Appraisal of Tests to Predict the Environmental Behaviour of Chemicals
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2.3
Degradation in the Gas Phase

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2.3.1 'DIRECT' METHODS TO ESTABLISH KINETIC RATE DATA RELEVANT TO ATMOSPHERIC CHEMISTRY

According to present knowledge, the homogeneous gas phase degradation of chemicals in the atmosphere proceeds largely by sunlight photolysis or by reaction with OH radicals and to a lesser extent in polluted air, by reaction with O_3, O, NO_3, etc. (see Section 2.2). A large body of laboratory data on the gas phase reactions of O, OH, O_3, etc. has been accumulated. The applications of laboratory methodologies as well as the reliability of their results are discussed in this section.

Methods for the study of gas-phase reaction rates belong essentially to two categories: static or flowing systems. In static systems, the reactive species are often generated by flash photolysis and detected by fast detection (photomultipliers, photodiodes) and recording devices. In flowing systems, the time scale is converted to a spatial coordinate along the flow tube. Radicals or other active species are typically generated by flash photolysis, microwave (radiowave electric) discharges or fast chemical reactions, and reactants or products are detected as a function of reaction time by a variety

of methods (e.g. absorption, resonance absorption, mass spectrometry, electron-spin resonance, laser magnetic resonance, resonance fluorescence). The individual techniques are described in more detail by Watson (1977) and Atkinson *et al.* (1979).

Methane is by far the most abundant organic molecule in the atmosphere (~1.5 p.p.m.) and thus represents the starting point for the chemistry of the 'clean' atmosphere. At the present time, it is generally accepted that the most important tropospheric sink for methane is its reaction with OH.

$$CH_4 + OH \longrightarrow CH_3 + H_2O \qquad (1)$$

Because of the importance of this sink, a large number of different laboratory methods have been applied to measure the rate constant of reaction (1) (see e.g. Baulch *et al.*, 1980). Table 2.3.1 presents a summary of these various techniques and their estimated rate constants.

While there is evidence that the two early studies summarized in Table 2.3.1 were slightly affected by secondary reactions, for all other studies the rate constants for reaction (1) are quite similar. The resulting mean k value is 8×10^{-15} cm^3 molecules^{-1} s^{-1} at 298 K with a reliability of ~15%. This confidence limit is equivalent to those reported for the most reliably measured rate constants of other gas-phase elementary reactions.

The study of the reactions of chlorine containing compounds has been stimulated by findings indicating their potential adverse impacts on the atmosphere. Model calculations simulating the chemistry of the stratosphere (Molina and Rowland, 1974) suggest that chlorine containing substances which are not rapidly degraded in the troposphere (i.e. freons) may escape to the stratosphere. These substances under stratospheric conditions may accelerate a catalytic cycle involving Cl atoms which could result in an additional pathway for the destruction of stratospheric ozone. For the purpose of estimating the influence of freons on the ozone layer, it was most important to obtain a reliable estimate of the rate constant for reaction (2).

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (2)$$

Within a three-year period the rate constant of reaction (2) was measured at room temperature in six independent studies using both static and flowing systems. The reaction was monitored either by Cl atom resonance absorption or by mass spectrometric ozone detection (see Baulch *et al.*, 1980). While the earliest study resulted in $k_2 = 1.85 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, the rate constants from the other five studies were nearly identical, ranging from 1.0 to 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} for k_2.

Reactions (1) and (2) are representative of a large number of abstraction reactions which are considered to be important in atmospheric chemistry and which have been measured in the laboratory by direct methods. Abstraction reactions are expected to show no pressure dependence, and this has actually

Table 2.3.1 Rate constants for $CH_4 + OH \rightarrow CH_3 + H_2O$ at room temperature

OH source	OH detection	$k_{298}(T)$ (cm^3 molecule^{-1} s^{-1})	System	Reference
Flash photolysis of H_2O	Time resolved absorption spectroscopy	1.7×10^{-14} (298 K)	Static	Horne and Norrish, 1967
$H + NO_2 \rightarrow OH + NO$, H atoms from micro-wave discharge in H_2	Electron-spin resonance	1.08×10^{-14} (300 K)	Flow	Wilson and Westenberg, 1967
Flash photolysis of H_2O	Resonance absorption	8.8×10^{-15} (300 K)	Static	Greiner, 1970
$H + NO_2 \rightarrow OH + NO$	Resonance fluorescence	$(7.9 \pm 0.4) \times 10^{-15}$ (298 K)	Static	Margitan *et al.*, 1974
Flash photolysis of H_2O	Resonance fluorescence	$(7.4 \pm 0.7) \times 10^{-15}$ (298 K)	Static	Davis *et al.*, 1974
$H + NO_2 \rightarrow OH + NO$	Laser magnetic resonance	$(9.5 \pm 1.4) \times 10^{-15}$ (296 K)	Flow	Howard and Evenson, 1976
Flash photolysis of H_2O	Resonance absorption	$(8.8 \pm 0.7) \times 10^{-15}$ (300 K)	Static	Zellner and Steinert, 1976
HONO photolysis	Product analysis, measurement of $k(OH + CH_4)$ relative to $k(OH + H_2)$	$(7.3 \pm 0.9) \times 10^{-15}$ (296 K)	Flow	Cox *et al.*, 1976

been observed for many specific reactions. Formerly, the temperature dependence of a rate constant was represented by constant activation energies. Only in the last decade with the application of more refined experimental methods has it been possible to experimentally verify a change of activation energy with temperature for abstraction reactions. With the temperature range applicable to the atmospheric degradation of chemicals (200–300 K), rate constants for many abstraction reactions have been measured and a constant activation energy is usually an adequate representation of their temperature dependence.

In large molecules, H atoms can frequently be abstracted by OH radicals at many different positions with a comparable rate. The total reaction rate constant will roughly consist of a sum of several 'partial' rate constants. For example, Greiner (1970) established that the reaction rates of many branched and unbranched alkanes with OH radicals can be represented by a single expression which (in a form slightly modified by Darnall *et al.*, 1978) fits within ±20% or better all available data for $OH + C_nH_{2n+2} + 2$, $n \geq 3$ between 300 and 500 K.

$$\begin{aligned} k = {} & N_1 \times 1.01 \times 10^{-12} \exp(-1635 \text{ cal mol}^{-1}/RT) \\ & + N_2 \times 2.41 \times 10^{-12} \exp(-850 \text{ cal mol}^{-1}/RT) \\ & + N_3 \times 2.10 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \end{aligned} \quad \text{(I)}$$

where N_1, N_2, N_3 are the numbers of primary, secondary, tertiary H atoms per molecule, respectively, or

$$\begin{aligned} k = {} & N_1 \times 6.5 \times 10^{-14} + N_2 \times 5.8 \times 10^{-13} \\ & + N_3 \times 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K} \end{aligned} \quad \text{(II)}$$

A similar expression was deduced by Perry *et al.* (1977) for the reactions of alkyl ethers with OH at room temperature:

$$k = N_1 \times 6.0 \times 10^{-13} + N_2 \times 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \text{(III)}$$

where N_1 and N_2 have the same meaning as above. The higher numbers in (III) as compared to (II) reflect the slightly lower C—H binding energies in ethers as compared to alkanes. Similar expressions might be valuable as a first approximation of the stability of large molecules in other homologeous series of compounds with respect to their reactions with OH.

A selection of abstraction reaction rate constants which have been obtained from 'direct' laboratory methods are tabulated in Table 2.3.2.

Photolysis by sunlight has a twofold importance for the degradation of chemicals in the atmosphere. First, the photolytical decomposition of molecules such as O_3, NO_2, and CH_2O generates the active species (OH, O, etc.) that take part in degradation processes. Direct laboratory measurements of absorption cross-sections and quantum yields of these molecules have contributed greatly to the understanding of the operative photochemical mechan-

Table 2.3.2 Selected reactions with rate constants

Abstraction reactions		k_{298}[cm^3 molecule^{-1} s^{-1}]	References
$CH_4 + OH$	$\rightarrow CH_3 + H_2O$	8.0×10^{-13}	1
$C_2H_6 + OH$	$\rightarrow C_2H_5 + H_2O$	2.9×10^{-13}	2
n-$C_4H_{10} + OH$	$\rightarrow$ products	2.6×10^{-12}	2
$CH_4 + O$	$\rightarrow CH_3 + OH$	1.7×10^{-17}	2
$H_2CO + OH$	$\rightarrow$ products	1.3×10^{-11}	1
$H_2S + OH$	$\rightarrow$ products	5.3×10^{-12}	1
$CHClF_2 + OH$	$\rightarrow CClF_2 + H_2O$	4.4×10^{-15}	1
$O_3 + OH$	$\rightarrow HO_2 + O_2$	6.7×10^{-14}	1
$NO + O_3$	$\rightarrow NO_2 + O_2$	1.8×10^{-14}	1
$HCO + O_2$	$\rightarrow HO_2 + CO$	5.1×10^{-12}	1
$CH_3O + O_2$	$\rightarrow H_2CO + HO_2$	6×10^{-16}	1
$HO_2 + NO$	$\rightarrow NO_2 + OH$	8.4×10^{-12}	1
$O + O_3$	$\rightarrow 2O_2$	9.5×10^{-15}	1
$Cl + O_3$	$\rightarrow OCl + O_2$	1.2×10^{-11}	1
Photolysis reactions		j(50 °N, summer, noon) [s^{-1}]	**References**
$O_3 + h\nu$	$\rightarrow$ products	4.5×10^{-4}	3
	$\rightarrow O(^1D) + O_2$	1.2×10^{-5}	3
$NO_2 + h\nu$	$\rightarrow$ products	8×10^{-3}	3
$CH_2O + h\nu$	$\rightarrow$ products	5.4×10^{-5}	4
$HNO_2 + h\nu$	$\rightarrow$ products	2.8×10^{-3}	3
$SO_2 + h\nu$	$\rightarrow$ products	4.5×10^{-7}	5
$NO_3 + h\nu$	$\rightarrow$ products	2.0×10^{-1}	6
Recombination/dissociation reactions		k_{298}[cm^3 molecule^{-1} s^{-1}, s^{-1}] at 1 atm in air	**References**
$O + O_2$	$\xrightarrow{M} O_3$	1.4×10^{-14}	7
$CH_3 + O_2$	$\xrightarrow{M} CH_3O_2$	2×10^{-12}	7
$NO_2 + OH$	$\xrightarrow{M} HNO_3$	1.0×10^{-11}	8
PAN	$\xrightarrow{M} NO_2 + CH_3C(O)OO$	3.7×10^{-4}	9
Addition reactions		k_{298}[cm^3 molecule^{-1} s^{-1}] at 1 atm	**References**
$OH + CO$	$\rightarrow$ products	2.8×10^{-13} (in air)	1
$OH + C_2H_4$	$\rightarrow$ products	8×10^{-12}	2
OH + propene	$\rightarrow$ products	2.6×10^{-11}	2
OH + benzene	$\rightarrow$ products	1.2×10^{-12}	2
OH + α-pinene	$\rightarrow$ products	5.5×10^{-11}	2
O + propene	$\rightarrow$ products	4.5×10^{-12}	2
O_3 + propene	$\rightarrow$ products	1.3×10^{-17}	2
O_3 + benzene	$\rightarrow$ products	7×10^{-23}	2

Reference: Baulch *et al.*, 1980 (1); Atkinson *et al.*, 1979 (2); Campbell, 1977 (3); Warneck *et al.*, 1978 (4); Penzhorn *et al.*, 1974 (5); Magnotta and Johnston, 1980 (6); Hampson and Garvdin, 1978 (7); Zellner, 1978 (8); Henry and Kenley, 1977 (9).

isms. On the other hand, certain groups of compounds may be directly photolysed, at significant rates, by light at wavelengths longer than about 295 nm. This wavelength range represents an appreciable portion of the light intensity being transmitted through the stratospheric ozone layer. The photolytical decomposition rate of chemical X in the troposphere is often characterized by the product $j_x[X]$, where

$$j_x = \int_{\lambda \geq 295\,\mathrm{nm}} \Phi(X, \lambda)\sigma(X, \lambda)J(\lambda)\,\mathrm{d}\lambda \qquad \text{(IV)}$$

Here $\Phi(\lambda)$ is the quantum yield, $\sigma(\lambda)$ is the absorption cross-section and $J(\lambda)$ is the solar flux. While the absorption cross-sections and quantum yields of small molecules for the most critical wavelength regions, around 300 nm, have been determined with great precision in laboratory experiments (see Baulch *et al.*, 1980), the actual contribution of the photodissociation to the gas-phase degradation of large organic molecules in the atmosphere still has to be fully explored. Some j_x values, based on laboratory experiments and calculated for certain solar flux conditions, are included in Table 2.3.2.

Another class of reactions not involved in the initial step but in later stages of the degradation process are recombination and thermal decomposition reactions. For example, alkyl radicals which are formed in the reaction of hydrocarbons with OH,

$$\mathrm{RH + OH} \longrightarrow \mathrm{R + H_2O} \qquad (3)$$

will usually add oxygen in the atmosphere.

$$\mathrm{R + O_2} \xrightarrow{\mathrm{M}} \mathrm{RO_2}$$

These reactions are followed by further oxidation reactions, ultimately yielding CO or CO_2. Another recombination process, which represents one of the more important smog reactions, is the addition of NO_2 to OH radicals to produce nitric acid molecules.

$$\mathrm{NO_2 + OH} \xrightarrow{\mathrm{M}} \mathrm{HNO_3} \qquad (5)$$

The nitric acid can be removed from the troposphere by rain. The rate constants for reactions such as (4) and (5) under atmospheric conditions are expected to be both pressure and temperature dependent in a complex manner. Many laboratory measurements of these reactions are available but they usually do not cover the range of conditions necessary to simulate the atmospheric processes. Fortunately, the theoretical understanding of recombination and unimolecular decomposition reactions has markedly advanced during the last decade (see e.g. Troe, 1979) and data obtained over a limited range of reaction conditions may be extrapolated to atmospheric conditions with fairly good confidence. Some selected rate constants for this group of reactions are also included in Table 2.3.2.

Finally, there is a class of reactions for which direct methods have proved as yet unsatisfactory for their complete analysis. These are the addition reactions involving a moderately thermally stable intermediate with a dissociation energy $\lesssim 25$ kcal mol^{-1}. The appreciable long lifetime of such intermediates can lead to different results for experiments performed at typical 'direct method' conditions (pressures $\lesssim 10$ torr, noble gases or N_2 as buffer gases) and those at atmospheric conditions ($p \sim 1$ atm, presence of O_2). For example, the very important reaction of CO with the OH radical,

$$CO + OH \longrightarrow CO_2 + H \qquad (6)$$

has been measured independently by many research groups and it has been established that there is a factor of 2 difference in k_6 between measurements made at low pressures and those at 1 atm in air. This difference has been suggested to be a result of the presence of oxygen rather than a pressure effect (Smith, 1977; Biermann *et al.*, 1978). Very recently, this 'oxygen effect' was observed for other reactions as well. For example, the consumption of CS_2 by OH was accelerated by several orders of magnitude in the presence of oxygen (Barnes *et al.*, 1983). Obviously, these effects are more readily observed at high pressures, which makes indirect methods, for example the use of large 'environmental chambers', perhaps more amenable for research in this area. These methods will be discussed in Section 2.3.2.

2.3.2 'ENVIRONMENTAL CHAMBER' APPLICATION TO ATMOSPHERIC PHOTO-OXIDATION STUDIES

Although absolute (non-comparative) experimental techniques provide accurate rate constant data for elementary reactions, these methods operate most efficiently at low pressures and are therefore technically difficult to apply at atmospheric pressure. The rates and product distributions of many atmospherically important reactions are, however, pressure dependent and extrapolation of rate constant data obtained at low pressure to atmospheric pressure is often difficult. Such absolute techniques are also inadequate for the investigations of many of the more complex processes occurring in the atmosphere. On the other hand, the recent use of environmental chambers in association with highly sensitive and selective analytical instrumentation has led to significant advances in our knowledge of atmospheric photo-oxidative reactions. Such chambers can simulate the complex reaction mechanisms occurring in the troposphere while automatically including less understood processes such as aerosol formation.

Environmental chambers have been used quite successfully in two major areas of atmospheric chemistry. First, they have been used to obtain time–concentration profiles of numerous reactants, products and intermediates under varying conditions of temperature, pressure and light intensity. From such concentration profiles it has been possible to extract

relative rate data for the reactions of tropospherically important substances with active species such as OH, NO_3, and O_3. This data has been primarily used for generation of kinetic models of atmospheric chemistry for use in air pollution control strategies. The second major use has been coupling of environmental chambers to *in situ* analytical techniques such as long path Fourier transform infrared (LP–FTIR) spectroscopy and long path differential optical (UV and visible) absorption spectroscopy. The combinations of these techniques have led to the detection of many important reaction intermediates and have yielded a wealth of mechanistic information in the p.p.b. and p.p.m. concentration ranges. The full utility of these combined techniques has yet to be fully exploited.

2.3.2.1 Types of 'Environmental Chambers'

Basically two types of environmental chambers have been employed in the study of atmospheric processes:

(1) chambers constructed from cylindrical glass tubes, normally pyrex, and closed (usually) by Teflon-coated metal end flanges or
(2) collapsible bags from Teflon or similar material ('tedlar bags').

The chambers vary greatly in size, ranging from 10 l to 6000 l. Many of them are surrounded by banks of fluorescent lamps which simulate, as far as is possible, natural sunlight. A few of the glass chambers are temperature controllable over temperature ranges extending in one case from −40°C to +40°C. Teflon bags have two major advantages over glass chambers. They are financially more attractive requiring only a small capital investment for setting up the experimental system and due to the collapsibility of the bag, they automatically compensate for pressure dilution effects caused by sampling during the course of experiments. On the other hand, they often suffer from the evaporation of organic chemicals from their inner surface. For examples of different types of chambers see Japar *et al.*, 1974, Barnes *et al.*, 1979, Carter *et al.*, 1979, Cox *et al.*, 1980, and Akimoto *et al.*, 1980.

2.3.2.2 Determination of Relative Reaction Rates

Although the initial purpose of environmental chambers was to provide a database for atmospheric computer models, one of their greatest successes in recent years has been their application in the determination of relative rate data, particularly for OH radical reactions with atmospherically important organic substances. Several relative-rate methods have been developed employing environmental chambers. Generally, a OH rate coefficient is determined for the test substance relative to that of a reference substance with an accurately known OH-rate constant, by following the concentration-time behaviour of both substances. Assuming that the reaction mechanisms are

sufficiently understood, these methods fall into the following categories:

(1) The monitoring of the rates of disappearance of the substances in an NO_x/air photolysis system (Lloyd *et al.*, 1976).

(2) The monitoring of the rates of disappearance of substances in a HONO/air photolysis system. This system has an advantage over (1) in that higher OH concentrations are produced which help to minimize secondary interference effects such as the photolysis of aldehydes, and it also allows the determination of rate constants for slower reacting species (Cox *et al.*, 1980).

(3) A newer 'dark' method (Barnes *et al.*, 1982) using peroxynitric acid (HO_2NO_2) in the presence of NO as the source of OH radicals through the reactions

$$HO_2NO_2 \longrightarrow HO_2 + NO_2$$
$$HO_2 + NO \longrightarrow OH + NO_2$$

(4) The monitoring of variation in CO_2 production from the reaction of OH with added CO as a function of reactant concentrations (Audley *et al.*, 1981). The non-photolytic source of OH in these studies was the heterogeneous reaction of H_2O_2 with NO_2,

$$H_2O_2 + NO_2 \longrightarrow OH + HNO_3$$

and finally,

(5) The determination of the relative disappearance rate in an environmental chamber where the photolysis of alkyl nitrites is used as a source of OH radicals. The photolysis of methyl nitrite, for example, produces methoxy radicals and NO.

$$CH_3ONO \xrightarrow{h\nu} CH_3O + NO$$

The alkoxy radicals react further with O_2 to give an aldehyde and HO_2 radicals which subsequently react with NO to produce OH radicals (Atkinson *et al.*, 1981),

$$CH_3O + O_2 \longrightarrow HCHO + HO_2$$
$$HO_2 + NO \longrightarrow OH + NO_2$$

In all the above types of experiments, the disappearance of the added substance was monitored using either GC, HPLC or FTIR. These relative rate techniques have been successfully applied to the measurement under conditions of atmospheric pressure and temperature of rate constants for the degradation by OH radicals of anthropogenic and natural tropospheric substances such as alkanes, alkenes, aldehydes, alcohols, aromatics and chlorinated aromatics (Atkinson *et al.*, 1979).

Although reaction with OH is considered to be the major degradation pathway for most substances in the troposphere, ozone is an important component of photochemical smog and reaction with O_3 can significantly

contribute to degradation of organic substances, particularly in the case of complex olefins. The reactions of O_3 are reasonably easy to study using environmental chambers. The general procedure is to mix ozone and an excess of the test substance in large dilution of air or N_2. The decrease in ozone concentration as a function of time is then followed by either measuring the attenuation by ozone absorption of light transmitted from a UV mercury lamp or by using a NO–O_3 chemiluminescence detector. The application of an environmental chamber to the determination of the rate constants of O_3 with a variety of olefins and aromatics at 1 atm can be found in Japar *et al.*, 1974, Pate *et al.*, 1976, and Adeniji *et al.*, 1981.

The reported experimental values agree reasonably well for terminal olefins but the scatter of values for internally double-bonded olefins is far beyond the estimated experimental precision. This scatter is attributed to secondary reaction interference with the O_3 consumption rate. The mechanisms of these secondary reactions are not sufficiently well understood to allow experimental compensation for such effects. This means that all rate constants for O_3-olefin reactions must be regarded as upper limit values. Kinetic and mechanistic studies are needed to better characterize the reactive intermediates formed in O_3-olefin reactions and in other secondary reactions of O_3. However, in this field the use of the environmental chamber-FTIR combination is allowing atmospheric scientists to make excellent progress.

Evidence has also recently emerged that under smog conditions the elimination of some aromatics such as phenols and cresols by NO_3 reactions would dominate their degradation by OH (Carter *et al.*, 1981). Carter and colleagues have also shown that frequently used industrial nitrogen containing compounds such as amines and hydrazines, when released to the atmosphere, can be rapidly consumed by reactions with O_3 as well as OH radicals. The above points demonstrate how incomplete our knowledge of degradation pathways for chemicals released to the troposphere is at the present time. These findings also point out the inherent danger in determining the atmospheric lifetime of an atmospheric pollutant based on a single degradation pathway, for example reaction with OH radicals, which may not be dominant under polluted conditions.

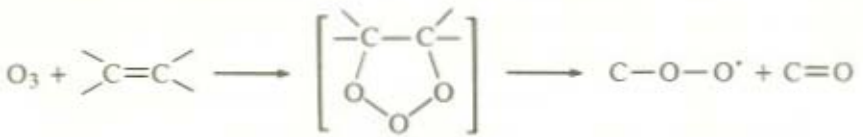
Nevertheless, because of ubiquitous distribution of the OH radical and its recognized importance in atmospheric degradation processes under unpolluted conditions, the intensive study of the reactions of OH and other atmospheric radicals has been taken as an initial step in describing and quantifying gas-phase atmospheric degradation processes.

2.3.2.3 Use of Large Reaction Vessels in Mechanistic Studies

As emphasized, the fate of many atmospheric chemicals in the gas phase is governed primarily by their reaction with OH and O_3. OH is particularly

important in that it is the major chain carrier of atmospheric reactions and determines the ability of other chemicals (e.g. O_3) to form oxidants. Because of the important role played by OH and O_3 in the degradation of atmospheric chemicals, much effect has gone into determining the mechanistic nature of these reactions. Reaction chambers coupled with GC and mass spectrometer analytical techniques have made remarkable progress in categorizing the various products from the OH and O_3 reactions with various chemicals, particularly hydrocarbons.

Much of the product identification for O_3-organic reactions has come from low pressure studies using fast flow photoionisation mass spectrometer techniques (Atkinson *et al.*, 1973). The early mechanistic explanations for ozone-alkene gas-phase reactions were based on the Criegee mechanism (Wei and Cvetanovic, 1963 and Criegee and Schröder, 1960) in which the initially formed 1, 2, 3 trioxolone fragments form a carbonyl compound and a reactive species (Criegee intermediate). A primary ozonide of any description has yet to be observed in the gas phase.



However, the intermediate dioxirane ($CH_2(O)_2$) has been identified in the low temperature reaction of O_3 with ethene (Lovas and Suenram, 1977 and Martinez *et al.*, 1977) and provides convincing evidence for the occurrence of the Criegee mechanism. In order to explain the excited molecular products and free radicals observed experimentally, O'Neal and Blumstein (1973) and Su *et al.* (1980) have suggested that the diradical ($CH_2(O)_2$) could rearrange by internal H-atom transfer together with some subsequent fragmentation steps to produce the excited molecular species. The general conclusion drawn over the years by various researchers is that the dioxirane will rearrange to form vibrationally excited formic acid which then subsequently fragments:

$$
\begin{aligned}
CH_2OO^* \longrightarrow HCO_2H^* &\longrightarrow CO + H_2O \\
&\longrightarrow CO_2 + H_2 \\
&\longrightarrow CO_2 + 2H \\
&\longrightarrow HCO_2H
\end{aligned}
$$

Bimolecular reactions are considered to be unimportant.

Although no direct monitoring of reactive intermediates formed in O_3-organic reactions has been made under atmospheric conditions, two research groups using reaction chamber/FTIR facilities have had some recent success in detecting a new major transitory product in the gas phase O_3–ethene reaction (Su *et al.*, 1980 and Niki *et al.*, 1981).

These groups have shown that as much as 38% of the CH_2O_2 species formed in the O_3–ethene reaction may take part in bimolecular reactions. They have also identified a new major product, formic acid anhydride, and suggest that its precursor is $HOCH_2OCHO$ formed by the reaction of thermally stabilized CH_2OO with CH_2O_2.

$$\begin{array}{lcl} O_3 + CH_2 = CH_2 & \longrightarrow & CH_2O + CH_2OO^* \\ CH_2OO^* & \longrightarrow & \text{products (62\%)} \\ CH_2OO^* + M & \longrightarrow & CH_2OO + M \quad (38\%) \\ CH_2OO + HCHO & \longrightarrow & HOCH_2OCHO \\ HOCH_2OCHO & \longrightarrow & (CHO)_2O + H_2 \end{array}$$

There have also been indications that the precursor to $(CHO)_2O$ undergoes gas to aerosol transformation at high concentrations (Niki *et al.*, 1981) suggesting that it could be a major aerosol precursor, at least in O_3–C_2H_4 reactions.

Another interesting development to come from reaction chamber/FTIR studies is the observation of a new intermediate hydroperoxy-hydroxy-methane (HO_2CH_2OH) formed in the reaction of HO_2 radicals with CH_2O radicals (Su *et al.*, 1979).

$$\begin{array}{lcl} HO_2 + CH_2O & \longrightarrow & HOOCH_2O \longrightarrow OOCH_2OH \\ OOCH_2OH + HO_2 & \longrightarrow & HOOCH_2OH + O_2 \end{array}$$

The fate of this new transient species, HO_2CH_2OH, in the photochemical oxidation of formaldehyde is considered to be either thermal or photochemically catalysed decomposition to ultimately yield HCO_2H and H_2O.

$$HO_2CH_2OH \longrightarrow H_2O + HCO_2H$$

The question as to whether such a transient species plays a role in the atmospheric photooxidation of CH_2O depends largely on the ability of the peroxyradical O_2CH_2OH to build up to high enough concentrations to allow it to react with HO_2 and/or NO.

There are several different reaction vessel methods available for obtaining mechanistic data for the reactions of OH radicals with organics. These include static small reactors where the OH is produced photolytically by the reaction of $O(^1D)$ atoms produced from the photodissociation of N_2O or NO_2 with H_2, H_2O or C_2H_6 (Henri and Carr, 1976; Cvetanovic, 1976 and Meagher and Heicklen, 1976) or by photolysis of H_2O_2 (Meagher and Heicklen, 1976) and the photolysis of HONO in large reaction vessels (Niki *et al.*, 1978; Cox *et al.*, 1980 and Kerr and Sheppard, 1981). The latter method based on the irradiation of HONO–NO–organic-air mixtures, with long path Fourier transform infrared spectroscopic or GC analysis, provides a potentially powerful tool for the elucidation of the mechanisms of OH radical initiated oxidation of chemicals under atmospheric conditions. In recent years, it has been convincingly demonstrated that OH radicals undergo predominantly

addition reactions with C_2H_4, C_3H_6 and other methyl-substituted olefins (Herron *et al.*, 1979). The resulting OH-adducts are expected to be collisionally deactivated in 1 atm of air. In the case of olefins containing weak allylic hydrogens, such as 1-butene, etc., it has been suggested that H-abstraction could occur 30% of the time (Atkinson *et al.*, 1977). The fate of the products from OH-addition or abstraction reactions with chemicals in the atmosphere is still very uncertain. However, in conjunction with computer modelling of smog chamber data, progress has been made in the interpretation of the complex secondary processes, occurring after the initial OH attack, for the simpler alkenes (C_2H_4, C_3H_6 and 2-C_4H_8) (Carter *et al.*, 1979) and for some aromatics (Atkinson *et al.*, 1980). There are several problems in the use of smog chamber data for the derivation of a specific chemical mechanism for atmospheric oxidation processes. For instance, in typical smog chamber experiments oxidation processes are initiated by both OH and O_3 and thus an adequate understanding of both OH and O_3-organic reaction mechanisms is required. In smog chamber experiments there are also, as yet, undefinable sources and sinks for chain carriers such as OH and HO_2. Such effects are commonly referred to as 'chamber effects'. A discussion of these interferences along with the utility and limitations of smog chamber data for computer modelling can be found in a review article by Carter *et al.* (1979).

2.3.2.4 Examples of Tropospheric Degradation by OH Radicals

Considering the importance of the OH radical the present state of our knowledge over the tropospheric degradation mechanisms for the following classes of compounds with OH radicals will be briefly outlined:

(a) alkanes
(b) alkenes
(c) aromatics
(d) aldehydes

Alkanes. The major degradation process for alkanes in the troposphere is their reaction with OH, which proceeds via H-abstraction. The initially formed alkyl radicals will react further with O_2.

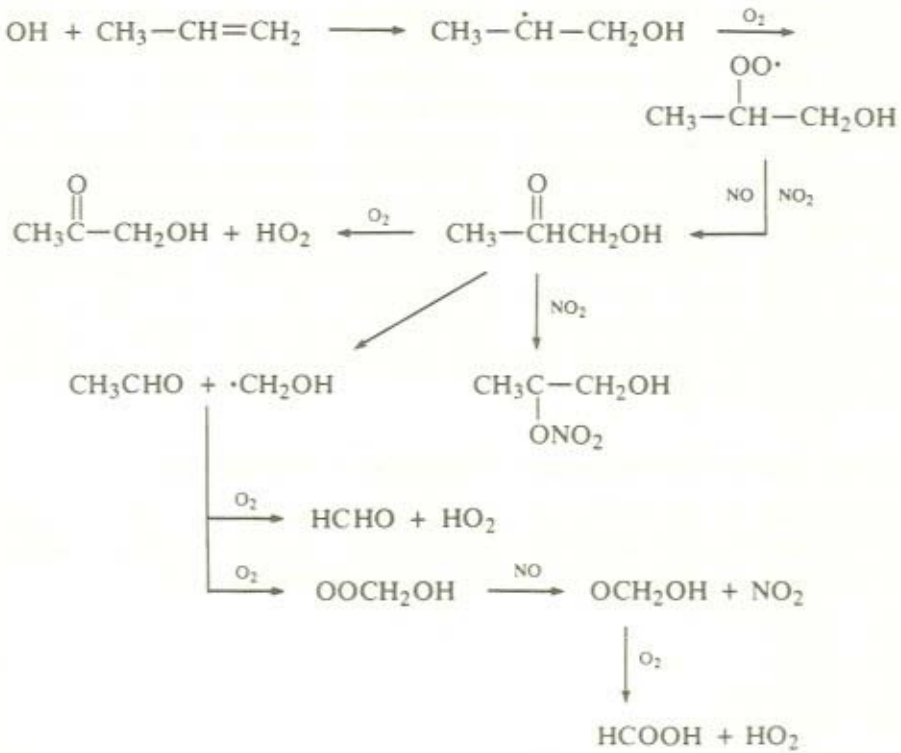
$$R + O_2 \longrightarrow RO_2$$

For the lower alkanes the subsequent steps can, for example, be represented as for C_2H_6:

$$C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2$$
$$C_2H_5O \longrightarrow CH_3 + HCHO$$
$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$$

The resulting aldehydes or ketones are further oxidized or photolysed.

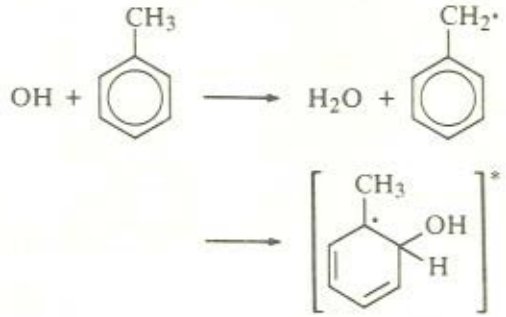
Alkenes. The initial reaction of OH with alkenes is one of addition (Atkinson *et al*., 1979). The reactions subsequent to the OH attack are also reasonably well understood. As in the case of the alkanes, the next step is the addition of O_2 forming a peroxy radical which can subsequently react with NO to form an alkoxy radical. This alkoxy radical can either decompose or further react with NO, NO_2 or O_2 forming nitrates and aldehydes or ketones, etc. Some of the possible pathways for the terminal addition of OH to propene are shown below.



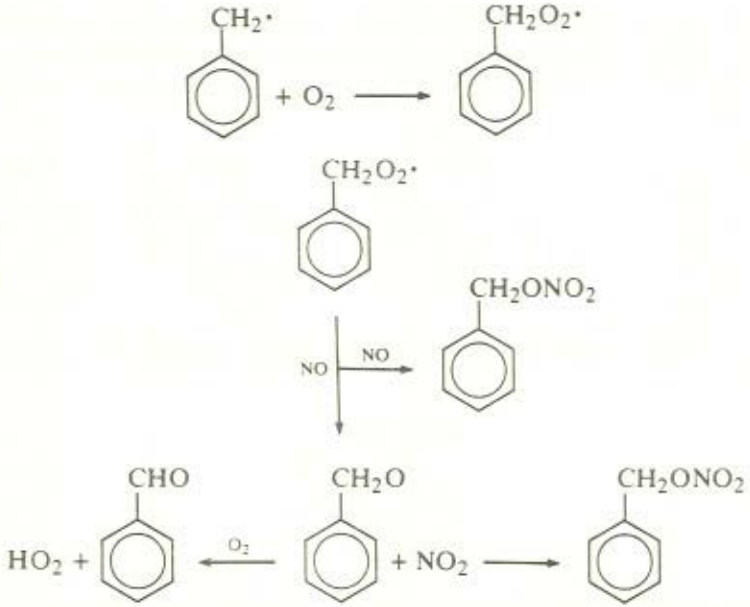
The expected major products will be formaldehyde or acetaldehyde which will react further in the atmosphere. For the alkenes with long side chains, H-atom abstraction will play a competing role and as will unimolecular isomerization of the alkoxy radicals. For the smaller alkenes in the atmosphere, reactions with OH are probably the major pathway of degradation, however, for highly branched and cyclic alkenes reactions with O_3 also play an important role.

Aromatics. The chemistry of OH-aromatic reactions is incompletely understood at present. Several good reviews are available detailing the progress in product analyses and the present status of the mechanistic understanding (Atkinson *et al*., 1979 and Atkinson *et al*., 1980). Using

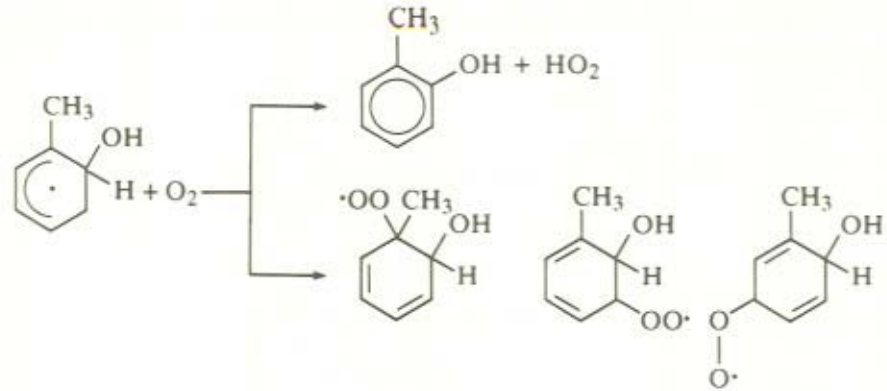
toluene as an example, the initial reaction of OH can be one of either addition or abstraction.



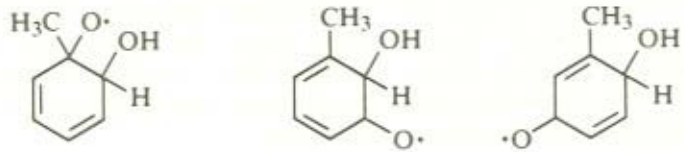
Obviously addition of OH to the benzene ring can occur at any of the *ortho, para* or *meta* positions forming a variety of OH-aromatic adducts but by analogy with O(^{3}P)-atom reactions (Gaffney *et al.*, 1976) attack at the *ortho* position is thought to be predominant. Under atmospheric conditions further reaction of these radicals with oxygen would be expected, with the subsequent formation of peroxide radicals. Thus, from the H-abstraction at the CH_3-substituted group on toluene, benzylaldehyde and benzylnitrate are the expected products. Benzaldehyde can further react with OH-radicals in a manner analogous to the aliphatic aldehydes.



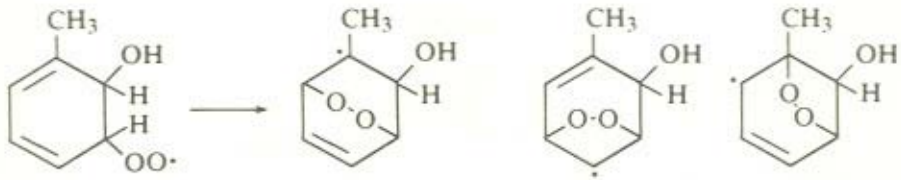
The radical formed by attack of OH at the benzene ring is also expected to react with oxygen.



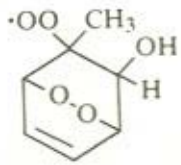
The peroxy radical can then react further with NO to form alkoxy radicals which through ring cleavage can lead to the many oxygenated species recently observed in aromatic oxidation systems (Darnall *et al*., 1979 and Takagi *et al*., 1980).



Atkinson *et al.* (1980) found, however, that the formation of α-dicarbonyls in NO_x–*o*-xylene–air systems was inconsistent with the above mechanism and postulated bicyclic aromatic–OH–O_2 adducts as the most reasonable alternative.



They envisage further reaction of these cyclized aromatic–OH–O_2 adducts with O_2.



These products could then react with NO to form an alkoxy radical or a stable nitrate. A series of highly favourable β-scission fragmentations of the

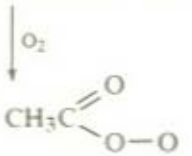
bicyclic peroxy alkoxy radicals could lead to the formation of α-dicarbonyl products. This reaction mechanism is highly speculative and has only been crudely outlined. Obviously a great deal more work is necessary in order to understand the detailed chemistry of such complex systems.

Aldehydes. With the exception of formaldehyde, which is also an important product from the photo-oxidation of methane in the atmosphere, aldehydes are important secondary products from the photodegradation of organic air pollutants. The aldehydes react with OH in a manner analogous to that of the alkanes. Formaldehyde, for example, yields the HCO radical which can further react with O_2 to form HO_2.

$$HCHO + OH \longrightarrow H_2O + HCO$$
$$HCO + O_2 \longrightarrow HO_2 + CO$$

Acetaldehyde reacts with OH to form CH_3CO which reacts further with O_2 to form the acetyl peroxy radical.

$$CH_3CHO + OH \longrightarrow CH_3CO + H_2O$$



This radical in the presence of NO_2 leads to the formation of peroxyacetylnitrate (PAN), one of the more notorious components of smog.

$$CH_3C(O)—O—O\cdot + NO_2 \rightleftharpoons CH_3C(O)—O—O—NO_2$$

Similar reaction pathways are expected for higher aldehydes. Although the quantum yields for photodissociation for most aldehydes and ketones in air at 1 atm are not well known, Cox *et al.* (1981) have demonstrated that direct photolysis can be one of the dominant loss processes. Using an assumed quantum yield of 1 for photodissociation, they demonstrated that for simple aldehydes, OH reaction and photolysis occur at apparently comparable rates. It should be stressed, however, that recent results of CH_3CHO photolysis indicate a quantum yield of only 0.21 (Weaver *et al.*, 1976). Such a low quantum yield would significantly increase the importance of the OH + aldehyde reaction. Much more experimental work is obviously needed on the photolysis rates of simple aldehydes and ketones in the atmosphere before the importance of the major degradation pathways can be quantified with certainty.

Degradation mechanisms have been published for other groups of compounds including alcohols, organic acids, sulphur containing compounds, and amines (see Atkinson *et al.*, 1979 and references therein).

2.3.3 APPRAISAL OF LABORATORY GAS PHASE TECHNIQUES

OH radicals are presently considered to be the most reactive species in initiating the destruction of organic chemicals in the atmosphere. Correspondingly, the inverse of the product (OH reaction rate constant) × (average atmospheric OH concentration) for a certain compound X should be a rough measure (at least an approximate upper limit) for the atmospheric lifetime (τ) of compound X.

$$\tau = (k(X + \mathrm{OH} \longrightarrow \text{products}) \times [\mathrm{OH}])^{-1}$$

For selected molecules, the atmospheric lifetimes are reported in Table 2.3.3.

Since typical transport times in the troposphere are of the order of 1 year (Junge, 1978), chemicals with an OH lifetime exceeding this period would be expected to be fairly homogeneously distributed throughout the troposphere. Field measurements for N_2O, CH_4, H_2, and some freons confirm this observation. This long lifetime will allow migration of these substances into

Table 2.3.3 Tropospheric lifetimes (τ) with respect to OH reactions assuming an average OH concentration 10^6 molecules cm^{-3}

Molecule	τ (years)	Reference	Molecule	τ (days)	Reference
N_2O	>163	3	C_2HCl_3	2.9	2
CF_2Cl_2	> 81	3	1,3,5-trimethyl-benzene	2.3	2
CHF_2Cl	7.4	1	H_2S	2.2	1
H_2	6.4	1	cyclohexane	1.6	2
CH_4	4.1	1	C_2H_4	1.4	2
CH_3CCl_3	2.7	1	diethylether	1.3	2
CH_3CN	1.6	4	diethylthioether	1.3	2
HCN	1.1	5	CH_2O	0.9	1
CH_3Cl	0.79	1	propene	0.44	2
O_3	0.68	1	phenol	0.41	4
peroxyacetyl-nitrate (PAN)	0.19	2	*o*-cresol	0.29	2
HNO_3	0.26	5	α-pinene	0.21	2
CO	0.12	1	$(CH_3)_2NH$	0.18	2
C_2H_6	0.12	2	1,3-butadiene	0.16	2
HCOOH	0.09	4	cyclohexene	0.16	2
CH_3OH	0.030	2	aniline	0.096	4
benzene	0.027	2			
o-xylene	0.027	2			
ethyl acetate	0.017	2			
n-C_4H_{10}	0.013	2			

Volz *et al.*, 1981; Baulch *et al.*, 1980 (1); Atkinson *et al.*, 1979 (2); Hampson and Garvin, 1978 (3); Wahner and Zetzsch, 1981 (4); Fritz *et al.*, 1981 (5))

the stratosphere, and in these cases, the possible chemical implications for the ozone layer must be considered. On the other hand, chemicals with OH lifetimes of the order of 1 day or even shorter will show large local concentration deviations and are not expected to reach the stratosphere.

Of course, the possible contributions of other initial degradation processes (photolysis, reaction with O, O_3) or non-degradation loss (wash-out, rain-out, dry deposition) have to be considered. With respect to the long-lived species, additional loss processes such as the destruction on active sites on the earth surface are of special importance.

Having established the rate for the initial degradation step of a chemical, a number of intermediates which may be harmful have to be considered. To account for these compounds, the complete degradation sequence of the chemical must be known. In many cases this situation is far from being realized, but encouragement can be taken from the fact that the general chemistry of the stratosphere is now considered to be fairly well understood. Acceptable agreement has been achieved between field measurements and model calculations based on data from laboratory experiments. The chemistry of the troposphere is considerably more complex, but through the use of large 'environmental' reaction chambers good progress has been made in recent years with respect to the elucidation of the general oxidation mechanisms. The present state of the art may be illustrated by the discussion of intentional release of certain chemicals to the atmosphere as smog inhibitors. In 1974, Heicklen (Jayanty *et al.*, 1974) proposed the use of diethylhydroxylamine (DEHA) for this purpose, and subsequently he vigorously pursued permissions from local authorities for field tests. In the meantime, medical tests have been performed on DEHA with respect to its toxicologic, carcinogenic and mutagenic effects. Rate constants have been determined for the reactions of DEHA with radicals (OH, O, HO_2) and smog chamber experiments have been performed on the overall effects of DEHA on smog formation in simulated atmospheres. However, neither the medical nor the physico-chemical tests have prompted definitive conclusions as to whether the release of DEHA to the polluted atmosphere is more beneficial than harmful (Maugh II, 1976; Heicklen, 1981a, b; Cupitt, 1981). This uncertainty is due to the unknown influences of weather conditions, the interactions between different degradation mechanisms in heavily polluted air, the contributions of heterogeneous reactions, etc.

2.3.4 CONCLUSIONS

Mechanistic and quantitative studies of OH radical reactions with organic chemicals are an important initial step in understanding the gas-phase degradation of these compounds in the atmosphere. Environmental chamber techniques can simulate complex reaction processes at atmospheric pressure

and have been useful in developing relative reaction rate data and in identifying important reaction intermediates. However, because present knowledge of degradation pathways is incomplete, estimates of atmospheric lifetime based only on a single reaction pathway (OH radical reactions) are inherently uncertain. This would be particularly true of processes in polluted air, where there remains a good deal of uncertainty as to the interactions among different degradation mechanisms. Further elucidation of these interactions will be essential to the prediction of quantitative transformations of organic substances in the polluted atmosphere.

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