Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions

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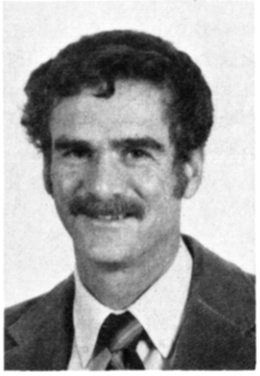

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I. Introduction

It has become well recognized during the past three decades that the gas-phase reactions of ozone (O_3) play an important role in the chemistry of the atmosphere.[1-6] With this recognition of O_3 as a reactive species in both the natural and polluted troposphere, together with the development of detailed chemical computer models for these complex reaction systems, measurements of O_3 reaction rate constants and the elucidation of the reaction mechanisms have been carried out. Prior to 1970 relatively few kinetic and mechanistic data were available for the reactions of O_3 with organics in the gas phase. Since then many kinetic, mechanistic, and product studies of these reactions for a large number of organics, mainly those containing unsaturated car-

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bon-carbon bonds, have been carried out.

In the polluted troposphere it was recognized early on that O_3, besides being one of the key products of photochemical air pollution,[7] is also reactive towards certain classes of organics, especially the alkenes,[8] and that O_3 reactions with such organics contribute to their consumption. In the natural troposphere, however, it was not until 1971 that it was recognized that O_3 also plays an important role in the chemistry of this region of the atmosphere, when Levy[9] postulated that the photolysis of O_3 to $O(^1D)$ atoms could lead to the generation of the hydroxyl (OH) radical, a key reactive specie.[6,10]

$$O_3 + h\nu\ (\lambda \lesssim 310\ \text{nm}) \rightarrow O(^1D) + O_2(^1\Delta_g)$$

$$O(^1D) + M\ (M = \text{air}) \rightarrow O(^3P) + M$$

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

In the clean troposphere, O_3 mixing ratios are generally around 10–40 ppb (parts per billion) at ground level,[11,12] generally increasing with increasing altitude to between ~30 and 100 ppb at 10 km, depending on the latitude and season.[6] The origin of this tropospheric O_3 has been a matter of some debate,[13] i.e., in situ photochemical production vs. downward transport from the lower stratosphere. The recent computer modeling data of Liu et al.[13] and Logan et al.[6] indicate that both processes are important, with the major region of O_3 formation by photochemical processes being in the upper troposphere. Ozone formation in the troposphere by photochemical routes occurs via the reaction sequence

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

In the stratosphere photolysis of O_3 and reaction with $O(^3P)$ atoms also become significant O_3 removal processes.[14] The chemistry of the troposphere and lower stratosphere[6,15,16] and of polluted urban atmospheres[3,17,18] has been discussed in detail elsewhere, and these articles and references therein should be consulted for details. It is now evident that for organics emitted into the troposphere, their reactions (both the rates and products) with O_3, along with those for photolysis, reaction with OH radicals[5,10,19] and, in certain cases, reaction with NO_3 radicals,[20-25] need to be known in order to assess the impact of these organic emissions on the ecosystem.

For atmospheric purposes, the lifetime τ_{O_3} of an organic due to reaction with O_3 is given by

$$\tau_{O_3} = (k[O_3])^{-1}$$

where k is the rate constant for the reaction of O_3 with the organic and $[O_3]$ is the O_3 concentration. Although the temperature decreases with increasing altitude throughout the troposphere, and hence the rate constant k also decreases with increasing altitude, the use of the room temperature rate constant allows the estimation of lower limit lifetimes due to reaction with O_3. When an O_3 concentration of 1×10^{12} molecule cm^{-3} (i.e., ~40 ppb at ground level) is used, the lower limit lifetimes with respect to reaction with O_3 shown in Table I as a function of the value of k are obtained.

TABLE I. Lifetimes τ_{O_3} of Organics Due to Reaction with O_3 at Various O_3 Reaction Rate Constants k (Calculated at an O_3 Concentration of 1×10^{12} molecule cm^{-3})

k, cm^3 molecule^{-1} s^{-1}	τ_{O_3}	k, cm^3 molecule^{-1} s^{-1}	τ_{O_3}
1×10^{-15}	0.3 h	1×10^{-19}	0.3 year
1×10^{-16}	3 h	1×10^{-20}	3 year
1×10^{-17}	1 day	1×10^{-21}	30 year
1×10^{-18}	10 day		

For most organics, reaction with the OH radical is an important atmospheric removal process[5,10,19] which competes with reaction with O_3. Kinetic data presently available show that all organics except the perhalogenated alkanes and CHF_3 react with the OH radical with rate constants of $\gtrsim 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K[10,26] (CHF_3 is the slowest reacting nonperhalogenated alkane studied to date, with a rate constant of $\sim 1.7 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K[26]). Thus, for all organics but the perhaloalkanes and CHF_3, OH radical rate constants at 298 K are $\gtrsim 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, which correspond[27] to atmospheric lifetimes (taking into account the temperature dependence of the rate constants) of $\lesssim 20$ years. Hence from Table I it is obvious that organics whose O_3 reaction rate constants at 298 K are $<10^{-20}$–10^{-21} cm^3 molecule^{-1} s^{-1} can be considered to be unreactive towards O_3 for atmospheric purposes. These considerations dictate to a large extent our approach to recommendations of rate constants for organics which react slowly with O_3, since we can regard O_3 reaction rate constants $\lesssim 10^{-20}$ cm^3 molecule^{-1} s^{-1} to be of negligible importance for atmospheric considerations.

In the present article, the available literature data through late 1984 concerning the gas-phase reactions of ozone with various classes of organics under conditions relevant to the atmosphere are discussed. Since the emphasis of this article is upon these reactions under atmospheric conditions, data obtained at low pressures or in the absence of O_2, which often exhibit chain characteristics and almost certainly have different reaction mechanisms subsequent to the initial reaction than when O_2 is present, are generally not discussed. In section II, the general experimental techniques used to determine the rate constants, products, and mechanisms are briefly discussed. In sections III–XI the available kinetic data for the different classes of organics are tabulated and evaluated, and wherever possible, recommendations for room temperature (298 K) rate constants and temperature-dependent parameters are given. Though the primary emphasis of this article deals with the kinetic data for these reactions, a discussion is also given in these sections of the present state of knowledge concerning their mechanisms. Finally, in section XII, the kinetic data available are discussed in terms of the atmospheric lifetimes of the various classes of organics, correlations with rate constants for reactions of these organics with other atomic and radical species, and a-prior predictive techniques.

The kinetic data are tabulated in separate tables for the alkanes and haloalkanes, acyclic monoalkenes, acyclic di- and trialkenes, cyclic alkenes, haloalkenes, alkynes, oxygen-, nitrogen-, and sulfur-containing organics, aromatics, organometallics, and organic radicals. These tables also indicate the experimental technique employed with abbreviations such as S-IR, where the

TABLE II. Reported Rate Constants k and Arrhenius Parameters for the Gas-Phase Reactions of O_3 with Alkanes and Haloalkanes

alkane	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref	temp range covered, K
methane	2.7×10^{-13}	15 350	$1.4 \times 10^{-24\,b}$	298	S-IR	Dillemuth et al.[65]	308-340
	$2.4 \times 10^{-14\,a}$	13 900^a	$1.4 \times 10^{-24\,a,b}$	298			
	1.2×10^{-13}	14 900	$1.4 \times 10^{-24\,b}$	298	S-IR	Schubert and Pease[67,68]	313-323
			$\leq 1.2 \times 10^{-21}$	298 ± 2	S-CL	Stedman and Niki[41]	
ethane	2.1×10^{-13}	13 900	$1.2 \times 10^{-23\,b}$	298	S-IR	Morrissey and Schubert[69]	c
	$5.8 \times 10^{-12\,a}$	14 700^a	$9.6 \times 10^{-24\,a,b}$	298			
propane	5.1×10^{-15}	12 100	$6.8 \times 10^{-24\,b}$	298	S-IR	Shubert and Pease[67,68]	304-323
	3.5×10^{-13}	14 300	$7.2 \times 10^{-24\,b}$	298	S-IR	Morrissey and Schubert[69]	c
	1.9×10^{-13}	14 600^a	$6.2 \times 10^{-24\,a,b}$	298			
n-butane	1.4×10^{-15}	11 100	$9.8 \times 10^{-24\,b}$	298	S-IR	Schubert and Pease[67,68]	298-323
isobutane	7.3×10^{-16}	10 300	$2.0 \times 10^{-23\,b}$	298	S-IR	Schubert and Pease[67,68]	298-323
1,1-difluoroethane	$2.18 \times 10^{-13\,a}$	15 800 ± 400	$6.0 \times 10^{-25\,b,d}$	298	S-IR	Dillemuth et al.[66]	307-362
1,1,1-trifluoroethane	$5.28 \times 10^{-13\,d}$	17 500 ± 500	$5.4 \times 10^{-26\,b,d}$	298	S-IR	Dillemuth et al.[66]	307-362

[a] O_2 excluded. [b] Calculated from the Arrhenius expression. [c] Not reported. [d] Reported O_3 disappearance rate data divided by a factor of 2 to take into account rapid reaction of O_3 with a product species.[66]

first letter(s) denote S, Static system; F, flow system; SF, stopped-flow system; and the second set of letters denote the detection technique; MS, mass spectrometry; PMS, photoionization mass spectrometry; IR, infrared absorption spectroscopy; FT-IR, Fourier transform-infrared absorption spectroscopy; UV, ultraviolet absorption; CL, chemiluminescence; and CA, chemical analysis by wet chemical techniques. These techniques are discussed in section II and, where appropriate, in the sections discussing the individual compounds.

The kinetic data are tabulated in the Arrhenius form of $k = Ae^{-E/RT}$, with the rate constants k being given, wherever available, at the individual temperatures studied, and where A and E are the Arrhenius preexponential factor and Arrhenius activation energy (the latter in cal mol^{-1} units), respectively. While this simple Arrhenius expression is known to be too simplistic for use over large temperature ranges, it is a convenient means of expressing the experimental data over limited temperature ranges. This is especially true for the available O_3 reaction rate constant data, which in the extreme cover only the relatively small temperature range of ~180 K to ~400 K.

II. Experimental Techniques

A. Kinetics Studies

The experimental techniques which have been utilized for the determination of rate constants for the reaction of O_3 with organics can be separated into two groups; namely absolute and relative rate techniques. These methods are briefly discussed below.

1. Absolute Rate Constant Techniques

a. Static and Stopped-Flow Systems. The general method which has been the most used in determining O_3 reaction kinetics is based on observing the rates of decay of O_3 (over the background O_3 decay rate) and/or the organic in a static system where the concentration of the other reactant is known. For reasons which are discussed below, the technique most frequently used involves monitoring the rate of decay of O_3 in the presence of a known excess concentration of the organic. In this case, if secondary reactions can be neglected, O_3 is consumed by

$$O_3 \xrightarrow{\text{wall}} \text{loss of } O_3 \qquad (1)$$

$$O_3 + \text{organic} \rightarrow \text{products} \qquad (2)$$

Hence

$$\frac{-d[O_3]}{dt} = (k_1 + k_2[\text{organic}])[O_3] \qquad (I)$$

where k_1 and k_2 are the rate constants for reactions 1 and 2. In the event that the organic concentration is in a large excess of the initial O_3 concentration (i.e., $[\text{organic}]/[O_3]_{\text{initial}} > 10$), then the organic concentration remains essentially constant throughout the reaction, and eq I simplifies to

$$\frac{-d\ln[O_3]}{dt} = k_1 + k_2[\text{organic}] \qquad (II)$$

Under these conditions pseudo-first-order decays of O_3 should be observed, and the slopes of straight-line plots of $\ln([O_3]_{t_0}/[O_3]_t)$ against time $(t - t_0)$ (where $[O_3]_{t_0}$ and $[O_3]_t$ are the O_3 concentrations at times t_0 and t, respectively) then yield the O_3 decay rate $-d\ln[O_3]/dt$. Plots of the O_3 decay rate as a function of the organic concentration should also be linear with a slope of k_2, the rate constant for the reaction of O_3 with the organic, and an intercept of k_1, the background O_3 decay rate. This method, i.e., the observation of pseudo-first-order O_3 decays in the presence of known excess organic concentrations, has been used in numerous studies, as, for instance, Niki and co-workers,[28-30] Becker et al.,[31] Herron and Huie,[32] Huie and Herron,[33] Adeniji et al.,[34] and Atkinson et al.[35,36]

However, under conditions where the initial organic concentration is of similar magnitude to the initial O_3 concentration, a complete second-order treatment of the data must be carried out. In the most general case, where the stoichiometry of the reaction of O_3 with the organic is not assumed to be unity, then, neglecting the background O_3 decay rate, the following integrated expressions hold:

$$\ln\left(\frac{[O_3]_{t_0}}{[O_3]_t}\right) = k_2^{O_3}\int_{t_0}^{t}[\text{organic}]dt \qquad \text{(III)}$$

and

$$\ln\left(\frac{[\text{organic}]_{t_0}}{[\text{organic}]_t}\right) = k_2^{\text{organic}}\int_{t_0}^{t}[O_3]dt \qquad \text{(IV)}$$

where $[\text{organic}]_{t_0}$ and $[\text{organic}]_t$ are the organic concentrations at times t_0 and t, respectively, and $k_2^{O_3}$ and k_2^{organic} are the apparent rate constants for reaction 2 derived from the O_3 decays and the organic decays, respectively. For nonunit stoichiometry, as is usually the case under these conditions (see below), then the values of $k_2^{O_3}$ and k_2^{organic} obtained from eq III and IV are not identical. Rate constant data have been obtained under conditions where the full second-order kinetic treatment must be used by, among others, Hanst et al.,[37] Bufalini and Altshuller,[38] Cox and Penkett,[39] and Japar et al.[40]

Experimental techniques using these static methods have included a stopped-flow system at ~4 Torr total pressure with mass spectrometric detection of O_3,[32,33] and O_3–organic reactions carried out at atmospheric pressure in Pyrex or Teflon reaction chambers at part-per-million concentrations of reactants, with O_3 being monitored by chemiluminescence instruments (see, for example, ref 28–30, 34–36, 40, and 41). These individual references should be consulted for further details of this general technique.

b. Flow Systems. Two flow techniques have been used to date to determine O_3 reaction rate constants with organics. Grimsrud et al.[42] used a conventional flow system, where the reaction time (~4–240 s) was changed by changing the reaction length and flow rate. The rate constants were calculated from the relationship

$$k = \frac{\ln([O_3]_{t_0}/[O_3]_t)}{\frac{1}{2}([\text{organic}]_t + [\text{organic}]_{t_0})(t - t_0)} \qquad \text{(V)}$$

where $[O_3]_{t_0}$ and $[\text{organic}]_{t_0}$ are the initial concentrations prior to entering the reaction tube, $[O_3]_t$ and $[\text{organic}]_t$ are the final concentrations at the outlet of the tube, and $(t - t_0)$ is the reaction time calculated from the flow rate and the flow-tube dimensions. Ozone was monitored by a chemiluminescence analyzer, and the organics were monitored by gas chromatography. It should be noted that eq V is based on the assumption of perfect plug-flow conditions—i.e., that axial diffusion is negligible. If the flow rates are low, axial diffusion can become nonnegligible, resulting in the reaction time being longer than assumed and hence yielding rate constants which are erroneously high. As indicated in the discussion of the specific compounds studied using this method, this indeed may have been a problem with this technique as used by Grimsrud et al.[42]

The other flow technique, used by Hanst et al.[37] and Bufalini and Altshuller,[38] is that of a stirred flow reactor, which differs from a conventional flow system in that the contents of the entire reactor are assumed to be well mixed. The rate constant k is then obtained from the expression

$$k = \frac{F}{V}\,\frac{([\text{organic}]_{t_0} - [\text{organic}]_f)}{[O_3]_f[\text{organic}]_f} = \frac{F}{V}\,\frac{([O_3]_{t_0} - [O_3]_f)}{[O_3]_f[\text{organic}]_f} \qquad \text{(VI)}$$

where F is the flow rate through the reactor, V is the volume of the reactor, $[\text{organic}]_{t_0}$ and $[O_3]_{t_0}$ are the concentrations of the organic and O_3, respectively, entering the reactor, and $[\text{organic}]_f$ and $[O_3]_f$ are the corresponding concentrations leaving the reactor. In the study of Hanst et al.[37] the reactants were monitored by infrared absorption spectroscopy, while in the study of Bufalini and Altshuller[38] the organics were monitored by gas chromatography and ozone was monitored by a wet chemical technique. Unfortunately, the accuracy of wet chemical techniques for monitoring O_3 is now open to question, and Hanst et al.[37] did not note the temperature at which their experiments were carried out, so both of these studies are considered to be primarily qualitative in nature for the purposes of this article.

c. Reaction Stoichiometry. In order for the apparent rate constant derived from either the static or the flow techniques to be a good approximation to the true elementary rate constant for the reaction of O_3 with an organic, the reactant whose rate of consumption is monitored must not be consumed to a significant extent by secondary reactions. However, at least for the organics which have been extensively studied, this has not always been the case. In particular, it has been shown that

(i) For conditions where $[\text{organic}] \gg [O_3]_{\text{init}}$, the presence of O_2 leads to a decrease in the rate constant derived from the O_3 decay rates [eq II] to a limiting value, with the concentration of O_2 necessary to decrease the derived rate constant to this limiting value being of the order of ~10^{15} molecule cm^{-3}.[31,32,40,43,44]

(ii) For the alkenes, when their concentration is not in large excess of the O_3 concentration, the reaction stoichiometry is not unity, and the O_3 rate constants $k_2^{O_3}$ derived from eq III increase dramatically as the $[\text{alkene}]/[O_3]$ ratio decreases.[40] Furthermore, for the O_3–propene system, Japar et al.[40] observed that the rate constants k_2^{alkene} derived from eq IV, even under conditions where $[\text{alkene}] \ll [O_3]$, were significantly higher than the values of $k_2^{O_3}$ obtained when $[O_3] \ll [\text{alkene}]$. This then implies that secondary reactions consuming the alkene (propene in this case) are more difficult to avoid than are secondary reactions involving O_3.

These observations of a decrease in the O_3 decay rates by O_2, and the dependence of O_3 and alkene decay rates and reaction stoichiometry on the $[\text{organic}]/[O_3]$ ratios, are more fully discussed by Japar et al.[40] Their data show[40] that secondary reactions can be important and that the optimum experimental conditions for determining rate constants which are close to those for the elementary reactions are those carried out in the presence of O_2 (e.g., at atmospheric pressure in air) at high $[\text{organic}]/[O_3]$ ratios, with the rate constants being derived by monitoring the O_3 decay rate.

2. Relative Rate Constant Techniques

This experimental technique, as used by Cvetanovic and co-workers[45,46] and by Kirchner et al.[47] is based upon monitoring the yields of the major products formed from two organics in the presence of O_3.

If the two reactions are

$$O_3 + \text{organic}_A \rightarrow \alpha_A\ \text{product}_A + \text{other products} (\text{rate constant } k_a)$$

$$O_3 + \text{organic}_B \rightarrow \alpha_B\ \text{product}_B + \text{other products} (\text{rate constant } k_b)$$

and if the [organic]/[O_3] ratios are sufficiently high so that the organic concentrations remain essentially constant during the reaction, then

$$\frac{\Delta[\text{product}_A]}{\Delta[\text{product}_B]} = \frac{k_a}{k_b}\frac{\alpha_A}{\alpha_B}\frac{[\text{organic}_A]}{[\text{organic}_B]} \qquad \text{(VII)}$$

Hence plots of ($\Delta[\text{product}_A]/\Delta[\text{product}_B]$) against ($[\text{organic}_A]/[\text{organic}_B]$) should yield straight lines of slope $k_a\alpha_A/k_b\alpha_B$. By determining α_A and α_B from product studies of the reactions of O_3 with the two organics, carried out individually, the rate constant ratio k_a/k_b may then be derived.

In order for this technique to be valid, α_A and α_B must be constant throughout the reaction and have the same values in the reactions of mixtures of organics with O_3 as in the single organic–O_3 reactions. However, the assumption that α remains constant throughout the reaction has been shown by Cox and Penkett[39] not to be valid, at least for the alkenes studied by them. Additionally, the studies of Vrbaski and Cvetanovic[45] and Wei and Cvetanovic[46] were carried out using high (Torr) concentrations of O_3 and organics, and secondary reactions were almost certainly important under those conditions. (Thus, for example, the work of Herron and Huie[48,49] and Martinez et al.[50] should be consulted in order to assess the importance of secondary reactions at lower organic and O_3 concentrations.) For such reasons the relative rate constant data obtained from these studies are open to question and in fact the data of Vrbaski and Cvetanovic[45] and Wei and Cvetanovic[46] do not agree well with more recent absolute data.[29,32,33,51] Hence, the data obtained by this relative rate technique are not considered in the following sections of this article.

B. Product and Mechanistic Studies

In general, these studies have used similar experimental techniques to those used for kinetic studies. Thus, for example, recent and relevant mechanistic studies have been those of Herron and co-workers[48–50] using a stopped flow system at 4–8 Torr total pressure with photoionization–mass spectrometric detection of radicals and stable products, and of Niki and co-workers[52–55] and Calvert and co-workers[56,57] using static systems at part-per-million concentrations of reactants in one atmosphere of air, with Fourier transform infrared (FT-IR) absorption spectroscopy being used for product detection and identification. These and other individual references should be consulted for details as to the experimental techniques used.

A number of other product studies using gas chromatography or other analytical techniques have been carried out (see, for example, ref 46, 58–64), but since these studies have not provided information as definitive as those described above and in the following sections, these are not discussed further in this article.

III. Alkanes and Haloalkanes

The reported kinetic data for the alkanes and the haloalkanes are given in Table II. Apart from the datum of Stedman and Niki[41] for methane, all of the reported data have been obtained by Dillemuth and co-workers[65,66] and Schubert and co-workers.[67–69] It can be seen from this table that if there is indeed an elementary reaction of O_3 with the alkanes or haloalkanes, the magnitude of the rate constants are such that these reactions are totally negligible for atmospheric purposes.

However, there are a number of reasons to believe that these data of Dillemuth et al.[65,66] and Schubert and co-workers[67–69] are not those for the elementary reactions of O_3 with the alkanes or haloalkanes: (1) If such reactions occur, they can only be reasonably considered to proceed via the (complex) pathway

$$O_3 + RH \rightarrow R + O_2 + OH$$

and the thermochemistry of this reaction is endothermic by 15, 18, and 21 kcal mol^{-1} for tertiary, secondary, and primary C–H bonds, respectively, and by 27 kcal mol^{-1} for methane,[70] all of which are higher than the reported Arrhenius activation energies listed in Table II. Since the Arrhenius activation energies are expected to be higher than the reaction endothermicities, the data in Table II indicate that the reported rate data do not correspond to the initial reactions. (2) The reported rate constants for the alkanes vary by only a factor of $\sim$20 from methane to isobutane (Table II), very different from the large increases in O(^{3}P) atom and OH radical rate constants observed from methane to isobutane of $\sim$5000 and $\sim$300, respectively.[10,71] Such a small change in the reported rate constants along the homologous alkane series is very surprising. (3) At these low reported rate constants, the presence of extremely small amounts of reactive impurities in the alkanes or haloalkanes could lead to chain-propagating reactions yielding erroneously high observed reaction rates. (4) Kleimenov and Nalbandian[72] used a flow system to study the reactions of O_3 with alkanes at $\sim$420 K, and interpreted their data in terms of the pyrolysis of O_3 to O_2 and an O(^{3}P) atom, followed by reaction of O(^{3}P) atoms with the alkanes. Knipe and Gordon[73] reviewed this topic and also concluded that the reactions observed by Dillemuth and co-workers and Schubert and co-workers involved O_3 dissociation and chain reactions initiated by oxygen atoms.

Thus, at this time it appears that there is no evidence for an elementary reaction between O_3 and the alkanes or haloalkanes. We recommend that for the reactions of O_3 with the alkanes and haloalkanes the rate constants given in Table II be considered to be upper limits, and, based on the thermochemical considerations indicated above, that the true rate constants are probably orders of magnitude less than these upper limits. In any case, these reactions can thus obviously be totally neglected for atmospheric, or indeed combustion, purposes.

TABLE III. Literature Rate Constants *k* and Arrhenius Parameters for the Reactions of O_3 with Acyclic Monoalkenes

alkene	*A*, cm^3 $molecule^{-1}$ s^{-1}	*E*, cal mol^{-1}	*k*, cm^3 $molecule^{-1}$ s^{-1}	*T*, K	technique	ref	temp range covered, K
ethene		~0	$(3.6 \pm 1.4) \times 10^{-18}$	303	S-IR	Cadle and Schadt[8]	303–323
			1.35×10^{-18}	*a*	F/S-IR	Hanst et al.[37]	
		4200 ± 400	$(2.66 \pm 0.33) \times 10^{-18}$	303	F-CA	Bufalini and Altshuller[38]	303–373
			3.3×10^{-18}	298 ± 2	S-CA	Bufalini and Altshuller[38]	
			1.38×10^{-19}	233	S-UV	DeMore[74]	178–233
			7.31×10^{-20}	225			
			4.48×10^{-20}	216			
			4.32×10^{-20}	208			
			1.83×10^{-20}	198			
			1.49×10^{-20}	193			
			1.25×10^{-20}	188			
			8.8×10^{-21}	188			
			7.0×10^{-21}	183			
	3.3×10^{-15}	4700 ± 200	5.0×10^{-21}	178			
			$(1.55 \pm 0.15) \times 10^{-18}$	299 ± 2	S-CL	Stedman et al.[28]	
	1.2×10^{-14}	4950 ± 200	2.8×10^{-17}[b]	298	S-UV	Becker et al.[31]	~284–347[c]
			$(2.24 \pm 0.13) \times 10^{-19}$	235.0	SF-MS	Herron and Huie[32]	235–362
			$(5.78 \pm 0.15) \times 10^{-19}$	266.9			
			$(9.33 \pm 0.37) \times 10^{-19}$	286.2			
			$(2.34 \pm 0.05) \times 10^{-18}$	309.4			
			$(3.84 \pm 0.08) \times 10^{-18}$	332.4			
			$(9.03 \pm 0.18) \times 10^{-18}$	362.0			
	9.00×10^{-15}	5081 ± 332	1.69×10^{-18}[b]	298			
			$(1.9 \pm 0.1) \times 10^{-18}$	299 ± 2	S-CL	Japar et al.[29]	
			$(1.9 \pm 0.1) \times 10^{-18}$	299	S-CL	Japar et al.[40]	
			$(1.69 \pm 0.13) \times 10^{-18}$	303	S-UV	Toby et al.[75]	
			4.4×10^{-19}	260 ± 2	S-CL	Adeniji et al.[34]	260–294
		~5800	1.6×10^{-18}	294 ± 2			
			$(1.43 \pm 0.19) \times 10^{-18}$	296 ± 2	S-CL	Atkinson et al.[36]	
			1.8×10^{-18}	*a*	S-FTIR	Niki et al.[52]	
			$(1.54 \pm 0.11) \times 10^{-18}$	291.8 ± 0.2	S-FTIR	Su et al.[56]	292–299
			$(1.80 \pm 0.11) \times 10^{-18}$	297.2 ± 0.3			
			$(2.10 \pm 0.05) \times 10^{-18}$	299.4 ± 0.6			
			$(1.36 \pm 0.34) \times 10^{-18}$	292.9 ± 0.2			
			$(1.72 \pm 0.05) \times 10^{-18}$	293.4 ± 0.2			
			$(1.68 \pm 0.85) \times 10^{-18}$	298.7 ± 0.5			
			$(1.64 \pm 0.07) \times 10^{-18}$	296.8 ± 0.2			
			$(1.16 \pm 0.12) \times 10^{-18}$	282.7 ± 0.3	S-FTIR	Kan et al.[57]	283–304
			$(1.23 \pm 0.01) \times 10^{-18}$	283.7 ± 0.8			
			$(1.39 \pm 0.01) \times 10^{-18}$	288.2 ± 0.7			
			$(1.41 \pm 0.06) \times 10^{-18}$	290.0 ± 0.5			
			$(1.64 \pm 0.05) \times 10^{-18}$	293.4 ± 0.4			
			$(1.68 \pm 0.04) \times 10^{-18}$	294.1 ± 0.1			
			$(1.70 \pm 0.04) \times 10^{-18}$	294.1 ± 0.2			
			$(2.35 \pm 0.01) \times 10^{-18}$	302.6 ± 0.3			
			$(2.28 \pm 0.04) \times 10^{-18}$	303.5 ± 0.2			
ethene-d_4			$(2.3 \pm 0.1) \times 10^{-18}$	299 ± 2	S-CL	Japar et al.[29]	
			$(1.98 \pm 0.07) \times 10^{-18}$	294.6 ± 0.5	S-FTIR	Su et al.[56]	
			$(2.05 \pm 0.16) \times 10^{-18}$	296.7 ± 0.5			
cis-1,2-ethene-d_2			$(2.15 \pm 0.44) \times 10^{-18}$	299.0 ± 0.3	S-FTIR	Su et al.[56]	
trans-1,2-ethene-d_2			$(1.86 \pm 0.18) \times 10^{-18}$	295.4 ± 0.5	S-FTIR	Su et al.[56]	
			$(2.15 \pm 0.14) \times 10^{-18}$	299.2 ± 0.5			
propene			6.2×10^{-18}	*a*	S-CA	Cadle and Schadt[8]	
			8.1×10^{-18}	*a*	F/S-IR	Hanst et al.[37]	
			1.26×10^{-17}	296	S-CA/CL	Cox and Penkett[39]	
			$(1.25 \pm 0.10) \times 10^{-17}$	299 ± 2	S-CL	Stedman et al.[28]	
	1.10×10^{-14}	3910 ± 200	1.45×10^{-17}[b]	298	S-UV	Becker et al.[31]	286–358
			$(2.08 \pm 0.02) \times 10^{-18}$	250.0	SF-MS	Herron and Huie[32]	250–362
			$(4.83 \pm 0.10) \times 10^{-18}$	266.9			
			$(7.37 \pm 0.15) \times 10^{-18}$	286.2			
			$(1.41 \pm 0.02) \times 10^{-17}$	309.4			
			$(1.76 \pm 0.02) \times 10^{-17}$	332.4			
			$(3.82 \pm 0.05) \times 10^{-17}$	362.0			
	6.14×10^{-15}	3769 ± 217	1.06×10^{-17}[b]	298			
			$(1.30 \pm 0.01) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
			$(1.32 \pm 0.03) \times 10^{-17}$	299	S-CL	Japar et al.[40]	
			5.1×10^{-18}	260 ± 2	S-CL	Adeniji et al.[34]	260–294
		~4000	1.26×10^{-17}	294 ± 2			
			$(1.04 \pm 0.14) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[36]	
propene-d_6			$(1.51 \pm 0.03) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
1-butene			1.03×10^{-17}	303	F-CA	Bufalini and Altshuller[38]	
			1.42×10^{-17}	298 ± 2	S-CA	Bufalini and Altshuller[38]	
			$(1.23 \pm 0.04) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
			$(1.69 \pm 0.05) \times 10^{-18}$	225.2	SF-MS	Huie and Herron[33]	225–363
			$(3.19 \pm 0.03) \times 10^{-18}$	247.1			

TABLE III (Continued)

alkene	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref	temp range covered, K
1-butene			$(4.28 \pm 0.08) \times 10^{-18}$	260.0	SF-MS	Huie and Herron[33]	225–363
			$(7.49 \pm 0.08) \times 10^{-18}$	282.2			
			$(1.37 \pm 0.05) \times 10^{-17}$	313.8			
			$(2.84 \pm 0.03) \times 10^{-17}$	363.1			
	2.93×10^{-15}	3350 ± 40	1.03×10^{-17}[b]	298			
			5.3×10^{-18}	260 ± 2	S-CL	Adeniji et al.[34]	260–294
		~3900	1.26×10^{-17}	294 ± 2			
2-methyl-2-propene			6.1×10^{-18}	[a]	F/S-IR	Hanst et al.[37]	
		2800 ± 400	$(2.32 \pm 0.33) \times 10^{-17}$	303	F-CA	Bufalini and Altshuller[38]	303–373
			1.8×10^{-17}	283	S-UV	Becker et al.[31]	
			$(1.36 \pm 0.02) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
			1.45×10^{-17}	295 ± 1	F-CL	Grimsrud et al.[42]	
			$(1.94 \pm 0.07) \times 10^{-18}$	225.2	SF-MS	Huie and Herron[33]	225–363
			$(3.67 \pm 0.07) \times 10^{-18}$	247.1			
			$(4.98 \pm 0.07) \times 10^{-18}$	260.0			
			$(8.47 \pm 0.12) \times 10^{-18}$	282.2			
			$(1.63 \pm 0.05) \times 10^{-17}$	313.8			
			$(3.12 \pm 0.03) \times 10^{-17}$	363.1			
	3.17×10^{-15}	3320 ± 46	1.16×10^{-17}[b]	298			
			1.2×10^{-17}	294 ± 2	S-CL	Adeniji et al.[34]	
cis-2-butene			4.9×10^{-17}	[a]	F/S-IR	Hanst et al.[37]	
			3.32×10^{-16}	303	F-CA	Bufalini and Altshuller[38]	
			1.41×10^{-16}	296	S-CA/CL	Cox and Penkett[39]	
			$(1.61 \pm 0.07) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]	
			$(4.86 \pm 0.03) \times 10^{-17}$	225.1	SF-MS	Huie and Herron[33]	225–364
			$(4.65 \pm 0.22) \times 10^{-17}$	226.8			
			$(5.31 \pm 0.08) \times 10^{-17}$	238.1			
			$(6.89 \pm 0.35) \times 10^{-17}$	251.3			
			$(8.65 \pm 0.18) \times 10^{-17}$	263.7			
			$(8.82 \pm 0.18) \times 10^{-17}$	277.3			
			$(9.98 \pm 0.17) \times 10^{-17}$	287.3			
			$(1.38 \pm 0.04) \times 10^{-16}$	308.9			
			$(1.36 \pm 0.06) \times 10^{-16}$	313.8			
			$(1.96 \pm 0.07) \times 10^{-16}$	336.2			
			$(2.01 \pm 0.23) \times 10^{-16}$	363.1			
			$(2.77 \pm 0.10) \times 10^{-16}$	363.5			
	3.11×10^{-15}	1900 ± 107	1.26×10^{-16}[b]	298			
			$(1.38 \pm 0.16) \times 10^{-16}$	297 ± 1	S-CL	Atkinson et al.[76]	
trans-2-butene		200 ± 300	$(4.32 \pm 0.66) \times 10^{-16}$	303	F-CA	Bufalini and Altshuller[38]	303–373
			3.33×10^{-16}	298 ± 2	S-CA	Bufalini and Altshuller[38]	
			2.57×10^{-16}	296	S-CA/CL	Cox and Penkett[39]	
			$(2.75 \pm 0.23) \times 10^{-16}$	299 ± 2	S-CL	Stedman et al.[28]	
			$(2.60 \pm 0.09) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]	
			$(5.98 \pm 0.07) \times 10^{-17}$	225.1	SF-MS	Huie and Herron[33]	225–364
			$(5.88 \pm 0.15) \times 10^{-17}$	226.8			
			$(6.86 \pm 0.12) \times 10^{-17}$	238.1			
			$(9.36 \pm 0.25) \times 10^{-17}$	251.3			
			$(1.14 \pm 0.03) \times 10^{-16}$	263.7			
			$(1.14 \pm 0.09) \times 10^{-16}$	277.3			
			$(1.34 \pm 0.05) \times 10^{-16}$	287.3			
			$(2.04 \pm 0.27) \times 10^{-16}$	308.9			
			$(1.93 \pm 0.02) \times 10^{-16}$	313.8			
			$(2.77 \pm 0.08) \times 10^{-16}$	336.2			
			$(3.17 \pm 0.25) \times 10^{-16}$	363.1			
			$(3.89 \pm 0.13) \times 10^{-16}$	363.5			
	5.96×10^{-15}	2088 ± 85	1.76×10^{-16}[b]	298			
			$(2.56 \pm 0.15) \times 10^{-16}$	299	S-CL	Japar et al.[40]	
			2.88×10^{-16}	294 ± 2	S-CL	Adeniji et al.[34]	
cis- + *trans*-2-butene	9.4×10^{-15}	2280 ± 150	2.00×10^{-16}[b]	298	S-UV	Becker et al.[31]	~281–352[c]
1-pentene			5.3×10^{-18}	[a]		Cadle and Schadt[8]	
			7.4×10^{-18}	[a]	F/S-IR	Hanst et al.[37]	
			$(1.07 \pm 0.04) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
cis-2-pentene			2.09×10^{-16}	296	S-CA/CL	Cox and Penkett[39]	
trans-2-pentene			3.15×10^{-16}	296	S-CA/CL	Cox and Penkett[39]	
cis- + *trans*-2-pentene			1.6×10^{-16}	[a]	F/S-IR	Hanst et al.[37]	
2-methyl-2-butene			7.47×10^{-16}	303	F-CA	Bufalini and Altshuller[38]	
			7.97×10^{-16}	296	S-CA/CL	Cox and Penkett[39]	
			$(4.93 \pm 0.16) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]	
			$(1.96 \pm 0.20) \times 10^{-16}$	226.8	SF-MS	Huie and Herron[33]	227–363
			$(2.24 \pm 0.07) \times 10^{-16}$	247.1			
			$(3.29 \pm 0.03) \times 10^{-16}$	284.0			
			$(6.79 \pm 0.15) \times 10^{-16}$	363.3			
	6.34×10^{-15}	1641 ± 155	3.97×10^{-16}[b]	298			

TABLE III (Continued)

alkene	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref	temp range covered, K
1-hexene		$\sim$0	$(8.8 \pm 1.4) \times 10^{-18}$	[a]	S-CA	Cadle and Schadt[8]	281–300
			1.01×10^{-17}	[a]	F/S-IR	Hanst et al.[37]	
			9.1×10^{-18}	298 ± 3	S-CA	Saltzman and Gilbert[77]	
			$(1.13 \pm 0.02) \times 10^{-17}$	303	F-CA	Bufalini and Altshuller[38]	
			1.25×10^{-17}	298 ± 2	S-CA	Bufalini and Altshuller[38]	
			1.36×10^{-17}	296	S-CA/CL	Cox and Penkett[39]	
			$(1.10 \pm 0.15) \times 10^{-17}$	299 ± 2	S-CL	Stedman et al.[28]	
			$(1.11 \pm 0.03) \times 10^{-17}$	299 ± 2	S-CL	Japar et al.[29]	
			1.08×10^{-17}	294 ± 2	S-CL	Adeniji et al.[34]	
			$(1.21 \pm 0.28) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[36]	
4-methyl-1-pentene			1.06×10^{-17}	296	S-CA/CL	Cox and Penkett[39]	
2-methyl-1-pentene			1.69×10^{-17}	296	S-CA/CL	Cox and Penkett[39]	
cis-3-methyl-2-pentene			$(4.56 \pm 0.08) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]	
trans-3-methyl-2-pentene			$(5.63 \pm 0.17) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]	
2,3-dimethyl-2-butene			$(1.51 \pm 0.08) \times 10^{-15}$	299 ± 2	S-CL	Japar et al.[29]	
			$(8.83 \pm 0.56) \times 10^{-16}$	226.8	SF-MS	Huie and Herron[33]	227–363
			$(8.30 \pm 0.37) \times 10^{-16}$	247.1			
			$(8.42 \pm 0.43) \times 10^{-16}$	284.0			
			$(1.41 \pm 0.09) \times 10^{-15}$	363.3			
	2.82×10^{-15}	584 ± 389	1.05×10^{-15} [b]	298			
1-heptene			8.1×10^{-18}	[a]	S-CA	Cadle and Schadt[8]	
			$(1.73 \pm 0.19) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[36]	
cis- + *trans*-2-heptene			8.8×10^{-17}	[a]	F/S-IR	Hanst et al.[37]	
1-octene			8.1×10^{-18}	[a]	S-CA	Cadle and Schadt[8]	
1-decene			1.08×10^{-17}	[a]	S-CA	Cadle and Schadt[8]	

[a] Room temperature, not reported. [b] Calculated from the Arrhenius expression. [c] Derived from the graphical data presented.

IV. Alkenes and Haloalkenes

A. Kinetic Data

The available literature absolute rate constant data for the reactions of O_3 with the acyclic monoalkenes, the acyclic dialkenes and trialkenes, the cyclic alkenes, and the haloalkenes are given in the following sections. These divisions between the classes of alkenes are somewhat arbitrary, but are useful because of the relatively large number of compounds studied. As discussed in Section II, the relative rate constant data have been neglected.

1. Acyclic Monoalkenes

The kinetic data for the reactions of O_3 with the acyclic monoalkenes are given in Table III. It can be seen that numerous studies have been carried out, most of which are in reasonable agreement, and most of which have been carried out only at room temperature. In the study of Becker et al.,[31] while it was observed that for propene the addition of O_2 reduced the derived rate constants markedly to an apparent limiting value for O_2 concentrations $\geq 3 \times 10^{15}$ molecule cm^{-3}, their data for ethene, propene, and 2-methyl-2-propene[31] are significantly higher than other recent data (Table III), and it must be concluded (as Becker et al.[31] themselves concluded for their ethene data) that insufficient concentrations of O_2 were present to minimize secondary reactions. Hence, these data of Becker et al.[31] will not be used in the following discussions and evaluations of the data base. The three earliest studies of Cadle and Schadt,[8] Hanst et al.[37] (for which the temperature was not noted), and Bufalini and Altshuller[38] also show significant discrepancies with later work. Cadle and Schadt,[8] Saltzman and Gilbert,[77] and Bufalini and Altshuller[38] used wet chemical techniques to monitor O_3, and the reliability and accuracy of these methods are open to question. In consequence, we will not consider the data obtained in these early investigations of ref 8, 37, 38, and 77 except for qualitative discussions. The data for the individual acyclic monoalkenes are discussed as follows:

a. Ethene, Ethene-d_2, and Ethene-d_4. The rate constants obtained by DeMore,[74] Stedman et al.,[28] Herron and Huie,[32] Japar et al.,[29,40] Toby et al.,[75] Adeniji et al.,[34] Su et al.,[56] Kan et al.[57] and Atkinson et al.[36] are plotted in Arrhenius form in Figures 1 and 2, together with the unweighted least-squares line. It can be seen that the experimental data fit the line to within better than ±30%. Furthermore, the two studies carried out over significant temperature ranges,[32,74] though the temperature ranges do not quite overlap, are in good agreement. The recent data of Su et al.[56] and Kan et al.[57] are also in excellent agreement with the calculated Arrhenius line. The unweighted least-squares analysis of these data yields the Arrhenius expression

$$k(\text{ethene}) = (1.20^{+0.31}_{-0.24}) \times 10^{-14} e^{-(5232\pm117)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where the indicated error limits are two least-squares standard deviations)

$$k(\text{ethene}) = 1.75 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty of ±30% at 298 K.

While the rate constant obtained by Hanst et al.[37] of $k = 1.35 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at room temperature (not specified) is in reasonable agreement with the above expression, the data of Cadle and Schadt[8] and Bufalini and Altshuller[38] are significantly higher. Possible reasons for these discrepancies have been noted above.

The available rate constants for ethene-d_4 and *cis*-

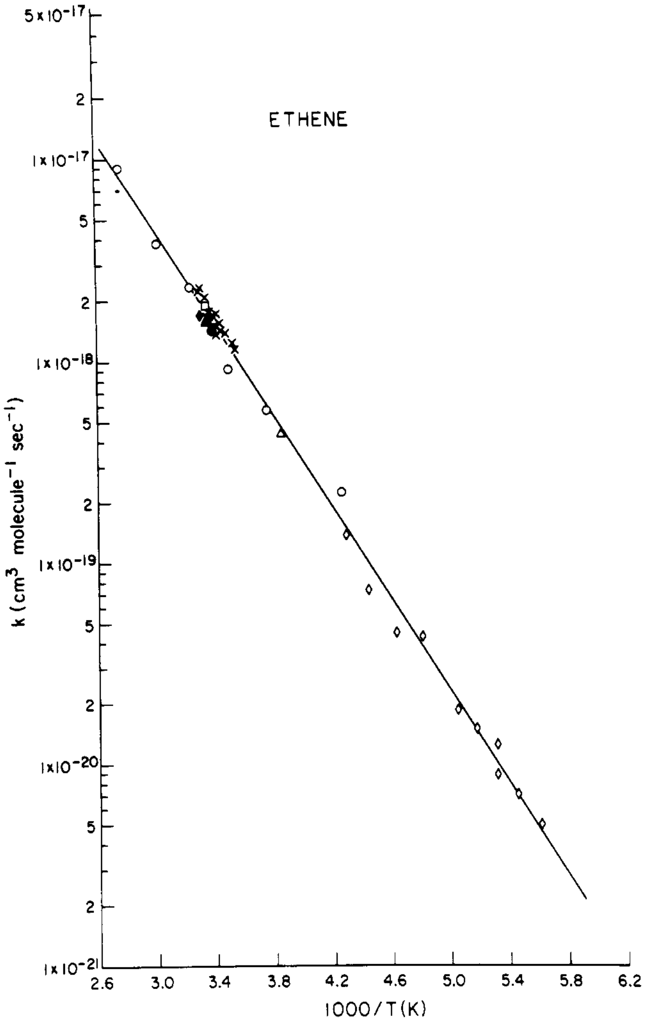


Figure 1. Arrhenius plot of selected (see text) literature rate constants for the gas-phase reaction of O_3 with ethene. (◇) DeMore;[74] (▲) Stedman et al.;[28] (○) Herron and Huie;[32] (□) Japar et al.;[29,40] (♦) Toby et al.;[75] (×) Su et al.,[56] Kan et al.;[57] (△) Adeniji et al.;[34] (●) Atkinson et al.;[36] (–) recommendation (see text).

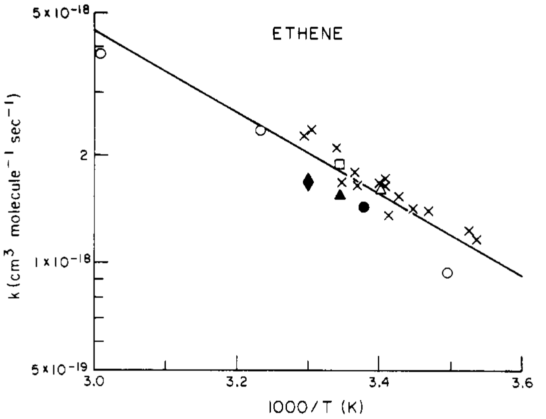


Figure 2. Arrhenius plot of selected (see text) literature rate constants at around room temperature for the gas-phase reaction of O_3 with ethene. (▲) Stedman et al.;[28] (○) Herron and Huie;[32] (□) Japar et al.;[29,40] (♦) Toby et al.;[75] (×) Su et al.,[56] Kan et al.;[57] (△) Adeniji et al.;[34] (●) Atkinson et al.;[36] (–) recommendation (see text).

and *trans*-ethene-d_2[29,56] are within 20% of the ethene data reported by these two groups,[29,56] indicating that isotope effects are minor. This is to be expected, since these reactions proceed via initial O_3 addition (see below).

b. Propene and Propene-d_6. Less data are available and over a shorter temperature range for propene than for ethene (Table III), and these are plotted in Arrhenius form in Figure 3. The temperature at which the rate constant obtained by Hanst et al.[37] is not known, so that datum cannot be included in Figure 3. It can be seen that the rate constants determined by Becker et al.[31] (which were not tabulated at the individual temperatures studied) are uniformly higher by ~40% than those of Herron and Huie;[32] the probable reasons for this have been discussed above for the ethene reaction. An unweighted least-squares analysis of the data of Cox and Penkett,[39] Stedman et al.,[28] Herron and Huie,[32] Japar et al.,[29,40] Adeniji et al.,[34] and Atkinson et al.[36] yields the Arrhenius expression

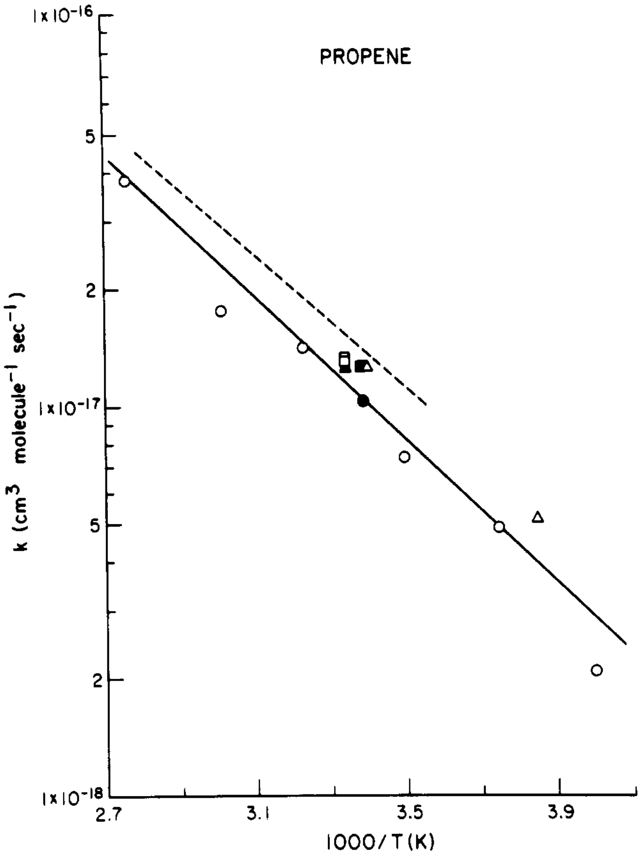


Figure 3. Arrhenius plot of selected (see text) literature rate constants for the gas-phase reaction of O_3 with propene. (■) Cox and Penkett;[39] (▲) Stedman et al.;[28] (○) Herron and Huie;[32] (□) Japar et al.;[29,40] (△) Adeniji et al.;[34] (●) Atkinson et al.;[36] (- - -) Becker et al.;[31] (–) recommendation (see text).

$$k(\text{propene}) = (1.32^{+2.72}_{-0.89}) \times 10^{-14} e^{-(4182 \pm 648)/RT}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

(the indicated errors in the Arrhenius parameters being two standard deviations)

$$k(\text{propene}) = 1.13 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at } 298\ \text{K}$$

with an estimated uncertainty of +40%, −20% at 298 K.

The sole reported rate constant for propene-d_6[29] at 299 ± 2 K is, as is the case for ethene-d_4 and ethene, very similar to that for propene, indicating that the isotope effect is small, as expected.

c. 1-Butene. Rate constants for the reactions of O_3 with 1-butene have been determined by Bufalini and Altshuller,[38] Japar et al.,[29] Huie and Herron,[33] and Adeniji et al.[34] The data of Japar et al.,[29] Huie and Herron,[33] and Adeniji et al.[34] are plotted in Arrhenius

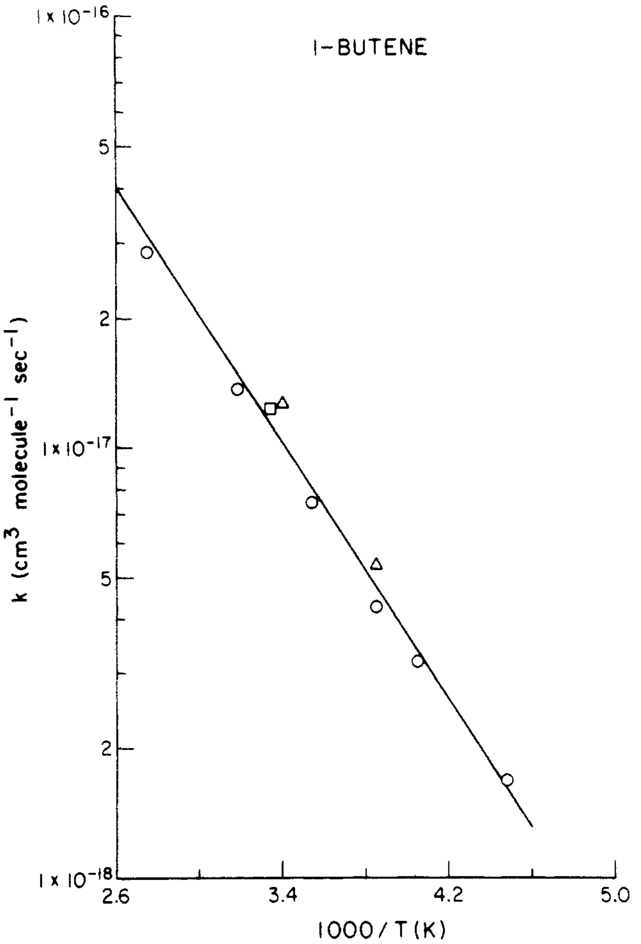


Figure 4. Arrhenius plot of selected (see text) rate constants for the gas-phase reaction of O_3 with 1-butene. (□) Japar et al.;[29] (○) Huie and Herron;[33] (△) Adeniji et al.;[34] (–) recommendation (see text).

form in Figure 4 (the rate constant of Bufalini and Altshuller[38] has been neglected for the reasons discussed above). These rate constant data are in good agreement with the unweighted least-squares Arrhenius line of

$$k(\text{1-butene}) = (3.46^{+1.19}_{-0.89}) \times 10^{-15} e^{-(3403 \pm 325)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where the error limits in the Arrhenius parameters are two standard deviations)

$$k(\text{1-butene}) = 1.10 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty at 298 K of ±30%.

d. 2-Methyl-2-propene (Isobutene). Rate constants have been determined by Hanst et al.,[37] Bufalini and Altshuller,[38] Becker et al.,[31] Japar et al.,[29] Grimsrud et al.,[42] Huie and Herron,[33] and Adeniji et al.[34] The data of Japar et al.,[29] Huie and Herron,[33] and Adeniji et al.[34] are plotted in Arrhenius form in Figure 5. These data show good agreement and an unweighted least-squares analysis yields the Arrhenius expression

$$k(\text{2-methyl-2-propene}) = (3.55^{+1.39}_{-1.00}) \times 10^{-15} e^{-(3364 \pm 182)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where the indicated error limits in the Arrhenius parameters are two least-squares standard deviations)

$$k(\text{2-methyl-2-propene}) = 1.21 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty of ±30% at 298 K.

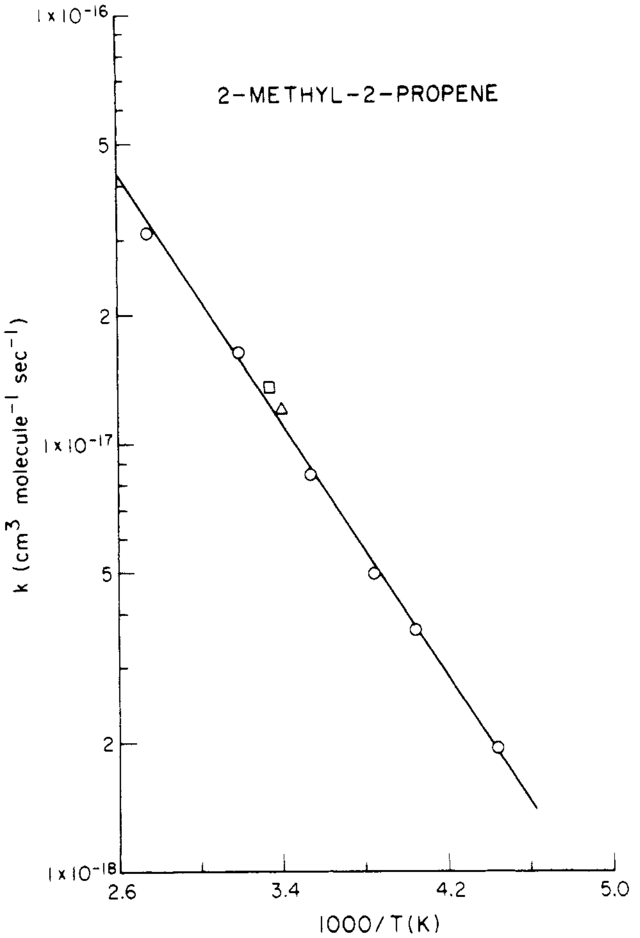


Figure 5. Arrhenius plot of selected (see text) rate constants for the gas-phase reaction of O_3 with 2-methyl-2-propene. (□) Japar et al.;[29] (○) Huie and Herron;[33] (△) Adeniji et al.;[34] (–) recommendation (see text).

The data of Hanst et al.,[37] Bufalini and Altshuller,[38] and Becker et al.[31] are significantly different (by factors of $\gtrsim 1.5$) than the data plotted in Figure 5, and the possible reasons for these discrepancies have been discussed above. The datum of Grimsrud et al.,[42] obtained using a slow-flow system, is ~25% higher than the recommendation. While this is certainly in agreement within the experimental uncertainties with the data shown in Figure 5, other somewhat higher discrepancies have been noted for α- and β-pinene[78] (see below), which may indicate that the data of Grimsrud et al.[42] tend to be uniformly high. This could well be due to nonideal flow characteristics at the slow-flow rates employed by Grimsrud et al.[42] (see section II).

e. *cis*-2-Butene. Rate constants for the reaction of O_3 with *cis*-2-butene have been determined by Hanst et al.,[37] Bufalini and Altshuller,[38] Cox and Penkett,[39] Japar et al.,[29] Huie and Herron,[33] and Atkinson et al.[76] The data from the latter four studies are plotted in Figure 6. While a significant amount of scatter is evident, the data are in reasonable agreement, and an unweighted least-squares analysis leads to the recommended Arrhenius expression

$$k(\textit{cis}\text{-2-butene}) = (3.52^{+1.79}_{-1.19}) \times 10^{-15} e^{-(1953 \pm 229)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(the indicated error limits in the Arrhenius parameters being two least-squares standard deviations)

$$k(\textit{cis}\text{-2-butene}) = 1.30 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty at 298 K of ±30%.

The data of Hanst et al.[37] and Bufalini and Altshuller[38] are factors of ~2.5 lower and ~2.2 higher, re-

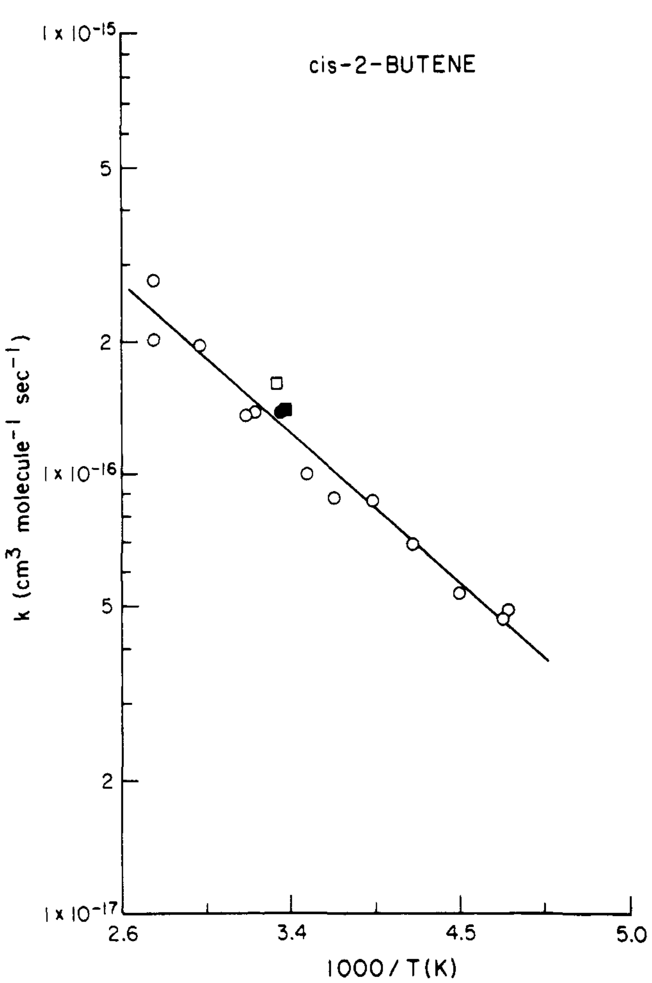


Figure 6. Arrhenius plot of selected (see text) rate constants for the gas-phase reaction of O_3 with *cis*-2-butene. (■) Cox and Penkett;[39] (□) Japar et al.;[29] (○) Huie and Herron;[33] (●) Atkinson et al.;[76] (–) recommendation (see text).

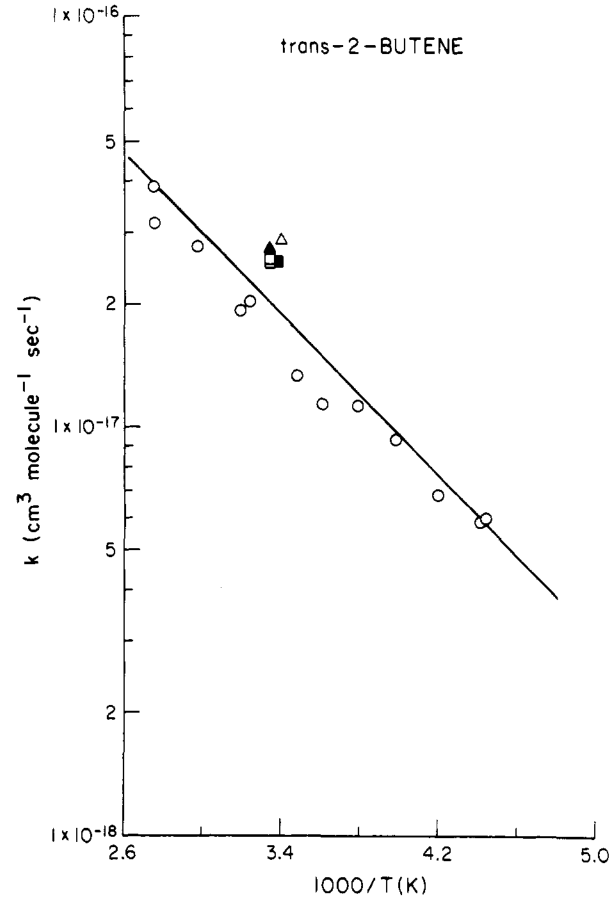


Figure 7. Arrhenius plot of selected (see text) rate constants for the gas-phase reaction of O_3 with *trans*-2-butene. (■) Cox and Penkett;[39] (▲) Stedman et al.;[28] (□) Japar et al.;[29,40] (○) Huie and Herron;[33] (△) Adeniji et al.;[34] (–) recommendation (see text).

spectively, than the rate constants recommended here.

f. *trans*-2-Butene. The rate constants obtained by Cox and Penkett,[39] Stedman et al.,[28] Japar et al.,[29,40] Huie and Herron,[33] and Adeniji et al.[34] are plotted in Arrhenius form in Figure 7. In this case, the agreement between the studies is not good, with the data of Huie and Herron[33] being significantly lower (by a factor of ~1.5) than those of Cox and Penkett,[39] Niki and coworkers,[28,29,40] and Adeniji et al.,[34] which are in excellent agreement among themselves. The fact that the stopped flow-mass spectroscopic data of Herron and Huie[32] and Huie and Herron[33] tend to be lower than most other studies is also evident, though to a much lesser extent, in Figures 1–6. The reasons for these differences are not known at the present time, but may involve the occurrence of secondary reactions in those studies yielding the higher apparent rate constants. The recent observation that the rate constants at room temperature for cyclopentene and cyclohexene obtained by Atkinson et al.[76] are lower by factors of ~1.6–3 than those determined by Japar et al.[29] and Adeniji et al.[34] (despite the use of basically similar experimental techniques) and that that of Atkinson et al.[76] for *cis*-2-butene (Figure 6) is in good agreement with Huie and Herron's data[33] tends to support the lower rate constants of Huie and Herron.[33]

However, in the absence of further data, we recommend the unweighted least-squares analysis of the data shown in Figure 7, which yields the Arrhenius expression

k(*trans*-2-butene) =

$$(9.08^{+10.63}_{-4.90}) \times 10^{-15} e^{-(2258\pm435)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(where the indicated errors are two least squares standard deviations)

k(*trans*-2-butene) =

$$2.00 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty at 298 K of +50%, −30% (i.e., ± approximately a factor of 1.5). Further work is obviously necessary to resolve the discrepancies between these data, at room temperature at a minimum.

g. 2-Methyl-2-butene. The rate constants obtained by Cox and Penkett,[39] Japar et al.,[29] and Huie and Herron[33] are plotted in Arrhenius form in Figure 8. The rate constant of Cox and Penkett[39] at 296 K, though in agreement with the earlier value of Bufalini and Altshuller,[38] is significantly higher than the more recent data of Japar et al.[29] and Huie and Herron[33]—the reasons for this discrepancy are not known at present.

The recommended Arrhenius line shown in Figure 8 is that obtained from an unweighted least-squares analysis of the data of Japar et al.[29] and Huie and Herron,[33] and is

k(2-methyl-2-butene) =

$$(6.17^{+6.45}_{-3.16}) \times 10^{-15} e^{-(1586\pm389)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(the indicated error in the Arrhenius parameters being two least-squares standard deviations)

k(2-methyl-2-butene) =

$$4.23 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}$$

with an estimated uncertainty at 298 K of +50%, −30% (i.e., ± approximately a factor of 1.5).

h. 2,3-Dimethyl-2-butene. Absolute rate constants

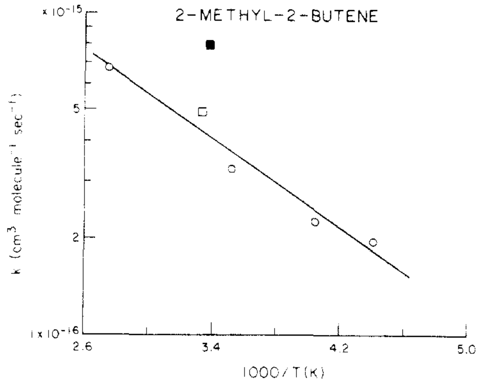


Figure 8. Arrhenius plot of selected (see text) rate constants for the gas-phase reaction of O_3 with 2-methyl-2-butene. (■) Cox and Penkett;[39] (□) Japar et al.;[29] (○) Huie and Herron;[33] (–) recommendation (see text).

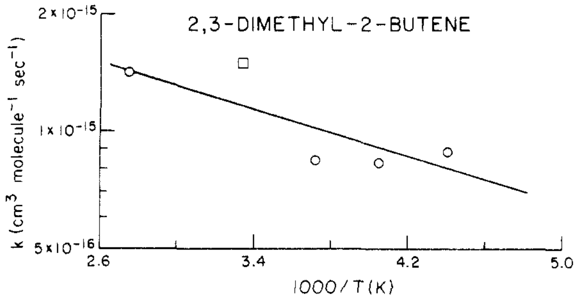


Figure 9. Arrhenius plot of rate constants for the gas-phase reaction of O_3 with 2,3-dimethyl-2-butene. (□) Japar et al.;[29] (○) Huie and Herron;[33] (–) recommendation (see text).

for this reaction have been obtained only by Japar et al.[29] and Huie and Herron,[33] and are plotted in Arrhenius form in Figure 9. The data are significantly scattered, with the rate constant of Japar et al.[29] at 299 K being a factor of ~1.4 higher than that derived by interpolation of the data of Huie and Herron.[33]

Our recommended Arrhenius expression is that obtained by an unweighted least-squares analysis of these data, and is

$$k(\text{2,3-dimethyl-2-butene}) = (3.71^{+9.83}_{-2.69}) \times 10^{-15} e^{-(690\pm703)/RT}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

(where the indicated error limits are two least-squares standard deviations)

$$k(\text{2,3-dimethyl-2-butene}) = 1.16 \times 10^{-15}\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K}$$

with an estimated uncertainty at 298 K of ± a factor of 1.5. Further studies concerning both the room temperature rate constant and the temperature dependence of this reaction are obviously necessary.

i. 1-Hexene. Although no temperature-dependent studies have been carried out for this particular alkene, several studies have determined rate constants at room temperature (Table III), and show good agreement. Based upon an unweighted least-squares analysis of the more recent rate constants obtained by Cox and Penkett[39] (which may be ~5–10% high[39]), Stedman et al.,[28] Japar et al.,[29] Adeniji et al.,[34] and Atkinson et al.,[36] we recommend

$$k(\text{1-hexene}) = 1.17 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K}$$

with an estimated uncertainty of ±30%.

j. Other Acyclic Monoalkenes. For the remaining alkenes listed in Table III, an insufficient number of reliable rate-constant determinations are available upon which to base any firm recommendations. However, based upon the above recommendations and the data given in Table III, generalizations can be made. The rate constants at room temperature for the 1-alkenes, propene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, and 1-decene, are all similar at ~1.2×10^{-17} cm³ molecule⁻¹ s⁻¹, within the scatter of a factor of ~1.5. While obviously more reliable data are necessary, we recommend using

$$k(\text{1-alkenes, RCH=CH}_2) = 1.2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K}$$

with an estimated uncertainty of +80%, −30%. This cited uncertainty reflects the possibility that a small increase in the rate constant with increasing chain length[36] may occur.

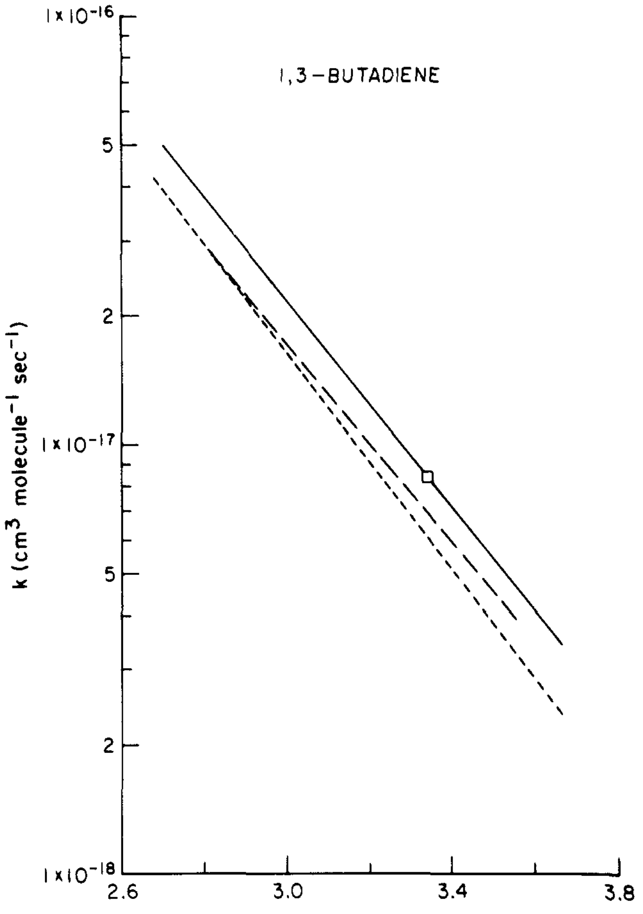


Figure 10. Arrhenius plot of the rate constants for the gas-phase reaction of ozone with 1,3-butadiene. (□) Japar et al.;[29] (– –) Becker et al.;[31] (- - -) Toby and Toby;[43] (–) recommendation (see text).

The rate constant for 2-methyl-1-pentene[39] is only a factor of ~1.5 higher than that for 2-methyl-2-propene, again indicating that a small increase in rate constant with increasing chain length may occur. While the magnitude of the rate constants for these terminal disubstituted alkenes, RR′C=CH₂, is surprisingly low, we tentatively recommend for this subclass that

$$k(\text{terminal disubstituted alkenes, RR}'\text{C=CH}_2) \simeq 1.2 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \text{ at 298 K}$$

with an estimated uncertainty of +80%, −20% at 298 K. This rate constant and uncertainty estimate are identical to that recommended above for the 1-alkenes, indicating the lack of any significant effect of a second substituent on the one olefinic carbon atom.

The data for *cis*- and *trans*-2-pentene and *cis*- and *trans*-3-methyl-2-pentene (Table III) again indicate that

TABLE IV. Reported Rate Constants *k* and Arrhenius Parameters for the Reaction of O_3 with Acyclic Dialkenes and Polyalkenes

alkene	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	at T, K	technique	ref	temp range covered, K
propadiene (allene)	1.7×10^{-15}	5500 ± 100	$(1.50 \pm 0.17) \times 10^{-19\,a}$	300	S-UV	Toby and Toby[79]	226–325
1,3-butadiene			8.1×10^{-18}	*b*	F/S-IR	Hanst et al.[37]	
			$(8.4 \pm 0.2) \times 10^{-18}$	299 ± 2	S-CL	Japar et al.[29]	
	5.45×10^{-14}	5330 ± 200	$6.7 \times 10^{-18\,a}$	298	S-UV	Becker et al.[31]	~286–358[c]
	1.05×10^{-13}	5800 ± 800	$(7.5 \pm 1.3) \times 10^{-18\,d}$	303	S-UV	Toby and Toby[43]	273–343
2-methyl-1,3-butadiene (isoprene)			1.27×10^{-17}	295 ± 1	S-FTIR	Arnts and Gay[80]	
			7.0×10^{-18}	260 ± 2	S-CL	Adeniji et al.[34]	260–294
		~3800	1.65×10^{-17}	294 ± 2			
			$(5.8 \pm 0.8) \times 10^{-18}$	278 ± 2	S-CL	Atkinson et al.[78]	278–323
			$(1.25 \pm 0.20) \times 10^{-17}$	296 ± 1			
			$(1.17 \pm 0.19) \times 10^{-17}$	296 ± 2			
	1.54×10^{-14}	4278 ± 854	$(1.76 \pm 0.34) \times 10^{-17}$	323 ± 1			
3,7-dimethyl-1,6-octadiene (dihydromyrcene)			6.8×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]	
3-methylene-7-methyl-1,6-octadiene (myrene)			1.25×10^{-15}	295 ± 1	F-CL	Grimsrud et al.[42]	
cis-3,7-dimethyl-1,3,6-octatriene (*cis*-ocimene)			2.0×10^{-15}	295 ± 1	F-CL	Grimsrud et al.[42]	
cis-2,*trans*-4-hexadiene			$(3.14 \pm 0.34) \times 10^{-16}$	294 ± 2	S-CL	Atkinson et al.[81]	
trans-2,*trans*-4-hexadiene			$(3.74 \pm 0.61) \times 10^{-16}$	294 ± 2	S-CL	Atkinson et al.[81]	
1,3,5-hexatriene[d]			$(2.62 \pm 0.34) \times 10^{-17}$	294 ± 2	S-CL	Atkinson et al.[81]	

[a] Calculated from the Arrhenius expression. [b] Room temperature, not reported. [c] Derived from the graphical tabulation given. [d] Value cited by Toby et al.[75] [e] Rate constants for *cis*-1,3,5-hexatriene and *trans*-1,3,5-hexatriene are identical to within ~10%.[81]

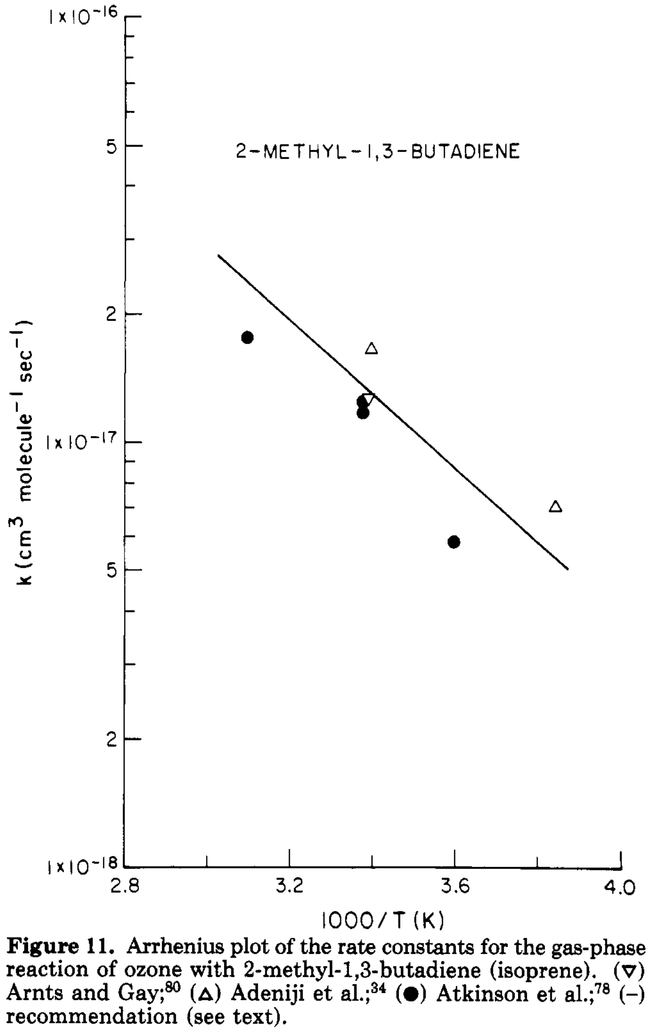


Figure 11. Arrhenius plot of the rate constants for the gas-phase reaction of ozone with 2-methyl-1,3-butadiene (isoprene). (▽) Arnts and Gay;[80] (△) Adeniji et al.;[34] (●) Atkinson et al.;[78] (–) recommendation (see text).

the major factor influencing the magnitude of the rate constants for the acyclic monoalkenes is the number of substituent groups, and not, to a first approximation, their precise identity. Thus, the rate constants for the *cis*- and *trans*-2-pentenes are only slightly higher than those for the corresponding *cis*- and *trans*-2-butenes, respectively,[39] and the rate constants for *cis*- and *trans*-3-methyl-2-pentene are very similar to that for 2-methyl-2-butene.[29] Hence, we recommend using the above recommended rate constants for *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene at 298 K for the corresponding cis and trans internal alkenes, trialkyl-substituted alkenes, and tetraalkyl-substituted alkenes, respectively, i.e., at 298 K

k(cis internal alkenes, RCH=CHR′) =

$$1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of +80%, −30%.

k(trans internal alkenes, RCH=CHR′) =

$$2.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of plus a factor of 2 and minus a factor of 1.5.

k(trialkyl-substituted alkenes RR′C=CHR″) =

$$4.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of plus a factor of 2 and minus a factor of 1.5.

k(tetraalkyl-substituted alkenes) =

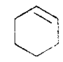
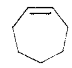
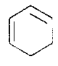
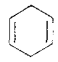
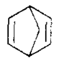
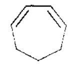
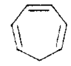
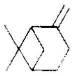
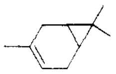
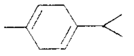
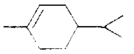
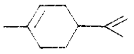
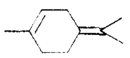
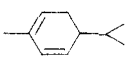
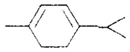
$$1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of plus a factor of 2 and minus a factor of 1.5. There is the possibility that the rate constants will, in the absence of steric hindrance effects, increase slightly with increasing substituent chain length.

2. Acyclic Dialkenes and Trialkenes

The absolute rate constant data available for the acyclic dialkenes and trialkenes are compiled in Table IV. Rate constants have been determined for propadiene (allene), 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), *cis*-2,*trans*-4-hexadiene, *trans*-2,*trans*-4-hexadiene, 1,3,5-hexatriene (a cis–trans mixture), and the three monoterpenes 3,7-dimethyl-1,6-octadiene (dihydromyrcene), 3-methylene-7-methyl-1,6-octadiene (myrcene), and *cis*-3,7-dimethyl-1,3,6-octatriene (*cis*-ocimene). Only for 1,3-butadiene and isoprene have more than one study been carried out. For propadiene, *cis*-2,*trans*-4- and *trans*-2,*trans*-4-hexadiene, 1,3,5-

TABLE V. Rate Constants k and Arrhenius Parameters for the Reaction of O_3 with Cycloalkenes, Cyclodialkenes, and Cyclotrialkenes

alkene	structure	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref
cyclopentene				$(8.13 \pm 0.79) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]
				5.73×10^{-16}	260 ± 2	S-CL	Adeniji et al.[34]
			~2300	9.69×10^{-16}	294 ± 2		
				$(2.75 \pm 0.33) \times 10^{-16}$	297 ± 1	S-CL	Atkinson et al.[76]
cyclohexene				5.9×10^{-17}	a	S-CA	Cadle and Schadt[8]
				$(1.60 \pm 0.15) \times 10^{-16}$	299 ± 2	S-CL	Japar et al.[29]
				1.18 ± 10^{-16}	260 ± 2	S-CL	Adeniji et al.[34]
			~2400	2.04×10^{-16}	294 ± 2		
				$(1.04 \pm 0.14) \times 10^{-16}$	297 ± 1	S-CL	Atkinson et al.[76]
cycloheptene				$(3.19 \pm 0.36) \times 10^{-16}$	297 ± 1	S-CL	Atkinson et al.[76]
1,3-cyclohexadiene				$(1.97 \pm 0.28) \times 10^{-15}$	297 ± 1	S-CL	Atkinson et al.[76]
1,4-cyclohexadiene				$(6.39 \pm 0.74) \times 10^{-17}$	297 ± 1	S-CL	Atkinson et al.[76]
bicyclo[2.2.1]-2-heptene				$(2.14 \pm 0.35) \times 10^{-15}$	297 ± 1	S-CL	Atkinson et al.[76]
bicyclo[2.2.2]-2-octene				$(7.28 \pm 0.90) \times 10^{-17}$	297 ± 1	S-CL	Atkinson et al.[76]
bicyclo[2.2.1]-2,5-heptadiene				$(4.68 \pm 1.29) \times 10^{-15}$	297 ± 1	S-CL	Atkinson et al.[76]
1,3-cycloheptadiene				$(1.56 \pm 0.21) \times 10^{-16}$	294 ± 2	S-CL	Atkinson et al.[81]
1,3,5-cycloheptatriene				$(5.39 \pm 0.78) \times 10^{-17}$	294 ± 2	S-CL	Atkinson et al.[81]
α-pinene				1.7×10^{-16}	294	S-CL	Ripperton et al.[82]
				1.45×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
				$(3.3 \pm 0.6) \times 10^{-16}$	298	S-CL	Japar et al.[30]
				$(6.2 \pm 1.3) \times 10^{-17}$	276 ± 1	S-CL	Atkinson et al.[78]
				$(8.3 \pm 1.3) \times 10^{-17}$	295 ± 1		
				$(8.4 \pm 1.9) \times 10^{-17}$	296 ± 2		
		9.4×10^{-16}	1452 ± 344	$(9.3 \pm 1.8) \times 10^{-17}$	324 ± 2		
β-pinene				3.6×10^{-17}	295 ± 1	F-CL	Grimsrud et al.[42]
				$(2.1 \pm 0.5) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[78]
Δ^3-carene				1.2×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
β-phellandrene				1.8×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
γ-terpinene				2.8×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
carvomenthene				5.2×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
d-limonene				6.4×10^{-16}	295 ± 1	F-CL	Grimsrud et al.[42]
terpinoline				$(7.3 \pm 2.2) \times 10^{-16}$	298	S-CL	Japar et al.[30]
				1.0×10^{-14}	295 ± 1	F-CL	Grimsrud et al.[42]
α-phellandrene				1.2×10^{-14}	295 ± 1	F-CL	Grimsrud et al.[42]
α-terpinene				8.8×10^{-14}	295 ± 1	F-CL	Grimsrud et al.[42]

[a] Not reported.

hexatriene, and the three acyclic monoterpenes, we do not give any rate constant recommendations since only a single study has been carried out for each of these alkenes. For 1,3-butadiene and 2-methyl-1,3-butadiene, however, our recommendations are as follows:

a. 1,3-Butadiene. The rate constant determined by Japar et al.[29] and the Arrhenius expressions of Becker et al.[31] and Toby and Toby[43] are plotted in Figure 10.

TABLE VI. Rate Constants k and Arrhenius Activation Energies E for the Reaction of O_3 with Haloalkenes

haloalkene	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref
vinyl fluoride		1.4×10^{-19}	260 ± 2	S-CL	Adeniji et al.[34]
	~7200	7.0×10^{-19}	294 ± 2		
1,1-difluoroethene		8×10^{-20}	290	S-UV	Becker et al.[31]
		1.9×10^{-19}	294 ± 2	S-CL	Adeniji et al.[34]
cis-1,2-difluoroethene		2.6×10^{-19}	294 ± 2	S-CL	Adeniji et al.[34]
trans-1,2-difluoroethene		2.1×10^{-18}	294 ± 2	S-CL	Adeniji et al.[34]
trifluoroethene		2.4×10^{-20}	260 ± 2	S-CL	Adeniji et al.[34]
	~7900	1.4×10^{-19}	294 ± 2		
tetrafluoroethene		5.0×10^{-19}	*a*	S-IR	Heicklen[83]
		9.2×10^{-20}	294 ± 2	S-CL	Adeniji et al.[34]
vinyl chloride		6.5×10^{-21}	295	S-UV	Sanhueza et al.[84]
		2.3×10^{-19}	*a*	S-FTIR	Gay et al.[85]
		$(2.45 \pm 0.45) \times 10^{-19}$	298	S-FTIR	Zhang et al.[86]
1,1-dichloroethene		$(3.7 \pm 1.0) \times 10^{-21}$	298	S-UV	Hull et al.[87]
cis-1,2-dichloroethene		6.2×10^{-20}	296	S-UV	Blume et al.[88]
		$<5 \times 10^{-21}$	*a*	S-FTIR	Niki et al.[54]
trans-1,2-dichloroethene		3.8×10^{-19}	296	S-UV	Blume et al.[88]
		$(1.80 \pm 0.29) \times 10^{-19}$	298	S-FTIR	Zhang et al.[86]
		1.2×10^{-19}	*a*	S-FTIR	Niki et al.[54]
		$(1.2 \pm 0.24) \times 10^{-19}$	300	S-FTIR	Niki et al.[55]
trichloroethene		$<3 \times 10^{-20}$	296 ± 2	S-CL	Atkinson et al.[36]
tetrachloroethene		$<2 \times 10^{-23}$	297	S-UV	Mathias et al.[89]
hexafluoropropene		7.7×10^{-20}	*a*	S-IR	Heicklen[83]
cis-1,3-dichloropropene		$(1.5 \pm 0.5) \times 10^{-19}$	295 ± 2	S-CL	Tuazon et al.[90]
trans-1,3-dichloropropene		$(6.7 \pm 0.8) \times 10^{-19}$	295 ± 2	S-CL	Tuazon et al.[90]
cis- + *trans*-octafluoro-2-butene		6.8×10^{-21}	*a*	S-IR	Heicklen[83]
2-(chloromethyl)-3-chloro-1-propene		$(3.9 \pm 0.5) \times 10^{-19}$	295 ± 2	S-CL	Tuazon et al.[90]

[a] Room temperature, not reported.

(The individual rate constants at the temperatures studied were not tabulated by either Becker et al.[31] or Toby and Toby,[43] a practice not to be condoned.) All three studies (together with that of Hanst et al.[37] at an unspecified room temperature) are in reasonable agreement. This may imply that for the 1,3-butadiene system sufficient O_2 was present in the study of Becker et al.[31] to terminate secondary reactions. In view of the larger error limits associated with the data of Toby and Toby[43,75] we recommend the 299 K rate constant of Japar et al.[29] with an Arrhenius activation energy of ~5.5 kcal mol^{-1} (the approximate average of the two literature values[31,43]), i.e.

$$k(\text{1,3-butadiene}) = (8.8 \times 10^{-14})e^{-5500/RT}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k(\text{1,3-butadiene}) = 8.1 \times 10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

with an estimated uncertainty at 298 K of ±40%.

b. 2-Methyl-1,3-butadiene (Isoprene). The rate constants reported by Arnts and Gay,[80] Adeniji et al.,[34] and Atkinson et al.[78] are plotted in Arrhenius form in Figure 11. The data of Adeniji et al.[34] are somewhat higher than the other rate constants; the reason for this discrepancy is not known at present.

Both temperature-dependent studies[34,78] reported an Arrhenius activation energy of ~4 kcal mole^{-1}. An unweighted least-squares treatment of the data in Figure 11, however, yields an Arrhenius activation energy of 3.0 kcal mol^{-1} because of the weighting caused by the two extreme temperature points, one from each of the two studies. For this reason, we prefer to use the mean of the room temperature (295 ± 3 K) rate constants (1.34×10^{-17} cm^3 molecule^{-1} s^{-1}) together with a "fitted" Arrhenius activation energy of 4.0 kcal mol^{-1} to obtain

$$k(\text{2-methyl-1,3-butadiene}) = 1.23 \times 10^{-14}\ e^{-4000/RT}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k(\text{2-methyl-1,3-butadiene}) = 1.43 \times 10^{-17}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\ \text{at 298 K}$$

with an estimated uncertainty of ±40% at 298 K.

3. Cycloalkenes, Cyclodialkenes and Cyclotrialkenes

The reported rate constants for the reactions of O_3 with these classes of alkenes are listed in Table V. Only for cyclopentene, cyclohexene, α-pinene, β-pinene, and terpinoline have more than a single study been carried out. Unfortunately, for cyclopentene, cyclohexene, α-pinene, and terpinolene, the reported room temperature rate constants are not in agreement, with discrepancies of up to a factor of ~4. Thus, we do not offer any recommendations of rate constants for this class of organics, except to recommend that further work be carried out to resolve the above mentioned discrepancies.

4. Haloalkenes

The available kinetic data for the reaction of O_3 with the haloalkenes are summarized in Table VI. Only for vinyl chloride, *cis*- and *trans*-1,2-dichloroethene, 1,1-difluoroethene, and tetrafluoroethene have more than a single study been carried out, and for these haloalkenes the agreement between the studies is not good. Thus, we make no recommendations for any of these haloalkenes.

The available data indicate that the reactions of O_3 with the haloalkenes are complicated by secondary reactions,[53-55,84] and thus the rate constant data given in Table VI should strictly be considered to be upper limits to the rate constants for the initial reactions. In particular, the reaction rate constants are markedly decreased in the presence of O_2,[84] and in the absence of O_2 or at high reactant concentrations a second-order dependence on O_3 (or the haloethene) has been observed for *cis*- and *trans*-dichloroethene[88] and 1,1-dichloroethene.[87] The most recent product studies of Niki

TABLE VII. Rate Constants and Arrhenius Parameters for the Reaction of O_3 with Alkynes

alkyne	*A*, cm^3 $molecule^{-1}$ s^{-1}	*E*, cal mol^{-1}	*k*, cm^3 $molecule^{-1}$ s^{-1}	*T*, K	technique	ref	temp range covered, K
acetylene		4800	$(7.8 \pm 2.8) \times 10^{-20}$	303	S-CA	Cadle and Schadt[101]	
			1.96×10^{-20}	283	S-UV	DeMore[74]	243–283
			1.05×10^{-20}	273			
			8.3×10^{-21}	273			
			2.3×10^{-21}	258			
			1.7×10^{-21}	248			
			1.3×10^{-21}	248			
	5.3×10^{-12}	10800 ± 400	5.0×10^{-22}	243			
			$(3.0 \pm 0.5) \times 10^{-20}$	294 ± 1	S-UV	DeMore[102]	
			$(8.6 \pm 0.9) \times 10^{-20}$	298 ± 2	S-CL	Stedman and Niki[41]	
			$(3.8 \pm 0.6) \times 10^{-20}$	297 ± 2	S-CL	Pate et al.[103]	
			$(7.8 \pm 1.2) \times 10^{-21}$	294 ± 2	S-CL	Atkinson and Aschmann[104]	
propyne			1.28×10^{-18}	298	S-IR	Dillemuth et al.[105]	
			$(2.2 \pm 1.2) \times 10^{-20}$	294 ± 1	S-UV	DeMore[102]	
			$(1.43 \pm 0.15) \times 10^{-20}$	294 ± 2	S-CL	Atkinson and Aschmann[104]	
1-butyne			1.79 ± 10^{-18}	298	S-IR	Dillemuth et al.[105]	
			$(4.0 \pm 1.3) \times 10^{-20}$	294 ± 1	S-UV	DeMore[102]	
			$(1.97 \pm 0.26) \times 10^{-20}$	294 ± 2	S-CL	Atkinson and Aschmann[104]	
2-butyne			$(3.3 \pm 0.5) \times 10^{-20}$	294 ± 1	S-UV	DeMore[102]	
diacetylene (butadiyne)			$(6^{+4}_{-3}) \times 10^{-20}$	297 ± 2	S-CL	Atkinson and Aschmann[106]	

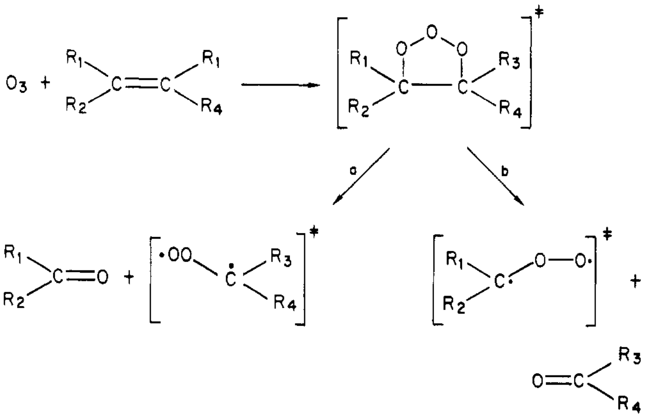
et al.[53–55] indicate that Cl atoms (in addition to OH and HO_2 radicals[53,55]) are generated in the reactions of O_3 with chloroalkenes and can react via secondary reactions with O_3 or the haloalkene. However, it should be noted that at part-per-million (ppm) concentrations of O_3 in the presence of large excess of the haloalkene in air, the O_3 decay rates may not be influenced to any marked degree by secondary reactions.

Assuming that the data in Table VI can be used for quantitative and comparative purposes, then the following generalizations can be made. For the fluorine- and chlorine-substituted ethenes (most of the data being from Adeniji et al.[34]), the room temperature rate constants decrease monotonically with the degree of substitution, with the exception of the *trans*-1,2-dihaloethenes, which for fluorine and chlorine atom substitution (the only two studied to date) are markedly more reactive than the 1,1 or cis-1,2 isomers. The fluorine- and chlorine-substituted propenes and butenes for which data are available (Table VI) also have rate constants markedly lower than those for the corresponding alkenes. Hence, these data indicate that chlorine substitution leads to a decrease of the rate constant with respect to the corresponding alkene, and that this decrease is more marked for chlorine substitution than for fluorine substitution, being orders of magnitude for vinyl chloride, trichloroethene, and tetrachloroethene. Since the OH radical rate constants for haloalkenes are generally less affected by halogen substitution than are those for the corresponding alkenes,[10,90] this indicates that, compared to the alkenes, the ozone reactions with the haloalkenes are generally of much less importance as an atmospheric loss process than are their OH radical reactions.

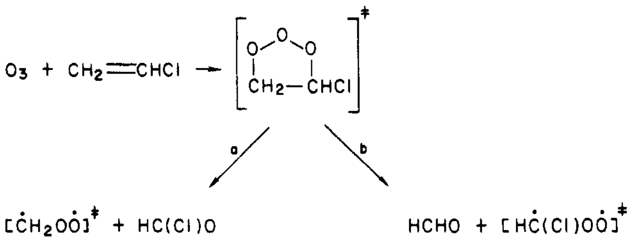
B. Mechanism

Most of the mechanistic and product data available concerning the reactions of O_3 with the alkenes have been obtained for the simple acyclic alkenes such as ethene, propene, and the 2-butenes. While numerous product studies have been carried out, the most definitive mechanistic data have emerged from the studies of Cox and Penkett,[39] Niki et al.,[52,54,91,92] Herron and co-workers,[48–50,93,94] and Calvert and co-workers.[56,57] These experimental data have been previously discussed by Calvert et al.[95] and Dodge and Arnts,[96] and much more recently by Herron et al.[97] and Atkinson and Lloyd,[18] and thus need not be discussed in detail here except to summarize the major overall conclusions.

It is now reasonably well established from these studies that the initial step in the O_3–alkene reaction is the formation of a "molozonide" which rapidly decomposes[97,98] to a carbonyl and a biradical, which is also initially energy rich:

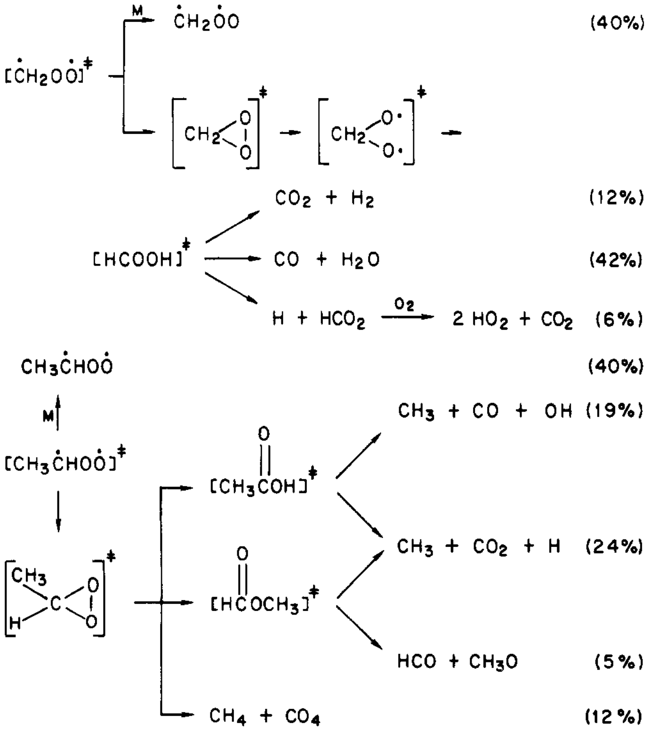


where [ ]‡ denotes an energy-rich species. On the basis of the work of Herron and Huie,[49] it has generally been assumed that $k_a \sim k_b$, at least for the alkenes. However, this assumption is probably not true for the haloalkenes, and recently Zhang et al.[86] have obtained a rate constant ratio of $k_a/k_b \sim 3.2$ for the decomposition of the "molozonide" formed from the reaction of O_3 with vinyl chloride



The energy rich biradicals $[R_1R_2\dot{C}O\dot{O}]^{\ddagger}$ can either be stabilized and undergo subsequent bimolecular reactions, or undergo unimolecular rearrangement and fragmentation. However, the details of these processes are only reasonably well understood for $[\dot{C}H_2O\dot{O}]^{\ddagger}$ and, to a lesser extent, for $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ and $[H\dot{C}(Cl)O\dot{O}]^{\ddagger}$. Indeed, the fractions of the initially energy-rich biradicals which are stabilized at atmospheric pressure and room temperature are not well-known.[18] For the $[\dot{C}H_2O\dot{O}]^{\ddagger}$ biradical formed from ethene, the fraction stabilized at atmospheric pressure has been determined to be 0.38,[56] 0.37,[57] and 0.35,[52] with obvious excellent agreement between these studies. For the higher biradicals such as $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ the situation is much less clear, with, for instance, reported stabilization yields of 0.18[92] and ~0.43 (the data of Cox and Penkett[39] as analyzed by Atkinson and Lloyd[18]) for $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$ from *cis*-2-butene. The sole data concerning stabilization factors for $[R_1R_2\dot{C}O\dot{O}]^{\ddagger}$ biradicals from other alkenes are those of Cox and Penkett[39] (see Atkinson and Lloyd[18] for a discussion of these data) and, with the exception of the biradicals from 1-hexene, are also of the order of ~0.4.[18] Recently Zhang et al.[86] have determined the fraction of stabilization of $[\dot{C}H_2O\dot{O}]^{\ddagger}$ from vinyl chloride to be 0.25, and rationalize this lower stabilization ratio (vs. that from ethene) by the fact that $[\dot{C}H_2O\dot{O}]^{\ddagger}$ formed from the reaction of O_3 with vinyl chloride is ~10 kcal mol^{-1} more energized than is $[\dot{C}H_2O\dot{O}]^{\ddagger}$ from the reaction of O_3 with ethene.

Based on analyses of product and mechanistic studies of the reactions of O_3 with ethene, propene, and *cis*- and *trans*-2-butene (ref 39, 48, 49, 52, 56, 57, 91, 92, 95, 96) Atkinson and Lloyd[18] have recommended that these species react under atmospheric conditions as shown below



where $\dot{C}H_2O\dot{O}$ and $CH_3\dot{C}HO\dot{O}$ denote thermalized biradicals. However, as noted above there are a number of uncertainties and ambiguities concerning the reactions of $[CH_3\dot{C}HO\dot{O}]^{\ddagger}$, including the fraction which is stabilized to $CH_3\dot{C}HO\dot{O}$ at room temperature and atmospheric pressure, and Herron et al.[97] and Atkinson and Lloyd[18] should be consulted for a more detailed discussion of the reactions of these and other biradicals.

The stabilized biradicals are known to undergo bimolecular reactions with aldehydes (ref 37, 52, 56, 57, 86, 91, 92), with SO_2 (ref 39, 56, 92, 94, 95), with CO,[56] and with H_2O,[39,95,99,100] and it is believed that they will also react with NO and NO_2.[18,97]

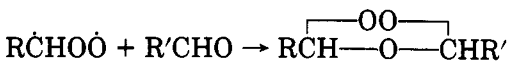
$$R\dot{C}HO\dot{O} + NO \rightarrow RCHO + NO_2$$

$$R\dot{C}HO\dot{O} + NO_2 \rightarrow RCHO + NO_3$$

$$R\dot{C}HO\dot{O} + SO_2 \xrightarrow{H_2O} RCHO + H_2SO_4$$

$$R\dot{C}HO\dot{O} + H_2O \rightarrow RCOOH + H_2O$$

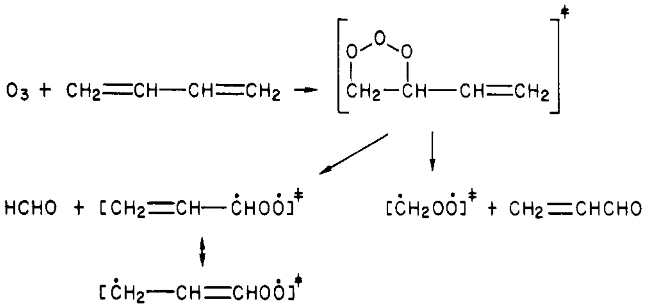
$$R\dot{C}HO\dot{O} + CO \rightarrow \text{products}$$

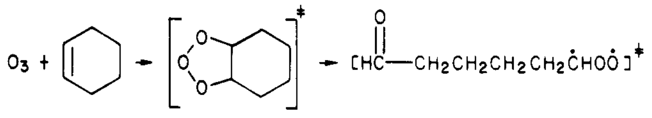


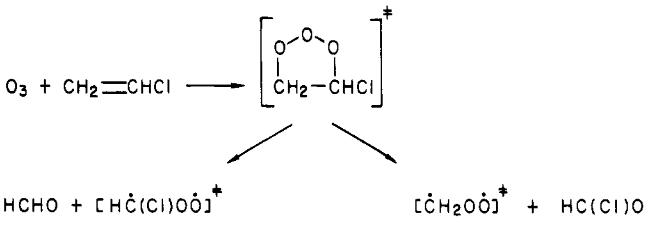
$$R\dot{C}HO\dot{O} + R'CHO \rightarrow \overbrace{RCH{-}O{-}CHR'}^{OO}$$

Under atmospheric and environmental chamber conditions, the reactions with NO, NO_2, or H_2O are expected to predominate, depending on their relative concentrations. For a detailed discussion of these reactions and their estimated rate constants, the articles of Herron et al.[97] and Atkinson and Lloyd[18] should be consulted.

While the above discussion has dealt mainly with the simple acyclic monoalkenes, the initial reactions for the di- and polyalkenes, the cyclic alkenes, and the haloalkenes are believed to be analogous.[54] For example, for 1,3-butadiene, cyclohexene, and vinyl chloride, the reactions are expected to proceed via[54]

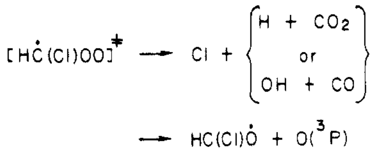






with the initially energy-rich biradicals undergoing subsequent reactions.

Niki and co-workers[54,55] have recently shown, from studies of the reaction of O_3 with *trans*-1,2-dichloroethene at room temperature and 700 Torr total pressure of air, that the yields of Cl and $O(^3P)$ atoms from the reactions

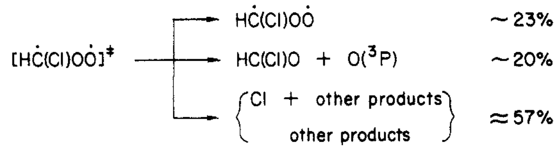


$$[H\dot{C}(Cl)OO]^{\ddagger} \rightarrow Cl + \left\{\begin{array}{c} H + CO_2 \\ \text{or} \\ OH + CO \end{array}\right\}$$
$$\rightarrow HC(Cl)\dot{O} + O(^3P)$$

are $\lesssim 0.7$[54] and 0.20,[54,55] respectively. Furthermore, peroxyformic acid, HC(O)OOH, has been observed from the reactions of O_3 with vinyl chloride,[53,54] 1,1-dichloroethene,[53,54] and *cis*- and *trans*-1,2-dichloroethene[53,54,86] with a yield in the *trans*-1,2-dichloroethene system (in the presence of a Cl atom scavenger) of ~ 0.23.[53] Lower peroxyformic acid yields of 0.04, 0.09, and 0.10 were obseved under similar experimental conditions for vinyl chloride, *cis*-1,2-dichloroethene, and 1,1-dichloroethene, respectively.[53] It was proposed[53] that HC(O)OOH resulted from the reaction of thermalized $H\dot{C}(Cl)O\dot{O}$ radicals with H_2O

$$HC(Cl)O\dot{O} + H_2O \rightarrow HC(O)OOH + HCl$$

though it could not be determined whether this reaction was heterogeneous or homogeneous in nature.[53] Thus, for the $[H\dot{C}(Cl)O\dot{O}]^{\ddagger}$ biradical formed from the reaction of O_3 with *trans*-1,2-dichloroethene, the reaction pathways at room temperature and atmospheric pressure appear to be



$$[H\dot{C}(Cl)O\dot{O}]^{\ddagger} \rightarrow \left\{\begin{array}{ll} H\dot{C}(Cl)O\dot{O} & \sim 23\% \\ HC(Cl)O + O(^3P) & \sim 20\% \\ \left\{\begin{array}{c} Cl + \text{other products} \\ \text{other products} \end{array}\right\} & \approx 57\% \end{array}\right.$$

However, the modes of reaction of the more complex excited biradicals, such as $[CH_2{=}CH\dot{C}HO\dot{O}]^{\ddagger}$ from isoprene and $[HCO(CH_2)_4\dot{C}HO\dot{O}]^{\ddagger}$ from cyclohexene shown above are presently unknown, and experimental data concerning the reactions of such biradicals under atmospheric conditions need to be obtained.

V. Alkynes

A. Kinetics

The available kinetic data for the reactions of O_3 with the alkynes are given in Table VII. Unfortunately, for the simple alkynes there is no general agreement as to the rate constants, and hence no recommendations are made. For acetylene, propyne, and 1-butyne the recent kinetic data of Atkinson and Aschmann[104] are, in general, lower than previous data. Thus, for acetylene the rate constant at 294 K of Atkinson and Aschmann[104] is a factor of ~4 lower than the rate constants obtained by Cadle and Schadt,[101] DeMore,[74,102] Stedman and Niki,[41] and Pate et al.,[103] when the temperature dependence of the rate constant is taken into account. The reasons for these discrepancies are not known, but may be due to the occurrence of surface reactions (as noted by DeMore[102]) and/or secondary reactions. It is probable that the rate constants determined by Dillemuth et al.[105] for propyne and 1-butyne are in error, being a factor of ~100 higher than the data of DeMore[102] and Atkinson and Aschmann.[104] It is thus obvious that further work is necessary to more fully characterize the kinetics of these reactions, including the determination of rate constants over a significant temperature range.

However, it is apparent that the alkynes are much less reactive than the alkenes, as also observed for the reactions of $O(^3P)$ atoms[107] and OH radicals[10,104] with this class of organics. These O_3 reactions are then of minor importance under atmospheric conditions, since the OH radical reactions have rate constants of $\sim 7 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for acetylene,[104] $\sim(6–8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for propyne and 1-butyne,[104] and $\sim 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for diacetylene[106] at room temperature.

B. Mechanism

The only-gas phase investigation of the products of these reactions has been that of DeMore.[102] The major products observed were α-dicarbonyls together with CO, CO_2, and carboxylic acids.[102] However, at least for acetylene, the time-dependent behavior of glyoxal formation suggested that it was not generated in a homogeneous gas-phase reaction since nearly all the glyoxal (~25% of the O_3 reacted) was formed during the initial stages of the reaction. Obviously further product and mechanistic studies are necessary before the reaction pathways for the alkynes can be elucidated.

VI. Aromatics

A. Kinetics

The available kinetic data for the reaction of O_3 with aromatics are given in Table VIII. No temperature dependence studies have been conducted. It can be seen that, except for styrene (see below), the aromatic hydrocarbons react very slowly with O_3, with rate constants $<10^{-20}$ cm^3 molecule^{-1} s^{-1} for the monocyclic aromatics. Thus, reaction of these compounds with O_3 is expected to be negligible under atmospheric conditions. The study of Pate et al.,[103] which yielded apparent rate constants for these reactions which, as expected, increase with the degree of substitution, must be regarded as the most definitive study. Styrene is best considered as a phenyl-substituted ethene, since for this organic the reaction with O_3 almost certainly occurs via O_3 addition to the $-CH{=}CH_2$ group. The rate constant for styrene is a factor of ~2 higher than that for propene, indicating that the phenyl group is somewhat more activating than a methyl group. Other than styrene, the most reactive of the aromatics studied are the cresols, and even for these aromatics the reactions with O_3 are of minor importance compared to their reaction with OH radicals[36,108] or NO_3 radicals.[20,23] It should be noted that the presence of any impurities or the formation of radical species in these reactions would lead to high apparent rate constants, and the data in Table VIII, especially for the aromatic hydrocarbons, must be considered to be upper limits.

Little is known concerning the mechanism and products for the reactions of O_3 with the aromatics. It is probable that styrene reacts in a manner analogous to that discussed in section IVB for the aliphatic alkenes, but the mechanism for the reaction with the other aromatics may well be quite different. Thus, Pate et al.[103] observed that the reactions of O_3 with the aromatic hydrocarbons lead to ring cleavage, forming α-dicarbonyls, with, for example, for 1,3,5-trimethylbenzene

$$2O_3 + 1,3,5\text{-}(CH_3)_3C_6H_3 \rightarrow 3CH_3COCHO$$

although small amounts of CO, CO_2, and HCOOH were also observed.[103] However, the mechanism for the formation of these products is presently unknown.

TABLE VIII. Rate Constants *k* for the Reaction of O_3 with Aromatic Compounds

aromatic	k, cm^3 $molecule^{-1}$ s^{-1}	T, K	technique	ref
benzene	$(7 \pm 4) \times 10^{-23}$	297 ± 2	S-CL	Pate et al.[103]
toluene	$(1.2 \pm 0.6) \times 10^{-20}$	298 ± 2	S-CL	Stedman and Niki[41]
	$(1.5 \pm 0.8) \times 10^{-22}$	297 ± 2	S-CL	Pate et al.[103]
o-xylene	$(7 \pm 2) \times 10^{-22}$	297 ± 2	S-CL	Pate et al.[103]
	$<1 \times 10^{-20}$	296 ± 2	S-CL	Atkinson et al.[36]
m-xylene	$(6 \pm 2) \times 10^{-22}$	297 ± 2	S-CL	Pate et al.[103]
	$<5 \times 10^{-21}$	296 ± 2	S-CL	Atkinson et al.[36]
p-xylene	$(4 \pm 2) \times 10^{-22}$	297 ± 2	S-CL	Pate et al.[103]
xylenes (isomeric mixture)	$<2 \times 10^{-19}$	*a*	F/S-IR	Hanst et al.[37]
	$\leq 5 \times 10^{-21}$	298 ± 2	S-CL	Stedman and Niki[41]
1,2,3-trimethylbenzene	$(1.6 \pm 0.4) \times 10^{-21}$	297 ± 2	S-CL	Pate et al.[103]
1,2,4-trimethylbenzene	$(1.3 \pm 0.3) \times 10^{-21}$	297 ± 2	S-CL	Pate et al.[103]
1,3,5-trimethylbenzene	$<1 \times 10^{-19}$	303	F-CA	Bufalini and Altshuller[38]
	$(2.2 \pm 0.6) \times 10^{-21}$	297 ± 2	S-CL	Pate et al.[103]
styrene	3.0×10^{-17}	303	F-CA	Bufalini and Altshuller[38]
	$(2.16 \pm 0.46) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[36]
o-cresol	$\sim 6 \times 10^{-19}$	300 ± 1	*b*	Atkinson et al.[108]
	$(2.55 \pm 0.39) \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[36]
m-cresol	2×10^{-19}	*a*	S-CL	Carter[109]
	$\sim 6 \times 10^{-19}$	300 ± 1	*b*	Atkinson et al[108]
	$(1.94 \pm 0.35) \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[36]
p-cresol	$\sim 6 \times 10^{-19}$	300 ± 1	*b*	Atkinson et al.[108]
	1.4×10^{-18}	*a*	*c*	Hendry[110]
	$(4.71 \pm 0.66) \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[36]
benzyl chloride	$<4 \times 10^{-20}$	296 ± 2	S-CL	Atkinson et al.[36]
biphenyl	$<2 \times 10^{-19}$	294 ± 1	*b*	Atkinson et al.[111]
naphthalene	$<2 \times 10^{-19}$	294 ± 1	*b*	Atkinson et al.[111]

[a] Room temperature, no reported. [b] Static system, with the loss of the aromatic being monitored in the presence of excess ozone. Hence these rate constants for the cresols must be expected to be upper limits due to secondary reactions of radical species formed in the initial reaction with the cresols. [c] Not reported.

TABLE IX. Rate Constants *k* for the Reaction of O_3 with Oxygen-Containing Organics

oxygenate	k, cm^3 $molecule^{-1}$ s^{-1}	T, K	technique	ref
formaldehyde	$\leq 2.1 \times 10^{-24}$	298	S-UV	Braslavsky and Heicklen[112]
acetaldehyde	$(3.4 \pm 0.5) \times 10^{-20}$	298 ± 2	S-CL	Stedman and Niki[41]
	$\leq 6 \times 10^{-21}$	296 ± 2	S-CL	Atkinson et al.[35]
glyoxal	$<3 \times 10^{-21}$	298 ± 2	S-CL	Plum et al.[113]
methylglyoxal	$(1.1 \pm 0.5) \times 10^{-21}$	297 ± 2	S-CL	Pate et al.[103]
	$<7 \times 10^{-20}$	296 ± 2	S-CL	Atkinson et al.[35]
	$<6 \times 10^{-21}$	298 ± 2	S-CL	Plum et al.[113]
ketene	$<7 \times 10^{-20}$	*a*	F/S-IR	Hanst et al.[37]
acrolein	7.4×10^{-19}	*a*	F/S-IR	Hanst et al.[37]
	$(2.8 \pm 0.5) \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[35]
crotonaldehyde (*trans*-$CH_3CH{=}CHCHO$)	7.4×10^{-19}	*a*	F/S-IR	Hanst et al.[37]
	$(9.0 \pm 1.8) \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[35]
methacrolein [$CH_2{=}C(CH_3)CHO$]	$(1.12 \pm 0.13) \times 10^{-18}$	296 ± 2	S-CL	Atkinson et al.[35]
	1.1×10^{-18}	*b*	*c*	Kamens et al.[114]
methyl vinyl ketone	$(4.77 \pm 0.59) \times 10^{-18}$	296 ± 2	S-CL	Atkinson et al.[35]
	4.0×10^{-18}	*b*	*c*	Kamens et al.[114]
3-penten-2-one (~30% *cis*, ~70% *trans*)	$(2.13 \pm 0.39) \times 10^{-17}$	296 ± 2	S-CL	Atkinson et al.[35]
2-cyclohexen-1-one	$(1.22 \pm 0.26) \times 10^{-18}$	296 ± 2	S-CL	Atkinson et al.[35]
cis-3-hexene-2,5-dione	$(1.8 \pm 0.2) \times 10^{-18}$	296 ± 2	S-CL	Tuazon et al.[115]
trans-3-hexene-2,5-dione	$(8.3 \pm 1.2) \times 10^{-18}$	296 ± 2	S-CL	Tuazon et al.[115]
furan	$(2.42 \pm 0.28) \times 10^{-18}$	298 ± 2	S-CL	Atkinson et al.[116]
2,5-dihydrofuran	1.61×10^{-17}	294 ± 2	S-CL	Adeniji et al.[34]

[a] Room temperature, not reported. [b] Ambient temperature, not reported. [c] Derived from computer modeling of experimental environmental chamber data.

VII. Oxygen-Containing Organics

A. Kinetics

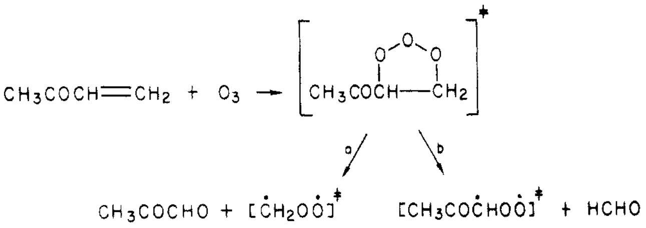
The available rate constant data for the reactions of O_3 with oxygen-containing organics are given in Table IX (except for the cresols, which are presented with the other aromatics in Table VIII). To date all of the rate constants for these organics have been determined at ~294–298 K. For those oxygen-containing compounds which do not contain unsaturated carbon–carbon bonds, e.g., formaldehyde, acetaldehyde, glyoxal, and methylglyoxal, the reactions are very slow, with rate constants of $<10^{-20}$ cm^3 $molecule^{-1}$ s^{-1} at ~298 K (the rate constant obtained by Stedman and Niki[41] for acetaldehyde is probably in error, since it is significantly higher than the upper limit subsequently determined by Atkinson et al.[35]). By analogy, it is expected that for other ethers, alcohols, aldehydes, and ketones not containing unsaturated carbon–carbon bonds the reactions will also be extremely slow, with room temperature rate constants of $\lesssim 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}. These reactions are hence of negligible atmospheric importance.

For the unsaturated carbonyls and ethers (other than ketene) however, much faster reactions are observed, with the most comprehensive set of data being those of Atkinson et al.[35] for the unsaturated carbonyls. The recent, more semiquantitative, data of Kamens et al.[114] for methacrolein and methyl vinyl ketone are in good agreement with the rate constants obtained more directly by Atkinson et al.[35] Because of this agreement for these carbonyls, we recommend the rate constants for these and other unsaturated carbonyls determined by Atkinson and co-workers.[35,115,116]

The only unsaturated ethers which have been studied are furan[116] and 2,5-dihydrofuran.[34] Both of these compounds react significantly slower than do the analogous alkenes: furan reacts ≳100 times slower than do the 2,4-hexadienes, and 2,5-dihydrofuran reacts 17–60 times slower than does cyclopentene. While the low reactivity of furan can be attributed to the effects of resonance stabilization which amounts to ~12 kcal mol^{-1},[116] the relatively low reactivity of 2,5-dihydrofuran is less obvious, especially since the oxygen is not immediately adjacent to the double bond.

B. Mechanism

Few data are available concerning the mechanisms of the reactions of O_3 with oxygen-containing organics. Since the reactions of O_3 with carbonyls not containing olefinic double bonds are of negligible importance, only oxygen-containing organics containing olefinic double bonds are considered below. Of these organics studied (Table IX), the relevant product data are few—the only published information being that of Kamens et al.[114] From a study of the reactions of O_3 with methacrolein and methyl vinyl ketone, methylglyoxal was observed as a product, along with other minor products. By analogy with the alkene reactions, these reactions are expected to yield[117]



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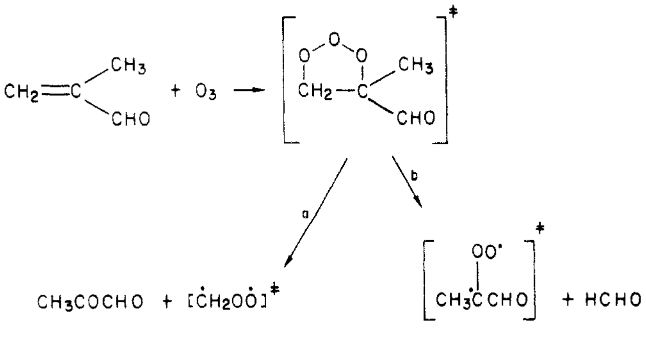


where the ratios of the decomposition pathways (a and b) are not known, nor are the subsequent fates of the initially energy-rich biradicals such as $[CH_3CO\dot{C}HO\dot{O}]^‡$, etc. The articles of Kamens et al.[114] and Lloyd et al.[117] should be consulted for the details of how these overall reactions have been treated in chemical computer modeling studies. It should be emphasized, however, that these treatments were based upon a very limited database, and must be considered to be highly uncertain and largely speculative in nature. Obviously much further mechanistic and product data are necessary before a better understanding of the reactions of O_3 with oxygen-containing organics containing olefinic double bonds, and indeed for oxygen-containing organics in general, is available.

VIII. Nitrogen-Containing Organics

The available kinetic data for the reaction of O_3 with nitrogen-containing organics are given in Table X. It can be seen that although data are available for a variety of different classes of compounds, including nitrites, nitriles, amines, hydrazines, and diazo compounds, none of these organics have been studied by more than one group. Thus, we make no recommendation regarding kinetic parameters for any of these reactions. In the remainder of this section, the kinetics and mechanisms for each of the different classes of compounds will be discussed separately, since in general the different classes react differently.

A. Nitrites

The reactions of O_3 with methyl nitrite and ethyl nitrite were studied by Hastie et al.,[118] who observed, using infrared absorption spectroscopy, a unit stoichiometry for the formation of the corresponding nitrates, indicating that the overall reaction proceeds via

$$RONO + O_3 \rightarrow RONO_2 + O_2$$

Although this is the only class of nitrogen-containing organics for which temperature-dependent kinetic data are available, these data must be considered to be uncertain since significantly different Arrhenius parameters were obtained for the two nitrites studied, though the approximate magnitude of the rate constants measured for the two compounds were reasonably similar over the temperature range studied. If the reaction indeed occurs via a simple elementary reaction as shown above, both methyl and ethyl nitrite would be expected to have similar Arrhenius parameters. That this is not so suggests that either the experimental data are incorrect or that the reaction mechanism is more complex than the one-step process given above or is possibly heterogeneous in nature.

B. Nitriles, Nitramines, and Nitrosamines

From Table X, the nitriles are seen to be unreactive, with only upper limit rate constants being obtained. Thus, O_3 reacts only very slowly with the C≡N group, as may be expected based on the strength of the C≡N bond and the lack of any obvious exothermic reaction pathways. Furthermore, the unreactivity of acrylonitrile, CH_2=CHCN, shows that, as again expected by analogy with the corresponding OH radical reaction,[124] the CN group is sufficiently electron withdrawing to markedly deactivate the olefinic double bond towards O_3 addition.

The two nitramines and nitrosamines studied to date are also unreactive towards O_3, with upper limit rate constants of ~3 × 10^{-20} cm^3 $molecule^{-1}$ s^{-1},[120] and thus these reactions are of negligible atmospheric importance. Based on analogy with the reactions of the alkyl

TABLE X. Rate Constants *k* and Arrhenius Parameters for the Reaction of O_3 with Nitrogen-Containing Organics

organic	*k*, cm^3 molecule^{-1} s^{-1}	*E*, cal mol^{-1}	*k*, cm^3 molecule^{-1} s^{-1} [a]	*T*, K	technique	ref
methyl nitrite			$(1.30 \pm 0.13) \times 10^{-20}$	298	S-IR	Hastie et al.[118]
			$(3.06 \pm 1.22) \times 10^{-20}$	316		
			F-GC	338		
	$(6.8^{+12.7}_{-4.5}) \times 10^{-13}$ [b]	5315 ± 344[b]	$(1.97 \pm 0.1) \times 10^{-19}$	352		
ethyl nitrite			$(1.17 \pm 0.14) \times 10^{-19}$	298	S-IR	Hastie et al.[118]
			$(1.60 \pm 0.23) \times 10^{-19}$	310		
			$(2.12 \pm 0.21) \times 10^{-19}$	324		
	$(3.2^{+3.4}_{-1.7}) \times 10^{-16}$ [b]	2351 ± 232[b]	$(2.52 \pm 0.35) \times 10^{-19}$	328		
methyl cyanide			$\leq 1.5 \times 10^{-19}$	299 ± 1	*c*	Pitts et al.[119]
ethyl cyanide			$\leq 1.0 \times 10^{-19}$	299 ± 1	*c*	Pitts et al.[119]
acrylonitrile			$< 1 \times 10^{-19}$	296 ± 2	S-CL	Atkinson et al.[36]
N-nitrosodimethylamine $[(CH_3)_2NNO]$			$< 3 \times 10^{-20}$	296 ± 2	S-FTIR	Tuazon et al.[120]
dimethylnitramine $[(CH_3)_2NNO_2]$			$< 3 \times 10^{-20}$	296 ± 2	S-FTIR	Tuazon et al.[120]
methylamine			$(2.13 \pm 0.29) \times 10^{-20}$	296 ± 2	S-CL	Tuazon et al.[121]
ethylamine			$(2.76 \pm 0.34) \times 10^{-20}$	296 ± 2	S-CL	Tuazon et al.[121]
dimethylamine			$(2.61 \pm 0.30) \times 10^{-18}$	296 ± 2	S-CL	Tuazon et al.[121]
trimethylamine			$(9.73 \pm 1.02) \times 10^{-18}$	296 ± 2	S-CL	Tuazon et al.[121]
pyrrole			$(1.57 \pm 0.20) \times 10^{-17}$	295 ± 1	S-CL	Atkinson et al.[122]
hydrazine			$\sim 3 \times 10^{-17}$ [d]	~298	S-FTIR	Tuazon et al.[123]
methylhydrazine			$> 1 \times 10^{-15}$	~298	S-FTIR	Tuazon et al.[123]
1,1-dimethylhydrazine			$> 1 \times 10^{-15}$	~298	S-FTIR	Tuazon et al.[123]
tetramethylhydrazine			$(1.27 \pm 0.14) \times 10^{-17}$	296 ± 2	S-CL	Tuazon et al.[121]
diazene (HN=NH)			$> 2 \times 10^{-16}$ [e]	296 ± 2	S-FTIR	Tuazon et al.[123]
methyldiazene $(CH_3N{=}NH)$			$> 2 \times 10^{-16}$ [e]	296 ± 2	S-FTIR	Tuazon et al.[123]
diazomethane (CH_2N_2)			$(3.3 \pm 0.1) \times 10^{-17}$	296 ± 2	S-FTIR	Tuazon et al.[123]
formaldehyde hydrazone $(H_2C{=}NNH_2)$			$(2.5 \pm 0.1) \times 10^{-17}$	296 ± 2	S-FTIR	Tuazon et al.[123]

[a] Error limits for CH_3ONO and C_2H_5ONO are two standard deviations of the least-squares analyses of the experimental data given. [b] The error limits are two least-squares standard deviations. [c] The decay of the organic, at part-per-million concentrations, was monitored by gas chromatography in the presence of excess O_3 in air. [d] Rate constant derived from the decay rate of hydrazine in the presence of excess O_3 and a radical trap. [e] Based on the rate of decay or upper limit thereof when formed by the reaction of hydrazine or methylhydrazine in excess O_3 in the presence of a radical trap. Given as a lower limit because some diazene or methyldiazene formation may be occurring while it reacts with O_3.

nitrites discussed above, *N*-nitrosodimethylamine may be expected to react to form the corresponding nitramine

$$(CH_3)_2NNO + O_3 \rightarrow (CH_3)_2NNO_2 + O_2$$

and this cannot be ruled out from the available data.

C. Amines

Recently, room temperature rate constants and product data for the reaction of O_3 with the simplest amines have been determined[121] (although the rate constants should be considered to be upper limits because of the possibility of secondary reactions consuming O_3). It can be seen from Table X that the room temperature rate constants increase markedly with the degree of substitution on the N atom, analogous to the trend observed for the reactions of $O(^3P)$ atoms with these amines[125] (but not with that for the corresponding OH radical reactions[10]). This strongly suggests that the reactions of O_3 with the amines are analogous to the corresponding $O(^3P)$ atom reactions[125–127] in that the reaction proceeds via initial addition at the N atom, followed by subsequent decomposition of the O_3–amine adduct.

$$R_3N + O(^3P) \rightarrow [R_3N^+\text{–}O^-]^\ddagger \rightarrow \rightarrow \text{products}$$

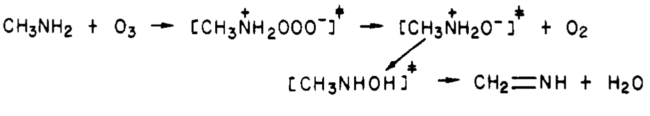
$$R_3N + O_3 \rightarrow [R_3N^+\text{–O-O-}O^-]^\ddagger \rightarrow \rightarrow \text{products}$$

This is further substantiated by the fact that the alternate reaction pathways involving H atom abstraction from N–H or C–H bonds

$$R_2NH + O_3 \rightarrow R_2N\cdot + OH + O_2$$

are too endothermic[70] to be of any importance.

While Tuazon et al.[121] have obtained preliminary product data for the reactions of O_3 with the three methylamines [the major products being NH_3, HCHO, and CH_3NHCHO from CH_3NH_2; $CH_3N{=}CH_2$ from $(CH_3)_2NH$; and HCHO and $(CH_3)_2NCHO$ from $(CH_3)_3N$, with other products being formed in lesser yields], the reaction mechanisms are not presently known. Thus, while the initial formation of $[R^3N^+\text{-}OOO^-]^\ddagger$ followed by decomposition and rearrangement reactions, e.g.



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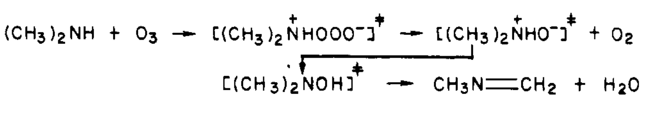


followed by reactions of $CH_2{=}NH$ and $CH_3N{=}CH_2$ with O_3[123] can account for certain of the products, there are still significant discrepancies between the observed products and those predicted on the basis of these reaction sequences.

D. Hydrazines

The reactions of the hydrazines with O_3 have also been extensively studied by Tuazon and co-workers,[121,123,128,129] and it can be seen from Table X that these compounds react significantly more rapidly with O_3 than do the simple amines, with monomethylhydrazine and 1,1-dimethylhydrazine reacting too fast to measure with the experimental technique employed. Other than tetramethylhydrazine, which probably reacts via a different mechanism than the other simple hydrazines (see below), the reaction rates appear to increase with increasing substitution, since monomethylhydrazine reacts with O_3 significantly faster than does hydrazine itself. It should be noted that, in contrast to most rate constant measurements, the rate constant given in Table X for N_2H_4 is based on the rate of N_2H_4 decay in excess O_3, rather than on the rate of O_3 decay in excess organic (see section II). An excess of *n*-octane was present as a radical trap in those experiments in order to minimize N_2H_4 consumption by OH radicals formed in the reaction.[123]

The initial reaction of O_3 with the hydrazines could occur in a manner analogous to the probable initial reaction of O_3 with the simple amines discussed above, i.e., addition at a nitrogen atom, presumably giving rise to either an *N*-hydroxy or a *C*-hydroxy intermediate

$$NH_2NH_2 + O_3 \rightarrow [H_2NN^+H_2OOO^-] \xrightarrow[-O_2]{} [H_2NN^+H_2O^-] \rightarrow [H_2NNHOH]^\ddagger$$

$$(CH_3)_2NN(CH_3)_2 + O_3 \rightarrow [(CH_3)_2NN^+(CH_3)_2OOO^-] \rightarrow \xrightarrow[-O_2]{} [(CH_3)_2N(CH_3)CH_2OH]^\ddagger$$

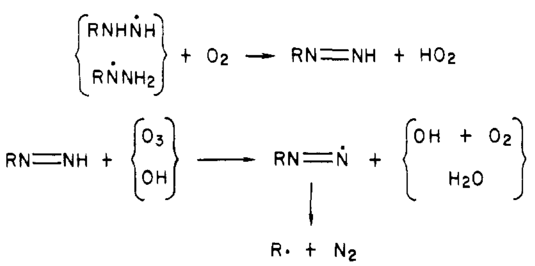
This latter reaction pathway is the only plausible initial reaction for tetramethylhydrazine, and it should be noted that tetramethylhydrazine reacts with O_3 only ~30% faster than does trimethylamine,[121] thus further supporting the conclusion that this hydrazine reacts with O_3 in a manner analogous to the amines.

However, for the other hydrazines studied to date (hydrazine, monomethylhydrazine, and 1,1-dimethylhydrazine) the additional initial reaction pathway involving H atom abstraction from the weak N–H bonds is possible, e.g.

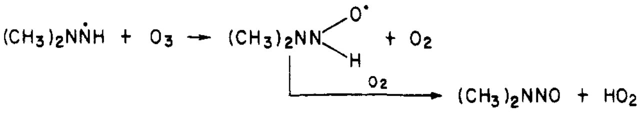
$$R_1R_2NNH_2 + O_3 \rightarrow R_1R_2N\dot{N}H + OH + O_2$$

This reaction pathway is estimated to be ~2 kcal mol^{-1} endothermic for N_2H_4,[70,130,131] which is consistent with the observed room temperature rate constants and reasonable estimates of the Arrhenius preexponential factors.[123] The fact that these three hydrazines react with O_3 significantly faster than do the corresponding amines and tetramethylhydrazine strongly suggests that they indeed react via a different mechanism, and supports the assumption that the hydrogen abstraction pathway is a dominant initial reaction for hydrazines containing an N–H bond.

Tuazon et al.[123] have obtained, using long pathlength FT-IR absorption spectroscopy, extensive product data concerning the reactions of N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$ with O_3, and these data have allowed plausible reaction pathways to be postulated.[123] In these reaction schemes, the $R_1R_2N\dot{N}H$ radicals [where R_1, R_2 = H or CH_3 for the hydrazines N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$] are proposed to react as follows for $RNH\dot{N}H$ or $R\dot{N}NH_2$ radicals:



though additional (and more uncertain) reactions, giving rise to diazomethane and other products, occur for R = CH_3.[123] For the $(CH_3)_2N\dot{N}H$ radical this reaction sequence cannot occur, and Tuazon et al.[123] have postulated other pathways leading to *N*-nitrosodimethylamine, the major observed product. These include



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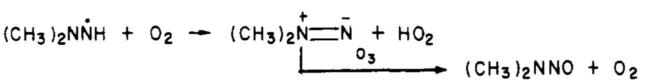


followed by reaction of the OH radicals formed in the initial reaction with the parent hydrazine. However, while the presence of OH radicals in these initial reactions has been confirmed by use of organic tracer compounds,[123] there are still significant uncertainties and inconsistencies in our present understanding of these reactions of O_3 with the simple hydrazines N_2H_4, CH_3NHNH_2, and $(CH_3)_2NNH_2$.

Even less is known concerning the mechanism of the reaction of O_3 with tetramethylhydrazine, and no extensive product study concerning this reaction has yet been carried out. As discussed above, since it lacks a weak N–H bond it probably reacts with O_3 differently than do the other hydrazines, being more closely analogous to the reaction of O_3 with the simple amines.

E. Diazenes, Diazomethane, and Hydrazones

The sole information concerning the gas-phase reaction of O_3 with these compounds is that of Tuazon et al.[123] These species were observed to be products in the reactions of the simple hydrazines with O_3 (see above) or of hydrazine with formaldehyde, and were observed to further react when formed in the presence of O_3. Table X gives the rate constants (or lower limits thereof) for the reactions of O_3 with diazene (HN=NH), methyldiazene (CH_3N=NH), diazomethane (CH_2N_2), and formaldehyde hydrazone (CH_2=NNH_2) derived by Tuazon et al.[123] Unlike the usual experimental procedure for deriving O_3 rate constants in static systems (see section II), these rate constants were derived from the rates of decay of the organic in the presence of excess O_3. For the two diazenes and diazomethane, the rate constants were derived from experiments with a radical trap present, so consumption of these compounds by reaction with OH radicals (which would otherwise be a problem with this technique) was minimized. No

TABLE XI. Rate Constants k and Arrhenius Parameters for the Reaction of O_3 with Sulfur-Containing Organics

organic	A, cm^3 molecule^{-1} s^{-1}	E, cal mol^{-1}	k, cm^3 molecule^{-1} s^{-1}	T, K	technique	ref	temp range covered, K
dimethyl sulfide			$<8.3 \times 10^{-19}$	296	SF-PMS	Martinez and Herron[132]	
thiirane (ethylene sulfide)			$<1.7 \times 10^{-20}$	296	SF-PMS	Martinez and Herron[133]	
tetrahydrothiophene			1.0×10^{-17}	298	S-UV	Kaduk and Toby[44]	
thiophene	1.05×10^{-13}	8400 ± 700	$7.2 \times 10^{-20\,a}$	298	S-UV	Kaduk and Toby[44]	303–373
			$<6 \times 10^{-20}$	298 ± 2	S-CL	Atkinson et al.[116]	

[a] Derived from cited Arrhenius expression.

radical trap was present in the single experiment where the formaldehyde hydrazone rate constant was derived, and hence this rate constant should be considered to be an upper limit. For the diazenes, the reactions were too rapid to derive anything but lower limit values.

As indicated in the previous section, the primary mode of reaction of O_3 with the diazenes is believed to be via H-atom abstraction from the N–H bonds yielding N_2 and H· or CH_3· radicals[123]

$$RN{=}NH + O_3 \rightarrow RN_2\cdot + OH + O_2$$

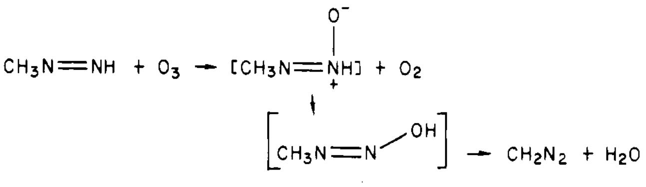
$$RN_2 \rightarrow R\cdot + N_2$$

However, $CH_3N{=}NH$ can also react with O_3 via H-atom abstraction from the C–H bonds, leading to CH_2N_2 formation.

$$CH_3N{=}NH + O_3 \rightarrow \cdot CH_2N{=}NH + OH + O_2$$

$$\cdot CH_2N{=}NH + O_2 \rightarrow CH_2N_2 + HO_2$$

or



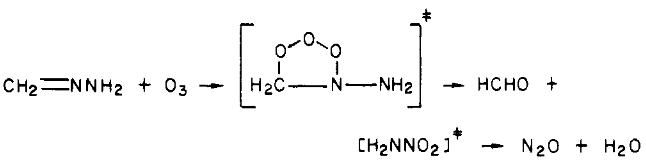
$$CH_3N{=}NH + O_3 \rightarrow [CH_3N{=}\underset{+}{\overset{O^-}{N}}H] + O_2$$
$$\updownarrow$$
$$[CH_3N{=}N{-}OH] \rightarrow CH_2N_2 + H_2O$$

However, both these pathways are speculative and it has not been definitively established whether diazomethane is indeed formed from the reaction of O_3 with methyldiazene.[123]

The major product observed to be formed when diazomethane or formaldehyde hydrazone was consumed was formaldehyde, though the formation of other products could not be ruled out.[123] For diazomethane, the obvious mode of reaction is

$$CH_2N_2 + O_3 \rightarrow CH_2O + N_2 + O_2$$

but it should be noted that the observed yield of HCHO was generally less than unity, so a more complex mechanism may be occurring. The formaldehyde hydrazone may react in a manner more analogous to the alkenes.



It is not clear whether N_2O is also a product of this reaction, and the mechanism for this reaction must also be considered to be uncertain.

IX. Sulfur-Containing Organics

Kinetic data are available for only four sulfur-containing organics, as shown in Table XI. For dimethyl sulfide, ethylene sulfide, and thiophene, only upper limits to the rate constants have been reported. The data of Kaduk and Toby[44] for thiophene were obtained in the presence of only low concentrations of O_2, and the presence of long chain reactions led to significant uncertainties in the determination of the initial rate constants. Also, the reactions of O_3 with dimethyl sulfide[132] and thiophene[44,116] displayed characteristics which indicate that the initial reactions with O_3 are slow, but form reactive species which initiate chain reactions destroying O_3, and which are terminated by reaction with the sulfur-containing organic. Thus, in the presence of such chain-propagating reactions, the observed reaction rates only approach those of the initial reaction at very high [reactant]/[O_3] ratios. In addition, we consider the rate constant obtained by Kaduk and Toby[44] for tetrahydrothiophene to be questionable, since it would be expected to be no more reactive than the other three sulfur-containing organics shown in Table XI. Thus, in the absence of further information, at the present time we would recommend that the rates of reaction of O_3 with sulfur-containing organics be considered to be unimportant for atmospheric purposes.

Although there are no kinetic data available for the reactions of O_3 with mercaptans, Glinski et al.[134,135] have shown that reaction must occur, since chemiluminescence ascribed to SO_2 phosphorescence or fluorescence was observed when O_3 reacted with CH_3SH under single-collision conditions.[135] However, in view of the fact that the room temperature rate constant for the reaction of O_3 with H_2S is less than 2×10^{-20} cm^3 molecule^{-1} s^{-1},[136] and because of the low rate constants for the organic sulfides in Table XI, the rate constants for the reaction of O_3 with the mercaptans are also probably too low for these reactions to be of any importance under atmospheric conditions.

X. Organometallics

Rate constants have been obtained for only tetramethyl- and tetraethyllead,[137,138] and these data are given in Table XII. Although reasonable agreement between the two studies was obtained for tetraethyllead, poor agreement was obtained for tetramethyllead, and significantly lower rate constants were obtained. No mechanistic or product data are available for these reactions; but it is possible that the reactions proceed via

TABLE XII. Rate Constants k for the Reaction of O_3 with Organometallics

organic	k, cm^3 $molecule^{-1}$ s^{-1}	T, K	technique	ref
tetramethyllead	$(1.26 \pm 0.40) \times 10^{-18}$	295 ± 3	S-GC	Harrison and Laxen[137]
	$(4.8 \pm 0.5) \times 10^{-19}$	*a*	*b*	Patel et al.[138]
tetraethyllead	$(1.09 \pm 0.18) \times 10^{-17}$	295 ± 3	F-GC	Harrison and Laxen[137]
	$(1.2 \pm 0.2) \times 10^{-17}$	*a*	*b*	Patel et al.[138]

[a] Not reported, room temperature. [b] Not reported.

TABLE XIII. Rate Constants and Arrhenius Parameters for the Reactions of O_3 with Radical Species

radical	A, cm^3 $molecule^{-1}$ s^{-1}	E, cal mol^{-1}	k, cm^3 $molecule^{-1}$ s^{-1}	T, K	technique[a]	ref
CH_3			$2.3 \times 10^{-12\,b}$	221	*e*	Simonaitis and Heicklen[142]
			$4.0 \times 10^{-12\,b}$	298		
			$\sim 6 \times 10^{-13\,c}$	*d*	DF-PMS	Washida et al.[143]
			$(2.20 \pm 0.31) \times 10^{-12}$	243	FP-PMS	Ogryzlo et al.[144]
			$(2.61 \pm 0.23) \times 10^{-12}$	298		
			$(2.95 \pm 0.27) \times 10^{-}$	347		
	5.4×10^{-12}	429 ± 159	$(2.97 \pm 0.42) \times 10^{-}$	384		
CH_3O			$<2 \times 10^{-15}$	298	*e*	Simonaitis and Heicklen[142]
CH_3O_2			$<2.4 \times 10^{-17}$	298	*e*	Simonaitis and Heicklen[142]
			$<5 \times 10^{-17}$	*d*		Sander and DeMore[145]

[a] DF = discharge-flow; FP = flash photolysis. [b] At approximately atmospheric pressure. Relative to k ($CH_3 + O_2$) $\sim 1.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K; 1.9×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 221 K.[146] [c] Relative to k (CH_3 + O) = 1.14×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[147] [d] Not reported; room temperature. [e] From analyses of complex reaction schemes.

initial H-atom abstraction from the alkyl C–H bonds: e.g.

$$Pb(CH_3)_4 + O_3 \rightarrow CH_2Pb(CH_3)_3 + OH + O_2$$

$$Pb(C_2H_5)_4 + O_3 \rightarrow CH_3\dot{C}HPb(C_2H_5)_3 + OH + O_2$$

This reaction pathway would account for the enhanced reactivity of tetraethyllead compared to tetramethyllead, since the secondary C–H bonds in $Pb(C_2H_5)_4$ are expected to be significantly weaker than the primary C–H bonds in $Pb(CH_3)_4$. If this reaction pathway is operable, secondary reactions involving OH radicals with the tetraalkylleads would occur, and this may be the reason for the discrepancies between the data of Harrison and Laxen[137] and Patel et al.[138] for $Pb(CH_3)_4$. Obviously much further work regarding these and other organometallic reactions is necessary in order to provide a wider data base for these organics.

In addition to these kinetic measurements, several studies have investigated the chemiluminescence from a variety of O_3–organometallic reactions, including $Ni(CO)_4$,[139] $Fe(CO)_5$,[139] $Zn(CH_3)_2$,[140] $Zn(C_2H_5)_2$,[140] AsH_3,[141] PH_3,[141] and SbH_3.[141] These data indicate that gas-phase reactions between O_3 and these organic species occur. However, since these data either pertain to nonorganometallics or do not yield definitive kinetic or mechanistic data, they are not discussed further here.

XI. Radical Species

The available kinetic data for the reactions of O_3 with radical species are summarized in Table XIII. For methoxy and methylperoxy radicals, the kinetic data were derived from complex reaction systems and only upper limit rate constants were derived. The rate constants obtained for the methyl radical show a considerable degree of scatter, but we favor the values of Ogryzlo et al.,[144] since these were obtained by the most direct technique. Because of the low concentration of O_3 and radicals in the atmosphere, and because both methyl and methoxy radicals react at significant rates with O_2 (which is present at a concentration $>10^5$ higher than O_3 in ambient atmospheres), these reactions can be considered to be of negligible importance in the atmosphere.

XII. Discussion and Conclusions

A. Rate Constant Trends and Correlations

As can be seen from the previous sections, kinetic data are now available for the reactions of O_3 with a variety of organics. For certain classes of organics, these data allow possible rate constant trends and correlations to be examined. The great majority of organics for which kinetic data are available and which react with O_3 at sufficiently high rates to be of possible atmospheric significance contain unsaturated carbon–carbon bonds (i.e., C=C or C≡C bonds), with the initial reaction involving O_3 addition across these unsaturated carbon–carbon bonds. However, certain nitrogen-containing compounds (such as the amines, hydrazines, diazo compounds, and hydrazones), and possibly certain organometallics, also react with O_3 at significant rates, apparently via different mechanisms than for those organics containing C=C or C≡C bonds. Unfortunately, the available kinetic data for these latter classes of organics are insufficient to allow any meaningful discussion of rate constant correlations and trends, and hence in this section discussion is restricted to organics containing unsaturated carbon-carbon bonds.

1. Correlations with OH Radical and $O(^3P)$ Atom Rate Constants

As noted previously,[10] O_3 is electrophilic in character, as are $O(^3P)$ atoms, OH radicals, and NO_3 radicals, and it may thus be expected that the rate constants for the addition reactions of these species to double and triple carbon–carbon bonds would exhibit some degree of correlation. Examples of the correlations between O_3 and OH radical and $O(^3P)$ atom and OH radical rate constants with a series of unsaturated organics are shown in Figures 12 and 13. It can be seen from these figures that while the correlation between $O(^3P)$ atom and OH radical rate constants for these organics con-

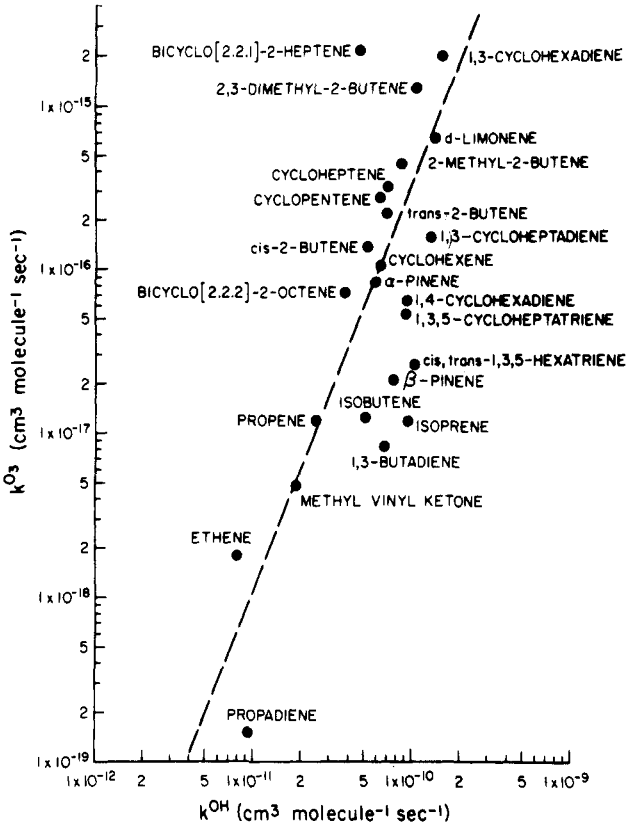


Figure 12. Plot of log k^{O_3} against log k^{OH} for a series of alkenes, cycloalkenes, and methyl vinyl ketone at room temperature. (The rate constants for OH radical reactions are taken from ref 10, 81, and 148–151.)

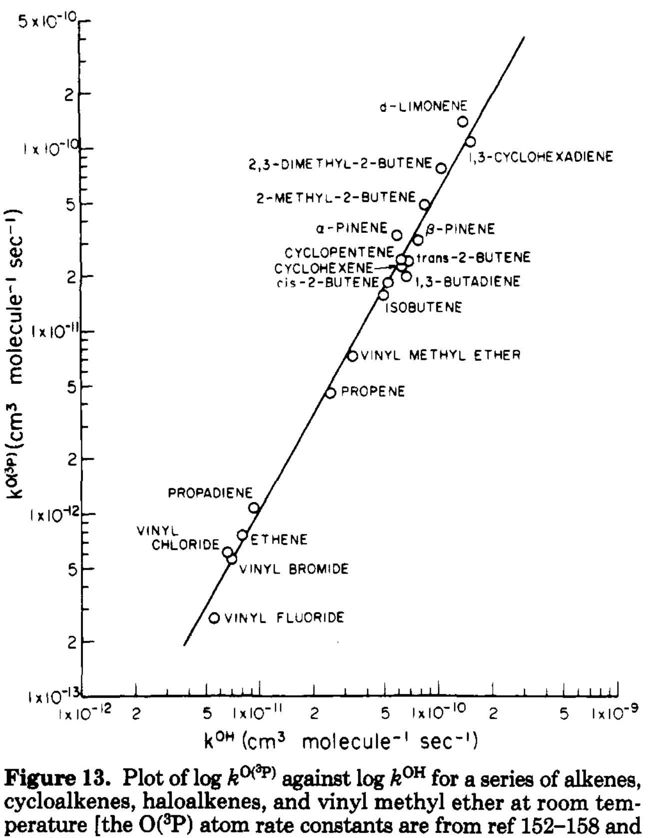
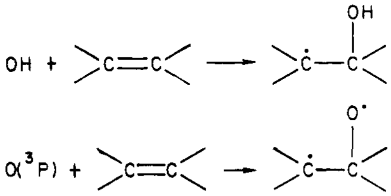
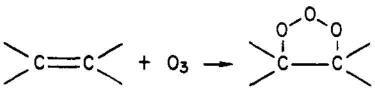


Figure 13. Plot of log $k^{O(^3P)}$ against log k^{OH} for a series of alkenes, cycloalkenes, haloalkenes, and vinyl methyl ether at room temperature [the O(^{3}P) atom rate constants are from ref 152–158 and the OH radical rate constants are from ref 10, 148, 149, and 151].

taining >C=C< bonds is excellent (Figure 13), that between O_3 and OH radicals is substantially more scattered (Figure 12). However, since OH radicals and O(^{3}P) atoms both react in a closely analogous manner by initially adding to one side of the unsaturated >C=C< or —C≡C— bond forming a radical species



(reaction of O(^{3}P) atoms with alkenes to form the alkene oxides in a single step being spin forbidden), while O_3 adds across the unsaturated >C=C< or —C≡C— bond to initially form a nonradical ozonide



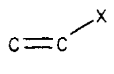
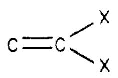
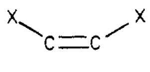
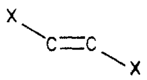
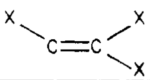
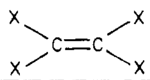
then these reactions are not strictly analogous. Indeed, as previously pointed out by Atkinson,[159] rate constant correlations are only accurate and useful if reactions which occur via analogous mechanisms are compared. Thus, except on a qualitative basis, and then only after the effects of conjugation and ring strain, as discussed in the following sections, are taken into account, we do not recommend the use of correlations with OH radical or O(^{3}P) atom rate constants to estimate rate constants for the reactions of O_3 with organics.

2. *Effects of Conjugation and Aromaticity*

It can be seen from Figure 12 that, except for 1,3-cyclohexadiene (discussed in the following section), the room temperature rate constants for the reaction of O_3 with conjugated di- and trialkenes are significantly low when compared with the O_3 reaction rate constants for the corresponding nonconjugated alkenes, and with predictions based upon correlation with the corresponding OH radical rate constants. In particular, 2-methyl-1,3-butadiene (isoprene) is similar in reactivity to propene, 1-butene, and 2-methyl-2-propene, and *cis*- and *trans*-1,3,5-hexatriene are less reactive at room temperature than the 2-butenes or the tri- and tetrasubstituted ethenes, while in terms of O(^{3}P) atom and OH radical reactions, 1,3-butadiene is of similar reactivity to *trans*-2-butene,[10] 2-methyl-1,3-butadiene is of comparable reactivity to 2-methyl-2-butene,[148] and *cis*- and *trans*-1,3,5-hexatriene are of comparable reactivity to 2,3-dimethyl-2-butene.[81] Thus, in general it can be concluded that conjugation has a more significant effect in reducing the rate constants for the reaction of O_3 with alkenes than is the case for OH radical or O(^{3}P) atom reactions. This again can be attributed to the differing initial reactions and transition states involved.

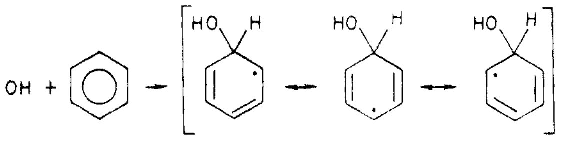
The most extreme effects of conjugation would obviously be seen in aromatic compounds, where the large resonance stabilization energy would be expected to have a large suppressing effect on the O_3, OH radical or O(^{3}P) atom rate constants. The rate constants for the reactions of OH radicals and O(^{3}P) atoms with benzene are factors of ~7 and ~40 lower, respectively, than their rate constants for reaction with ethene;[10] while O_3 reacts with benzene over 4 orders of magnitude

TABLE XIV. Effects of Substituent Identity, Number, and Orientation about the Carbon-Carbon Double Bond on Room Temperature Rate Constants for the Reaction of O_3 with Organics, Relative to the Room Temperature Rate Constant for the Reaction of O_3 with Ethene

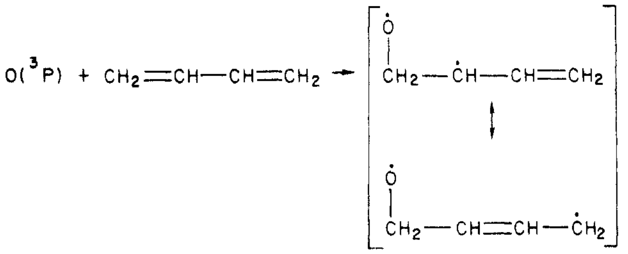
	number and orientation					
substituent, X						
C_6H_5	12					
CH_3	6.5	6.9	74	114	240	660
$COCH_3$	2.7		1.0	4.7		
CHO	0.16					
CH_2Cl		0.22				
CN	<0.1					
F	0.4	<0.11	0.15	1.2	0.014	0.29
Cl	≤0.004	0.002	<0.003	≤0.2	≤0.02	<0.00001

slower than it does with ethene. The relatively low rate constant for the reaction of O_3 with furan discussed in section VIIA is consistent with this effect, since furan also has some aromatic character. This extreme effect of aromaticity in suppressing O_3 rate constants is consistent with, and can be considered to be an extension of, the negative effects of conjugation on these rate constants.

The fact that conjugation and resonance stabilization have much larger effects on suppressing O_3 rate constants than on the corresponding OH radical or $O(^3P)$ atom rate constants can be attributed to the fact that while in all three systems resonance (or conjugation) stabilization is lost or reduced in the transition state, the radical (or biradical) formed in the reaction of OH radicals or $O(^3P)$ atoms with aromatics or conjugated alkenes remains resonance stabilized, compensating for the loss of aromaticity or reduction of conjugation stabilization in the transition state: e.g.



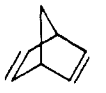
and



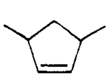
However, since an analogous stabilization of the molozonide intermediate formed in the initial O_3 reaction cannot occur, there is no compensation for the loss of aromaticity or conjugation stabilization in the initial reaction, and thus the effects of conjugation or aromaticity on suppressing the rate constant are much larger.

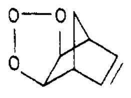
3. *Effects of Ring Strain*

A further reason for the relatively poor correlation between O_3 and OH radical rate constants, at least for the cycloalkenes, appears to be due to the differing effects of ring strain on the kinetics of these reactions. While ring strain effects on OH radical rate constants with cycloalkenes appear to be negligible or minor,[81,149] Atkinson et al.[76] have shown that ring strain has a significant effect on the rate constants for the reactions of O_3 with a series of cycloalkenes and nonconjugated cyclodialkenes. They also showed that the rate constant per double bond correlated better with the difference in the ring strain energy between the cycloalkene and the corresponding structure with one less double bond (i.e., the "relative" strain energy) than with the strain energy released when the bond is totally broken. For example, for bicyclo[2.2.1]-2,5-heptadiene (I) the rate constant appears to be more influenced by the difference in strain energy between I and II than the strain energy difference between I and III. Such a correlation is in accord with current mechanistic theories that these O_3 addition reactions proceed via formation of a 1,2,3-trioxide ring intermediate (structure IV, as discussed in section IVB), since the difference between the ring strain energy of the 1,2,3-trioxide (IV) and II should be approximately independent of the cycloalkene or nonconjugated cyclodialkene being studied, since the strain energies of polycyclic ring compounds are approximately the sum of the strain energies of the individual rings.[70]


I


II


III



IV

It is interesting that O_3 reacts with 1,3-cyclohexadiene ~6 times faster than with its acyclic analogue 2,4-hexadiene and with 1,3-cycloheptadiene a factor of ~2 slower than with 2,4-hexadiene (see Table V). While this order-of-magnitude difference in the rate constants between 1,3-cyclohexadiene and 1,3-cycloheptadiene could be due in part to the fact that 1,3-cycloheptadiene has a slightly higher relative strain energy,[70,81] the magnitude of the difference suggests that other factors may also be involved. It should also be noted that the rate constant for the reaction of O_3 with 1,3,5-cycloheptatriene is even lower than that for 1,3-cycloheptadiene, by a factor of ~3, despite the fact that 1,3,5-hexatriene reacts with O_3 a factor of ~3 faster than does 1,3-butadiene.[81] This could also be due in part to the effect of relative ring strain, since 1,3,5-cycloheptatriene is estimated to have a negative relative strain energy of ~2 kcal $mole^{-1}$,[70] but this cannot be accurately assessed because the rate constant for its acyclic analogue, 2,4,6-octatriene, is not known. Obviously, additional data are required to more unambiguously assess the combined effects of ring strain and conjugation on the rate constants for the reaction of O_3

TABLE XV. Effect of Substituent CHO and CH_3CO Groups on Room Temperature O_3 Reaction Rate Constants

carbonyl	10^{18} × k^a	alkene	10^{18} × k^b	substituent effect
$CH_2{=}CHCHO$	0.28	$CH_2{=}CH_2$	1.75	0.16
$CH_3CH{=}CHCHO$	0.90	$CH_3CH{=}CH_2$	11.3	0.08
$CH_2{=}C(CH_3)CHO$	1.12	$CH_2{=}CHCH_3$	11.3	0.10
$CH_3COCH{=}CH_2$	4.77	$CH_2{=}CH_2$	1.75	2.7
$CH_3COCH{=}CHCH_3$	21.3	$CH_2{=}CHCH_3$	11.3	1.9

[a] In cm^3 $molecule^{-1}$ s^{-1}, from reference 35. [b] In cm^3 $molecule^{-1}$ s^{-1}, from the present recommendations for the alkenes at 298 K.

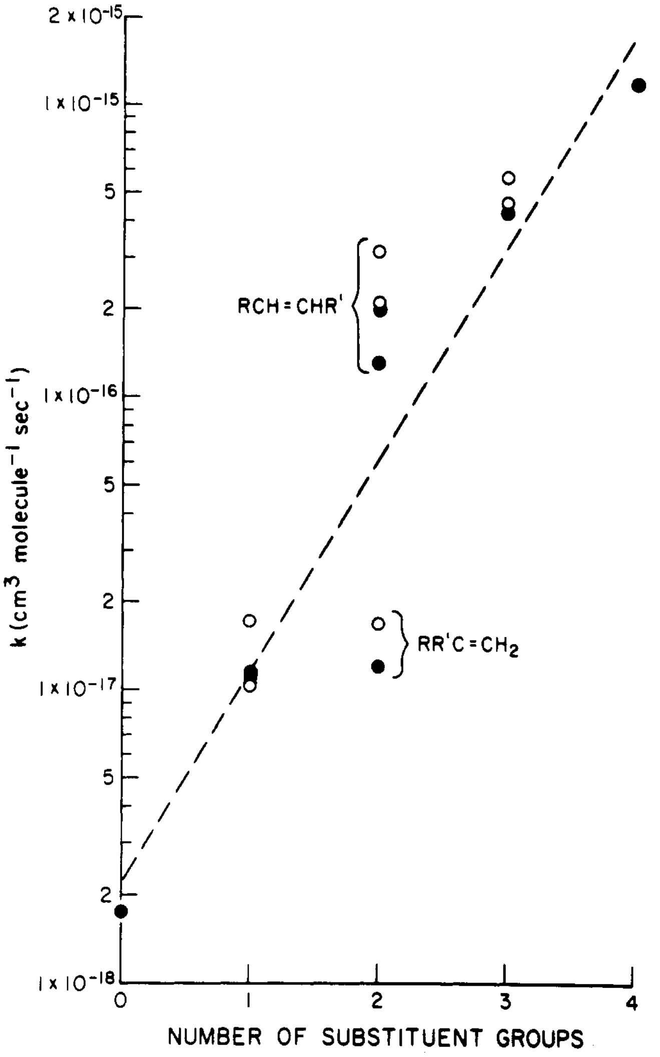


Figure 14. Plot of the room temperature rate constants for ethene and alkyl-substituted ethenes against the number of alkyl substituents. (●) Alkenes for which recommended rate constants have been given here; (○) alkenes for which insufficient data are available for recommendations to be given.

with cyclodialkenes and cyclotrialkenes.

4. Substituent Effects

Based upon the data in Tables III–VIII, the most important single factor in determining how rapidly O_3 reacts with a carbon–carbon double bond is the nature, number, and orientation of substituents around that bond. The available data concerning these effects are summarized in Table XIV, where the factors by which the room temperature O_3 rate constant is changed when one or more H atoms on ethene is replaced by various substituents for which data are available are given. (The effects of substitution by ethyl and larger alkyl groups are not shown since the data are limited and, as discussed in section IVA, these effects appear to be similar to CH_3 substitution). It can be seen that some substituents, such as phenyl, methyl (and, section IVA, higher alkyl groups), and acetyl groups tend to enhance the room temperature O_3 reaction rate constants, whereas others, such as formyl, chloromethyl, cyano, chloro, and fluoro substituent groups tend to suppress the O_3 reaction rate constant. In general, as expected, electron-withdrawing substituents tend to suppress the rate constants, while electron-donating substituents such as methyl or other alkyl groups tend to enhance the rate constant. This effect is totally consistent with the electrophilic nature of O_3 as a reactant towards $>C{=}C<$ and $-C{\equiv}C-$ bonds. As further shown in Table XV, replacement of an H atom by a CHO group on an olefinic double bond decreases the room temperature O_3 reaction rate constant by a factor of ~8 ± 2, while replacement of an H atom by a $COCH_3$ group increases the rate constant by a factor of ~2–3.

In terms of the effects of number and orientation of substituents about olefinic double bonds, the only complete and reliable data set concerns the effects of alkyl substituents. However, less reliable, and in some cases only upper limit, data concerning the effects of Cl- and F-atom substitution are also available. Although, as shown in Table XIV and Figure 14, the enhancement of the rate constant due to alkyl substitution increases with the number of substituents, it does not increase in a simple proportional manner, and for the two-substituent case the effect of orientation around the olefinic double bond is significant with the trans-1,2-isomer being significantly more reactive than the cis-1,2-isomer. In particular, the terminal alkenes $RR'C{=}CH_2$ are an order of magnitude less reactive than are the internal alkenes $RCH{=}CHR'$. This situation is different from that for $O(^3P)$ atom and OH radical reactions, for which the rate constants increase monotonically with the degree of substitution around the olefinic double bond.[10,152,153,156] The effects of orientation for the disubstituted alkenes are also important for the diones and the haloalkenes, with the internal dihaloalkenes reacting faster than the terminal dihaloalkenes, and with the *trans*-1,2-dihaloalkene or the *trans*-3-hexene-2,5-dione isomers reacting appreciably faster than the corresponding cis isomers. Further evidence for a large cis vs. trans effect comes from the room temperature rate constants for the reactions of O_3 with the 1,3-dichloropropenes,[90] where the rate constant for the trans isomer is a factor of ~4.5 higher than that for the cis isomer (Table VI). There is no obvious explanation for this effect, except to note that steric factors may to some extent be contributing.

5. Arrhenius Parameters

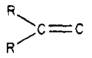
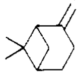
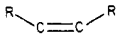
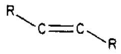
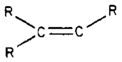
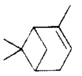
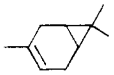
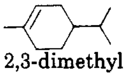
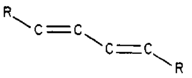
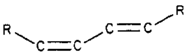
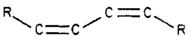
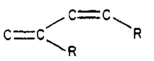
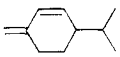
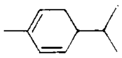
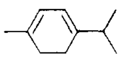
The effects of the number and orientation of substituents on the Arrhenius preexponential factors (which reflect steric and orientation effects) and the Arrhenius activation energies (which reflect energetic factors) would obviously be much more useful than effects on the room-temperature rate constants in elucidating the causes of the above-noted substituent effects. Unfortunately, temperature dependence studies are for the most part limited to the simple acyclic al-

TABLE XVI. Arrhenius Preexponential Factors, A, and Activation Energies, E, for the Reactions of O_3 and OH Radicals with Selected Alkenes

	O_3[a]		OH		
alkene	$10^{14} \times A$, $cm^3\ molecule^{-1}\ s^{-1}$	E, kcal mol^{-1}	$10^{12} \times A$, $cm^3\ molecule^{-1}\ s^{-1}$	E, kcal mol^{-1}	ref
ethene	1.2	5.2	1.7	−0.94	Atkinson and Lloyd[18]
propene	1.3	4.2	4.1	−1.08	Atkinson and Lloyd[18]
1-butene	0.35	3.4	7.6	−0.93	Atkinson and Lloyd[18]
2-methyl-2-propene	0.36	3.4	9.2	−1.00	Atkinson and Pitts[160]
cis-2-butene	0.35	2.0	10.4	−0.97	Atkinson and Pitts[160]
trans-2-butene	0.91	2.3	11.2	−1.09	Atkinson and Lloyd[18]
2-methyl-2-butene	0.62	1.6	19.1	−0.90	Atkinson and Pitts[152]
2,3-dimethyl-2-butene	0.37	0.7			
1,3-butadiene	8.8	~5.5	14.5	−0.93	Atkinson et al.[161]
2-methyl-1,3-butadiene	1.2	~4.0	23.6	−0.81	Kleindienst et al.[151]

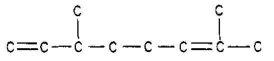
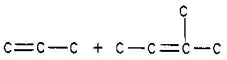
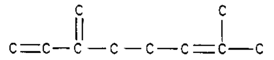
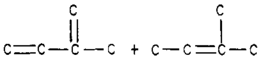
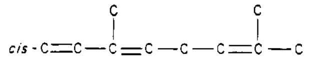
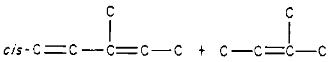
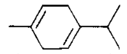
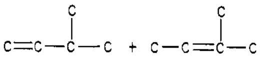
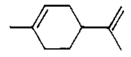
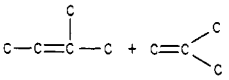
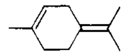
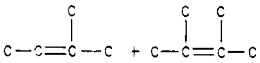
[a] Recommended values from this review.

TABLE XVII. Summary of Recommended Room Temperature O_3 Rate Constants for Acyclic Alkenes or Unstrained Cycloalkenes with Varying Degrees and Configuration of Alkyl Substitution, Compared with Experimental Data

general structure	$10^{16}k$ (recommended), $cm^3\ molecule^{-1}\ s^{-1}$	alkene	$10^{16}k$ (obsd[a]), $cm^3\ molecule^{-1}\ s^{-1}$
R—C=C	0.12	propene	0.11[b]
		1-butene	0.11[b]
		1-pentene	0.05–0.11
		1-hexene	0.12[b]
		1-heptene	0.08–0.17
		1-octene	0.08
		1-decene	0.11
		4-methyl-1-pentene	0.11
	0.12	2-methyl-2-propene	0.12[b]
		2-methyl-1-pentene	0.17
			0.21–0.36
	1.3	*cis*-2-butene	1.30[b]
		cis-2-pentene	2.1
		cyclohexene	0.6–2.0
	2.0	*trans*-2-butene	2.0[b]
		trans-2-pentene	3.2
	4.3	2-methyl-2-butene	4.2[b]
		cis-3-methyl-2-pentene	4.6
		trans-3-methyl-2-pentene	5.6
			0.83–3.3
			1.2
			5.2
$R_2C=CR_2$	12	2,3-dimethyl-2-butene	11.6[b]
C=C(R)—C=C	0.14	isoprene	0.143[b]
	3.7	*trans*-2, *trans*-4-hexadiene	3.7
	3.1	*cis*-2, *trans*-4-hexadiene	3.1
	~3[c]	1,3-cyclohexadiene	19.7
	0.14–3[d]		1.8
(C=C—C=C)—R_3	>3		120
(C=C—C=C)—R_4	>>3		880

[a] Unless indicated otherwise, the range of values shown in the data tables is given. The appropriate tables should be consulted for references. [b] Recommended value. [c] Assumed to be the same as the cis,trans isomer. [d] Assumed to be between the rate constants for isoprene and the 2,4-hexadienes.

TABLE XVIII. Comparison of Measured and Estimated Room Temperature Rate Constants for the Reaction of O_3 with Di- and Trialkenes with Non-conjugated Double Bond Systems

structure	structures for compds used to estimate k	$10^{16}k$, cm^3 molecule^{-1} s^{-1}	
		estd[a]	obsd[b]
 $C{=}C{-}\overset{C}{C}{-}C{-}C{-}C{=}\overset{C}{C}{-}C$ (dihydromyrcene)	 $C{=}C{-}C + C{-}C{=}\overset{C}{C}{-}C$	4.4	6.8
 $C{=}C{-}\overset{C}{\overset{\Vert}{C}}{-}C{-}C{-}C{=}\overset{C}{C}{-}C$ (myrcene)	 $C{=}C{-}\overset{C}{\overset{\Vert}{C}}{-}C + C{-}C{=}\overset{C}{C}{-}C$	4.4	12.5
 $cis\text{-}C{=}C{-}\overset{C}{C}{=}C{-}C{-}C{=}\overset{C}{C}{-}C$ (ocimene)	 $cis\text{-}C{=}C{-}\overset{C}{C}{=}C{-}C + C{-}C{=}\overset{C}{C}{-}C$	4.4-7.3[c]	20
 (γ-terpinene)	 $C{=}C{-}\overset{C}{C}{-}C + C{-}C{=}\overset{C}{C}{-}C$	8.4	2.8
 (*d*-limonene)		4.4	6.4
 (terpinolene)	 $C{-}C{=}\overset{C}{C}{-}C + C{-}\overset{C}{C}{=}\overset{C}{C}{-}C$	15	7,[d] 100

[a] Estimated based on recommended values for compounds listed in second column. [b] Except as noted, from Grimsrud et al.[42] [c] The rate constant for *cis*-3-methyl-1,3-pentadiene is not known, but is expected to be between that for 2-methyl-1,3-butadiene (isoprene) and the 2,4-hexadienes. [d] From Japar et al.[30]

kenes, and even for these, many of the Arrhenius parameters are uncertain. Table XVI summarizes the Arrhenius parameters for those alkenes for which we have given recommended values, and also shows, for comparison, the Arrhenius parameters for the corresponding OH radical reactions.

It can be seen that the Arrhenius preexponential factors for the O_3 reactions are lower by several orders of magnitude than those for the corresponding OH radical reactions. This is reasonable in view of the nature of the transition state involved, and supports the generally recognized mechanism for the initial O_3–alkene reaction involving concerted addition of O_3 to both sides of the double bond forming a cyclic intermediate. These O_3 reactions thus have a much lower probability for the appropriate orientation when O_3 and the alkenes collide than does simple addition of a radical to one end of the bond.

It can be seen from Table XVI that for the reaction of O_3 with the substituted ethenes the Arrhenius activation energy decreases monotonically with the number of substituents, while no obvious trend is observed for the Arrhenius preexponential factor. Thus, the major effect of alkyl substitution is to decrease the energy of the activated complex. This trend is qualitatively similar to the effect of increasing alkyl radical substitution on ethene for $O(^3P)$ atom reactions,[152,153,156] but is totally different from the case for OH radical reactions, where the Arrhenius activation energies are essentially constant at -1 kcal mol^{-1}, and the Arrhenius preexponential factors increase monotonically with the degree of substitution.[10] These differences between O_3 and $O(^3P)$ atom reactions and OH radical reactions with the alkenes almost certainly arise because of the fact that the OH radical reactions have a zero or negligible energy barrier towards reaction, and the observed differences in the temperature dependencies are effectively due to collision rate effects, and not reaction energetics.

6. Estimation of Rate Constants

a. Alkenes with Single or Nonconjugated Double Bond Systems. As discussed in section IVA, the rate constants for the acyclic alkenes and nonconjugated dialkenes indicate that to a first approximation the room temperature rate constants are determined by the degree and configuration of alkyl substitution about the double bond, and not by the precise identity of the alkyl substituent. This is also expected to hold for cycloalkenes with relatively low-strain six-membered rings. By analogy, for conjugated acyclic dialkenes the rate constant is anticipated to be determined mainly by the degree and configuration of alkyl substitution about the C═C—C═C bond system, although data are available for only a few of the many possible configurations. This suggests an obvious technique for estimation of O_3 rate constants for this class of organics, based on our recommended rate constant for the simplest representative alkenes. These recommendations for alkenes with varying degrees and configurations of alkyl substitution are given in Table XVII, together with the experimental data for the more complex alkenes, and these can be compared with the "estimated" values.

It can be seen from Table XVII that this estimation technique works reasonably well for the monoalkenes, including the six-membered cycloalkenes, with the possible exceptions of α- and β-pinene and Δ^3-carene, where ring strain effects may be nonnegligible. For the acyclic conjugated dialkenes, insufficient data are available to test this technique, though based on the poor agreement between the observed and estimated rate constants for 1,3-cyclohexadiene it does not appear to be particularly useful for the cyclodialkenes. While no data are available for the dialkenes with the same number and orientation of substituents as those in α- and β-phellandrene and α-terpinene, the observed rate constants are consistent with our estimates of the lower limit values.

For alkenes with nonconjugated double bonds (including alkenes with both conjugated and nonconjugated double bond systems), it may be anticipated that the rate constants per nonconjugated double bond or conjugated double bond system are additive (as appears to be the case for OH radical reactions[149]), with the rate constant for each system being that for the simpler alkenes with the same degree and configuration of alkyl substitution around the double bonds. Kinetic data against which this assumption can be tested are available primarily from the study of Grimsrud et al.[42] for the reaction of O_3 with a number of acyclic and cyclic monoterpenes having separated double bond systems. Table XVIII shows a comparison of the observed rate constants for these monoterpenes with the rate constants so estimated, together with the structures of the simpler alkenes used to derive the estimated rate constants.

It can be seen from Table XVIII that the agreement between the estimated and observed rate constants is good to within approximately a factor of 2–3. For terpinoline, the estimated rate constant is consistent only with the lower of the two reported measurements, and suggests that the rate constant determined by Grimsrud et al.[42] may be in error. Obviously additional measurements of these rate constants are clearly desirable in order to more unambiguously test this estimation technique. However, this agreement to within a factor of ~3, with the possible exception of terpinoline, suggests that for acyclic alkenes or cycloalkenes with only low strain six-membered rings, the room temperature rate constants can be approximately estimated based on the number of double bonds or conjugated double bond systems and the degree and configuration of substitution around these double bond systems.

b. Organics with More Than One Type of Substituent. A more difficult problem is the estimation of O_3 rate constants for organics with more than one type of substituent on the carbon–carbon double bond. This problem is difficult not only because of the limited data available concerning the effects of multiple substituents other than for alkyl groups, but also because of the even more limited number of compounds which have more than one type of substituent for which kinetic data are available, and which can be used to test estimation techniques. In particular, other than the two 1,3-dichloropropene isomers, the only mixed-substituent compounds which have been studied to date are methacrolein, crotonaldehyde, and 2-penten-2-one, which have both CH_3 and either CHO or $COCH_3$ substituent groups about the carbon–carbon double bond. However, these latter three compounds can be used to explore the utility of simple estimation techniques.

TABLE XIX. Comparison of Observed and Estimated Room Temperature O_3 Rate Constants for Selected Organics with Multiple Substituents Around the Carbon–Carbon Double Bond

	$10^{18}k$, cm^3 molecule^{-1} s^{-1}		
		estd	
organic	obsd	method A[a]	method B[a]
$CH_2{=}C(CH_3)_2$	12	74	
cis-$CH_3CH{=}CHCH_3$	130	74	
trans-$CH_3CH{=}CHCH_3$	200	74	
$(CH_3)_2C{=}CHCH_3$	423	480	
$(CH_3)_2C{=}C(CH_3)_2$	1160	3100	
$CH_2{=}C(CH_3)CHO$	1.12	1.8	0.30
trans-$CH_3CH{=}CHCHO$	0.90	1.8	4.9
$CH_3CH{=}CHCOCH_3$ (30% cis, 70% trans)	21.3	31	54–83
cis-$CH_3COCH{=}CHCOCH_3$	1.8	13	22
trans-$CH_3COCH{=}CHCOCH_3$	8.3	13	35
$CH_2{=}CCl_2$	0.25–0.65	0.036	0.0058
cis-$CHCl{=}CHCl$	0.062	0.036	0.063
trans-$CHCl{=}CHCl$	0.18–0.38	0.036	0.097
$CHCl{=}CCl_2$	<0.03	0.005	0.0045
$CCl_2{=}CCl_2$	<0.00002	0.0007	0.00027
$CH_2{=}CF_2$	0.19	0.28	0.045
cis-$CHF{=}CHF$	0.26	0.28	0.49
trans-$CHF{=}CHF$	2.1	0.28	0.76
$CHF{=}CF_2$	0.14	0.11	0.099
$CF_2{=}CF_2$	0.092	0.045	0.017

[a] Calculated for the chloroethenes using the rate constant of Zhang et al.[86] for vinyl chloride.

One obvious way to estimate rate constants for reactions of compounds with more than one type of substituent is to start with the room temperature rate constant for the reaction of O_3 with ethene, and to assign to each substituent the multiplicative factor by which addition of the substituent changes the ethene rate constant (tabulated in the first column in Table XIV). Thus, for example, for both crotonaldehyde and methacrolein, the ethene rate constant would be multiplied by 6.5 (for CH_3) and by 0.16 (for CHO) to obtain the estimated rate constant. This technique is simple, data are available concerning the (enhancement/suppression) factors for a number of substituents (Table XIV), and it can readily be tested against compounds with multiple numbers of the same substituents. Table XIX compares the experimental room temperature O_3 rate constant reactions for the di-, tri-, and tetramethyl-substituted ethenes, the haloalkenes, and the three mixed-substituent oxygenates listed above against the rate constants estimated in this manner (indicated as method A in the table). It can be seen that, except for isobutene, *cis*-3-hexene-2,5-dione, and certain of the haloalkenes, the estimated and experimental rate constants agree to within a factor of 3, which can be considered to be good considering the simplicity of this technique.

An alternate estimation technique for the mixed-substituent organics, which takes into account to some extent the effects of substituent configuration, utilizes the O_3 rate constant for the methyl-substituted ethene with the same degree and configuration of methyl substituents about the carbon–carbon double bond as the substituents (of all types) in the subject organic, and for each substituent (other than methyl) to multiply the rate constant by the (enhancement/suppression) factor for that substituent, divided by the enhancement factor for methyl (first column of Table XIV). Thus, the O_3 rate constant for methacrolein is estimated by multiplying the isobutene rate constant by 0.16 (for CHO) and dividing by 6.5 (for CH_3), and likewise the rate constant for crotonaldehyde (which exists in the trans form) is obtained by multiplying the *trans*-2-butene rate constant by the same factors. The rate constants estimated in this way for the three mixed-substituent oxygenates, the 3-hexene-2,5-dione isomers, and the haloalkenes are indicated in Table XIX (as method B), where they can be compared with the estimates using method A and the experimental data.

It can be seen that this second technique (method B) does not predict the rate constants for these three mixed-substituent oxygenates and the 3-hexene-2,5-dione isomers quite as well as does the first, more simplistic method (A). In particular, method B predicts that, since O_3 reacts much more rapidly with *trans*-2-

TABLE XX. Comparison of Rate Constants and Loss Rates for Selected Organics in the Presence of 7×10^{11} molecule cm^{-3} (30 ppb) of O_3, 1×10^6 cm^{-3} of OH Radicals, and 2.4×10^8 cm^{-3} (10 ppt) of NO_3 Radicals[a]

	O_3		OH^b		NO_3^c	
organic	k^{O_3}, cm^3 $molecule^{-1}$ s^{-1}	loss rate, day^{-1}	k^{OH}, cm^3 $molecule^{-1}$ s^{-1}	loss rate, day^{-1}	k^{NO_3}, cm^3 $molecule^{-1}$ s^{-1}	loss rate, day^{-1}
alkanes						
n-butane	$<10^{-23}$	$<6 \times 10^{-7}$	2.6×10^{-12}	0.2	3.6×10^{-17}	0.0007
alkenes and haloalkenes						
ethene	1.8×10^{-18}	0.11	8.1×10^{-12}	0.7	1.1×10^{-16}	0.002
propene	1.1×10^{-17}	0.7	2.5×10^{-11}	2	7.6×10^{-15}	0.16
trans-2-butene	2.0×10^{-16}	12	7.0×10^{-11}	6	3.8×10^{-13}	8
2-methyl-2-butene	4.2×10^{-16}	25	8.7×10^{-11}	8	9.9×10^{-12}	205
2,3-dimethyl-2-butene	1.2×10^{-15}	70	1.1×10^{-10}	10	6.1×10^{-11}	1300
isoprene	1.4×10^{-17}	0.8	9.6×10^{-11}	8	5.8×10^{-13}	12
α-pinene	8×10^{-17}	5	6.0×10^{-11}	5	6.1×10^{-12}	130
d-limonene	6×10^{-16}	36	1.4×10^{-10}	12	1.4×10^{-11}	290
trichloroethene	$<3 \times 10^{-20}$	<0.002	2.3×10^{-12}	0.2		
alkynes						
acetylene	7.8×10^{-21}	0.0005	7×10^{-13}	0.06		
propyne	1.4×10^{-20}	0.0008	6.2×10^{-12}	0.5		
aromatics						
toluene	$<1 \times 10^{-20}$	<0.0006	6.4×10^{-12}	0.6	3.6×10^{-17}	0.0007
o-cresol	2.6×10^{-19}	0.02	4.1×10^{-11}	3.5	2.2×10^{-11}	450
O-, N-, and S-containing						
methacrolein	1.1×10^{-18}	0.07	2.9×10^{-11}	2.5		
methyl vinyl ketone	4.8×10^{-18}	0.3	1.9×10^{-11}	1.6		
dimethyl sulfide	$<8 \times 10^{-19}$	<0.05	9.8×10^{-12}	0.8	9.7×10^{-13}	20
furan	2.4×10^{-18}	0.15	4.0×10^{-11}	3.5	1.4×10^{-12}	29
thiophene	$<6 \times 10^{-20}$	<0.004	9.6×10^{-12}	0.8	3.2×10^{-14}	0.7
pyrrole	1.6×10^{-17}	1.0	1.2×10^{-10}	10	4.9×10^{-11}	1000
hydrazine	$\sim 3 \times 10^{-17}$	~2	6.5×10^{-11}	6		
monomethylhydrazine	$>1 \times 10^{-15}$	>60	6.1×10^{-11}	5		
trimethylamine	9.7×10^{-18}	0.6	6.1×10^{-11}	5		

[a] Note that this OH radical concentration is appropriate only during daytime hours, and this NO_3 radical concentration is appropriate only during nighttime. [b] Rate constants taken from ref 10, 18, 24, 104, 116, 122, and 148–150. [c] Rate constants taken from ref 21–25 and 162.

butene than it does with isobutene, then the same would be true for crotonaldehyde compared to methacrolein, contrary to the experimental data which shows that they both have similar rate constants. However, the *trans*-1,2-dihaloethenes do react significantly more rapidly with O_3 than do the *cis*-isomers and method B is indeed somewhat more successful in predicting rate constants for these organics. However, in general it appears that the simplest technique (method A) should be used for the estimation of O_3 rate constants for organics for which no experimental data are available. Clearly, much more data are required, including in particular temperature dependence studies in order that steric and energetic factors can be considered separately, before reliable estimation techniques for mixed-substituent organics can be developed.

B. Atmospheric Lifetimes

As indicated in the Introduction, organics emitted into the atmosphere can be removed by reactions with O_3 and OH and NO_3 radicals, or by photolysis. In order to estimate the atmospheric lifetimes of these organics the rates of these various loss processes need to be known. In this review, we have discussed the reactions of organics with O_3, which is present in the unpolluted lower troposphere at concentrations of ~30 ppb[11] (~7×10^{11} molecule cm^{-3}), and Figure 15 shows the approximate range and magnitude of O_3 rate constants for the various classes of organics for which kinetic data are available, together with their atmospheric half-lives relative to removal by reaction with O_3. (It should be noted that these calculations have used the 298 K O_3 rate constants, and hence underestimate the actual atmospheric lifetimes, since the temperature, and hence the O_3 rate constants, decrease with increasing altitude in the troposphere). It can be seen that for the organics studied to date, the rate constants vary over a wide range ($<10^{-20}$ to $\sim 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}) and thus so do the atmospheric half-lives. Reaction with O_3 is a very rapid removal process for such organics as the internal alkenes and the hydrazines, and is totally negligible for the aromatic and saturated hydrocarbons.

Of course, the atmospheric half-lives shown in Figure 15 are upper limits since most organics can also react with other species present in the troposphere (i.e., OH and NO_3 radicals) and certain of these organics can also be removed by photolysis. Since most of the organics discussed in this review do not absorb light significantly at wavelengths which reach the lower troposphere ($\lambda \gtrsim 290$ nm), removal by photolysis is generally not important, though atmospheric photolysis of the nitrites and diazo compounds and certain oxygenates is sufficiently rapid that photolysis is probably their major daytime removal process. Table XX compares, for selected organics, the room temperature rate constants and the approximate corresponding atmospheric loss rates for reaction with O_3 (over a 24-h period), with OH radicals during daytime hours, and with NO_3 radicals during nighttime hours. Representative concentrations of these species have been chosen to be; O_3, 30 ppb = 7×10^{11} molecule cm^{-3}; OH, 1×10^6 molecule cm^{-3}; and NO_3, 10 ppt = 2.4×10^8 molecule cm^{-3}. The OH radical rate constants are from ref 10, 18, 24, 104, 116, 122, and 148–150, while the NO_3 radical rate constants are from Atkinson et al.[21-25,162] (These NO_3 radical rate constants are all linearly dependent on the value of the equilib-

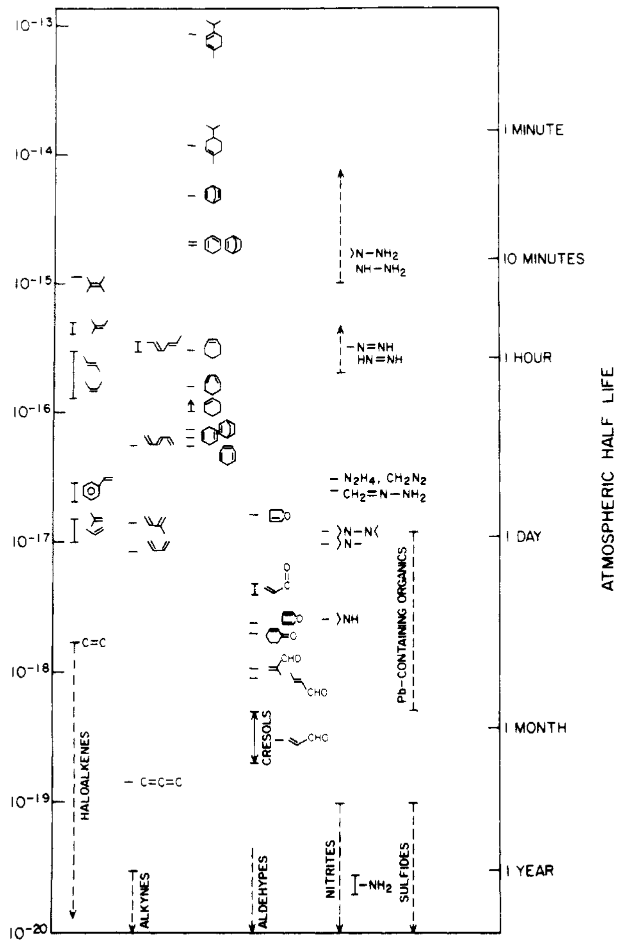


Figure 15. Room temperature rate constants for the reaction of O_3 with representative organics and classes of organics, and corresponding atmospheric half-lives relative to removal by reaction with O_3 for an O_3 concentration of 7×10^{11} molecule cm^{-3} (30 ppb).

rium constant used for the reactions $NO_2 + NO_3 \rightleftarrows N_2O_5$; a value of $2.4 \times 10^{-27}(T/300)^{0.32}e^{11080/T}$ cm^3 molecule^{-1} [163,164] was used here.) It can be seen that under these atmospheric conditions the reactions with O_3 are important for the higher alkenes, the monoterpenes, and the hydrazines. For the other organics for which kinetic data are available, reaction with O_3 is of generally negligible or minor importance.

Interestingly, nighttime reaction with the NO_3 radical can be an important, or in fact dominant, loss process for certain organics—for example, the higher alkenes (including the monoterpenes), furan, pyrrole, and dimethyl sulfide [and it is likely that the aliphatic amines and the hydrazines react rapidly (with rate constants $\sim 10^{-11}$ cm^3 molecule^{-1} s^{-1}) with NO_3 radicals]. Further work concerning the reactions of the NO_3 radical are obviously urgently needed for atmospheric purposes, since reaction with the NO_3 radical may be an important removal process for certain of the other organics listed.

C. Conclusions

It can be seen from the previous sections of this article that a large number of kinetic studies have been carried out with a variety of organics, allowing estimates of atmospheric lifetimes to be obtained. However, as discussed in the first part of this section, insufficient data are presently available to allow reliable estimates of O_3 rate constants, and thus atmospheric lifetimes, for organics for which no experimental data are presently available, with the possible exceptions of the simple alkenes, certain di- and trialkenes with separated double bond systems and certain haloalkenes. In addition, only for a few simple alkenes are reliable temperature-dependence data available. Finally, it should be noted that major uncertainties exist concerning the mechanism of the reaction of O_3 with essentially all classes of organics except the simple alkenes under atmospheric conditions, and again the details are only well established for ethene itself. Thus, although there exists a large body of data available concerning the atmospheric reactions of O_3 with organics, it is clear that further studies are called for, and such studies would have both theoretical and applied significance.

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