

CHM 5423 – Atmospheric Chemistry
Notes on reactions of organics in the troposphere (Chapter 5)

5.1 Introduction

In general, the lifetime of a molecule in the troposphere is governed by a variety of processes. Some molecules decompose by photodissociation. Other molecules, particularly polar molecules, can be physically removed from the troposphere by rainout, washout, and deposition. Molecules can also be removed by chemical reaction. Finally, molecules with no significant removal processes in the troposphere can migrate into the stratosphere. In this chapter, we focus on the chemical reactions of organic molecules.

Organic molecules are an important trace constituent in the lower atmosphere of the Earth. Organic molecules have both natural and anthropogenic sources, and can be released directly into the atmosphere as a primary pollutant, or can form from the transformation of other organic molecules as secondary pollutants. In this chapter we examine the main reactions of general classes of organic molecules in the troposphere.

5.2 Oxidizing species in the troposphere

While the general tendency of organic molecules in the troposphere is to go from reduced to oxidized molecules, the reactions do not begin with the direct reaction of molecules with molecular oxygen. Instead, reactions are initiated with oxidant molecules, generally radical species that exist at low concentration. In this section we indicate the major oxidant species found in the troposphere.

OH (daytime)

Hydroxyl radical is the main oxidizing species in the troposphere. It exists at extremely low concentrations, typically $\sim 1 \times 10^6$ molecules/cm³, with large fluctuations around this value. Hydroxyl radical also has an extremely short lifetime in the troposphere. Because of this, and because the major sources of hydroxyl radicals are all photochemical reactions, it is an important reactant in the daytime, but essentially absent at night.

The main source of hydroxyl radical in the troposphere is from photodissociation of ozone, followed by reaction of excited oxygen atoms with water molecules.



The threshold wavelength for photodissociation of ozone to produce $\text{O}({}^1\text{D}) + \text{O}_2({}^1\Delta)$ is 310. nm. At wavelengths shorter than this, the quantum yield for production of $\text{O}({}^1\text{D})$ is approximately 0.9. The other main photodissociation pathway is



which produces ground state products. The oxygen atom produced by reaction 2.3 does not have sufficient energy to react with water molecules, and usually reforms ozone by the termolecular recombination reaction



At wavelengths longer than 310. nm the quantum yield for the production of $\text{O}({}^1\text{D})$ atoms was expected to quickly drop to zero. In fact, while the quantum yield decreases, it remains in the region 0.1-0.2 (Fig 3.3, Chapter 3). This is because a second, spin forbidden process that forms an $\text{O}({}^1\text{D})$ atom and a $\text{O}_2({}^3\Sigma)$ molecule occurs.

The fate of the electronically excited oxygen atom produced in reaction 2.1 is either quenching, to form a ground state oxygen atom, or reaction with a water molecule to form two hydroxyl radicals. The fraction of $\text{O}({}^1\text{D})$ atoms forming hydroxyl radical is a sensitive function of relative humidity, which governs the concentration of water molecules in the gas phase.

Two other minor sources of hydroxyl radical are also photochemical processes. They are



Photodissociation of organic peroxides (ROOH) can also produce hydroxyl radical, but concentrations of organic peroxides are generally lower than the concentration of hydrogen peroxide.

It is estimated that ~ 80% of OH radical production is from ozone photodissociation, with the remaining molecules generated by reactions 2.5, 2.6, and other minor processes. While there are a few non-photochemical sources of hydroxyl radical, they are much less important, though they do generate small concentrations of hydroxyl radical at night.

O₃ (daytime + nighttime)

The main source of ozone in the troposphere is photodissociation of nitrogen dioxide



followed by the termolecular recombination reaction forming ozone. Nitrogen oxides are often found as a pollutant in urban areas, and so ozone concentrations in such regions are generally higher than in rural areas. In fact, concentrations of NO, NO₂ and O₃ in the daytime are linked by the Leighton mechanism, which will be discussed later.

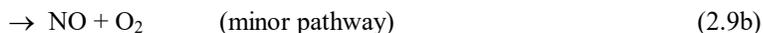
While ozone is produced by a photochemical process, it has a half-life in the troposphere of a few days, and so is present both in the daytime and at night. A typical ozone concentration is ~ 1. x 10¹² molecule/cm³, with fluctuations around this value between daytime and night time, and based on geographic location.

NO₃ (night time)

Nitrogen trioxide is produced by the reaction of nitrogen dioxide with ozone



During the daytime nitrogen trioxide disappears due to photodissociation, which is fast due to the fact that the molecule absorbs light throughout the visible region of the spectrum

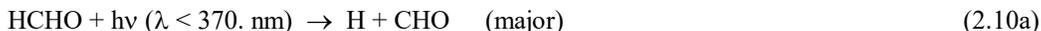


At night, when photodissociation does not occur, concentrations of nitrogen trioxide gradually increase as NO₂ is converted to NO₃ by reaction 2.8.

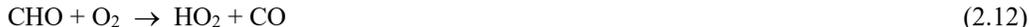
A typical concentration of NO₃ is ~ 1. x 10⁹ molecule/cm³.

HO₂ (daytime)

Hydroperoxyl radical is generated photochemically in the troposphere. The main source of hydroperoxyl radical is photodissociation of aldehydes. For example



HO₂ is then generated by termolecular or bimolecular reaction of the major products of the photodissociation reaction



Larger aldehydes are also capable of generating H and CHO radicals and so are additional sources of hydroperoxyl radical.

Since the lifetime of hydroperoxyl radical is short, it is found at high concentrations only during the daytime. Typical concentrations of hydroperoxyl radical are $\sim 2.0 \times 10^8$ molecule/cm³.

Cl (daytime)

There is some evidence that Cl atoms can play a role in the chemistry of remote regions over the ocean. Chlorine atoms can be generated by a number of processes, the most important of which is believed to be reaction with nitrogen oxides such as dinitrogen pentoxide



Chlorine atom concentrations are estimated to be $\sim 1. \times 10^2$ molecules/cm³. Because chlorine atoms are expected to be chemically reactive, they could play a role in the chemical processes over mid-ocean, where concentrations of other oxidizing species are also low.

A summary of typical 24-hour average concentrations of major oxidizing species in the troposphere is given in Table 2.1. It is important to remember that actual concentrations of these species vary widely from these "average" values, and that in some cases average values themselves have a great deal of uncertainty. However, these average values are useful in estimating half-lives for molecules in the troposphere.

Table 2.1 - Typical concentrations of oxidizing species in the troposphere

Molecule	Time present	24-hour average concentration (molecule/cm ³)
OH	day	$1. \times 10^6$
O ₃	day and night	$1. \times 10^{12}$
NO ₃	night	$1. \times 10^9$
HO ₂	day	$2. \times 10^8$
Cl	day	$1. \times 10^2$

5.3 Reactions of alkanes

Alkanes make up an important class of molecules found in the troposphere. In addition, many other organic molecules go through reactions similar to those of alkanes. This makes alkanes a useful starting point in a discussion of the oxidation of organic molecules.

In giving reactions of molecules in the troposphere we will proceed from an initial molecule to stable intermediate or final products. We will concentrate on the main pathways for reaction as well as important side reactions, and will discuss both daytime and night time reactions of molecules.

Methane + OH

Methane (CH₄) is the most abundant alkane in the atmosphere, due in part to its unusually long lifetime with respect to reaction with OH radical. The reaction of hydroxyl radical with methane and other alkanes is the

abstraction reaction, where a hydrogen atom is removed from the alkane to form an alkyl radical and water, followed by subsequent reactions of the alkyl radical, as will be discussed. The main sequence of reactions for the daytime oxidation of methane are as follows:



The general sequence of reactions is alkane \rightarrow alkylperoxy radical \rightarrow alkoxy radical \rightarrow aldehyde. Reaction 3.1 is slow while the other reactions extremely fast.

The rate constant for reaction 3.1 at 298. K is $k_{bi} = 6.2 \times 10^{-15} \text{ cm}^3/\text{molecule}\cdot\text{s}$. Using our typical 24-hour average hydroxyl radical concentration, $[\text{OH}] = 1. \times 10^6 \text{ molecule}/\text{cm}^3$, we get

$$k_f = k_{bi} [\text{OH}] = 6.2 \times 10^{-9} \text{ s}^{-1} \quad (3.5)$$

$$t_{1/2} = \ln(2)/k_f = 1.2 \times 10^8 \text{ s} = 3.5 \text{ years} \quad (3.6)$$

where k_f is the effective first order rate constant for the reaction. The half-life for methane is sufficiently long that methane has the opportunity to mix well throughout the troposphere, though there are small differences between the methane concentration in the Northern and Southern hemispheres, as crossover of gases across the tropics takes place on the same timescale as the half-life.

Alkane + OH

Larger alkanes react in the same manner as methane, though there are usually a variety of possible initial products from the abstraction reaction. Rate constants for the alkane + OH reaction are usually fit to an equation of the form

$$k_{bi} = B T^n \exp(- C/T) \quad (3.7)$$

where B, C, and n are fitting parameters obtained from experimental data. For all alkanes other than methane the value $n = 2$ is used in eq 3.7. Values for the fitting parameters for eq 3.7 for several alkanes are given in Table 3.1.

Table 3.1 - Rate constant data for the alkane + OH reaction*

Alkane	k_{bi}^{298} ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	B ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	C (K)	n
methane	0.00618×10^{-12}	0.0965×10^{-18}	1082.	2.58
ethane	0.254×10^{-12}	15.2×10^{-18}	498.	2.
propane	1.12×10^{-12}	15.5×10^{-18}	61.	2.
n-butane	2.44×10^{-12}	16.9×10^{-18}	- 145.	2.
2-methylpropane	2.19×10^{-12}	11.6×10^{-18}	- 225.	2.
n-pentane	4.0×10^{-12}	24.4×10^{-18}	- 183.	2.
2-methylbutane	3.7×10^{-12}			
2,2-dimethylpropane	0.85×10^{-12}	18.0×10^{-18}	189.	2.
n-hexane	5.45×10^{-12}	15.3×10^{-18}	- 414.	2.

* Values for k_{bi} are given at 298. K. Fitting parameters for finding k_{bi} at other temperatures are for use in the equation $k_{bi} = B T^n \exp(- C/T)$.

For most alkanes there are a variety of products that can form from the abstraction reaction. For example, for the reaction of hydroxyl radical with propane, there are two products



One would expect the distribution of products should depend on three factors - a statistical factor (the number of equivalent hydrogens in the alkane), the ease of breaking the C-H single bond, and the stability of the alkyl radical formed from the reaction.

Typical values for C-H bond strengths in alkanes are ~ 410. kJ/mol for a primary hydrogen, ~ 395. kJ/mol for a secondary hydrogen, and ~ 385. kJ/mol for a tertiary hydrogen. Therefore, breaking the C-H bond for a tertiary hydrogen is easiest to accomplish, while breaking a C-H bond in a primary hydrogen is most difficult to accomplish. The stability of the alkyl radical formed follows the same pattern, with tertiary alkyl radicals expected to be most stable and primary alkyl radicals least stable.

Models have been developed for predicting the rate constant for reaction 3.1 and the branching ratio for the distribution of alkyl radicals formed (branching ratio is similar to primary quantum yield in photochemistry, and represents the fraction of particular products formed per reactant molecule). One simple model is as follows:

$$k_{bi} = N_p k_p + N_s k_s + N_t k_t \quad (3.9)$$

In this equation N_p , N_s , and N_t are the number of primary, secondary, and tertiary hydrogen atoms in the alkane, and k_p , k_s , and k_t are rate constants for reaction of each type of hydrogen atom. Typical values for these rate constants (at $T = 298. \text{ K}$) are $k_p = 4.5 \times 10^{-14} \text{ cm}^3/\text{molecule}\cdot\text{s}$, $k_s = 4.7 \times 10^{-13} \text{ cm}^3/\text{molecule}\cdot\text{s}$, and $k_t = 1.95 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$.

If we use eq 3.9 to predict the overall rate constant and branching ratio for the propane + OH reaction at $T = 298. \text{ K}$, we get

$$k_{bi}^{298} = 6 (4.5 \times 10^{-14}) + 2 (4.7 \times 10^{-13}) = 1.21 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s} \quad (3.10)$$

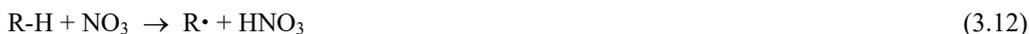
$$\phi(\text{CH}_3\text{CHCH}_3) = [2 (4.7 \times 10^{-13})]/(1.21 \times 10^{-12}) = 0.78 \quad (3.11)$$

Both the overall rate constant for the reaction and the branching ratio are in reasonably good agreement with experimental results. More sophisticated models, which account for additional features in the parent alkane, have also been developed.

Using the data in Table 3.1, half-life values for small alkanes with respect to the hydroxyl radical reaction can be found. Except for methane ($t_{1/2} = 3.5$ years) and ethane ($t_{1/2} = 32$ days), alkane half-lives are typically a week or less.

Alkane + NO₃

Alkanes can also react at night with NO₃, which gradually forms after sunset. The general reaction is again abstraction of a hydrogen atom, and may be written as



Although night time concentrations of NO₃ are larger than daytime concentrations of OH, the rate constant for reaction 3.12 is much slower than that for the corresponding abstraction reaction with hydroxyl radical. For example, using $[\text{NO}_3] = 1. \times 10^9 \text{ molecule}/\text{cm}^3$ and $k_{bi}^{298}(\text{CH}_3\text{CH}_2\text{CH}_3) = 1.7 \times 10^{-17} \text{ cm}^3/\text{molecule}\cdot\text{s}$, we get $k_f = 1.7 \times 10^{-8} \text{ s}^{-1}$, about 100 times smaller than the value $k_f = 1.12 \times 10^{-6} \text{ s}^{-1}$ for the effective first order rate constant for the daytime reaction of propane with OH. Reaction 3.12 is therefore a minor pathway for the reaction of alkanes in the troposphere. The reaction is nevertheless of some importance, as it is a minor source for nitric acid and it removes NO_x from the troposphere.

Alkyl radical reaction

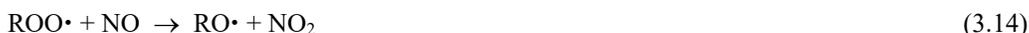
The only significant reaction of the alkyl radical formed from the abstraction of a hydrogen from an alkane is formation of an alkylperoxy radical by the three body process



where $ROO\cdot$ is an alkylperoxy radical. The effective bimolecular rate constant for this reaction, at 1 atm pressure and 298. K, is $k_{bi} = 1 - 2 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$, leading to a half-life for alkyl radicals of $t_{1/2} \sim 10 \text{ nsec}$. The reaction is essentially instantaneous in the troposphere. There is no other competing reaction involving alkyl radicals in the troposphere.

Alkylperoxy radical reactions

The main daytime reaction of alkylperoxy radicals in the troposphere is with NO . There are two reactions that take place



For small alkylperoxy radicals reaction 3.14 dominates. For large alkylperoxy radicals the recombination reaction can become important. For example, looking at n-alkylperoxy radicals, the branching ratio for reaction 3.15 increases from $\phi = 0.02$ (for n-propylperoxy radical) to $\phi = 0.36$ (for n-octylperoxy radical). So reaction 3.15 can become important for large alkylperoxy radicals. Note that reaction 3.15 effectively removes NO_x from the atmosphere, as reactions and photodissociation of $RONO_2$ are slow compared to physical removal.

Alkylperoxy radicals can also react with hydroperoxyl radical (HO_2) or with other alkylperoxy radicals by recombination. For the reaction with hydroperoxyl radical a variety of products have been observed.



The first reaction (3.16a) is an important source of organic peroxides in the troposphere. The other two reactions form small amounts of oxygenated compounds (carbonyls, alcohols).

The reactions of alkylperoxy radicals are similar to those with hydroperoxyl radical, and can therefore lead to a variety of products. Since concentrations of alkylperoxy radicals are generally much smaller than hydroperoxyl radical concentrations, the alkylperoxy self-reactions make only a small contribution to the fate of these radicals in the troposphere.

The reaction of $ROO\cdot$ (3.14 and 3.15) and with hydroperoxyl radical (3.16 a-c) are of comparable importance during the daytime, and so are sensitive to differences in the concentration of NO and HO_2 from their typical 24-hour average values. The half-life for the daytime reaction of $ROO\cdot$ by any of these processes is about 1 minute, and so the reactions are relatively fast.

At night, alkylperoxy radicals will react with nitrogen trioxide.



Reaction 3.17 forms alkoxy radical and converts nitrogen trioxide back to nitrogen dioxide. The reaction is slow, but it is the only significant night time reaction involving alkylperoxy radical.

Alkoxy radical reactions

There are a variety of reactions of the alkoxy radicals formed by reaction 3.14 and other minor reactions. The actual reactions taking place depend on the size and structure of the alkoxy radical as well as concentrations of potential reactants.

Alkoxy radicals can react with molecular oxygen to form stable carbonyl compounds by the process



For example, methoxy radical will react to form formaldehyde



Because of the high concentration of molecular oxygen in the troposphere, reaction 3.18 is fast. For $\text{CH}_3\text{O}\cdot$ radical at 1 atm pressure and 298. K the half-life for the reaction is 70. μsec .

While reaction 3.18 is fast, there are other processes that can be competitive with this reaction in the troposphere. For larger alkoxy radicals decomposition is also a fast process.



The energy for the bond breaking required for reaction 3.20 to occur comes from the excess energy in the alkoxy radical formed by reaction 3.14. Bond breaking tends to favor the formation of the more stable alkyl radical. For example



Reaction 3.21 b forms a more stable alkyl radical and so is favored in the decomposition reaction.

Large alkoxy radicals can also undergo isomerization, leading to the formation of "alkyl-like" radicals. Isomerization requires a minimum of a four carbon chain so that isomerization can occur through a six atom ring transition state. For example



The radical formed from isomerization, while technically not an alkyl radical, will react essentially react as alkyl radicals react.

The relative importance of isomerization, decomposition, and reaction with molecular oxygen depends on several factors. For radicals sufficiently large that they can undergo isomerization, this is the dominant process. In the absence of isomerization, reaction with O_2 is usually the fastest process for small alkoxy radicals. For larger radicals and in the absence of isomerization decomposition can also become a significant process. Note that whichever reaction takes place, the half-life for the reaction is very short ($\sim 10\text{-}100 \mu\text{sec}$).

Table 3.2 gives the branching ratio for reaction with O_2 , decomposition, and isomerization for several alkoxy radicals.

Table 3.2 - Branching ratios for reactions of selected alkoxy radicals

Radical	ϕ_{O_2}	ϕ_{dec}	ϕ_{iso}
$CH_3O\cdot$	~ 1	$< 10^{-5}$	-
$CH_3CH_2CH_2CH_2O\cdot$	0.2	0.002	0.8
$CH_3CH_2CH(O)CH_2CH_3$	0.7	0.3	-

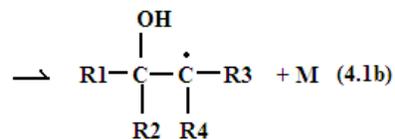
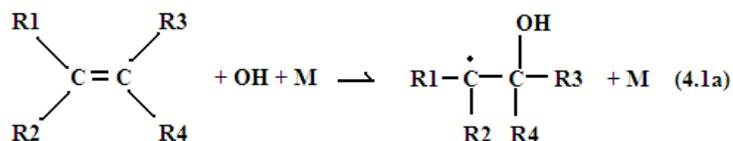
5.4 Reactions of alkenes and alkynes

Unlike alkanes, alkenes can undergo both abstraction and addition reactions. During the daytime the major reactions are with hydroxyl radical and ozone. The ozone reaction will also occur at night, though ozone concentrations will be somewhat lower at night than during the day.

Alkene + OH

Hydroxyl radicals can abstract hydrogens from alkenes in the same way they abstract hydrogen from alkanes. The sequence of reactions is generally the same as for the alkane + OH reactions. Because of this, and because abstraction is generally much slower than addition for the reaction of hydroxyl radical with alkenes, we will not discuss the sequence of reactions any further.

Hydroxyl radical can also react with alkenes by addition at the C=C double bond. The reaction can be modeled as a termolecular recombination reaction. For most alkenes, there are two possible sets of products. Note that R1, R2, R3, and R4 represent either H atoms or alkyl groups.



For example, the reaction of 1-methyl ethene ($CH_3CH=CH_2$) gives two possible products



We would expect that the branching ratio should be larger for the reaction that forms the more stable radical. This is in fact usually observed. For the above reaction, for example, $\phi_{4.2a} = 0.65$ at $T = 298$. K.

The above reaction exhibits a negative value for E_a , the activation energy, as is often the case for recombination reactions. As previously discussed, this apparent negative activation energy is a consequence of the

actual mechanism for the reaction being more complicated than as shown in eq 4.1. As a result, the addition reaction becomes faster at lower temperature.

Table 4.1 gives the Arrhenius parameters for the alkene + OH addition reaction for several molecules, as well as the value for the bimolecular rate constant at $T = 298$. K. For two of the alkenes (ethene and propene) the high pressure (bimolecular) limit has not actually been reached, and so a more complicated expression for k_{bi} should be used, as discussed in the Chapter 4 handout (eq 4.22 or 4.23 of the Chapter 4 handout).

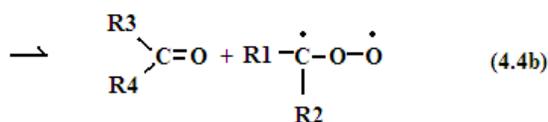
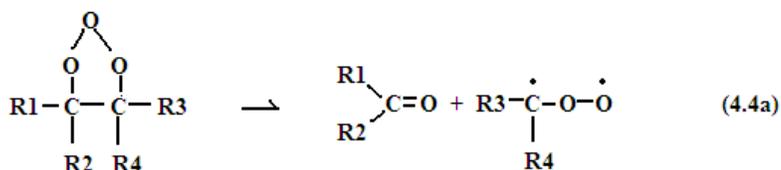
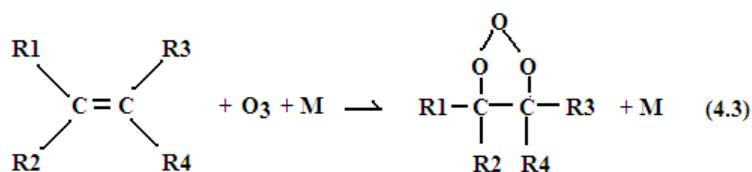
Table 4.1 - Rate constant data for the alkene + OH reaction*

Alkene	k_{bi}^{298} ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	A ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	E_a (kJ/mol)
ethene	8.52×10^{-12}	1.96×10^{-12}	- 3.64
propene	26.3×10^{-12}	4.85×10^{-12}	- 4.19
1-butene	31.4×10^{-12}	6.55×10^{-12}	- 3.88
cis-2-butene	56.4×10^{-12}	11.0×10^{-12}	- 4.05
trans-2-butene	$640. \times 10^{-12}$	10.1×10^{-12}	- 4.57
2-methylpropene	51.4×10^{-12}	9.47×10^{-12}	- 4.19
1-pentene	31.4×10^{-12}	-	-
cyclopentene	$67. \times 10^{-12}$	-	-

* Values for k_{bi} are given at 298. K and 1.0 atm. Fitting parameters for finding k_{bi} at other temperatures are for use in the equation $k_{bi} = A \exp(-E_a/RT)$.

Alkene + O₃

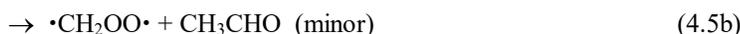
Unlike alkanes, alkenes can also react with ozone (O₃). Although ozone is almost exclusively produced by photochemical processes, it typically has a lifetime of several days in the troposphere. Therefore the alkene + O₃ reaction occurs at night as well as during the day. The reaction is by addition, and initially produces an ozonide, which then decomposes to give a carbonyl compound and a Criegee intermediate (diradical), which can then undergo a variety of additional reactions. The reaction can be written as follows



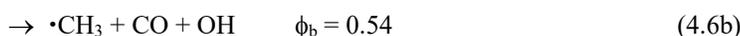
The addition reaction initially produces an ozonide (4.3), reducing the bond order of the alkene double bond. This is followed by a breaking of the C-C single bond for the carbons attached to ozone, along with breaking one of the O-O

bonds. In most cases this will lead to the formation of two sets of products (4.4a,b), a carbonyl compound and an Criegee intermediate. This intermediate can be observed in solution, where it is stabilized by interaction with solvent molecules. The $\dot{\text{C}}\text{H}_2\text{OO}\cdot$ Criegee intermediate has recently been identified in the gas phase using infrared spectroscopy.

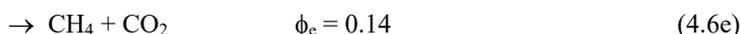
As is the case for many other reactions, in cases where there are several sets of potential products we can predict the products more likely to form based on the stability of the radicals that are produced. For example, for the reaction of propene with ozone there are two sets of possible products



The Criegee intermediate formed from the decomposition of the ozonide in the alkene + O_3 reaction has a large amount of energy, and can participate in a variety of subsequent reactions. One study found the following branching ratios for $\text{CH}_3\dot{\text{C}}\text{HOO}\cdot$ (at $p = 1.0$ atm and $T = 298$. K)



$$\phi_{\text{c+d}} = 0.17$$



In some cases mechanisms for the formation of these various products have been proposed. The stabilized Criegee intermediate formed by the quenching reaction (4.6a) will undergo further reaction, as will the radicals formed from the other pathways.

Table 4.1 gives the Arrhenius parameters for the alkene + OH addition reaction for several molecules, as well as the value for the bimolecular rate constant at $T = 298$. K.

Table 4.2 - Rate constant data for the alkene + O_3 reaction*

Alkene	k_{bi}^{298} ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	A ($\text{cm}^3/\text{molecule}\cdot\text{s}$)	E_a (kJ/mol)
ethene	1.6×10^{-18}	9.14×10^{-15}	21.45
propene	10.1×10^{-18}	5.51×10^{-15}	15.61
1-butene	9.64×10^{-18}	3.36×10^{-15}	14.50
cis-2-butene	$125. \times 10^{-18}$	3.22×10^{-15}	8.05
trans-2-butene	$190. \times 10^{-18}$	6.64×10^{-15}	8.80
2-methylpropene	11.3×10^{-18}	2.70×10^{-15}	13.57
1-pentene	10.0×10^{-18}	-	-
cyclopentene	$570. \times 10^{-18}$	1.8×10^{-15}	2.91

* Values for k_{bi} are given at 298. K. Fitting parameters for finding k_{bi} at other temperatures are for use in the equation $k_{\text{bi}} = A \exp(-E_a/RT)$.

The most important feature of the alkene + O_3 reaction is the yield of hydroxyl radical for different alkenes. In general, larger alkenes produce more hydroxyl radicals per alkene. For example, the yield of OH radical for some small alkenes are $\phi_{\text{OH}} \sim 0.10$ (for ethene), $\phi_{\text{OH}} \sim 0.25$ (for propene), and $\phi_{\text{OH}} \sim 0.40$ (for 1-butene). Since these

reactions can occur at night, they represent a non-photochemical source of hydroxyl radical, and so lead to extremely low concentrations of OH at night ($< 10^2$ molecule/cm³).

During the daytime both the alkene + OH reaction and the alkene + O₃ reactions are important. Values for the effective first order rate constants for addition of OH and addition of O₃ are given in Table 4.3, along with branching ratios and values for half-life. Half-lives for alkenes with respect to reaction are on the order of a few hours, with both the addition reaction with OH and the addition reaction with O₃ being important. At night the only significant reaction taking place is the alkene + O₃ reaction.

Table 4.3 - Effective first order rate constants, branching ratios, and lifetimes for alkene addition reaction

Alkene	k _f (OH)*	k _f (O ₃)*	φ _{OH}	φ _{O₃}	t _{1/2}
ethene	8.52 x 10 ⁻⁶ s ⁻¹	1.6 x 10 ⁻⁶ s ⁻¹	0.84	0.16	19.0 hr
1-butene	31.4 x 10 ⁻⁶ s ⁻¹	9.64 x 10 ⁻⁶ s ⁻¹	0.70	0.30	4.7 hr
1-hexene	37. x 10 ⁻⁶ s ⁻¹	11.0 x 10 ⁻⁶ s ⁻¹	0.77	0.23	4.0 hr

* Values for k_{bi} are given at 298. K and 1.0 atm pressure, using [OH] = 1.0 x 10⁶ molecule/cm³, [O₃] = 1.0 x 10¹² molecule/cm³.

Alkene + NO₃

The night time addition reaction of alkenes with NO₃ is slow, but represents a potential source of organic nitrates in the troposphere. For larger alkenes the abstraction reaction can also occur, but this will also be slow in comparison with reaction with ozone.

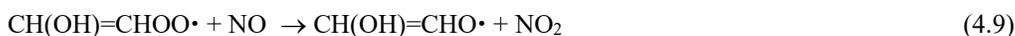
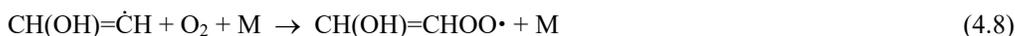
Alkynes

The main daytime reaction of alkynes is the addition reaction with hydroxyl radical. For example, for acetylene, the reaction is



The effective bimolecular rate constant for the reaction, at 298. K and 1.0 atm pressure, is k_{bi} = 9.0 x 10⁻¹³ cm³/molecule•s, leading to a half-life t_{1/2} = 8.9 days, using our typical value [OH] = 1.0 x 10⁶ molecule/cm³. The reaction is in the falloff region for acetylene, and so k_{bi} will show some dependence on pressure. Larger alkynes react in the same way as acetylene, with k_{bi} = (5 - 30) x 10⁻¹² cm³/molecule•s. For these larger alkynes the reaction is in the high pressure limit, and so behaves as if it is a bimolecular reaction.

The subsequent reactions of the radical formed by reaction 4.7 are as one would expect based on the reactions of alkyl radicals



The final product is glyoxyl, (CHO)₂, a dicarbonyl compound. Other products, such as formic acid (HCOOH) have also been observed in laboratory studies.

Alkynes do not appear to react to a significant extent with O₃, or in an addition reaction with NO₃ at night. For alkynes larger than acetylene there is of course the possibility of abstraction of a hydrogen in the alkyl groups present, either by OH in the daytime, or NO₃ at night.