into cloud water. The lifetime of CH_3OOH in the troposphere due to photolysis and reaction with the

OH radical is calculated to be ≈ 2 days. Methyl hydroperoxide is then a temporary sink of radicals, with its wet or dry deposition being a tropospheric loss process for radicals.

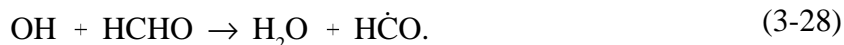
The only important reaction for the methoxy radical in the troposphere is with O_2 to form HCHO and the HO_2 radical,



Formaldehyde is a "first-generation" product that reacts further, by photolysis:



where the percentages are for overhead sun conditions (Rogers, 1990) and also by reaction with the OH radical,



In the troposphere, the H atom and $\dot{H}CO$ (formyl) radical produced in these processes react solely with O_2 to form the HO_2 radical:



The lifetimes of HCHO due to photolysis and OH radical reaction are ≈ 4 h and 1.5 days, respectively, leading to an overall lifetime of ≈ 3 h for overhead sun conditions.

The final step in the oxidation of CH_4 in the earth's atmosphere involves the oxidation of CO by reaction with the OH radical (the only tropospheric reaction of CO) to form CO_2 :



The lifetime of CO in the lower troposphere is ≈ 2 mo.

The overall reaction sequence leading to CO_2 formation, through the HCHO and CO intermediate products, is shown in Figure 3-2.

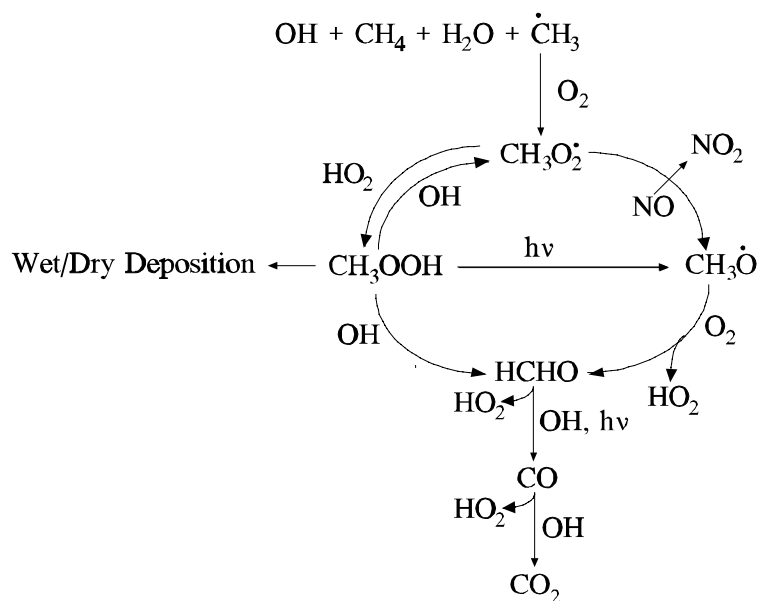


Figure 3-2. Atmospheric reactions in the complete oxidation of methane.

There is competition between NO and the HO₂ radical for reaction with the CH₃O₂ radical, and the reaction route depends on the rate constants for these two reactions and the tropospheric concentrations of HO₂ radicals and NO. The rate constants for the reaction of the CH₃O₂ radicals with NO (Reaction 3-22) and HO₂ radicals (Reaction 3-23) are of comparable magnitude (Atkinson et al., 1992a). Based on the expected HO₂ radical concentration in the troposphere, Logan et al. (1981) calculated that the reaction of the CH₃O₂ radical with NO dominates for NO mixing ratios of >30 ppt (equivalent to an NO concentration of $>7 \times 10^8$ molecules cm⁻³ in the lower troposphere). For NO mixing ratios <30 ppt, the reaction of the CH₃O₂ radical with HO₂ dominates.

Hydroperoxy radicals formed from, for example, Reactions 3-26, 3-29, and 3-30 can react with NO, O₃, or themselves, depending mainly on the concentration of NO. The reaction with NO leads to regeneration of the OH radical,



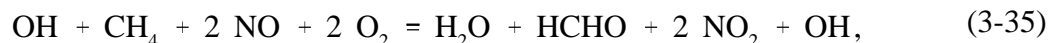
whereas the reactions with O₃ and HO₂ radicals lead to a net destruction of tropospheric O₃:



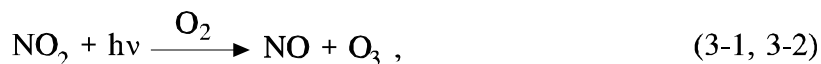
This net loss of tropospheric O₃ occurs because the photolytic production of the OH radical from O₃, via the intermediary of the O(¹D) atom, represents a loss process for tropospheric O₃. Hence, the absence of any O₃ formation from the CH₄ oxidation cycle is equivalent to a net O₃ loss. Using the rate constants reported for Reactions 3-32 and 3-34 (Atkinson et al., 1992a) and the tropospheric O₃ mixing ratios given above, it is calculated that the HO₂ radical reaction with NO dominates over reaction with O₃ for NO mixing ratios >10 ppt. The rate constant for Reaction 3-33 is such that an NO mixing ratio of this magnitude also means that the HO₂ radical reaction with NO dominates over the self-reaction of HO₂ radicals.

There are therefore two regimes, depending on the fate of HO₂ and CH₃O₂ radicals: (1) a high-NO regime in which HO₂ and CH₃O₂ radicals react with NO to convert NO to NO₂, regenerate the OH radical, and, through the photolysis of NO₂, produce O₃; and (2) a low-NO regime in which HO₂ and CH₃O₂ radicals combine (Reaction 3-23), and HO₂ radicals undergo self-reaction and react with O₃ (Reactions 3-33 and 3-34), leading to a net destruction of O₃ and inefficient OH radical regeneration (see also Ehhalt et al., 1991; Ayers et al., 1992).

Under high-NO conditions, the oxidation of CH₄ leading to the formation of HCHO can be written as the net reaction,



indicating the conversion of two molecules of NO to NO₂ and regeneration of the OH radical. Because NO₂ photolyzes to form O₃ in the presence of O₂,

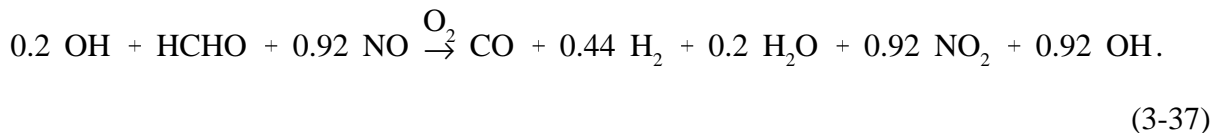


the oxidation of CH₄ to HCHO under high-NO conditions can be written as



showing the formation of O₃ from CH₄ oxidation in the troposphere. The reaction cycles oxidizing CH₄ to HCHO, converting NO to NO₂, and forming O₃ are shown schematically in Figure 3-3.

In a similar manner, under high-NO conditions, the photolysis of HCHO and its reaction with the OH radical is given approximately by



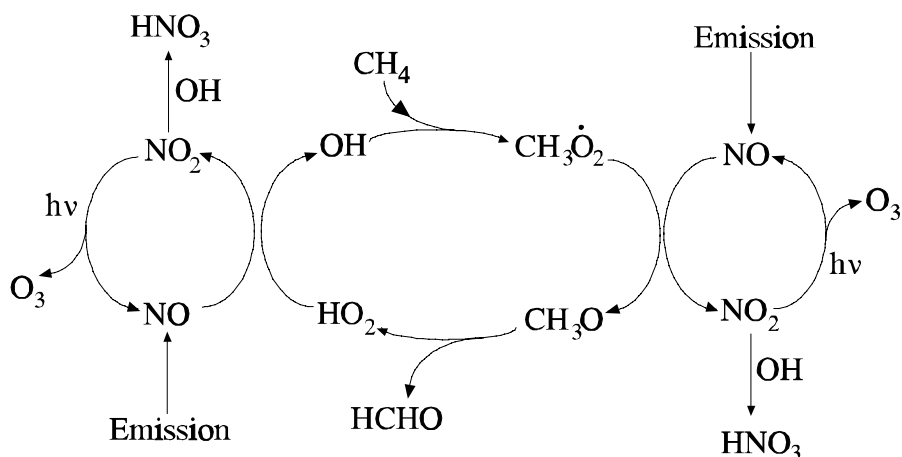


Figure 3-3. *Cyclic reactions of methane oxidation to formaldehyde, conversion of nitric oxide to nitrogen dioxide, and concomitant formation of ozone in the atmosphere.*

Formaldehyde photooxidation is thus a source of HO₂ radicals (and of OH radicals in high-NO conditions) (Ehhalt et al., 1991), especially in urban areas where the concentration of HCHO is elevated because it is produced during the oxidation of anthropogenic nonmethane VOCs (Finlayson-Pitts and Pitts, 1986).

Nitric oxide mixing ratios are sufficiently low in the lower troposphere over marine areas that oxidation of CH₄ will lead to a net destruction of O₃ (low-NO conditions), as discussed by Carroll et al. (1990) and Ayers et al. (1992). However, in the upper troposphere and over continental areas impacted by NO_x emissions from combustion sources, NO mixing ratios are high enough (high NO-conditions) for CH₄ oxidation to lead to net O₃ formation (Carroll et al., 1990; World Meteorological Organization, 1992).

3.2.3.4 Cloud Processes in the Methane-Dominated Troposphere

In addition to the dry and wet deposition of certain products of the NO_x-CH₄-air photooxidation (e.g., wet and dry deposition of HNO₃ and CH₃OOH [Atkinson, 1988, and references therein; Hellpointner and Gäb, 1989]), cloud processes can have significant effects on the gas-phase chemistry of the clean troposphere (Lelieveld and Crutzen, 1990, 1991; Warneck, 1991, 1992). Lelieveld and Crutzen (1990, 1991) have postulated from modeling studies that the uptake of HCHO, HO₂ radicals, and N₂O₅ into clouds can decrease markedly the production of O₃. The incorporation of HCHO into cloudwater removes HCHO from the gas phase and, hence, reduces the gas-phase formation of HO₂. The uptake of HO₂ radicals into cloudwater has the same effect. Moreover, the aqueous-phase reactions of CH₂(OH)₂ (the hydrated form of HCHO) lead to the formation of O₂• which reacts with dissolved O₃ to act as a sink for O₃ during cloudy periods. During nighttime, N₂O₅ formed in the gas phase from Reactions 3-3, 3-12, and 3-13 can be readily incorporated into cloudwater with hydrolysis to HNO₃, precluding the reformation of NO_x during the following day from Reactions 3-13 and 3-14. Dentener and Crutzen (1993) have also concluded from a computer modeling study that

the heterogeneous reactions of NO_3 radicals and N_2O_5 on aerosols can have significant effects on global O_3 mixing ratios and on OH concentrations by reducing NO_x levels.

The net effect of these cloud processes is to reduce the gas-phase concentrations of HCHO, NO_x , HO_x , and O_3 . Additional, but related, processes can occur in the polluted troposphere (see, for example, Jacob et al., 1989; Dentener and Crutzen, 1993; Section 3.2.5).

3.2.4 Photochemistry of the Polluted Atmosphere

Human activities lead to the emissions of NO_x ($\text{NO} + \text{NO}_2$) and both CH_4 - and nonmethane organic compounds (NMOC) into the atmosphere (Table 3-1). Methane emissions are important on a global scale (World Meteorological Organization, 1992), whereas nonmethane VOC emissions are most important in urban and regional areas. In addition to the emissions of nonmethane VOCs from anthropogenic sources, large quantities of biogenic nonmethane VOCs (mainly of isoprene [2-methyl-1, 3-butadiene] and monoterpenes, $[\text{C}_{10}\text{H}_{16}]$) are emitted, both in polluted and nonpolluted areas, into the atmosphere from vegetation (see, for example, Isidorov et al., 1985; Lamb et al., 1987; Arey et al., 1991a,b).

Table 3-1. Estimated Emissions of Methane, Nonmethane Organic Compounds, Nitrous Oxide, and Nitrogen Oxides into the Earth's Atmosphere from Biogenic and Anthropogenic Sources^a

Chemical	Emissions (Tg/year ^b)	
	Biogenic Sources	Anthropogenic Sources
CH_4^c	≈150	≈350
NMOC ^d	≈1,000	≈100
N_2O (as N) ^e	≈7	≈6
NO_x (as N) ^f	≈10	≈40

^aSee Appendix A for abbreviations and acronyms.

^bTeragram = 10^{12} g, or $\approx 10^6$ metric tons.

^cFung et al. (1991a); World Meteorological Organization (1992). Emissions from ruminants, rice paddies, and biomass burning are considered as anthropogenic emissions.

^dLogan et al. (1981); World Meteorological Organization (1992), with biogenic emissions being assumed to be 50% isoprene and 50% monoterpenes.

^ePrinn et al. (1990).

^fNational Research Council (1991); World Meteorological Organization (1992); biogenic sources ≈50% from soils and ≈50% from lightning.

Analogous to the photooxidation of CH_4 , the interaction of NO_x with nonmethane VOCs from anthropogenic and biogenic sources under the influence of sunlight leads to the formation of photochemical air pollution (National Research Council, 1991). In urban areas, emissions of NO_x and VOCs from human activities (combustion sources, including transportation; industrial sources; solvent usage; landfills; etc.) dominate over biogenic sources (National Research Council, 1991; Chameides et al., 1992). However, the emissions

of VOCs from vegetation have been implicated in the formation of photochemical air pollution in urban (Chameides et al., 1988; 1992) as well as rural areas (Trainer et al., 1987; Roselle et al., 1991; Chameides et al., 1992).

In essence, the chemistry of the polluted urban and regional atmosphere is an extension of that of the clean, CH₄-dominated troposphere, with a number of additional complexities due to the number and types of VOCs emitted from anthropogenic and biogenic sources. At least in certain urban areas, the NMOC content of ambient air is similar to the composition of typical gasolines (Mayrsohn and Crabtree, 1976; Mayrsohn et al., 1977; Harley et al., 1992; see Section 3.4.3). For example, gasolines typically consist of ≈55 to 65% alkanes, ≈5 to 10% alkenes, and ≈25 to 35% aromatic hydrocarbons (Lonneman et al., 1986; Sigsby et al., 1987), whereas in Los Angeles, CA, the ambient urban air composition is ≈50 to 55% alkanes, ≈5 to 15% alkenes, ≈25 to 30% aromatic hydrocarbons, and ≈5 to 15% carbonyls (Grosjean and Fung, 1984; California Air Resources Board, 1992). Emissions of NO_x and VOCs are dealt with in detail in Section 3.4.1.

3.2.4.1 Tropospheric Loss Processes of Volatile Organic Compounds

The chemical loss processes of gas-phase VOCs include photolysis and chemical reaction with the OH radical during daylight hours, reaction with the NO₃ radical during nighttime hours, and reaction with O₃, which often is present throughout the 24-h period (Atkinson, 1988).

As discussed earlier, photolysis of chemical compounds in the troposphere is restricted to the wavelength region above ≈290 nm. Because of the strength of chemical bonds, the tropospheric wavelength region in which photolysis can occur extends from ≈290 to 800 nm, and this wavelength region often is referred to as the "actinic" region. For photolysis to occur, a chemical compound must be able to absorb radiation in the actinic region (and hence have a nonzero absorption cross-section, σ_λ , in this wavelength region). Having absorbed radiation, a chemical compound must then undergo chemical change (i.e., have a nonzero quantum yield, ϕ_λ , for photodissociation or photoisomerization). The quantum yield, ϕ_λ , is defined as (number of molecules of the chemical undergoing change)/(number of photons of light absorbed). The photolysis rate, $k_{\text{photolysis}}$, for the process,



is given by

$$k_{\text{photolysis}} = \int J_\lambda \sigma_\lambda \phi_\lambda d\lambda, \quad (3-39)$$

where J_λ is the radiation flux at wavelength λ , and σ_λ and ϕ_λ are the absorption cross-section and photolysis quantum yield, respectively, at wavelength λ . Photolysis is therefore a pseudo-first-order process (depending on the radiation flux and spectral distribution) and the lifetime of a chemical with respect to photolysis is given by

$$\tau_{\text{photolysis}} = k_{\text{photolysis}}^{-1}. \quad (3-40)$$

For the reaction of a VOC with a reactive species, X (for tropospheric purposes, X = OH, NO₃, and O₃), the lifetime for the reaction process, C + X → products, is given by

$$\tau_x = (k_x[X])^{-1} \quad (3-41)$$

and depends on the concentration of the reactive species X and the rate constant (k_x) for reaction of the VOC with X. In general, the ambient atmospheric concentrations of OH radicals, NO₃ radicals, and O₃ are variable, depending on time of day, season, latitude, altitude, etc. For the purpose of comparing lifetime calculations for various classes of VOCs, average ambient tropospheric concentrations of these three species often are used. The concentrations used here have been presented in the sections above and are OH radicals, a 12-h average daytime concentration of 1.6×10^6 molecule cm⁻³ (equivalent to a 24-h average concentration of 8×10^5 molecule cm⁻³) (Prinn et al., 1992); NO₃ radicals, a 12-h nighttime average concentration of 5×10^8 molecule cm⁻³ (Atkinson, 1991); and O₃, a 24-h average of 7×10^{11} molecule cm⁻³ (30 ppb) (Logan, 1985).

The major classes of VOCs are the alkanes, alkenes (including alkenes from biogenic sources), aromatic hydrocarbons, carbonyl compounds, alcohols, and ethers (see California Air Resources Board, 1992). The calculated lifetimes with respect to the individual atmospheric loss processes of compounds representing a range of reactivities in each class are given in Table 3-2. Note that the lifetimes given are dependent on the reaction rate constants and the assumed ambient concentrations of OH radicals, NO₃ radicals, and O₃. Uncertainties in the ambient concentrations of the reactive species translate directly into corresponding uncertainties in the lifetimes.

The following brief discussions of the tropospheric chemistry of the important classes of VOCs are based on the recent review and evaluation article of Atkinson (1994), which should be consulted for further details of the tropospheric reactions of VOCs.

Alkanes

Because gasoline and diesel fuels contain alkanes of carbon number C₄ to ≥C₁₅, a large number of alkanes are present in ambient air (see, for example, Grosjean and Fung, 1984; California Air Resources Board, 1992; Section 3.4). Table 3-2 shows that the only important tropospheric loss process for the alkanes is by reaction with the OH radical, with calculated lifetimes of the C₃ to C₁₀ alkanes ranging from ≈1 to 15 days. As for methane, the OH radical reaction proceeds by H-atom abstraction from the various C-H bonds. The nighttime reactions of the NO₃ radical with alkanes (calculated to be generally of minor importance, but see Penkett et al. [1993]) also proceed by initial H-atom abstraction. For an alkane (RH), the initially formed radical is an alkyl radical (R),

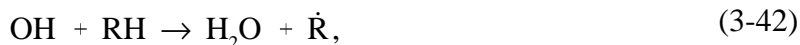


Table 3-2. Calculated Tropospheric Lifetimes of Selected Volatile Nonmethane Organic Compounds Due to Photolysis and Reaction with Hydroxyl and Nitrate Radicals and with Ozone^a

Organic	Lifetime Due to Reaction with			h ν
	OH	NO ₃	O ₃	
<i>n</i> -Butane	5.7 days	2.8 years	>4,500 years	
2-Methylbutane	3.7 days	290 days	>4,500 years	
<i>n</i> -Octane	1.7 days	250 days	>4,500 years	
Ethane	1.7 days	230 days	10 days	
Propene	6.6 h	4.9 days	1.6 days	
Isoprene	1.7 h	0.8 h	1.3 days	
Limonene	1.0 h	3 min	2.0 h	
Benzene	12 days	>4 years	>4.5 years	
Toluene	2.4 days	1.9 years	>4.5 years	
<i>m</i> -Xylene	7.4 h	200 days	>4.5 years	
Formaldehyde	1.5 days	80 days	>4.5 years	4 h
Acetaldehyde	11 h	17 days	>4.5 years	6 days
Acetone	66 days	—	>4.5 years	60 days
2-Butanone	13 days	—	>4.5 years	
Methanol	15 days	>77 days	—	
Ethanol	4.4 days	>50 days	—	
Methyl <i>t</i> -butyl ether	4.9 days	—	—	
Ethyl <i>t</i> -butyl ether	1.6 days	—	—	
Methylglyoxal	10 h	—	>4.5 years	2 h

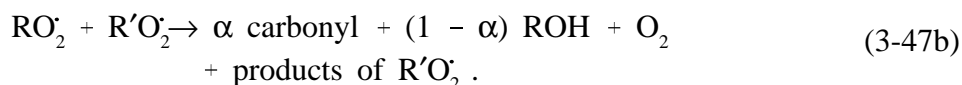
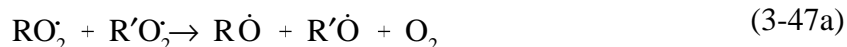
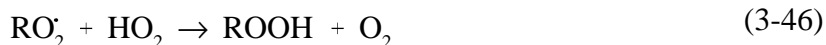
^aSee Appendix A for abbreviations and acronyms.

Sources: Lifetimes resulting from reaction with OH, NO₃, and O₃ were calculated using rate constants given in Atkinson and Carter (1984) and Atkinson (1989, 1991, 1994); data for photolysis lifetimes are from Horowitz and Calvert (1982), Meyrahn et al. (1982, 1986), Plum et al. (1983), and Rogers (1990). The OH radical, NO₃ radical, and O₃ concentrations used (molecule cm⁻³) were: OH, 12-h average of 1.6 × 10⁶; NO₃, 12-h average of 5 × 10⁸; O₃, 24-h average of 7 × 10¹¹.

which rapidly adds O₂ to form an alkyl peroxy radical (RO₂),



with the simplest of the RO₂ radicals being the methylperoxy radical, described in Section 3.2.3.3 dealing with methane oxidation. Alkyl peroxy radicals can react with NO, NO₂, and HO₂ radicals, and other organic peroxy radicals (R'O₂):

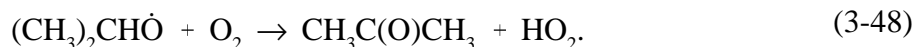


The reactions with organic peroxy radicals are expected to be of less importance in the troposphere than the other reactions listed. Because low NO conditions occur even in air masses in urban areas, the HO₂ radical reactions with RO₂ radicals and the subsequent chemistry must be considered. However, because of space constraints and a general lack of knowledge concerning the tropospheric chemistry of RO₂ radicals under low-NO conditions, only the reactions occurring under high-NO conditions are presented and discussed here. For the ≥C₃ alkyl peroxy radicals, in addition to the reaction pathway leading to NO-to-NO₂ conversion (Reaction 3-44a), a second reaction pathway leading to formation of an alkyl nitrate becomes important:

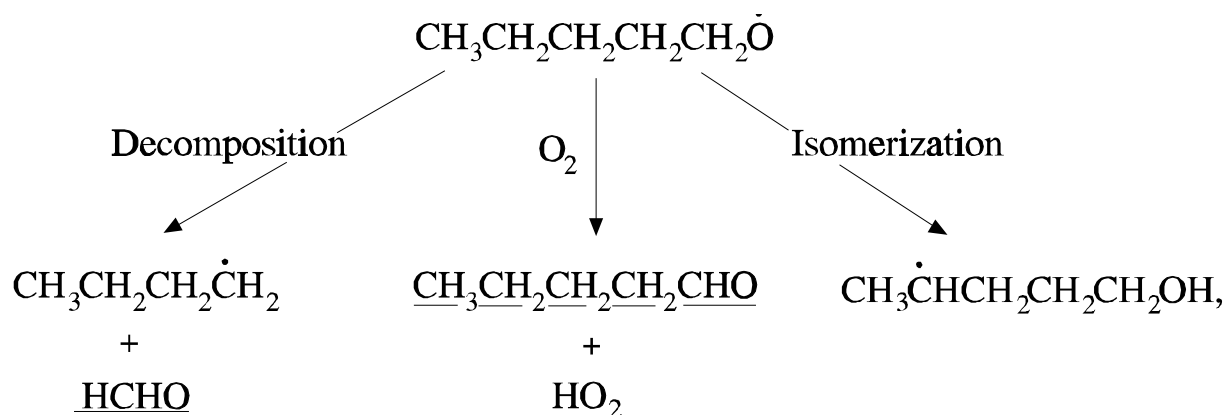


For a given alkyl peroxy radical, the alkyl nitrate yield increases with increasing pressure and with decreasing temperature (Carter and Atkinson, 1989a).

Analogous to the case for the methoxy radical, those alkoxy radicals (RO₂) formed from the higher alkanes that have an abstractable H atom can react with O₂ to form the HO₂ radical and a carbonyl; for example,



In addition, unimolecular decomposition by C-C bond scission and unimolecular isomerization via a six-member transition state (Atkinson and Carter, 1991; Atkinson, 1994) can be important for the larger alkoxy radicals. For example, the following chemistry can occur for the 1-pentoxy radical:



with the alkyl radicals C_4H_9 and $\text{HOCH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCH}_3$ undergoing further reaction.

The majority of the reaction rate constants and reaction pathways in the alkane degradation schemes are arrived at by analogy from the chemistry of C_1 - C_3 alkyl, alkyl peroxy, and alkoxy radicals (Atkinson, 1990, 1994; Carter, 1990; Atkinson et al., 1992a). A number of areas of uncertainty still exist for the tropospheric chemistry of the alkanes (Atkinson, 1993). These include the relative importance of alkoxy radical reaction with O_2 , decomposition and isomerization, and the reactions occurring subsequent to the isomerization reaction; the formation of alkyl nitrates from the reactions of the peroxy radicals with NO ; and reactions of the alkyl peroxy radicals with HO_2 and other peroxy radicals, reactions that can be important in the nonurban troposphere.

Alkenes (Anthropogenic and Biogenic)

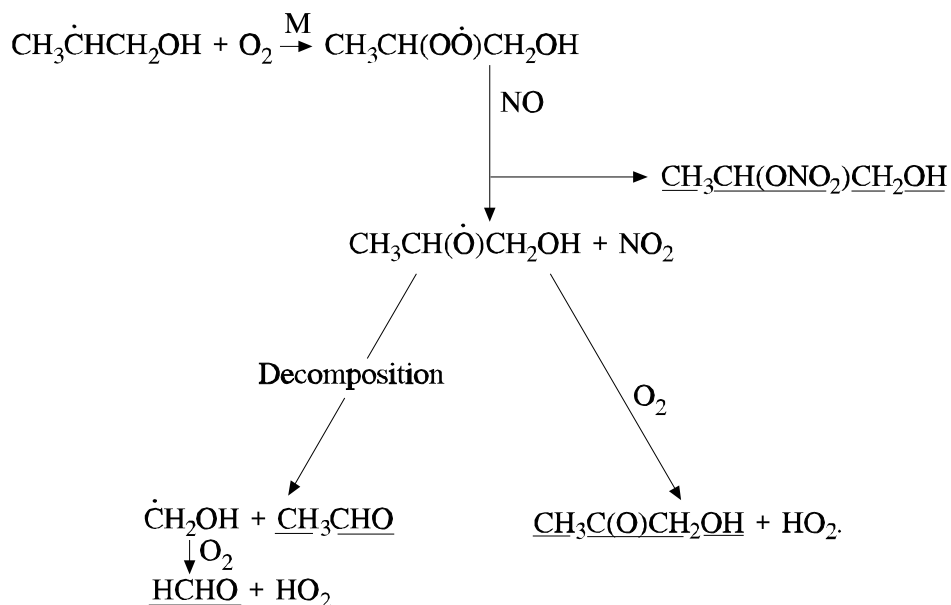
The alkenes emitted from anthropogenic sources are mainly ethene, propene, and the butenes, with lesser amounts of the $\geq \text{C}_5$ alkenes. The major biogenic alkenes emitted from vegetation are isoprene (2-methyl-1,3-butadiene) and $\text{C}_{10}\text{H}_{16}$ monoterpenes (Isidorov et al., 1985; Winer et al., 1992), and their tropospheric chemistry is currently the focus of much attention (see, for example, Hatakeyama et al., 1989, 1991; Arey et al., 1990; Tuazon and Atkinson, 1990a; Pandis et al., 1991; Paulson et al., 1992a,b; Paulson and Seinfeld, 1992a; Zhang et al., 1992; Hakola et al., 1993, 1994).

As evident from Table 3-2, the alkenes react with OH and NO_3 radicals and O_3 . All three processes are important atmospheric transformation processes, and all three reactions proceed by initial addition to the $>\text{C}=\text{C}<$ bonds. These reactions are briefly discussed below.

Hydroxyl Radical Reactions. As noted above, the OH radical reactions with the alkenes proceed mainly by OH radical addition to the $>\text{C}=\text{C}<$ bonds. For example, the OH radical reaction with propene leads to the formation of the two OH -containing radicals,



The subsequent reactions of these radicals are similar to those of the alkyl radicals formed by H-atom abstraction from the alkanes. Taking the $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{OH}$ radical as an example, under high- NO conditions, the following chemistry occurs:



The underlined species represent products that, although stable, can undergo further reaction; and, hence, they can lead to "second-generation" products. For the simple $\leq \text{C}_4$ alkenes, the intermediate OH-containing radicals appear to undergo mainly decomposition at room temperature and atmospheric pressure of air. Hence, for propene, the "first-generation" products of the OH radical reaction in the presence of NO are HCHO and CH_3CHO , irrespective of which OH-containing radical is formed.

However, this is not the case for the more complex alkenes of biogenic origin. The product studies of Tuazon and Atkinson (1990a) and Paulson et al. (1992a) for the OH radical reaction with isoprene in the presence of NO_x show that the products expected from reaction schemes analogous to that shown above for propene (i.e., HCHO + methyl vinyl ketone [$\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$] and HCHO + methacrolein [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$], arising from initial OH radical addition to the $\text{CH}_2=\text{CH}-$ and $\text{CH}_2=\text{C}<$ bonds, respectively) do not account for the entire reaction pathways. The product yields obtained from the studies of Tuazon and Atkinson (1990a) and Paulson et al. (1992a) are methyl vinyl ketone, 34%; methacrolein, 24%; 3-methylfuran, 5%; organic nitrates, $\approx 12\%$; and unidentified carbonyl compounds, $\approx 25\%$ (Tuazon and Atkinson, 1990a; Paulson et al., 1992a; Atkinson, 1994). The HCHO yield was consistent with being a co-product formed with methyl vinyl ketone and methacrolein (Tuazon and Atkinson, 1990a). Aerosol formation for isoprene photooxidation has been shown to be negligible under atmospheric conditions (Pandis et al., 1991; Zhang et al., 1992).

To date, few quantitative product studies have been carried out for the monoterpenes (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1993, 1994). Arey et al. (1990) and Hakola et al. (1993, 1994) have observed the C_7 - C_{10} carbonyl compounds, as had been based on the analogous reaction scheme shown above for propene, but with total carbonyl formation yields of $\leq 50\%$. These data (Arey et al., 1990; Hakola et al., 1993, 1994) indicate the formation of other products in significant, and often dominant, yields. Hatakeyama et al. (1991) used Fourier transform infrared (FTIR) absorption spectroscopy and reported carbonyl compounds to be formed in high yield from α -pinene and β -pinene, in apparent disagreement with the data of Arey et al. (1990) and Hakola et al. (1994). Although Hatakeyama et al. (1991) ascribed these carbonyl products to those expected from oxidative

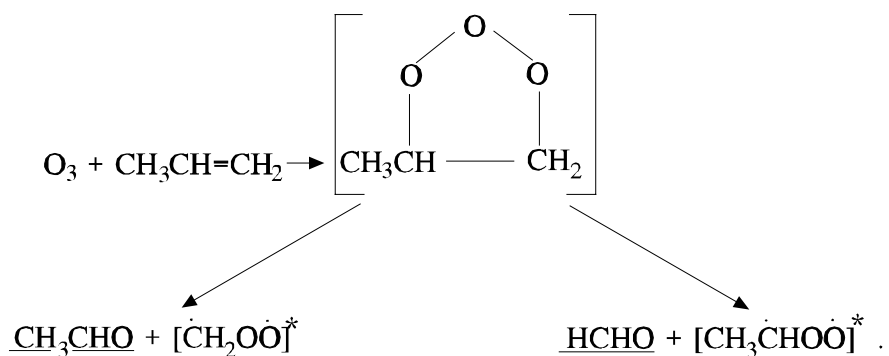
cleavage of the $>C=C<$ bonds, it is possible that the yields reported for these carbonyls included contributions by other, as yet unidentified, carbonyl-containing products.

Nitrate Radical Reactions. The NO_3 radical reactions proceed by reaction schemes generally similar to the OH radical reactions, except that, when NO_3 radicals are present, NO concentrations are low (see above) and $\text{RO}_2 + \text{RO}_2$ and $\text{RO}_2 + \text{HO}_2$ radical reactions are expected to dominate over $\text{RO}_2 + \text{NO}$ reactions. For propene, the initial reaction is



followed by a series of reactions that are expected (Atkinson, 1991) to lead to the formation of, among others, carbonyls and nitrate-carbonyls (for example, HCHO , CH_3CHO , $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CHO}$, and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$ from propene). Few data are presently available concerning the products and detailed mechanisms of NO_3 -alkene reactions (Atkinson, 1991, 1994, and references therein). In particular, the reaction products and mechanisms for the NO_3 radical reactions with isoprene and the monoterpenes are still not quantitatively understood (Kotzias et al., 1989; Barnes et al., 1990; Hjorth et al., 1990; Skov et al., 1992).

Ozone Reactions. The O_3 reactions also proceed by addition of O_3 to the alkene, to form an energy-rich ozonide that rapidly decomposes to form carbonyls and energy-rich biradicals ($[]^*$):



The energy-rich biradicals, $[\dot{\text{C}}\text{H}_2\text{OO}]^*$ and $[\text{CH}_3\dot{\text{C}}\text{HOO}]^*$, undergo collisional stabilization or decomposition:



There are still significant uncertainties concerning the reactions of the energy-rich biradicals (Horie and Moortgat, 1991; Atkinson, 1990, 1994), with recent studies showing the production of OH radicals in high yields for several alkenes (Niki et al., 1987; Paulson et al., 1992a; Atkinson et al., 1992b; Paulson and Seinfeld, 1992b; Atkinson and Aschmann, 1993).

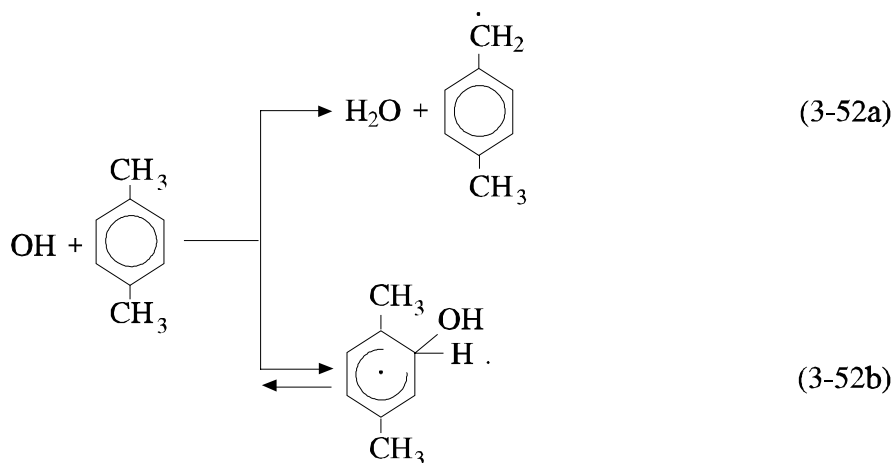
For isoprene, the major products are methacrolein and methyl vinyl ketone (Kamens et al., 1982; Niki et al., 1983; Paulson et al., 1992b). Paulson et al. (1992b) derived an OH radical and an O(³P) atom formation yield of 0.68 ± 0.15 and 0.45 ± 0.2 , respectively, from the O₃ reaction with isoprene, indicating the dominance of secondary reactions. However, Atkinson et al. (1992b) derived a significantly lower OH radical formation yield of 0.27 (uncertain to a factor of ≈ 1.5). Clearly, further studies of this important reaction are needed.

The only quantitative studies of the gas-phase O₃ reactions with the monoterpenes are those of Hatakeyama et al. (1989) for α - and β -pinene and Hakola et al. (1993, 1994) for a series of monoterpenes. Additionally, Atkinson et al. (1992b) derived OH radical formation yields from these reactions under atmospheric conditions.

Several groups (Gäb et al., 1985; Becker et al., 1990, 1993; Simonaitis et al., 1991; Hewitt and Kok, 1991) have reported the formation of H₂O₂ and organic peroxides from O₃ reactions with alkenes. However, there are significant disagreements in the quantitative results reported by Becker et al. (1990, 1993) and Simonaitis et al. (1991).

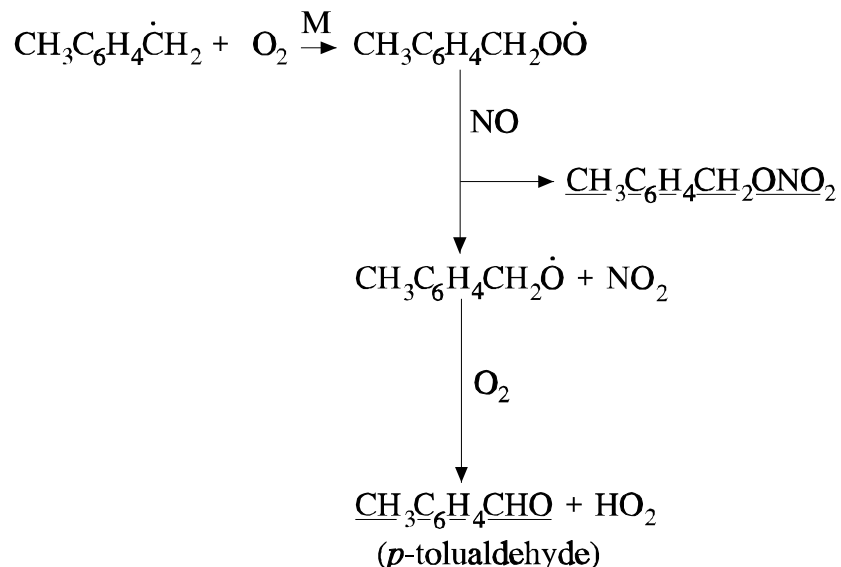
Aromatic Hydrocarbons

The chemistry of aromatic hydrocarbons is one of the major sources of uncertainty in the atmospheric chemistry of VOCs (National Research Council, 1991; Atkinson, 1994). The most abundant aromatic hydrocarbons in urban atmospheres are benzene, toluene, the xylenes, and the trimethylbenzenes (Grosjean and Fung, 1984; California Air Resources Board, 1992). As shown in Table 3-2, the only tropospherically important loss process for benzene and the alkyl-substituted benzenes is by reaction with the OH radical. For the alkyl-substituted benzenes, the OH radical reactions proceed by two pathways: (1) H-atom abstraction from the C-H bonds of the alkyl substituent groups and (2) OH radical addition to the aromatic ring, as shown below, for *p*-xylene:



with the OH radical addition pathway being reversible above ≈ 325 K (Atkinson, 1989).

The radical formed in Reaction 3-52a reacts analogously to an alkyl radical (Atkinson, 1994), leading, in the presence of NO, to aromatic aldehydes and organic nitrates.



The OH-containing radical formed in Reaction 3-52b can undergo reaction with both NO₂ and O₂. Knispel et al. (1990) reported rate constants for the reactions of NO₂ and O₂ with the OH-containing radicals formed from benzene and toluene. The magnitude of the rate constants they obtained implies that, in the troposphere, the major reactions of these radicals will be with O₂. Laboratory studies of the formation of selected products from the gas-phase reactions of the OH radical with toluene, *o*-xylene, and 1,2,3-trimethylbenzene (Atkinson and Aschmann, 1994), and, in particular, of the formation of the ring-cleavage product 2,3-butanedione from *o*-xylene, are consistent with the kinetic data of Knispel et al. (1990). Thus, at least for the monocyclic aromatic hydrocarbons such as benzene, toluene, and the xylenes, the OH-aromatic adducts formed in Reaction 3-52b react with O₂ under atmospheric conditions. However, care must be taken in using product yields obtained in the laboratory at higher than ambient NO₂ concentrations because data may be influenced by the NO₂ reaction and, hence, may not be applicable to the O₂ reaction with the OH-aromatic adduct. Clearly, the products formed and their yields from the O₂ and NO₂ reactions with the OH-aromatic adducts need to be determined, and the detailed reaction mechanisms elucidated.

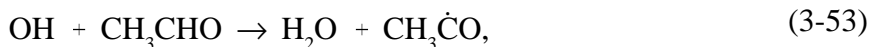
Despite these uncertainties, however, products from the OH radical addition pathway have been identified, and their formation yields determined (Atkinson, 1994, and references therein). The major products identified from the OH radical addition pathway are phenolic compounds (e.g., phenol from benzene and *o*-, *m*-, and *p*-cresol from toluene) and α-dicarbonyls (glyoxal, methylglyoxal, and 2,3-butanedione) resulting from the cleavage of the aromatic ring (see, for example, Atkinson, 1990, 1994, and references therein). Significant fractions (≥50% for benzene, toluene, and the xylenes) of the reaction products are, however, still not accounted for.

Carbonyl Compounds

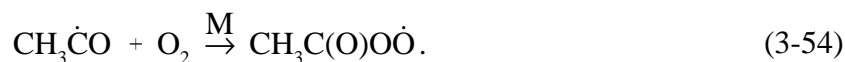
As noted above, the OH radical reactions with the alkanes, alkenes, and aromatic hydrocarbons lead, often in large yield, to the formation of carbonyl compounds. Likewise, carbonyls are formed during the reactions of NO₃ radicals and O₃ with alkenes. As a first approximation, the carbonyl compounds of tropospheric interest are HCHO (see Section 3.2.3.3), acetaldehyde, and the higher aliphatic aldehydes; benzaldehyde; acetone, 2-butanone, and the higher ketones; and simple dicarbonyls such as glyoxal, methylglyoxal, and 2,3-butanedione.

The tropospheric photooxidation of isoprene leads to the formation of methyl vinyl ketone (CH₃C(O)CH=CH₂) and methacrolein (CH₃C(CHO)=CH₂). The OH radical-initiated reactions of these two carbonyl compounds in the presence of NO_x have been studied by Tuazon and Atkinson (1989, 1990b).

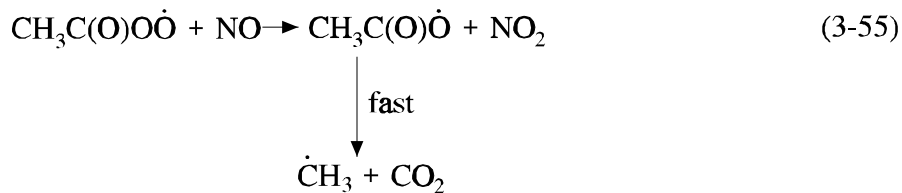
The tropospherically important loss processes of the carbonyls not containing >C=C< bonds are photolysis and reaction with the OH radical. As shown in Tables 3-2, photolysis is a major tropospheric loss process for the simplest aldehyde (HCHO) and the simplest ketone (CH₃C(O)CH₃), as well as for the dicarbonyls. For the higher aldehydes and ketones, the OH radical reactions are calculated to be the dominant gas-phase loss process (Table 3-2). For CH₃CHO, the reaction proceeds by H-atom abstraction from the -CHO group to form the acetyl (CH₃CO) radical,



which rapidly adds O₂ to form the acetyl peroxy radical:



This O₂ addition pathway is in contrast to the reaction of O₂ with the formyl (HCO) radical formed from HCHO, which reacts by an H-atom abstraction pathway (Reaction 3-30). The acetyl peroxy radical reacts with NO and NO₂,



with the NO₂ reaction forming the thermally unstable PAN. The higher aldehydes also lead to PANs (Roberts, 1990); for example, propionaldehyde reactions lead to the formation of

peroxypropionyl nitrate (PPN). Although the rate constant at atmospheric pressure for the thermal decomposition of PAN (Atkinson et al., 1992a) is such that the lifetime of PAN, with respect to thermal decomposition, is ≈ 30 min at 298 K in the lower troposphere, the thermal lifetime of PAN is calculated to be several hundred years in the upper troposphere. Reaction with OH radicals or photolysis, or both, therefore will dominate as the loss processes of PANs in the upper troposphere (Atkinson et al., 1992a).

The transport of PAN out of urban areas into colder air masses (e.g., to higher altitude) leads to PAN becoming a temporary reservoir of NO_x , allowing the long-range transport of NO_x to less polluted areas. Release of NO_2 in these less polluted areas via Reaction 3-56, with subsequent photolysis of NO_2 , then leads to O_3 formation and the pollution of remote areas.

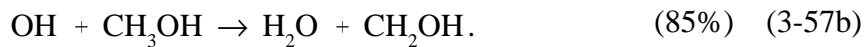
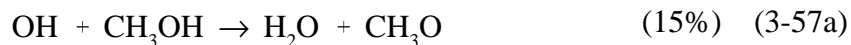
Because the $\dot{\text{C}}\text{H}_3$ radical formed from the NO reaction with $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ leads to HCHO formation, the OH radical reaction with CH_3CHO subsequently leads to the formation of HCHO. The same process occurs for propionaldehyde, which reacts to form CH_3CHO and then HCHO. Benzaldehyde appears to behave as a phenyl-substituted aldehyde, with respect to its OH radical reaction, and the analog to PAN is then peroxybenzoyl nitrate, PBzN ($\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONO}_2$).

The formation of HCHO from CH_3CHO and of CH_3CHO and then HCHO from propionaldehyde are examples of "cascading", in which the photochemical degradation of emitted VOCs leads to the formation of further VOCs, typically containing fewer carbon atoms than the precursor VOC. This process continues until the degradation products are removed by wet and dry deposition or until CO or CO_2 are the degradation products. The reactions of each of these VOCs (i.e., the initially emitted VOC and its first-, second-, and successive-generation products), in the presence of high concentrations of NO, can lead to the formation of O_3 .

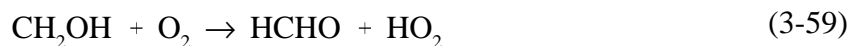
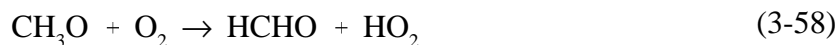
As discussed in Section 3.2.3.3 for HCHO, the photolysis of carbonyl compounds can lead to the formation of new radicals that result in enhanced photochemical activity. The OH radical reactions of the ketones are generally analogous to the reaction schemes for the alkanes and aldehydes.

Alcohols and Ethers

A number of alcohols and ethers are used in gasolines and in alternative fuels. The alcohols include methanol, ethanol, and *tert*-butyl alcohol, and the ethers include methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). Table 3-2 shows that in the troposphere these VOCs react only with the OH radical. The relatively long calculated lifetime of methanol in the troposphere (15 days), due to reaction with the OH radical (Table 3-2), suggests that methanol also will be removed from the troposphere by wet and dry deposition and that these physical loss processes may dominate the OH radical reactions preceded by H-atom abstraction from the C-H bonds (and to a minor extent from the O-H bonds in the alcohols), for example, for methanol,



In the troposphere, both of the CH₃O and CH₂OH radicals react only with O₂ to form HCHO.



The overall reaction is then



The reaction sequence for ethanol is similar (Atkinson, 1994). Product studies of the OH radical-initiated reactions of MTBE and ETBE in the presence of NO_x have been carried out by Japer et al. (1990), Smith et al. (1991a, 1992), Tuazon et al. (1991), and Wallington and Japar (1991). The major products from MTBE are *tert*-butyl formate, HCHO, and methyl acetate [CH₃C(O)OCH₃] and, from ETBE, *tert*-butyl formate, *tert*-butyl acetate, HCHO, CH₃CHO, and ethyl acetate. The available product data and the reaction mechanisms have been reviewed by Atkinson (1994), and that reference should be consulted for further details.

In addition to the use of alcohols and ethers in gasolines and alternative fuels, unsaturated alcohols have been reported as emissions from vegetation (Arey et al., 1991a; Goldan et al., 1993), and kinetic and product studies have begun to be reported for these biogenic VOCs (Grosjean et al., 1993a).

Primary Products and Areas of Uncertainty for the Tropospheric Degradation Reactions of Volatile Organic Compounds

The tropospheric degradation reactions of the alkanes, alkenes (including those of biogenic origin), aromatic hydrocarbons, carbonyls (often formed as products of the degradation reactions of alkanes, alkenes, and aromatic hydrocarbons), and other oxygenates have been briefly discussed above. A more lengthy and detailed discussion of the atmospheric chemistry of alkanes, alkenes, aromatic hydrocarbons, and oxygen- and nitrogen-containing organic compounds emitted into the atmosphere from anthropogenic and biogenic sources and of their atmospheric transformation products is given in the review and evaluation of Atkinson (1994), which also provides an assessment of the uncertainties in the product yields and the reaction rate constants. The first-generation products of the alkanes, alkenes, and aromatic hydrocarbons follow (unfortunately, complete product distributions have not been obtained for most of the VOCs studied).

Alkanes.

- Carbonyl compounds (i.e., aldehydes and ketones) are formed as major products for the smaller (≤C₄) alkanes.
- Alkyl nitrates are formed from the ≥C₃ alkanes studied to date. The yields increase with the size of the alkane from ≈4% for propane to ≈30% for *n*-octane.
- δ-Hydroxycarbonyls are expected to be formed after the alkoxy radical isomerization reaction. To date, no direct evidence for the formation of these compounds exists. For the larger alkanes, the formation yields of these compounds could be high.

- Alkyl hydroperoxides are formed under low-NO conditions.
- Alkyl peroxy nitrates (ROONO_2) are formed but have short lifetimes (a few seconds at 298 K) due to thermal decomposition.
- Alcohols are formed from the combination reactions of the peroxy radicals under low-NO experimental conditions. These compounds are expected to be formed in low concentrations in the troposphere.

The major uncertainties in the atmospheric chemistry of the alkanes concern the formation of RONO_2 from the reactions of the peroxy radicals with NO (Reaction 3-44b) and the reactions of the alkoxy radicals in the troposphere. These uncertainties affect the amount of NO to NO_2 conversion occurring and, hence, the amounts of O_3 that are formed during the NO_x -air photooxidations of the alkanes.

Alkenes.

- Carbonyl compounds (aldehydes and ketones) are formed as major products of the OH radical, NO_3 radical, and O_3 reactions.
- Organic acids are formed from the O_3 reactions, but probably in low yields.
- Hydroxynitrates and nitratocarbonyls are formed from the OH radical reactions and NO_3 radical reactions, respectively. The hydroxynitrates are formed in low yields from the OH radical reactions, whereas the nitratocarbonyls may be major products of the NO_3 radical reactions.
- Hydroxycarbonyls and carbonyl-acids are also expected to be formed, although few, if any, data exist to date.
- Decomposition products are produced from the initially energy-rich biradicals formed in the O_3 reactions; these include CO, CO_2 , esters, hydroperoxides, and, in the presence of NO_x , peroxyacyl nitrates (RC(O)OONO_2 and PANs).

The major areas of uncertainty concern the products and mechanisms of the O_3 reactions (in particular, the radical yields from these reactions that affect the O_3 formation yields from the NO_x -air photooxidations of the alkenes) and the reaction products and mechanisms of the OH radical reactions with the alkenes containing more than four carbon atoms.

Aromatic Hydrocarbons.

- Phenolic compounds, such as phenol and cresols, have been shown to be major products of the atmospheric reactions of the aromatic hydrocarbons under laboratory conditions.
- Aromatic aldehydes, such as benzaldehyde, are formed in $\leq 10\%$ yield.
- α -Dicarbonyls, such as glyoxal, methylglyoxal, and biacetyl, are formed in fairly high (10 to 40%) yields. These dicarbonyls photolyze rapidly to form radicals and, therefore, are important products with respect to the photochemical activity of the aromatic hydrocarbons.
- Unsaturated carbonyl or hydroxycarbonyl compounds are formed, although there is little direct information concerning the formation of these products.

There is a lack of knowledge of the detailed reaction mechanisms and products for the aromatic hydrocarbons under tropospheric conditions (i.e., for the NO_x concentrations encountered in urban and rural areas). It is possible that the products observed in laboratory studies and their formation yields are not representative of the situation in the troposphere. This then leads to an inability to formulate detailed reaction mechanisms for the atmospheric

degradation reactions of the aromatic hydrocarbons, and the chemical mechanisms used in urban airshed models then must rely heavily on environmental (or "smog") chamber data.

Oxygenated Compounds.

- The products observed from the atmospheric photooxidations of oxygenated organics are carbonyls, organic acids (e.g., RC(O)OH), esters, alcohols, and, in the presence of NO_x , PANs.

The major area of uncertainty concerns the importance of photolysis of carbonyl compounds in the troposphere, and the products formed. In particular, there is a lack of information concerning the absorption cross-sections and photodissociation quantum yields for most of the aldehydes and ketones other than HCHO , CH_3CHO , and CH_3COCH_3 .

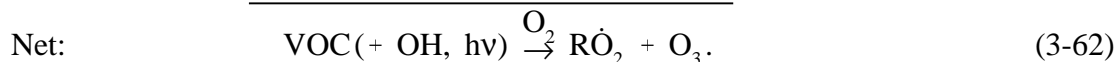
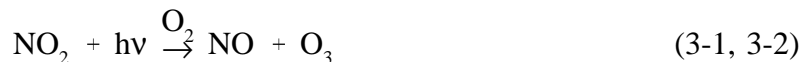
3.2.4.2 Chemical Formation of Ozone in Polluted Air

Major Steps in Ozone Formation

As discussed earlier, NO_x and VOCs interact under the influence of sunlight to form O_3 and other photochemical air pollutants. The major steps in this process are the conversion of NO to NO_2 by peroxy radicals, with the photolysis of NO_2 leading to O_3 production. In the absence of a VOC, Reactions 3-1 through 3-3,



do not lead to any net formation of O_3 . The reaction of a VOC with the OH radical, or its photolysis, leads to the formation of HO_2 and organic peroxy (RO_2) radicals, which react with NO under high- NO conditions:



with the alkoxy (RO) radical producing further HO_2 or RO_2 radicals or both, and, hence, resulting in further production of O_3 . This process is shown schematically in Figure 3-4.

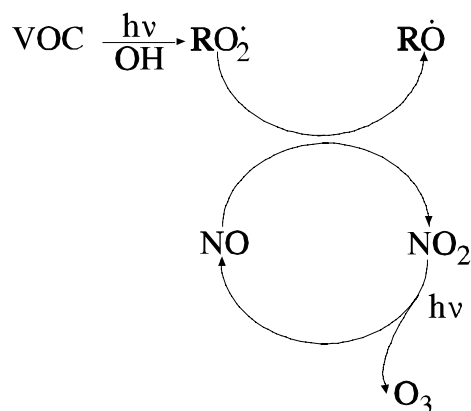
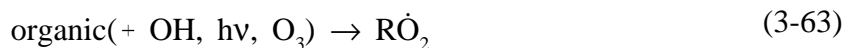


Figure 3-4. Major steps in production of ozone in ambient air ($R = H$, alkyl or substituted alkyl, or acyl).

The general time-concentration profiles for selected species during irradiation of an NO_x -VOC-air mixture are shown in Figure 3-5 for a constant light intensity and in Figure 3-6 for diurnally varying light intensity. These general features of an NMOC- NO_x -air irradiation are described by the reactions described below.

The conversion of NO to NO_2 occurs through the oxidation reactions:



The maximum concentration of NO_2 is less than the initial $\text{NO} + \text{NO}_2$ concentration because NO_2 is removed through the reaction



This reaction removes radicals (OH and NO_2) and NO_x from the system. In addition to the removal of NO_x through Reaction 3-15, NO_x also can be removed through the formation of temporary reservoir species such as organic nitrates (Reaction 3-44b) and PAN (Reaction 3-56).

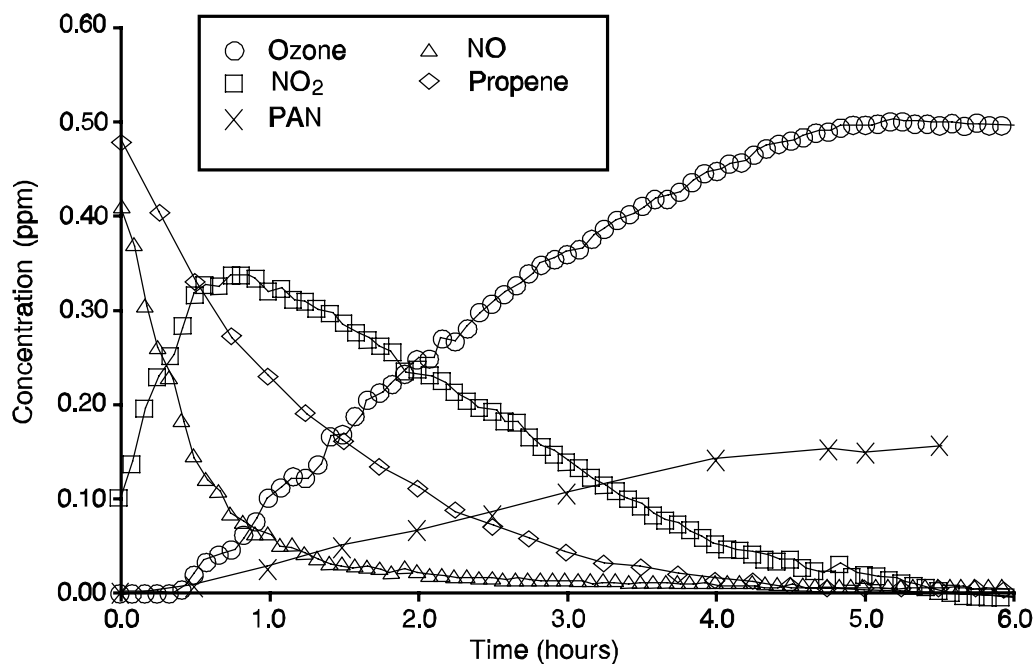


Figure 3-5. Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an indoor chamber with constant light intensity.

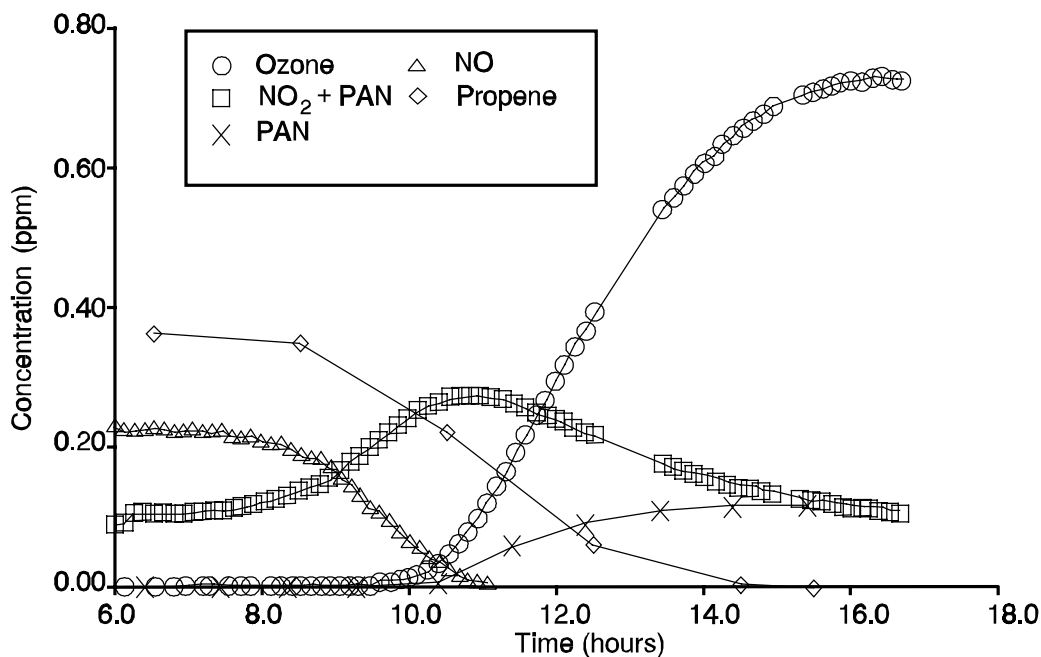


Figure 3-6. Time-concentration profiles for selected species during irradiations of a nitrogen oxide-propene-air mixture in an outdoor chamber with diurnally varying light intensity.



The O_3 concentration increases with the NO_2/NO concentration ratio, and O_3 formation ceases when NO_2 (and hence NO_x) has been removed by reaction.

Formation of PAN occurs by Reaction 3-56. Because of Reactions 3-55 and 3-56, the PAN concentration also increases with the NO_2/NO concentration ratio, and PAN formation also ceases when NO_x has been depleted.

The removal processes for NO_x are by reaction of NO_2 with the OH radical to form HNO_3 (Reaction 3-16), the formation of organic nitrates from the $\text{ROO} + \text{NO}$ Reaction 3-44b pathway, and the formation of PAN through Reaction 3-56. The initially present NO_x is converted to organic nitrates, HNO_3 , and thermally unstable PANs. At ambient temperature, the PANs will gradually thermally decompose to yield NO_2 and the acylperoxy radicals; hence, the ultimate fate of NO_x will be to form HNO_3 and organic nitrates.

Effects of Varying Initial Nitrogen Oxide and Nonmethane Volatile Organic Compound Concentrations

As discussed in Section 3.2.4.2, NO_x and VOC interact in sunlight to form O_3 and other photochemical air pollutants. The formation of O_3 from the NO_x and VOC precursors is nonlinear with respect to the precursor emissions (or ambient concentrations). As discussed in detail in Section 3.6, computer models incorporating emissions, meteorology, and chemistry are necessary for a full understanding of the complexities of the NO_x -VOC- O_3 system. The major reactions in irradiated VOC- NO_x -air mixtures (see Section 3.2.4.2) include



which is in competition with Reaction 3-15,



which removes both radicals and NO_x .



Based on these reactions, as the VOC/NO_x ratio decreases, Reaction 3-15 competes more successfully with Reaction 3-61 in removing radicals from the system for a constant source of OH radicals, and, thus, slows down the formation of O_3 (and vice-versa). The ultimate amount of O_3 formed depends on the NO_2 available for photochemical processing through

Reactions 3-44a, 3-1, 3-2, and 3-3. Because of the diurnal light intensity variation and the length of daylight available for reactions and photolysis to occur, O₃ formation from VOC-NO_x-air mixtures, especially as a function of the VOC/NO_x ratio, is complex and depends on the time or distance scale being considered (for example, transport of urban plumes to rural areas) (Wolff, 1993; Finlayson-Pitts and Pitts, 1993). In general, reducing the VOC/NO_x ratio by reducing VOC emissions slows down the formation rate of O₃, leading to lower O₃ levels in urban areas and in areas downwind of urban complexes. Reduction of NO_x emissions leads to a more rapid formation of O₃, although with less O₃ formed, and, hence, inner-urban areas may experience higher O₃ levels with NO_x control than with VOC control, whereas suburban and rural areas may have lower O₃ levels with NO_x control (Trainer et al., 1993; Olszyna et al., 1994).

Effects of Biogenic Nonmethane Volatile Organic Compound Emissions

Biogenic VOC emissions can be important in urban and rural areas (Trainer et al., 1987; Chameides et al., 1988, 1992; Roselle et al., 1991) and can contribute to O₃ formation in much the same way as anthropogenic VOCs. Modeling simulations in which urban biogenic VOC emissions are first included and then excluded from the calculations generally indicate little effect of the biogenic emissions on the predicted O₃ levels. This is not unexpected from the shape of the O₃ isopleths at high VOC/NO_x ratios (Chameides et al., 1988; Section 3.6). However, results of modeling studies in which anthropogenic VOC emissions are removed from the simulations (but anthropogenic NO_x emissions are left unaltered) suggest that anthropogenic NO_x together with biogenic VOCs may form sufficient O₃ to exceed the NAAQS, at least in certain areas (Chameides et al., 1988). Thus, for the anthropogenic and biogenic VOC emissions considered by Chameides et al. (1988) for Atlanta, GA, changes in either the anthropogenic VOC emissions or biogenic VOC emissions have little effect on O₃ levels. Therefore, as discussed for the Atlanta region (Chameides et al., 1988), NO_x control may be more favorable than VOC control in urban areas with substantial biogenic NMOC emissions.

Although it is known that isoprene is reactive with respect to the formation of O₃ (Section 3.2.4.3) and that the monoterpenes react rapidly with OH radicals, NO₃ radicals, and O₃, the O₃-forming potentials of the various monoterpenes emitted into the atmosphere are not known.

3.2.4.3 Hydrocarbon Reactivity with Respect to Ozone Formation

As discussed in Section 3.2.4, VOCs are removed and transformed in the troposphere by photolysis and by chemical reaction with OH radicals, NO₃ radicals, and O₃. In the presence of sunlight, the degradation reactions of the VOCs lead to the conversion of NO to NO₂ and the formation of O₃ and various organic products. However, different VOCs react at differing rates in the troposphere because of their differing tropospheric lifetimes (Table 3-2). The lifetimes of most VOCs with respect to reaction with OH radicals and O₃ are in the range ≈1 h to ≈10 years. In large part, because of these differing tropospheric lifetimes and rates of reaction, VOCs exhibit a range of reactivities with respect to the formation of O₃ (Altshuller and Bufalini, 1971, and references therein).

A number of "reactivity scales" have been developed over the years (see, for example, Altshuller and Bufalini, 1971, and references therein; Darnall et al., 1976), including the rate of VOC disappearance in NO_x-VOC-air irradiations, the rate of NO to NO₂ conversion in NO_x-VOC-air irradiations, O₃ formation in NO_x-single VOC-air irradiations, eye

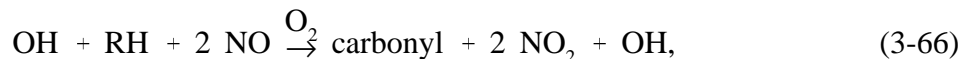
irritation, and the rate constant for reaction of the VOC with the OH radical. It appears, however, that a useful definition of "reactivity" is that of "incremental reactivity" (*IR*), defined as the amount of O₃ formed per unit of VOC added or subtracted from the VOC mixture in a given air mass under high-NO conditions (Carter and Atkinson, 1987, 1989b):

$$IR = \Delta[O_3]/\Delta[VOC], \quad (3-65)$$

at the limit of $\Delta[VOC] \rightarrow 0$. The concept of incremental reactivity and some further details of this approach are illustrated by the general reaction mechanism for the photooxidation of an alkane, RH:

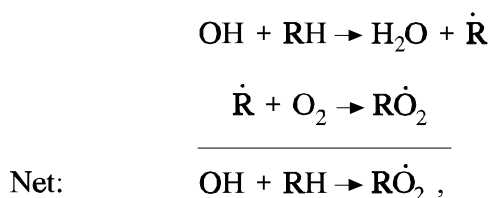


The net reaction,

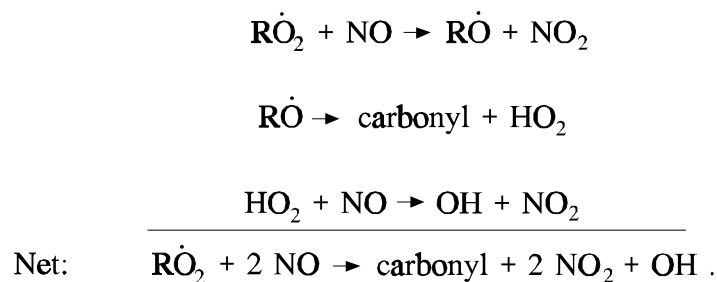


can be viewed as involving the two separate reaction sequences:

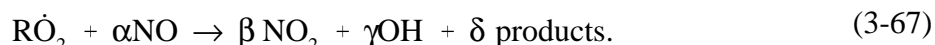
(1) the formation of organic peroxy ($\dot{R}O_2$) radicals from the reactions,



and (2) the conversion of NO to NO₂ and the formation of O₃ and other products,



The photolysis of NO₂ then leads to O₃ formation (Reactions 3-1 and 3-2). The first reaction sequence determines how fast $\dot{\text{R}}\text{O}_2$ radicals are generated from the VOC, which is called "kinetic reactivity" (Carter and Atkinson, 1989b). For the case given above, where the only reaction of the VOC is with the OH radical, the kinetic reactivity depends solely on the OH radical reaction rate constant. The second reaction sequence, leading to NO to NO₂ conversion, regeneration of OH radicals, and the formation of product species, determines the efficiency of formation of O₃ from the $\dot{\text{R}}\text{O}_2$ radicals formed from the first reaction sequence and is termed "mechanistic reactivity" (Carter and Atkinson, 1989b). The second reaction sequence can be represented as



In general, the faster a VOC reacts in the atmosphere, the higher the incremental reactivity. However, the chemistry subsequent to the initial reaction does affect the O₃-forming potential of the VOC. Thus, the existence of NO_x sinks in the reaction mechanism (low values of β or values of α-β > 0) leads to a decrease in the amount of O₃ formed. Examples of NO_x sinks are the formation of organic nitrates and PANs (which are also sinks for radicals). The generation or loss of radical species can lead to a net formation or net loss of OH radicals (γ > 1 or γ < 1, respectively). This, in turn, leads to an enhancement or suppression of radical concentrations in the air parcel and to an enhancement or suppression of the overall reactivity of all VOCs in that air parcel by affecting the rate of formation of $\dot{\text{R}}\text{O}_2$ radicals.

These effects vary in importance depending on the VOC/NO_x ratio. Nitrogen oxides sinks are most important at high VOC/NO_x ratios (NO_x-limited), affecting the maximum O₃ formed; although the formation or loss of OH radicals is most important at low VOC/NO_x ratios, affecting the initial rate at which O₃ is formed (Carter and Atkinson, 1989b). In addition to depending on the VOC/NO_x ratio (Table 3-3), incremental reactivity depends on the composition of the VOC mixture and on the physical conditions encountered by the air mass (including the dilution rate, light intensity, and spectral distribution (Carter and Atkinson, 1989b; Carter, 1991).

Table 3-3. Calculated Incremental Reactivities of Selected Volatile Organic Compounds as a Function of the Volatile Organic Compound/Nitrogen Oxide Ratio for an Eight-Component Volatile Organic Compound Mixture^a and Low-Dilution Conditions^b

NMOC	VOC/NO _x Ratio (ppmC/ppm)			
	4	8	16	40
CO	0.011	0.022	0.016	0.005
Ethane	0.024	0.041	0.018	0.007
<i>n</i> -Butane	0.10	0.16	0.069	0.019
<i>n</i> -Octane	0.068	0.12	0.027	-0.031
Ethene	0.85	0.90	0.33	0.14
Propene	1.28	1.03	0.39	0.14
<i>trans</i> -2-Butene	1.42	0.97	0.31	0.054
Benzene	0.038	0.033	-0.002	-0.002
Toluene	0.26	0.16	-0.036	-0.051
<i>m</i> -Xylene	0.98	0.63	0.091	-0.025
Formaldehyde	2.42	1.20	0.32	0.051
Acetaldehyde	1.34	0.83	0.29	0.098
Methanol	0.12	0.17	0.066	0.029
Ethanol	0.18	0.22	0.065	0.006
Urban Mix	0.41	0.32	0.088	0.011

^aEight-component VOC mixture used to simulate NMOC emissions in an urban area.

^bSee Appendix A for abbreviations and acronyms.

Source: Carter and Atkinson (1989b).

The O₃-forming potentials of large numbers of VOCs, including emissions from automobiles using gasoline and various alternative fuels such as methanol and ethanol blends and compressed natural gas, have been investigated by airshed computer models (Chang and Rudy, 1990; Chang et al., 1991a; Derwent and Jenkin, 1991; Andersson-Sköld et al., 1992; McNair et al., 1992, 1994; Carter, 1994). Consistent with the modeling studies of Carter and Atkinson (1987, 1989b), these computer-modeling studies show that VOCs differ significantly in terms of their O₃-forming potential, for single-day as well as multiday conditions (Derwent and Jenkin, 1991; Andersson-Sköld et al., 1992; Carter, 1994; McNair et al., 1994). However, there are some differences between the O₃-forming potentials derived by Derwent and Jenkin (1991) for multiday transport conditions over Europe and by Carter (1994) for 1-day urban airshed "maximum incremental reactivity" conditions, especially for HCHO, an important direct emission and atmospheric transformation product of most VOCs.

Recent modeling studies have been carried out by Carter (1994) and McNair et al. (1994) to determine the O₃-forming potential of alternative fuels. Emissions from vehicles using 85% methanol and 15% gasoline (M-85) were shown to have ≈40% of the O₃-forming

potential of emissions from gasoline-fueled vehicles. Emissions from vehicles using liquefied petroleum gas (LPG) and compressed natural gas (CNG) were shown to have O₃-forming potentials that are ≈50% and ≈18%, respectively, of the O₃-forming potential of emissions from gasoline-fueled vehicles (McNair et al., 1994).

3.2.5 Photochemical Production of Aerosols

The chemical processes involved in the formation of O₃ and other photochemical pollutants from the interaction of NO_x and VOCs lead to the formation of OH radicals and oxidized VOC reaction products that often are of lower volatility than the precursor VOC. The OH radicals that oxidize the VOCs and lead to the generation of RO₂ radicals and conversion of NO to NO₂ (with subsequent photolysis of NO₂ form O₃) also react with NO₂ and sulfur dioxide (SO₂) to form HNO₃ and H₂SO₄, respectively, which can become incorporated into aerosols as particulate nitrate (NO₃) and sulfate (SO₄²⁻). The low-volatility VOC reaction products can condense onto existing particles in the atmosphere to form secondary organic aerosol matter. Hence, O₃ formation, acid formation, and secondary aerosol formation in the atmosphere are so related that controls aimed at reducing O₃ levels can impact (positively or negatively) acid and secondary aerosol formation in the atmosphere.

3.2.5.1 Phase Distributions of Organic Compounds

Chemical compounds are emitted into the atmosphere in both gaseous and particle-associated forms. The emissions from combustion sources (e.g., vehicle exhaust) are initially at elevated temperature, and compounds that may be in the particle phase at ambient atmospheric temperature may be in the gas phase when emitted. In addition, atmospheric reactions of gas-phase chemicals can lead to the formation of products that then condense onto particles, or self-nucleate (Pandis et al., 1991; Wang et al., 1992; Zhang et al., 1992). Measurements of ambient atmospheric gas- and particle-phase concentrations of several classes of organic compounds indicate that the phase distribution depends on the liquid-phase vapor pressure, PL (Bidleman, 1988; Pankow and Bidleman, 1992). The available experimental data and theoretical treatments show that, as a rough approximation, organic compounds with PL > 10⁻⁶ torr at ambient temperature are mainly in the gas phase (Bidleman, 1988). As expected, the gas-particle phase distribution in the atmosphere depends on the ambient temperature, with the chemical being more particle-associated at lower temperatures. The gas-to-particle adsorption-desorption process can be represented as,



where A is the gas-phase compound, F is the particle-phase compound, and TSP is the total suspended particulate matter. The relationship among these three species is expressed using a particle-gas partition coefficient, K:

$$K = F/(\text{TSP})A. \quad (3-69)$$

Because K is a constant at a given temperature, if TSP increases (for example, in going from a clean remote atmosphere to an urban area), F/A also must increase and the chemical becomes more particle-associated (Pankow and Bidleman, 1991, 1992).

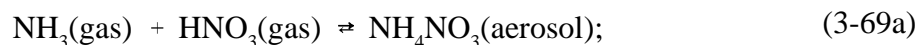
Gaseous and particulate species in the atmosphere are subject to wet and dry deposition. Dry deposition refers to the uptake of gases and particles at the earth's surface by vegetation, soil, and water, including lakes, rivers, oceans, and snow-covered ground. Wet deposition refers to the removal of gases and particles from the atmosphere through incorporation into rain, fog, and cloud water, followed by precipitation to the earth's surface. These processes are discussed further in Section 3.6.

For gases, dry deposition is important primarily for HNO_3 , SO_2 , and H_2O_2 as well as for O_3 and PAN, whereas wet deposition is important for water-soluble gases such as HNO_3 , H_2O_2 , phenols, and, under atmospheric conditions, SO_2 . Dry deposition of particles depends on the particle size; those of a mean diameter of ≈ 0.1 to $2.5 \mu\text{m}$ have lifetimes with respect to dry deposition of ≈ 10 days (Graedel and Weschler, 1981; Atkinson, 1988), sufficient for long-range transport. However, particles are efficiently removed from the atmosphere by wet deposition (Bidleman, 1988).

Particles can form in the atmosphere by condensation or by coagulation, generally occurring by coagulation in urban and rural areas. The photooxidation reactions of VOCs typically lead to the formation of more oxidized and less volatile product species. When the vapor pressures exceed the saturated vapor pressure (i.e., vapor pressure $< 10^{-6}$ Torr), the products will become particle-associated (Pandis et al., 1991, 1992). Accumulation-size particles are in the size range 0.08 to $2.5 \mu\text{m}$ diameter (Whitby et al., 1972).

In urban areas, the major sources of particulate matter (Larson et al., 1989; Solomon et al., 1989; Wolff et al., 1991; Hildemann et al., 1991a,b; Rogge et al., 1991, 1993; Chow et al., 1993) are

- direct emissions of elemental carbon from, for example, diesel-powered vehicles (Larson et al., 1989);
- direct emissions of primary organic carbon from, for example, meat cooking operations, paved road dust, and wood-burning fireplaces and other combustion sources (Hildemann et al., 1991a,b; Rogge et al., 1991, 1993);
- secondary organic material formed in the atmosphere from the atmospheric photooxidations of gas-phase NMOC (Turpin and Huntzicker, 1991; Pandis et al., 1992);
- the conversion of NO and NO_2 to HNO_3 , followed by neutralization by NH_4 or through combination with other cations to form aerosol nitrates:



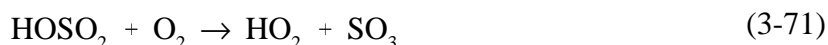
- the conversion of SO_2 (and other sulfur-containing species) to H_2SO_4 , which has sufficiently low volatility to move to the aerosol phase; and
- emission into the atmosphere of "fine dust", for example, crustal material.

Because the fine-particle size range is the same magnitude as the wavelength of visible light, particulate matter present in the atmosphere leads to light scattering and absorption, and hence to visibility reduction (Larson et al., 1989; Eldering et al., 1993).

3.2.5.2 Acid Deposition

As noted above, the chemical processes involved in the formation of O_3 and other photochemical pollutants from the interaction of NMOC and NO_x also lead to the formation of acids in the atmosphere. The two major acidic species in ambient air are HNO_3 and H_2SO_4 , arising from the atmospheric oxidation of NO_x and SO_2 , respectively. Reduced sulfur compounds emitted from biogenic sources and certain anthropogenic sources also may lead to SO_2 or sulfonic acids (Tyndall and Ravishankara, 1991).

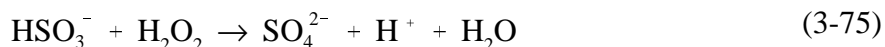
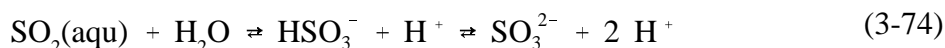
The major sulfur-containing compound emitted into the atmosphere from anthropogenic sources is SO_2 . In the troposphere, the important loss processes of SO_2 are dry deposition (Atkinson, 1988, and references therein), reactions within cloud water, and gas-phase reaction with the OH radical. The rate constant for the reaction of SO_2 with the OH radical is such that the lifetime of SO_2 with respect to gas-phase reaction with the OH radical is ≈ 15 days. The reaction proceeds by (Stockwell and Calvert, 1983; Atkinson et al., 1992a)



The reaction of SO_3 with water vapor is slow in the gas-phase (Atkinson et al., 1992a) and, hence, this may be a heterogeneous reaction. Because of its low vapor pressure, H_2SO_4 exists in the aerosol or particle phase in the atmosphere.

Dry deposition is an important atmospheric loss process for SO_2 , because SO_2 has a fairly long lifetime, due to gas-phase chemical processes, and also has a high deposition velocity. A lifetime, in relation to dry deposition of 2 to 3 days, appears reasonable (Schwartz, 1989).

Sulfur dioxide is not very soluble in pure water (Schwartz, 1989). However, the presence of pollutants such as H_2O_2 or O_3 , in the aqueous phase, displaces the equilibrium and allows gas-phase SO_2 to be incorporated into cloud, rain, and fog water, where it is oxidized rapidly (Schwartz, 1989; Pandis and Seinfeld, 1989, and references therein):



In addition, aqueous sulfur can be oxidized in a process catalyzed by transition metals such as iron(III) (Fe^{3+}) and manganese(II) (Mn^{2+}) (Graedel et al., 1986b; Weschler et al., 1986; Pandis and Seinfeld, 1989).



The oxidation rate of aqueous sulfur by O_3 decreases as the pH decreases (i.e., as the acidity increases) and this oxidation route is therefore self-limiting and generally of minor importance in the atmosphere. The oxidation of SO_2 by H_2O_2 appears to be the dominant aqueous-phase oxidation process of SO_2 (Chandler et al., 1988; Gervat et al., 1988; Schwartz, 1989; Pandis and Seinfeld, 1989; Fung et al., 1991b), although the transition metal-catalyzed oxidation of SO_2 may also be important (Jacob et al., 1989). It should be noted that aqueous-phase H_2O_2 arises, in part, from the absorption of HO_2 radicals and H_2O_2 into the aqueous phase, with HO_2 radicals being converted into H_2O_2 (Zuo and Hoigne, 1993).

The oxidation of SO_2 to sulfate in clouds and fogs is often much faster than the homogeneous gas-phase oxidation of SO_2 initiated by reaction with the OH radical. The gas-phase oxidation rate is ≈ 0.5 to $1\% \text{ h}^{-1}$, whereas the aqueous-phase (cloud) oxidation rate may be as high as 10 to $50\% \text{ h}^{-1}$ (Schwartz, 1989).

The oxidation of NO_x to HNO_3 and nitrates was discussed in Section 3.2.3. During daylight hours, oxidation occurs by the gas-phase reaction of NO_2 with the OH radical:



with the lifetime of NO_2 due to Reaction 3-15 calculated to be ≈ 1.4 days. Nitric acid is removed from the troposphere by wet and dry deposition, with wet deposition being efficient. During nighttime hours, NO_2 can be converted into NO_3 radicals and N_2O_5 :



with N_2O_5 undergoing wet or dry deposition, or both. The reader is referred to Schwartz (1989) for further discussion of the conversion of NO_x to NO_3 and HNO_3 and of acid deposition.

3.3 Meteorological Processes Influencing Ozone Formation and Transport

Day-to-day variability in O_3 concentrations is, to a first approximation, the result of day-to-day variations in meteorological conditions. This section presents a succinct overview of those atmospheric processes that affect the concentrations of O_3 and other oxidants in urban and rural areas. Included in this list of processes are the vertical structure and

dynamics of the PBL; transport processes, including thermally-driven mesoscale circulations such as lake and sea breeze circulations; complex terrain effects on transport and dispersion; vertical exchange processes; deposition and scavenging; and meteorological controls on biogenic emissions and dry deposition.

3.3.1 Meteorological Processes

3.3.1.1 Surface Energy Budgets

Knowledge of the surface energy budget is fundamental to an understanding of the dynamics of the PBL. The PBL is defined as that layer of the atmosphere in contact with the surface of the earth and directly influenced by the surface characteristics. In combination with synoptic winds, it provides the forces for the vertical fluxes of heat, mass, and momentum. The accounting of energy inputs and outputs provides a valuable check on modeled PBL dynamics.

Figure 3-7 illustrates the surface radiation budget for short-wave (wavelength roughly $<0.4 \mu\text{m}$) and long-wave radiation. The radiation budget for the surface can be described in terms of its components as

$$Q_{\text{sfc}} = K\downarrow - K\uparrow + L\downarrow - L\uparrow + Q_{\text{H}} + Q_{\text{E}}. \quad (3-78)$$

where $K\downarrow$ is the incoming short-wave radiation, $K\uparrow$ is the outgoing short-wave radiation, $L\downarrow$ is the incoming long-wave radiation from the atmosphere, $L\uparrow$ is the outgoing long-wave radiation, and Q_{H} and Q_{E} are the heat flux and latent heat flux to the soil, respectively. On a global annual average, Q_{sfc} is assumed to be near zero (i.e., the planet is not heating or cooling systematically, an assumption clearly being questioned with the growing debate on climatic change). On a day-to-day basis, however, Q_{sfc} will certainly vary from zero and will cause changes in surface temperature. Cloud cover, for example, will reduce the amount of short-wave radiation reaching the surface and will modify all the subsequent components of the radiation budget. Moreover, the redistribution of energy through the PBL creates thermodynamic conditions that influence vertical mixing. The treatment of energy budgets has been attempted on the scale of individual urban areas. These studies are summarized by Oke (1978).

For many of the modeling studies of the photochemical production of O_3 , the vertical mixing has been parameterized by a single, well-mixed layer. However, because this is a great simplification of a complex structure, and because the selection of rate and extent of vertical mixing may influence local control options, future modeling and observational studies need to address the energy balances so that more realistic simulations can be made of the structure of the PBL.