The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere†

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The gas-phase reactions of ozone with unsaturated hydrocarbons are significant sources of free radical species (including $^\bullet$OH) and particulate material in the Earth's atmosphere. In this tutorial review, the kinetics, products and mechanisms of these reactions are examined, starting with a discussion of the original mechanism proposed by Criegee and following with a summary presentation of the complex, free radical-mediated reactions of carbonyl oxide (Criegee) intermediates. The contribution of ozone–terpene reactions to the atmospheric burden of secondary organic aerosol material is also discussed from the viewpoint of the formation of non-volatile organic acid products from the complex chemistry of ozone with α-pinene. Throughout the article, currently accepted understanding is supported through the presentation of key experimental results, and areas of persistent or new uncertainty are highlighted.

1 Introduction

The reactions of ozone with alkenes have been the subject of detailed study for many decades. In the condensed phase, the reactions are an important component of the arsenal of the synthetic organic chemist, while in the gas phase, the reactions turn out to be important sources of free radicals and secondary organic aerosol in the Earth's atmosphere. In this review, we focus on the gas-phase ozonolysis of alkenes and their importance for atmospheric chemistry. It turns out that a detailed understanding of many aspects of the physical chemistry of the reactions is required in order to properly understand their implications for the atmosphere. General features of the mechanism of the reactions have been known for some time, but there are subtleties that are still not properly understood. For example, the formation of $^\bullet$OH radicals from the reactions is of key importance for the atmosphere, but a proper understanding of the process requires detailed information about vibrational excitation and energy transfer in the intermediates. Similarly, reactions of ozone with terpenes are known to generate a large number of involatile oxygenated compounds that have been detected in secondary organic aerosol (SOA). However, the exact nature of the nucleating species in SOA formation is not known, and the detailed mechanism of formation of the various oxygenated species is not clearly understood. Atmospheric ozonolysis was most recently reviewed by Calvert *et al.*[1] as part of a book dealing with the atmospheric oxidation of alkenes in general. Part of what we have tried to do here is to summarise some of the key aspects of that review and provide a guide to more recent developments. In a review of this length, it is impossible to present an exhaustive account of what is known of the reactions. Instead, we attempt to provide a flavour of what is well established, and which aspects of the reactions are uncertain and should be the subject of further study.

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† One of a collection of reviews on the theme of gas kinetics.

2 General discussion of the gas-phase ozonolysis mechanism

The mechanisms of gas-phase ozone–alkene reactions are complex. The basis of the current understanding was provided by Criegee, in the 1940s, following extensive studies of ozonolysis reactions occurring in the condensed phase.[2] As represented in Fig. 1, initiation involves the concerted [3 + 2] cycloaddition of ozone to the double bond of the alkene forming a cyclic 1,2,3-trioxolane intermediate species (hereafter referred to as the primary ozonide, POZ) in which a σ bond remains between the C atoms and a bridge comprising three O atoms has been inserted.

This process is highly exothermic, by some 200–250 kJ mol^{-1}, and this excess energy is retained within the adduct, leading to a very rapid decomposition of the POZ. Cycloreversion, involving homolytic cleavage of the remaining C–C and one of the O–O bonds, gives rise—in the case of asymmetrically substituted alkenes—to the formation of two pairs of products, in each case a carbonyl molecule and a carbonyl oxide reactive intermediate.[1] A fraction of the excess energy will be dissipated in translating and rotating the two POZ fragments but a significant amount will remain as vibrational excitation in both entities. While this energy is insufficient for decomposition of the carbonyl molecule, sufficient vibrational and rotational excitation resides in the carbonyl oxide to permit further unimolecular reactions to occur. In contrast to the gas phase, the condensed-phase ozonolysis of alkenes proceeds differently after rupture of the POZ as the carbonyl and carbonyl oxide fragments remain in close proximity to one another, due to solvent cage effects, and they recombine to form a 1,2,4-trioxolane cyclic adduct (the secondary ozonide, SOZ) in which the carbon atoms of the original alkene π-system are no longer directly bonded. Under gas-phase conditions, with very much lower molecular densities and no cage effects, such *prompt* recombination chemistry is very unlikely (except, perhaps, in the case of internally unsaturated cycloalkenes) as the nascent fragments from POZ decomposition separate rapidly. In essence, the remainder of this article is a discussion of these processes: what is the chemical fate of carbonyl oxides and what is the significance of this for the chemistry of the Earth's atmosphere?

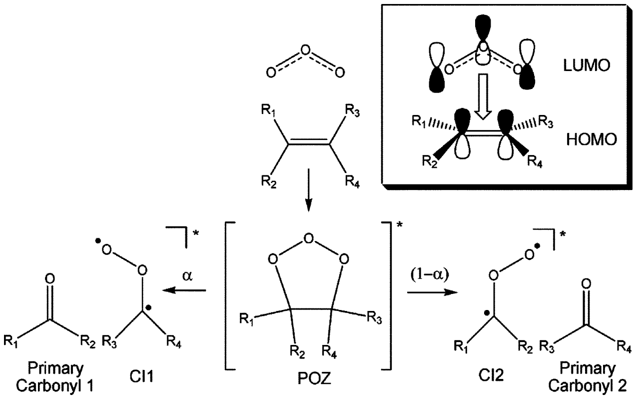

Fig. 1 Ozonolysis initiation: [3 + 2] cycloaddition of ozone to alkene double bond. Inset figure represents interacting frontier orbitals; R = alkyl or H.

The nature and chemistry of gas-phase carbonyl oxides has been the subject of much scientific interest, study and debate for several decades,[1] and this is reflected in the nomenclature encountered in the literature for these species.[3] They have variously been referred to as Criegee intermediates, carbonyl oxides, dioxymethylenes and peroxymethylenes, and this inconsistency reflects the ongoing debate about their electronic structure and chemistry. In discussions of atmospheric chemistry, the term Criegee intermediate (CI) is almost exclusively used—by unofficial convention—and this will be the case in the remainder of this article except where specific intermediate structures are being discussed.

Electronic structure of Criegee intermediates

Before progressing, it is worth noting that chemical species attributed as being CIs have not, to date, been observed directly in the gas phase, despite their intermediacy in ozone–alkene reactions first being postulated by Criegee in 1949.[2] This fact is usually attributed to their supposed very short lifetimes yet, as shall be discussed in a subsequent section, current, indirect experimental data suggest that this may not be the case or the cause. In Fig. 1, CIs have been represented as biradicals, with two sites of spin density. Of course, they could equally have been represented as zwitterions and it should be appreciated, as supported by electronic structure calculations, that these two "cartoon" views represent limiting canonical forms and that the true electronic nature of a given CI is best represented as something between the two (Fig. 2).

One example of how the electronic structure of a CI directly impacts atmospheric chemistry concerns the formation of $^{\bullet}$OH (which will be discussed in much more detail later) from the isomerisation and subsequent decomposition of monoalkyl-substituted carbonyl oxides.[4] The isomerisation requires that the alkyl-substituent group is on the same side of the CI as the terminal O atom (*i.e.*, that these groups are in a *syn* conformation) although this may not necessarily be the case (*i.e.*, they may have an *anti* conformation). For methylcarbonyl oxide ($CH_3{}^{\bullet}CHOO^{\bullet}$) electronic structure calculations suggest a significant zwitterionic character—meaning that the C–O bond of the CI has significant π character—with an energy barrier of around 120 kJ mol^{-1} for conversion between *syn* and *anti* forms (see Fig. 3).

This dictates that when formed they behave as distinct and different chemical entities. For the simplest CI, $^{\bullet}CH_2OO^{\bullet}$, structure calculations suggest a planar, biradical structure[5] with some singlet-π character whereas for dimethylcarbonyl oxide, $(CH_3)_2{}^{\bullet}COO^{\bullet}$, calculations indicate significantly more zwitterionic character.[6]

Experimental, observational evidence for the existence of Criegee intermediates—certainly in the gas phase—is ample

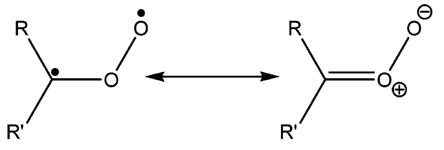

Fig. 2 Resonance canonicals for a Criegee intermediate; R = alkyl, H.

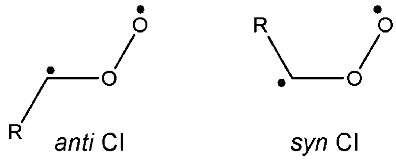

Fig. 3 Conformation of *anti* and *syn* Criegee intermediates. R = alkyl. The energy barrier to rotational inter-conversion is about 120 kJ mol^{-1}.

but, to date, entirely indirect. By contrast, a significant number of CIs have been prepared, observed and studied in solution at room temperature and by matrix isolation at cryogenic temperatures.[3] It should also be stated that none of the CIs prepared in such studies were from ozone–alkene reactions (*e.g.*, the photolysis of a diazo compound in oxygen-saturated solution is one of the most often employed preparative methods) and that the structures of these carbonyl oxides are considerably mesomerically stabilised and not representative of atmospherically-relevant CIs.

In order to indicate why the existence of CIs in gas-phase ozone–alkene reactions is generally accepted, it is necessary to present some of the indirect experimental evidence alluded to above, along with support from the results of appropriate theoretical electronic structure calculations.

The gas-phase chemistry of Criegee intermediates

Formation. The principal evidence for the intermediacy of CIs in ozone–alkene reactions concerns the formation and decomposition of the primary ozonide. That the initial gas-phase ozone–alkene reaction is an addition process is supported by the observation of a small deuterium isotope effect (*i.e.*, inconsistent with any H-atom abstraction processes) for the reactions of ozone with ethene and propene, and their fully-deuterated analogues.[1] Additional evidence is provided by observation of the fact that reaction rate coefficients for ozone–alkene reactions increase with the degree of alkyl-substitution around the $>C{=}C<$ core: this is similar to the case for the reactions of alkenes with $^{\bullet}OH$ and $NO_3^{\bullet}$ radicals, for which the addition mechanism is well established.[4] That the initial reaction is a concerted cycloaddition is consistent with experimentally determined Arrhenius *A* factors that are some two to three orders of magnitude smaller for ozone–alkene reactions than for the corresponding $^{\bullet}OH$– and $NO_3^{\bullet}$–alkene reactions,[4] for which radical addition is to one end of the π system and, hence, entropies of activation are less negative. One way of rationalising the dependence of ozone–alkene reaction rate coefficients on the degree of alkyl substitution around the $>C{=}C<$ core is to consider the interacting frontier orbitals.[7] Increasing the electron density around the π system (*e.g.*, by alkyl substitution) serves to raise the energy of the highest occupied molecular orbital (HOMO), bringing it closer to that of the lowest unoccupied molecular orbital (LUMO) of ozone. This enhances the effective HOMO–LUMO overlap and interaction, thus lowering the energy barrier to POZ formation.[8] As the LUMO corresponds to the ozone π system, in each case, the energy of the HOMO should correlate with Arrhenius activation barriers and, hence, with the logarithm of rate coefficients. This linear relationship is the basis of many "correlation-type" structure activity relationships (SARs) which have been presented in the literature for reaction processes pertinent to tropospheric chemistry.[8] On top of the orbital-energy dependence, the particularity of the concerted cycloaddition process (*i.e.*, that the bridging addition of ozone occurs at both ends of the $>C{=}C<$ core simultaneously) means that any asymmetry in the size/shape of the alkene HOMO, at each end of the double bond, will provide additional constraint to the relative spatial positions of the interacting ozone and alkene molecules. Consistent with these frontier orbital considerations is the correlation-type SAR for gas-phase ozone–alkene reaction parameters presented by this laboratory.[9] Logarithm values of measured (room temperature) rate coefficients were shown to correlate with calculated HOMO energies (E_{HOMO}) for a variety of alkene species (Fig. 4(a)).

However, compared to similar SARs constructed for $^{\bullet}OH$–alkene and $NO_3^{\bullet}$–alkene rate data, the data for ozone–alkene reactions are significantly scattered about the straight-line relationship. Data for asymmetrically-substituted alkenes were seen to deviate from a linear relationship constructed from data for simple symmetrically-substituted alkenes, and the magnitude of the deviation scaled with a measure of asymmetry in the lobes of the HOMO at each end of the alkene double bond (Fig. 4(b)).

To conclude this part of the discussion, it should also be remarked that measured yields of primary carbonyl products (those formed directly from the decomposition of the POZ) for a large variety of ozone–alkene reactions systems sum to one‡—in support of the mechanism represented in Fig. 1.[1,4] It is necessary that such measurements were made under "$^{\bullet}OH$-free conditions" (usually achieved through the addition of a hydrocarbon scavenger species, in sufficient concentration such that $\geq 95\%$ of any adventitiously formed $^{\bullet}OH$ react with the scavenger) as this reactive radical is an intermediate product of the ozone–alkene reaction, as discussed in the next section.

Unimolecular reactions. In discussing the unimolecular chemistry of carbonyl oxides it is useful to begin by making a distinction between unsubstituted and substituted CIs. The former is the simplest CI possible, $^{\bullet}CH_2OO^{\bullet}$, which is formed during the ozonolysis of ethene and terminal alkenes (*i.e.*, 1-alkenes). The latter type of CI may be either monosubstituted ($R^{\bullet}CHOO^{\bullet}$; for which the distinction between *syn* and *anti* forms has already been mentioned) or disubstituted ($RR'^{\bullet}COO^{\bullet}$). In general, for all CI types, unimolecular reaction is believed either to involve dissociation (perhaps involving prior isomerisation), giving radical fragments, including $^{\bullet}OH$, or isomerisation to dioxirane. As stated in the introduction, the formation of $^{\bullet}OH$ is of particular importance to the chemistry of the Earth's troposphere as this radical is the principal initiator of oxidation for virtually all VOCs, and is reactive towards many other atmospherically important trace species.[10] The formation of $^{\bullet}OH$ from ozone–alkene reactions will be dealt with at much greater length in section 3.

The unimolecular chemistry of $^{\bullet}CH_2OO^{\bullet}$, at 298 K and 1 atmosphere total pressure, is relatively well established.[11]

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‡ Examples of where this is not the case will be discussed and interpreted in a later section of this article.

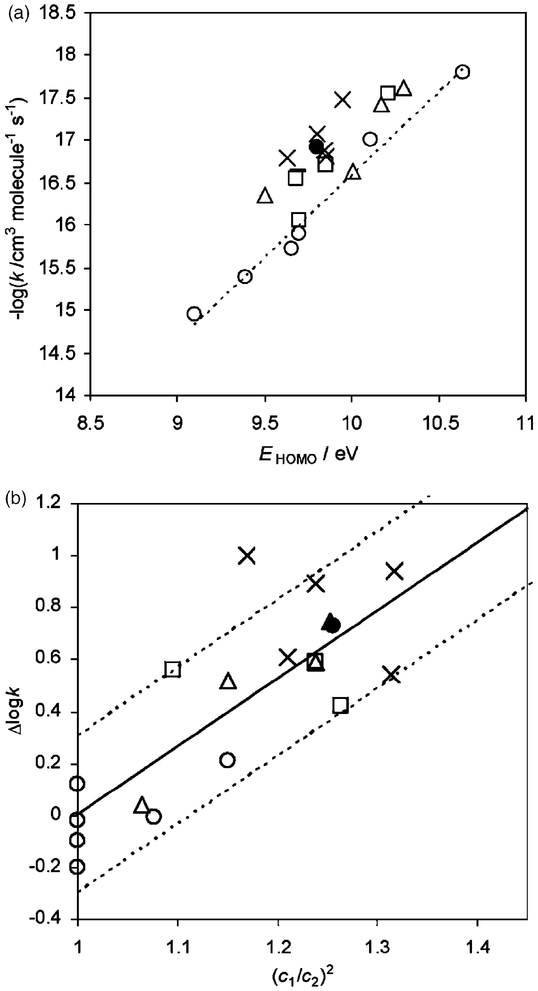
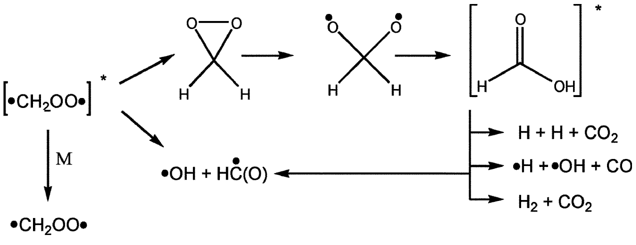


Fig. 4 (a) Correlation plot of $-\log(k_{298\,\mathrm{K}}/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1})$ *vs.* calculated E_{HOMO} for the reactions of ozone with a variety of alkenes, including: simple alkenes (open circles); methylene-substituted cycloalkanes (open squares); chlorinated alkenes (open triangles); 2-methylpropene (filled circle); other asymmetric 1-alkenes (crosses). Plot is based on data from ref. 9, omitting data for monoterpenes. (b) Plot of deviation in $\Delta\log k$ ($= \log(k_{\mathrm{correlation\ prediction}}) - \log(k_{\mathrm{measured}})$) *vs.* square of ratio of carbon p_x, p_y and p_z orbital contributions (*i.e.*, their coefficents) to the HOMO, at each end of the alkene double bond, for a variety of different alkenes. Plot is based on data from ref. 9, omitting data for monoterpenes. The dotted lines indicate a change of a factor ±2 in the rate constant relative to the observed linear correlation (central solid line).

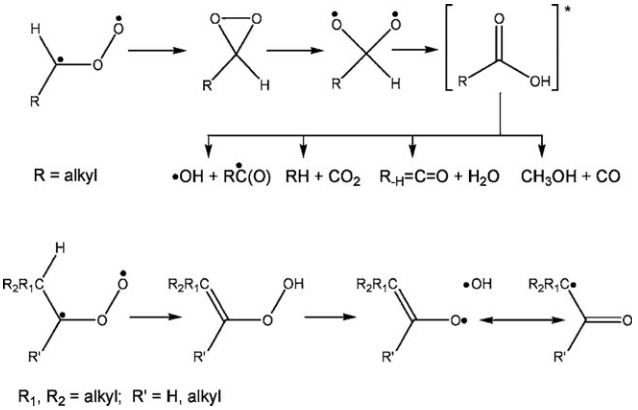
Observed stable reaction products include HC(O)H, CO, CO_2, H_2O and HC(O)OH. Direct and indirect evidence of $^{\bullet}$OH formation has also been reported in a compelling number of studies. The mechanism of $^{\bullet}CH_2OO^{\bullet}$ decomposition is generally believed to occur as indicated in Scheme 1.

The upper channel involves ring closure of the CI to form an excited dioxirane (which has been observed in the gas-phase ozonolysis of ethene by microwave spectroscopy) which then isomerises to an activated (or "hot") formic acid molecule before fragmenting. $^{\bullet}$OH formation from ethene ozonolysis is often ascribed to a concerted reaction channel involving direct rearrangement and decomposition of the CI through a four-membered transition state.[1] Deuterium substitution experiments suggest, however, that this latter is, at most, a minor source of $^{\bullet}$OH and that it is fragmentation of "hot" formic acid that is responsible (*e.g.*, see ref. 12). Implicit with the above discussions of the unimolecular chemistry of CIs, and of course the POZ, is the assumption that these species are so vibrationally excited—due to the exothermicity of the initiation step—that they simply decompose. Again, theoretical calculations suggest that, except for very large cyclic alkenes, the POZ exclusively decomposes at atmospherically relevant temperatures and pressures.[13] In the case of CIs, however, this is not the case and their lifetimes (with respect to unimolecular isomerisation/decomposition) are such that they may be stabilised, or quenched, by collision with N_2 or O_2 molecules—a process whose efficiency will be pressure dependent. This then provides the possibility of bimolecular reactions involving CIs or additional thermal unimolecular processes. Measurements and atmospheric implications of time- and pressure-dependent $^{\bullet}$OH radical formation, and various measures of yields of stabilised Criegee intermediates (SCIs), will be described and discussed subsequently.



Scheme 1

In addition to the chemistry indicated in Scheme 1 for $^{\bullet}CH_2OO^{\bullet}$, it is proposed that disubstituted and *syn*-monosubstituted CIs can isomerise *via* a five-membered transition state to an excited vinylhydroperoxide species (over a barrier of about 60 kJ mol^{-1}) which can decompose to yield $^{\bullet}$OH and a vinyloxyl radical.[1] The formation of $^{\bullet}$OH *via* this "hydroperoxide" channel was first proposed in gas-phase studies of 2,3-dimethyl-2-butene ozonolysis by Niki *et al.*,[14] who further suggested that the proportion of vibrationally excited CI that did not isomerise to a vinylhydroperoxide (and subsequently decompose) was collisionally stabilised. For disubstituted CIs, experimental product studies suggest that the "hydroperoxide" channel is dominant (*e.g.*, values for the yield of $^{\bullet}$OH from the ozonolysis of 2,3-dimethyl-2-butene are close to unity) and, hence, that dimethyldioxirane formation (with a barrier of about 100 kJ mol^{-1}) is at most a minor process.[15] Further to this, if dioxirane formation does occur to a small extent, there is no evidence for the formation of products from the decomposition of a "hot ester" analogous to the "hot acid" channel discussed above for $^{\bullet}CH_2OO^{\bullet}$.[1] For *anti* monosubstituted CIs, there is significant indirect evidence for the occurrence of a "hot acid" channel by observation of products that include methane, CO_2, ketene, H_2O, methanol and CO; and, perhaps, $^{\bullet}$OH.[12,16] For *syn* monosubstituted CIs it is assumed that dioxirane formation does not compete with isomerisation to a vinylhydroperoxide and subsequent $^{\bullet}$OH release. The chemistry described above for mono- and disubstituted CIs is summarised in Scheme 2.



Scheme 2

Bimolecular reactions. As already stated, if collisional quenching stabilises the excited CI sufficiently (*i.e.*, such that its lifetime with respect to unimolecular processes is longer than the time required for bimolecular encounters), reaction between stabilised Criegee intermediates and other atmospherically important trace species may become possible.[1,17] For example, reactions between SCIs and H_2O, SO_2, $CH_3C(O)H$, $CF_3C(O)CF_3$, $CH_3C(O)OH$, CH_3OH, $HC(O)OH$ and NO_2 have been reported in the literature. Of these, the most atmospherically important are likely to be those of SCIs with H_2O (a reaction which may be a significant source of organic acids and H_2O_2 in the atmosphere) and with NO_x in the urban atmosphere. To date, only one direct-kinetic study of a bimolecular reaction of a SCI has been reported—a study of the reaction between methylcarbonyl oxide and acetaldehyde (ethanal).[18] In addition to this, however, a number of relative-rate studies[1] of SCI reactions have been reported but any absolute rate data which have been estimated from such studies must be viewed as highly uncertain. This uncertainty obviously extends to a detailed understanding of the atmospheric implications of such chemistry and this is something which needs to be addressed in the laboratory. However, it is still not clear how this could be achieved at the present time. Some mechanistic aspects of the bimolecular reactions of SCIs will be discussed further in a subsequent section of the present article.

Free radical formation in gas-phase ozone–alkene reactions. Owing to the central importance of •OH in the chemistry of the Earth's troposphere, this section will focus on current understanding of the formation of this species (and other free radical co-products), the experimental evidence that underpins this understanding, and areas where experimental and theoretical study are still very much required.

The formation of •OH in ozone–alkene reactions has been discussed in the literature for some decades and was observed directly by the emission of vibrationally excited radicals at low pressure (*ca.* 1 Torr) as early as 1972 (*e.g.*, see refs. 1 and 10). Later, low-pressure (4 Torr) flow-tube experiments (employing photoionisation mass spectrometric detection) provided product data that were consistent with the formation of •OH which, at this time, was attributed to the decomposition of excited CIs giving H atoms which subsequently reacted with O_3.

$$^{\bullet}\mathrm{H} + \mathrm{O}_3 \rightarrow {}^{\bullet}\mathrm{OH}\ (v \leq 9) + \mathrm{O}_2 \qquad \text{(R1)}$$

Some years after these studies, evidence was provided for the formation of •OH at atmospheric pressure, from the reaction of ozone with 2,3-dimethyl-2-butene. A reaction stoichiometry ($\Delta[\text{alkene}]/\Delta[O_3]$) of 1.7 ± 0.1 was measured for the reaction and the *excess* consumption of the alkene—*i.e.*, the chemistry represented in Fig. 1 dictates a stoichiometry of one—was attributed to reaction with adventitiously produced •OH.[14] Direct formation of •OH from the decomposition of excited CIs was suggested and the hydroperoxide mechanism postulated. Since these early investigations, a large number of published studies have added to the significant body of indirect evidence for the direct formation of •OH and, further to this, many of these have provided quantitative information about the efficiency with which it is produced (*i.e.*, so-called •OH yields) in various ozone–alkene reaction systems. Compelling, albeit indirect, evidence for the intermediacy of •OH in the ozone–alkene reaction mechanism was provided by this laboratory from studies in which ozone was reacted with an alkene (2-methyl-2-butene) in the presence of various pairs of "tracer" species, selected according to the criteria that they are reactive towards •OH but (relatively) unreactive towards O_3 and other radical species likely to be formed in the ozonolysis reaction (*e.g.*, peroxyl radicals, including the hydroperoxyl radical, $HO_2^{\bullet}$).[19] The consumption of the two tracers was expected solely to be due to reaction with •OH and, hence, the relative changes in their concentration should be dictated by their relative reactivity towards this radical.

$$\text{Tracer A} + \text{X} \rightarrow \text{products} \qquad \text{(R2)}$$

$$\text{Tracer B} + \text{X} \rightarrow \text{products} \qquad \text{(R3)}$$

Here, X (which may or may not be •OH) is the reactive intermediate responsible for the consumption of tracers A and B. In essence, these were relative-rate studies in which relative-rate coefficients ($k_{\mathrm{A+X}}/k_{\mathrm{B+X}}$) were determined, from measured concentration data for the two tracers (according to expression E1), and compared with the ratio of rate coefficients for the reactions of these species with •OH ($k_{\mathrm{A+OH}}/k_{\mathrm{B+OH}}$), calculated using rate parameters taken from the literature.

$$\ln([\mathrm{A}]_0/[\mathrm{A}]_i) = (k_{\mathrm{A+X}}/k_{\mathrm{B+X}})\ln([\mathrm{B}]_0/[\mathrm{B}]_i) \qquad \text{(E1)}$$

Here, $[A]_0$ and $[A]_i$ (and similarly for tracer B) are the initial concentration of tracer A and the concentration of this species after a certain extent of 2-methyl-2-butene consumption by reaction with ozone. The results of this study are summarised in Fig. 5, in which the relative-rate coefficient data for the various tracers have been expressed relative to ethene; O_3 reacts with ethene *ca.* 200 times slower than it does with 2-methylbut-2-ene, so ethene consumption is virtually exclusively through its reaction with •OH.

Quantitative •OH yields have been obtained from studies in which any of this radical formed was completely reactively "scavenged", by the addition of high concentrations of a hydrocarbon species (which is unreactive towards ozone), or

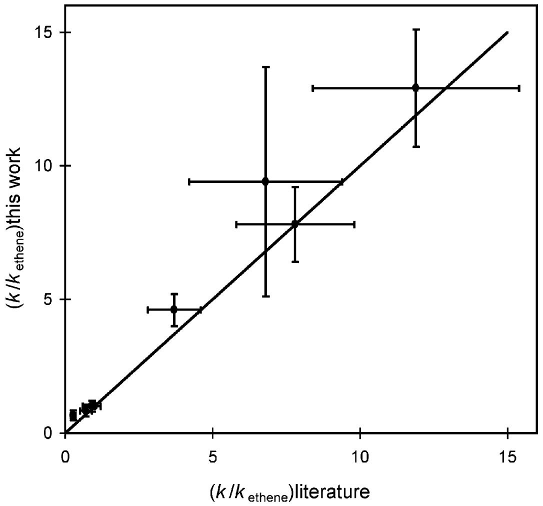


Fig. 5 Plot of measured (298 K) rate coefficients, relative to that for ethene, *vs.* relative literature values for the reactions of $^{\bullet}$OH with various hydrocarbons. Data from ref. 19.

partially "scavenged" through reaction with a carefully selected "tracer" hydrocarbon which was added in relatively low concentration (*e.g.*, see ref. 20). In these former studies, $^{\bullet}$OH yields were inferred either by measuring yields of products of the $^{\bullet}$OH-scavenger chemistry (*e.g.*, the yields of cyclohexanol and cyclohexanone from the reaction of $^{\bullet}$OH with cyclohexane—see Scheme 3), or by observing and quantitatively interpreting the effect of varying concentrations of added scavenger on the reaction stoichiometry.

In the latter, tracer-type, studies $^{\bullet}$OH yields were obtained by observing the amount of hydrocarbon tracer compound (*e.g.*, 1,3,5-trimethylbenzene) *e.g.*, ref. 21 that was consumed in the presence of ozone and an alkene, and by considering the relative reactivity of $^{\bullet}$OH radicals towards the added tracer and towards the parent alkene, for the conditions of the experiment. The results of the two types of experiment have generally been in very good accord. To date, $^{\bullet}$OH yields have been reported for almost 50 different alkenes (including simple acyclic alkenes, cyclic alkenes, conjugated dienes, monoterpenes and sesquiterpenes) from such indirect studies. Currently preferred $^{\bullet}$OH yields (*i.e.*, those recommended by IUPAC, for example, for inclusion in models of atmospheric chemistry) for a variety of ozone–alkene reactions are listed in Table 1.[20]

It is of value to make a few simple remarks about these data at this point. The $^{\bullet}$OH yield for the reaction of ozone with ethene is small (0.16); the yields for *Z*- and *E*-2-butene are somewhat larger (0.33 and 0.64, respectively, mean value = 0.49); and the yield for 2,3-dimethyl-2-butene is significantly larger again (0.90). By considering these simple systems, it may be assumed that only one CI structure, for each of the alkenes, is responsible for the $^{\bullet}$OH formation observed. On going from ethene (no alkyl substitution in the CI) to the 2-butenes (one methyl substituent) to 2,3-dimethyl-2-butene (two methyl substituents) the $^{\bullet}$OH yield increases from relatively near zero, to near 0.5, to near 1.0. Obviously, there are some subtleties in the data that are being ignored here but this trend is entirely consistent with $^{\bullet}$OH formation from the hydroperoxide mechanism, if it is assumed that 1,2-disubstituted alkenes produce *syn* and *anti* monosubstituted CIs with equal probability.§ Thus, by assuming that *syn* alkyl-substituted CIs produce $^{\bullet}$OH with unit efficiency, and that monosubstituted CIs are formed with a *syn* (or *anti*) configuration 50% of the time, a structure activity relationship (SAR) for $^{\bullet}$OH formation efficiency can be proposed. To predict $^{\bullet}$OH yields for asymmetric alkenes, knowledge of the relative amounts of the two CIs which can be formed is also required (*i.e.*, the branching ratio, α, in Fig. 1). This information is available for many asymmetric alkenes in the form of reported yields of primary carbonyl species (again, see Fig. 1). These considerations and assumptions were the basis of a SAR developed and presented by this laboratory. Predictions made using this SAR, for a large variety of alkene species, are compared to their corresponding measured values in Fig. 6.[21]

In the time since the results of the majority of these indirect investigations were published, several direct studies of $^{\bullet}$OH formation from gas-phase ozone–alkene reactions have been

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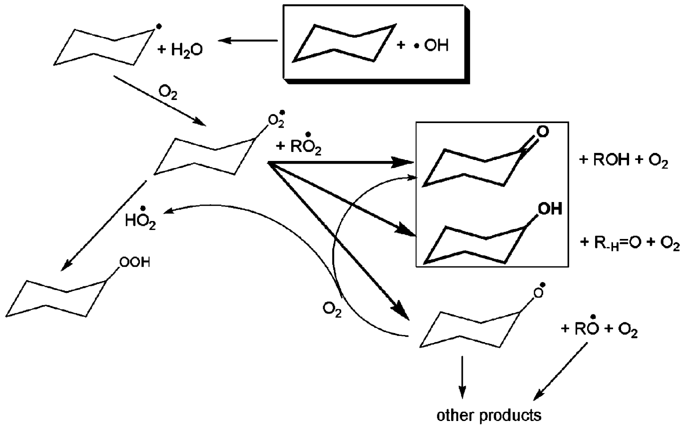
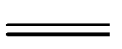
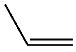
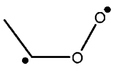
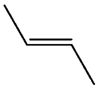
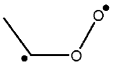
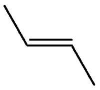
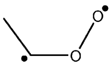
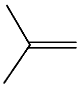
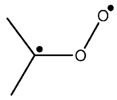
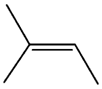
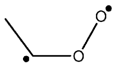
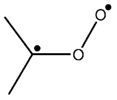
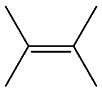
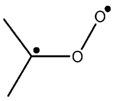
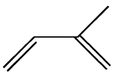
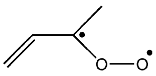
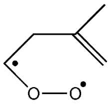
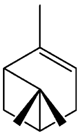
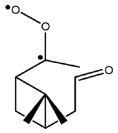
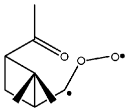
§ Some important factors being overlooked here are: $^{\bullet}$OH formation from the decomposition of $^{\bullet}CH_2OO^{\bullet}$ (which must be occurring, but by a different mechanism—see section 2); absolute knowledge of the proportions of *syn*- and *anti*-substituted CI that are formed from the 2-butenes, and the fact that *Z*- and *E*-2-butene exhibit clearly different $^{\bullet}$OH yields; and the fact that the $^{\bullet}$OH yield from 2,3-dimethyl-2-butene is less than one, and that yields of stabilised CI have been reported for this alkene.



Scheme 3

Table 1 Expected CI structures and IUPAC-preferred •OH yields for the reactions of ozone with several different simple alkenes and α-pinene

Alkene	Structure	CIs	IUPAC-preferred •OH yield
Ethene		•CH_2OO•	0.16
Propene		•CH_2OO•  (*syn* and *anti*)	0.34
Z-2-Butene		 (*syn* and *anti*)	0.33
E-2-Butene		 (*syn* and *anti*)	0.64
2-Methylpropene		•CH_2OO• 	0.62
2-Methyl-2-butene		  (*syn* and *anti*)	0.88
2,3-Dimethyl-2-butene			0.90
Isoprene		•CH_2OO•  (*syn* and *anti*)  (*syn* and *anti*)	0.25
α-Pinene		  (*syn* and *anti*)	0.80

Errors in OH yields are typically on the order of 0.1–0.2; the reader is referred to ref. 20 for more detailed discussion.

reported. The most significant of these employed a high-pressure flow system in which •OH radicals were detected, over a timescale of tens-of-milliseconds, by laser induced fluorescence (LIF).[16,22] As detailed in the next section, the results of these studies were, initially, surprising and appeared inconsistent with the indirect, atmospheric pressure determinations of •OH yields outlined above.

Time-resolved studies of •OH formation. As detailed above, there has been a long-held view that CIs are formed with vibrational excitation, and that decomposition occurs promptly from the excited species. However, it might be expected that the vibrationally excited CI would be at least partially stabilised at atmospheric pressure, the condition under which most of the •OH yield experiments have been carried out. For the more substituted alkenes such as 2,3-dimethyl-2-butene, •OH yields approach unity at atmospheric pressure, suggesting that if stabilisation is occurring it is only a very minor fate of the CI. By studying the pressure dependence of the reactions of ozone with selected alkenes, Anderson and co-workers[16,22] have been able to shed light on the details of the mechanism. These workers measured •OH yields from the ozonolysis of a number of alkenes using a fast-flow reactor coupled to detection by laser induced fluorescence (LIF). Experiments were carried out over short reaction times (*ca.* 10 ms) and at a variety of pressures ranging from 1 Torr to a few hundred Torr in some cases. They found that the •OH yields for the substituted alkenes studied dropped as the pressure increased. (For the ozonolysis of ethene—where the mechanism of •OH formation is different from the other

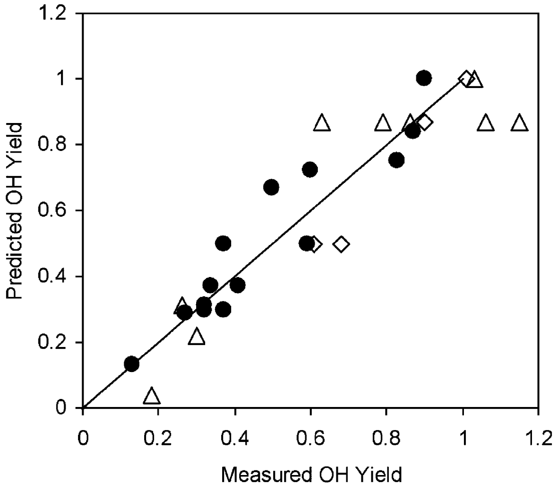


Fig. 6 Plot of predicted *vs.* measured $^{\bullet}$OH yields for a variety of ozone–alkene reactions: simple alkenes (open circles); terpenes (open triangles); internally unsaturated cyclic alkenes (open triangles). Figure based on data from ref. 21.

compounds—the yield was observed to be independent of pressure.) The pressure dependence of the yields makes sense if it is assumed that $^{\bullet}$OH is generated promptly from vibrationally excited CIs, and that this process is in competition with collisional stabilisation. However, the majority of $^{\bullet}$OH-yield measurements reported have been made at atmospheric pressure, and on the face of it the two sets of observations appear inconsistent. In a subsequent paper, these authors showed that at longer reaction times, of around one second, the $^{\bullet}$OH yield increased, approaching values consistent with previous atmospheric pressure determinations (Fig. 7).[22]

This observation can be explained if it is assumed that there are two distinct mechanisms leading to the formation of $^{\bullet}$OH: (i) prompt formation from a vibrationally excited CI; and (ii) longer-timescale formation from the decomposition of an initially stabilised CI as illustrated in Scheme 4.

This observation brings with it the possibility that *syn*- and disubstituted-CIs—which are assumed to give $^{\bullet}$OH radicals with more-or-less unit efficiency—could undergo bimolecular reactions at high pressures before being able to decompose to give $^{\bullet}$OH radicals. This has important implications for atmospheric chemistry, because it is possible that $^{\bullet}$OH yields measured in the laboratory are modified in the atmosphere by potential bimolecular reactions of the stabilised CI. As detailed in a subsequent section, in order to at least partially test this hypothesis, the present authors carried out a series of experiments in which $^{\bullet}$OH yields for the ozonolysis of 2-methyl-2-butene were measured in the presence of species that are believed to react with CIs;[23] species added were water, SO_2, acetic acid and butanone. It was discovered that, even at the highest concentrations added, there was no discernible change in the measured $^{\bullet}$OH yield implying that bimolecular reactions with *syn*- and disubstituted CIs were not occurring. The observation that the presence of these species does not interfere with $^{\bullet}$OH formation is important from the perspective of atmospheric chemistry, because it indicates that $^{\bullet}$OH yields measured in the laboratory can be applied to atmospheric models. One interpretation of these observations is that the quenching of vibrationally excited CIs gives either *anti*-CIs (for which the kinetics of bimolecular reactions may be relatively rapid, as detailed in a subsequent section) or the hydroperoxide that then leads to $^{\bullet}$OH formation. Some tentative evidence for this possibility has been obtained from flow-tube studies using Fourier transform infrared spectroscopy to detect transient reaction intermediates which may be responsible for $^{\bullet}$OH formation. At 200 Torr, an intermediate with the expected lifetime was detected in the reaction of 2,3-dimethyl-2-butene with ozone, but its spectrum did not correspond to that expected for $(CH_3)_2{}^{\bullet}COO^{\bullet}$, rather, it appeared consistent with the corresponding hydroperoxide product of isomerisation.[24] Unfortunately, there were technical difficulties with these initial experiments that made it impossible to obtain a clean spectrum of the intermediate.

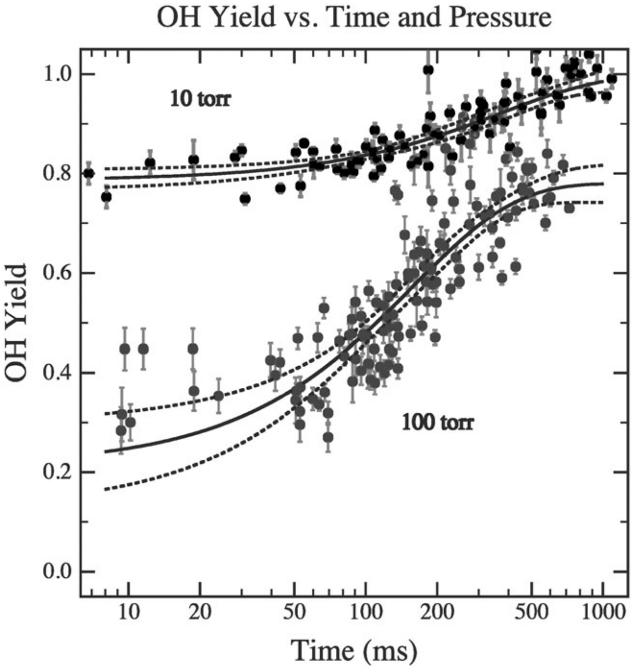
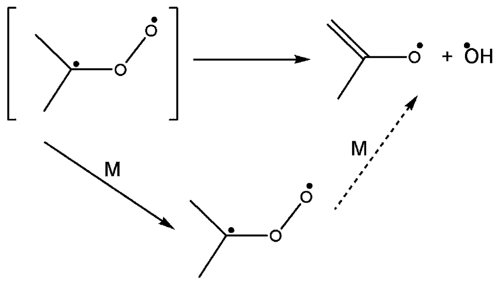


Fig. 7 Results of time-resolved study of $^{\bullet}$OH formation from the ozonolysis of 2,3-dimethyl-2-butene, at 10 and 100 Torr total pressure, by Kroll *et al.*[22] Reprinted with permission from ref. 22. Copyright 2001 American Chemical Society.

Stabilised Criegee intermediates (SCI). Fractional yields of stabilised Criegee intermediates have been reported for around 15 different ozone–alkene reactions under ambient



Scheme 4

conditions.[1,17] It should be appreciated that *such reported yields of SCI* correspond to the proportion of a given CI that, following its formation from the POZ and any subsequent collisional deactivation, is capable of participating in bimolecular reactions with molecular reaction partners. In fact, this is how all of the yields of SCI reported to date have been obtained: a species capable of reacting with the SCI (often referred to as a Criegee intermediate scavenger or trapping agent) is added in excess to a reacting ozone–alkene mixture and the products of the scavenging chemistry are used to infer the yield of the SCI. The product measured may be predominantly derived from the scavenger (*e.g.*, H_2SO_4 aerosol formed following SCI + SO_2) or from the Criegee intermediate itself (*e.g.*, the co-product of the SCI + SO_2 reaction, a carbonyl species).

$$R_1R_2{}^\bullet COO^\bullet + SO_2 \rightarrow SO_3 + R_1R_2C{=}O \qquad (R4)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (R5)$$

SCI scavengers, other than SO_2, that have been employed in such studies include HC(O)H, and H_2O, with SCI yields being derived from quantitative measurements of hydroxymethylformate, and hydroperoxide adducts, respectively.[1] From a simple consideration of the mechanisms represented by Fig. 1, and Schemes 1 and 2, it is expected that, for a variety of alkenes, yields of ${}^\bullet$OH should be anti-correlated with yields of SCI—or, at the very least, they should vary in opposite senses when comparing a given ozone–alkene reaction with others. As can be seen in Fig. 8, which is a plot of SCI yield *vs.* one minus ${}^\bullet$OH yield, this is seen to be the case although the relationship is not linear and does not tend towards the origin.

The observed non-linearity is consistent with the fact that other unimolecular fates are available to substituted CIs (*e.g.*, dioxirane formation) and that these also occur over timescales that preclude the possibility of bimolecular reactions in these experiments. That the plot does not tend to the origin suggests that even for disubstituted CIs (as for the specific case of 2,3-dimethyl-2-butene, for which data are included in the plot), which would be expected to exclusively isomerise to vinylhydroperoxide intermediates and release ${}^\bullet$OH, a small proportion of CIs are produced in a form that is stabilised at 298 K and 1 atm. As a final note, it is worth remarking that the data for cyclopentene, cyclohexene and cycloheptene appear anomalous when compared to those for the other alkenes included in the figure. The measured ${}^\bullet$OH yields for these species[1] vary between 0.36 (for cycloheptene) and 0.62 (for cyclopentene), values which are not inconsistent with reported ${}^\bullet$OH yields for acyclic 1,2-disubstituted alkenes (*e.g.*, *Z*- and *E*-2-butene) and this suggests that the SCI yields reported for these species are anomalously small when compared to the data for acyclic ozone–alkene reactions. There are two probable reasons for this, both of which result from the cyclic structure of these alkenes. First, once the POZ has been formed and ruptured, the excess energy of the cycloaddition reaction remains entirely within a single species—an intermediate with a carbonyl group at one end and a carbonyl oxide at the other—and cannot be dissipated as a result of energy transfer into translation and rotation modes of two separate fragments.[13] This may serve to accelerate unimolecular reactions involving the CI part of the intermediate, thus reducing the fraction that can be collisionally stabilised. Evidence for this can be seen in the significantly larger yields of CO_2 and (co-produced) acyclic aldehydes observed from the ozonolysis of these three cycloalkenes (Scheme 5) compared to the products of a CO_2-elimination pathway for CIs derived from simple acyclic alkenes.[1]

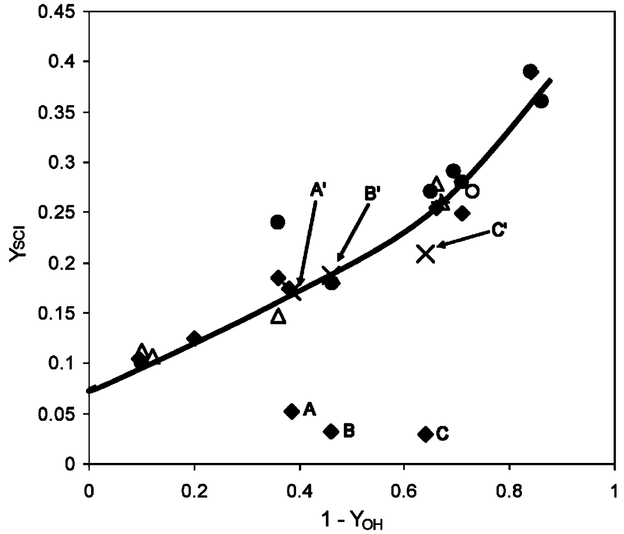
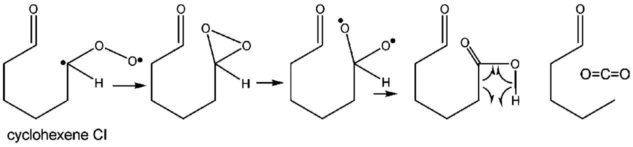


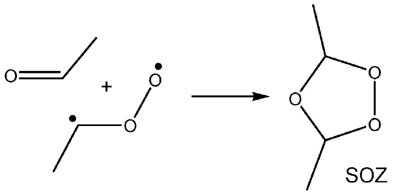
Fig. 8 Plot of measured yields of stabilised Criegee intermediate (Y_{SCI}) *vs.* 1 − ${}^\bullet$OH yield (1 − Y_{OH}) for a variety of ozone–alkene reactions. Data reported by various groups of workers: Hatakeyama and Akimoto[17] (filled diamonds); Paulson and co-workers[25,26] (filled circles); and Rickard *et al.*[21] (open triangles—anomalous reported measurement for β-pinene omitted). Data included for simple alkenes (ethene, propene, *Z*-2-butene, *E*-2-butene, *Z*-2-pentene, 2-methylpropene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, 1-butene, 1-pentene, 1-octene, 1-tetradecene), cyclic alkenes (methylenecyclohexane, cyclopentene (A), cyclohexene (B), 1-methylcyclohexene, cycloheptene (C)) and monoterpenes (α- and β-pinene). The *y*-ordinate data for the points labelled A′, B′ and C′ correspond to the same three cycloalkenes and are the sum of measured SCI yields and acyclic aldehyde yields[2] (these latter assumed to be formed *via* CO_2 elimination).

Second, the bifunctional nature of the intermediate means it is entirely feasible that the carbonyl oxide end can reactively interact with the carbonyl end—conceivably, given sufficient stabilisation, this could even allow the formation of a SOZ species by back biting.[13]

Kinetics of bimolecular reactions of SCIs. As already stated, to date, only one direct kinetic study has been reported of the kinetics of a bimolecular reaction of a SCI.[18] In this study, under (presumed) conditions of room temperature and one atmosphere of pressure, the reaction of $CH_3{}^\bullet CHOO^\bullet$ with acetaldehyde ($CH_3C(O)H$) was studied in a steady-state flow reactor.



Scheme 5



(R6)

Ozone and *E*-2-butene were introduced at the head of the tube, and excess acetaldehyde was added through a sliding injector at various distances along the cell in order to "trap" any SCI present after different reaction times. Evidence of bimolecular reaction was provided by observing secondary ozonide formation, by FT-IR spectroscopy. Detailed numerical simulations of these time-dependent SOZ data were performed by adopting a mechanism in which the SCI was assumed either to react with added acetaldehyde or to transform unimolecularly. A rate coefficient of 1×10^{-12} cm^3 molecule^{-1} s^{-1} was obtained for the bimolecular reaction (R6) and a unimolecular loss rate coefficient of 76 s^{-1}. As can be seen from Fig. 7, the time-resolved experiments of Kroll *et al.* indicate a rate constant for $^{\bullet}$OH formation from $(CH_3)_2{}^{\bullet}COO^{\bullet}$ (and by inference SCI decomposition) that is considerably smaller than this value. Furthermore, a study made in our laboratory suggested that bimolecular reactions of SCIs are very slow. Again, formation of $^{\bullet}$OH from the reaction of ozone with 2-methyl-2-butene was measured, in the absence and presence of large (and atmospherically unrealistic) concentrations of various SCI trapping agents.[23] In these experiments, the $^{\bullet}$OH yield was observed to be insensitive to the presence, or absence, of the different SCI scavengers employed, for the conditions of these studies—see Fig. 9.

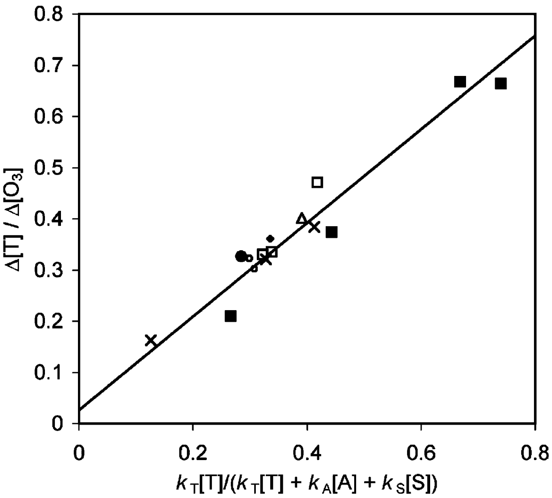


Fig. 9 Plot of Δ[T]/Δ[O$_3$] *vs.* k_T[T]/(k_T[T] + k_A[A] + k_S[S]) (*i.e.*, the first term is the amount of tracer consumed through reaction with OH and the latter is the proportion of OH that will react with the tracer) for various 2-methyl-2-butene ozonolysis experiments. T = $^{\bullet}$OH tracer compound (1,3-dimethylbenzene), A = alkene, and S = SCI scavenger. Data obtained in the absence of SCI scavenger (open squares) and in the presence of: 20 000 ppmv H$_2$O (crosses), 100 ppmv SO$_2$ (filled circle), 500 ppmv SO$_2$ (open triangle), 100 ppmv butanone (filled diamond), 150 ppmv acetic acid (filled square). Data also included for experiments carried out using 1,3,5-trimethylbenzene as the $^{\bullet}$OH tracer, in the absence of any SCI scavenger. Reprinted with permission from ref. 23. Copyright 2001 American Chemical Society.

From Kroll *et al.*'s study of the pressure dependence of $^{\bullet}$OH formation,[16] it is possible to put an upper limit on the rate coefficient for dissociation of the CI to give $^{\bullet}$OH, and on this basis, Johnson *et al.* were able to place upper limits on the bimolecular rate coefficients for the reaction of CIs with the scavenger species added. These upper limits are set out in Table 2.

Kroll *et al.*'s later work[22] showed that the timescale of SCI decomposition is significantly longer than the value used by Johnson *et al.* and the upper limits in the table can probably be reduced by an order of magnitude. It is important to note that these upper limits refer to the reaction of the added scavenger species with stabilised CIs that generate $^{\bullet}$OH; the experiments gave no information about stabilised *anti*-CIs, which, at least to a first approximation, do not generate $^{\bullet}$OH. The mechanistic implications of this chemistry are also interesting. It is well accepted that CIs react with H$_2$O, SO$_2$, carbonyls and organic acids, but Table 2 implies that at least for some CIs, these reactions are relatively slow. On the face of it, the large bimolecular rate coefficient obtained by Paulson and co-workers (of the order of 1×10^{-12} cm^3 molecule^{-1} s^{-1}) for the reaction of SCI with acetaldehyde does not seem consistent with the rather low upper limits for the rate constants of other bimolecular reactions. A possible explanation is that different types of CI are being examined in the two studies, with the *anti*-CI reacting quickly, while the *syn*- and disubstituted-CIs (which give $^{\bullet}$OH radicals) react rather more slowly. Indeed there is some theoretical evidence to support this view. Ryzhkov and Ariya[27] carried out density functional calculations on the reactions of CIs with water. They concluded that the reaction of *anti*-$CH_3{}^{\bullet}CHOO^{\bullet}$ with water occurs with a rate constant several orders of magnitude larger than the reactions of either *syn*-$CH_3{}^{\bullet}CHOO^{\bullet}$ of $(CH_3)_2{}^{\bullet}COO^{\bullet}$ with water. Of course, as already suggested in this article, it may be possible that excited CIs which are capable of producing $^{\bullet}$OH are relatively rapidly collisionally stabilised in the form of unsaturated hydroperoxide intermediate molecules—thus preventing their participation in (relatively slower) bimolecular reactions involving the types of species typically employed as SCI scavengers in experimental studies.

In contrast to these inferred slow bimolecular processes, Presto and Donahue[28] have shown that the reaction of NO$_2$ with SCI that lead to $^{\bullet}$OH radical formation is a relatively fast process. These authors examined $^{\bullet}$OH yields from the ozonolysis of selected alkenes in the presence of NO$_2$. For 2,3-dimethyl-2-butene, they observed a decrease in the $^{\bullet}$OH yield and a proportional increase in acetone yield as pressure was increased. They concluded that at the higher pressures, vibrational excitation in the CI was being quenched and that reaction (R7) is an efficient process.

$$(CH_3)_2{}^{\bullet}COO^{\bullet} + NO_2 \rightarrow (CH_3)_2C(O) + {}^{\bullet}NO_3 \quad \text{(R7)}$$

They suggested a rate coefficient for this reaction of about 10^{-13} cm^3 molecule^{-1} s^{-1}. The bimolecular process is likely to have a low barrier (it is a radical–radical reaction), while the unimolecular decomposition is likely to have a higher barrier. Thus, the impact of the reactions on atmospheric chemistry is likely to be strongly temperature dependent. If the proposed rate coefficient for this process is realistic, under very polluted

Table 2 Upper limit bimolecular rate coefficient estimates for the reactions of CIs with various molecular partners[23]

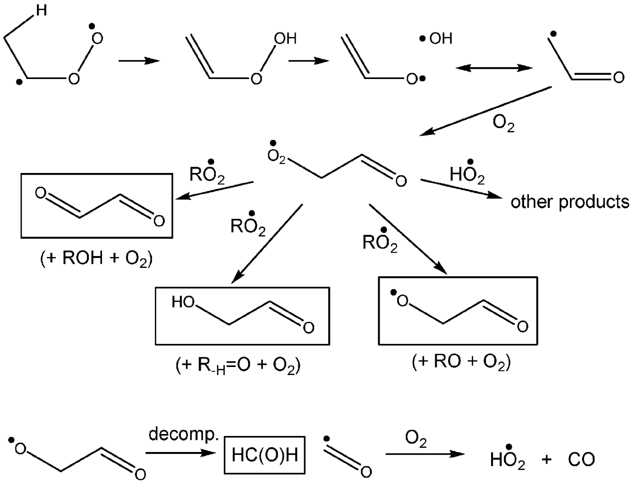
Reactant	H_2O	SO_2	Butanone	Acetic acid
$[S]_{max}{}^{a}$/molecule cm^{-3}	5×10^{17}	1×10^{16}	2.5×10^{15}	4×10^{15}
k/cm^3 molecule^{-1} s^{-1}	$\leq 1 \times 10^{-16}$	$\leq 4 \times 10^{-15}$	$\leq 2 \times 10^{-14}$	$\leq 1 \times 10^{-14}$

[a] $[S]_{max}$ is the maximum concentration of substrate used in the experiments.

urban conditions (of ozone, alkenes and NO_x) it may be that reaction (R7) is competitive with the unimolecular decomposition of SCI to produce $^{\bullet}$OH radicals. Clearly, the kinetics of processes such as reaction (R7) and the (potential) reaction of SCI with NO (which is usually the dominant component of NO_x) need to be fully elucidated.

Chemistry of the radical co-produced with $^{\bullet}$OH

According to the chemistry represented in the lower part of Scheme 2 the radical co-produced with $^{\bullet}$OH is a vinyloxyl-type radical ($R(O^{\bullet})C{=}CR'R''$) which, notionally, is in resonance with an acetonyl-type radical ($RC(O)C^{\bullet}R'R''$). Electronic structure calculations suggest that the majority of spin density for such a species will reside on the C atom adjacent to the carbonyl moiety[29] and this dictates that, under atmospheric conditions, the acetonyl-type radical will combine with molecular oxygen to form an acetonylperoxyl radical. There has been relatively little discussion of the chemistry of these radicals in ozone–alkene studies in the literature and yet some general features of their gas-phase chemistry are known or can be estimated by analogy to similar systems. For example, it is known that peroxyl radicals are relatively unreactive in that they tend to react with other radical species including—in the context of atmospheric chemistry—oxides of nitrogen (NO, NO_2 = "NO_x") and other peroxyl radicals ($HO_2{}^{\bullet}$ and $RO_2{}^{\bullet}$, where R is a carbon-containing group).[30] To date, the great majority of experimental gas-phase ozone–alkene studies have been carried out under static conditions and, hence, necessarily under "NO-free" conditions (NO is reactive towards O_3). Thus, the acetonylperoxyl-type radical will be expected to react with other peroxyl radicals formed during the course of the ozone–alkene reaction—*viz.*, $RO_2{}^{\bullet}$ (formed from $^{\bullet}$OH-scavenging chemistry or from carbon-containing fragments of CIs) and $HO_2{}^{\bullet}$. Reaction with $RO_2{}^{\bullet}$ will lead to a combination of closed-shell and radical products, and reaction with $HO_2{}^{\bullet}$ will, to an uncertain degree, terminate the radical chain through the formation of organic hydroperoxide molecules. To exemplify this chemistry, the fate of *syn*-methylcarbonyl oxide can be considered (see Scheme 6).



Scheme 6

Isomerisation of the CI will give an excited vinylhydroperoxide which rapidly decomposes to yield $^{\bullet}$OH and vinyloxyl radicals. As already stated, this latter is more realistically represented as $^{\bullet}CH_2C(O)H$ and in the presence of molecular oxygen this will form the corresponding peroxyl radical. Reactions of this radical with other peroxyl radicals will be expected to yield glyoxal (HC(O)C(O)H), glycoaldehyde ($HC(O)CH_2OH$) or an acyloxyl radical ($HC(O)CH_2O^{\bullet}$). This oxyl radical is expected to rapidly decompose to a formyl radical ($HC(O)^{\bullet}$) and a secondary carbonyl product, formaldehyde (methanal). Any formaldehyde product measured, for example, during the ozonolysis of *Z*-2-butene (which involves only one CI, methylcarbonyl oxide) is clearly secondary in nature as it cannot be formed directly from the POZ. This is not the case, *e.g.*, for the ozonolysis of propene (which produces both $^{\bullet}CH_2OO^{\bullet}$ and $CH_3{}^{\bullet}CHOO^{\bullet}$ intermediates) where formaldehyde is formed directly from a proportion of the decomposing POZ. Formaldehyde formation from the ozonolysis of *Z*-2-butene (Tuazon *et al.*[31] report a yield of 0.161 ± 0.030) must be as a result of secondary processes (*e.g.*, as represented in Scheme 6) as the primary carbonyl product is acetaldehyde alone. Similarly, secondary-carbonyl yields can be inferred for a significant variety of simple acylic alkenes for which carbonyl product data have been reported. Thus, the combined yields of secondary carbonyl[1] (as defined by example above), α,β-dicarbonyl[1] (*e.g.*, glyoxal) and β-hydroxycarbonyl[1] products (*e.g.*, glycoaldehyde) should increase with increasing yield of $^{\bullet}$OH—*i.e.*, consistent with the decomposition of vinylhydroperoxide intermediates and the subsequent radical chemistry. This assertion is supported by Fig. 10 in which combined product yields, as just stated, are plotted against yields of "hydroperoxide $^{\bullet}$OH".

These latter are measured $^{\bullet}$OH yields minus any contribution to the formation of this radical made by the decomposition of $^{\bullet}CH_2OO^{\bullet}$ (which will occur during the ozonolysis of 1-alkenes), with an assumed fractional $^{\bullet}$OH yield of 0.16 per peroxymethylene intermediate formed. The plot is clearly linear but the slope is less than one. This presumably reflects the fact that other peroxyl radical reactions are occurring, which do not form the products discussed above—*e.g.*, chain terminating reactions involving $HO_2{}^{\bullet}$. To summarise this discussion of the gas-phase chemistry of Criegee intermediates, the chemistry of methylcarbonyl oxide is represented, in outline, in Scheme 7.

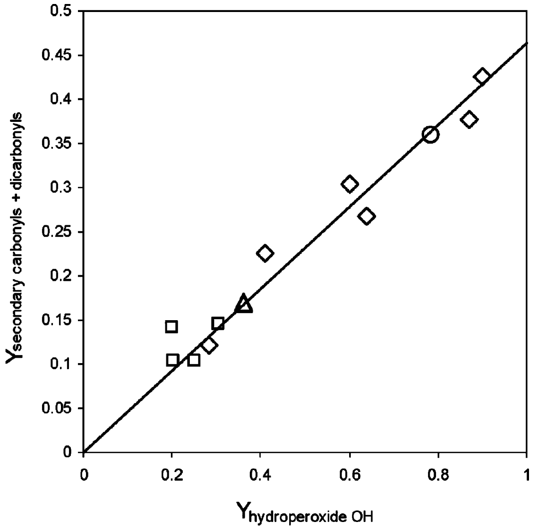
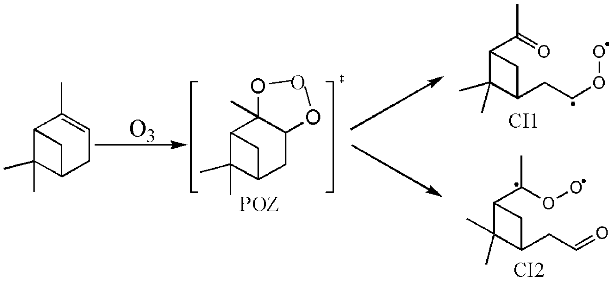


Fig. 10 For various ozone–alkene reactions: plot of the combined reported yields of secondary carbonyls and dicarbonyl products *vs.* yield of OH from the decomposition of substituted CIs (see text). Data included for ethene, propene, *Z*- and *E*-2-butene, 2-methylpropene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, *Z*-3-hexene, *Z*-4-octene and 2-methyl-1-butene.

3 Precursors to secondary organic aerosol formation

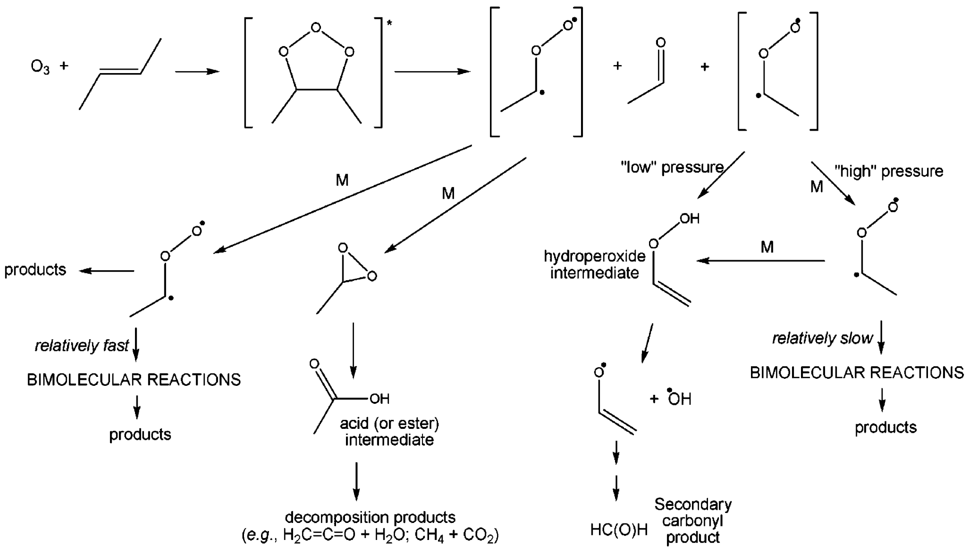
The reactions of ozone with larger biogenic species such as the terpenes ($C_{10}H_{16}$ hydrocarbons) are important sources of $^{\bullet}OH$ for the same reasons that the ozonolysis of simpler unsaturated compounds are. However, in addition, these former reactions are important sources of particulate matter in the atmosphere, generally known as secondary organic aerosol (SOA). As detailed above, the mechanisms for the reactions of ozone with simple unsaturated hydrocarbons are far from fully understood. For these more complex systems, there are additional difficulties in interpreting the experimental observations. The ozonolysis of α-pinene is expected to produce two CIs (ignoring differences of *syn*- and *anti*-conformation), as illustrated in Scheme 8, and is thus expected to give products that have a carbonyl functionality at one end of the molecule, and a functionality resulting from chemistry of the CI at the other end.



Scheme 8

This is indeed the case for products such as pinonaldehyde, pinonic acid and norpinonic acid. However, products such as pinic and norpinic acid require further oxidation of the carbonyl moiety (Fig. 11).

What this appears to indicate is the occurrence of intramolecular reactions involving both ends of the reaction intermediates—the extent to which these occur is likely to be determined by particular features of the terpene concerned. Even though it is the most extensively studied, there is significant uncertainty in the mechanism for the ozonolysis of α-pinene, and the following discussion will be limited to this reaction. Uncertainties in the understanding of this mechanism can be exemplified by what is understood about the formation of pinonaldehyde. Structurally, this product is very closely related to both of the CIs by simply possessing one fewer oxygen atoms. The yield of pinonaldehyde from the reaction appears to be fairly well established at about 20%.[1] However, as Alvarado *et al.* commented in 1998,[32] it is not obvious, mechanistically, how it is formed. These authors showed that direct loss of an O atom from either of the CIs formed in the reaction (CI1 or CI2) was not significant, and they suggested that the reaction



Scheme 7

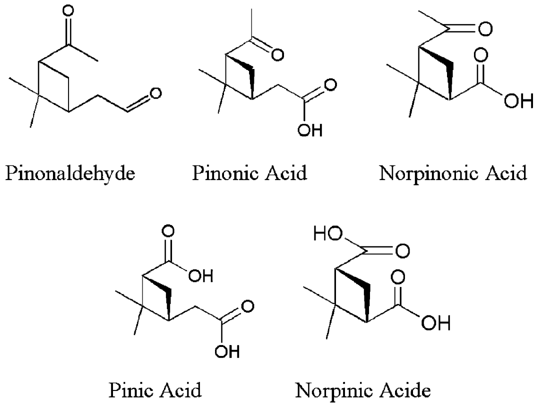
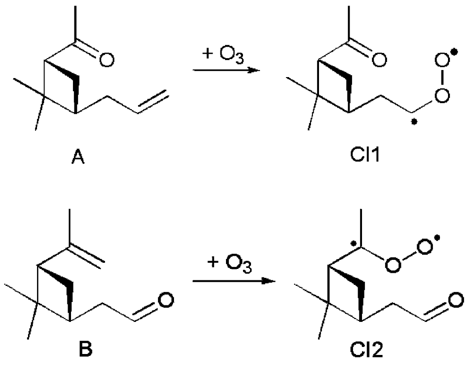


Fig. 11 Structures of several identified products of the gas-phase ozonolysis of α-pinene.

of CI1 with H_2O was a possible source. Yu *et al.*[33] believed the major source of pinonaldehyde in their experiments to be O-atom loss from CI1, the reaction of secondary •OH with α-pinene accounting for the remainder. Kamens *et al.*[34] also argued that pinonaldehyde was generated in the reaction of •OH with α-pinene. Warschied and Hoffmann[35] have presented results showing that the yield of pinonaldehyde varies between 20% (at ≤1% relative humidity) to 50% (at 80% relative humidity). Their quantitative experiments were carried out without an •OH scavenger (in the presence of large concentrations of cyclohexane, experimental difficulties prevented quantitative measurements, but qualitatively the results were similar). It is not immediately clear how 50% of the reaction could generate pinonaldehyde, given that the yield of •OH from the reaction is close to 80% and that the co-products of the •OH-forming chemistry are not believed to yield pinonaldehyde. These studies show clearly that there is no consensus on the mechanism leading to formation of even the first generation of products.

Secondary organic aerosol is known to contain substantial quantities of organic acids, and these compounds have been proposed as nucleating species for aerosol formation and growth; for example, a study at the EUPHORE chamber in Valencia concluded that pinic acid is the key nucleating species in the ozonolysis of α-pinene.[36] One of the key questions to be asked in trying to understand the mechanism of organic acid formation in α-pinene ozonolysis mechanism is which CI gives rise to which product. Until recently, this question has been answered largely by inference, but recent work in our laboratory is beginning to answer the question, at least in the case of the major identified organic acid products. By synthesising compounds that only give one or other of the CIs on ozonolysis—as illustrated in Scheme 9—it is possible to extract important information about which compounds are generated *via* which CI.



Scheme 9

The enone (A)[37] and enal (B)[38] have each been synthesised, and the acid products of their gas-phase reaction with ozone measured under various experimental conditions by gas chromatography with mass spectrometric detection. What is observed is that most of the identified products can be associated with one or other of the CIs; for example, pinic acid is seen to be generated exclusively from CI2, as expected, while norpinonic acid is formed only *via* CI1. On the other hand, pinonic acid is inferred to be generated from both CIs, by three separate mechanisms. For the reactions of ozone with α-pinene, and the enone (A) and the enal (B) precursors, measured yields of pinonic and norpinonic acid are plotted as a function of experiment relative humidity (RH), in Fig. 12(a) and (b).

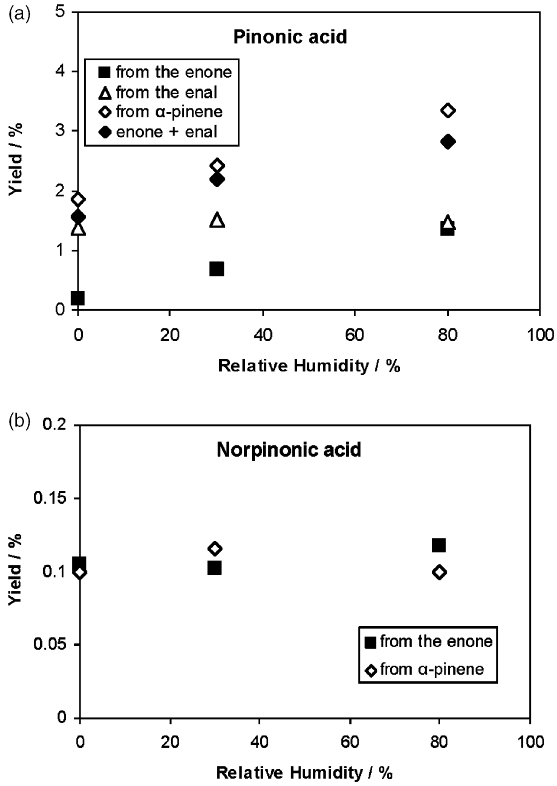
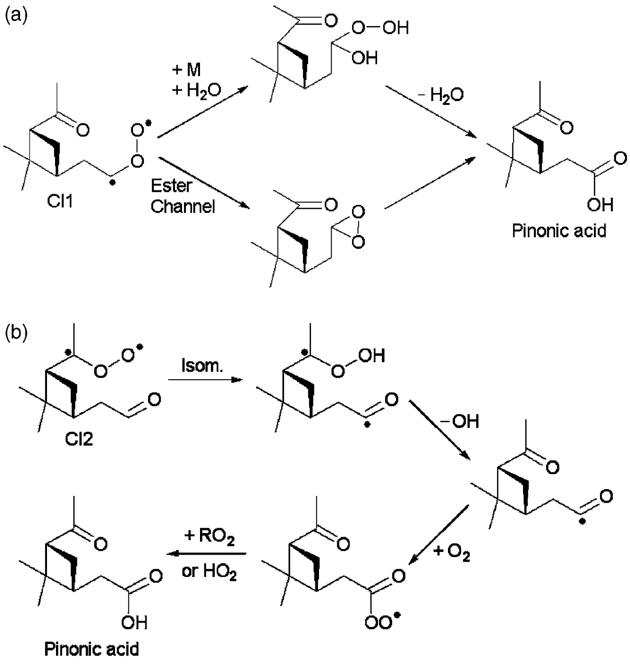


Fig. 12 (a) Pinonic acid yields from the ozonolysis of enone and enal precursors, and from α-pinene measured at different relative humidities. Figure reproduced from ref. 37 - Reproduced by permission of the PCCP Ownership Board. (b) Norpinonic acid yields from the ozonolysis of the enone precursor and α-pinene measured at different relative humidities. Norpinonic acid formation was not observed from the ozonolysis of the enal precursor. Figure reproduced from ref. 37 - Reproduced by permission of the PCCP Ownership Board.



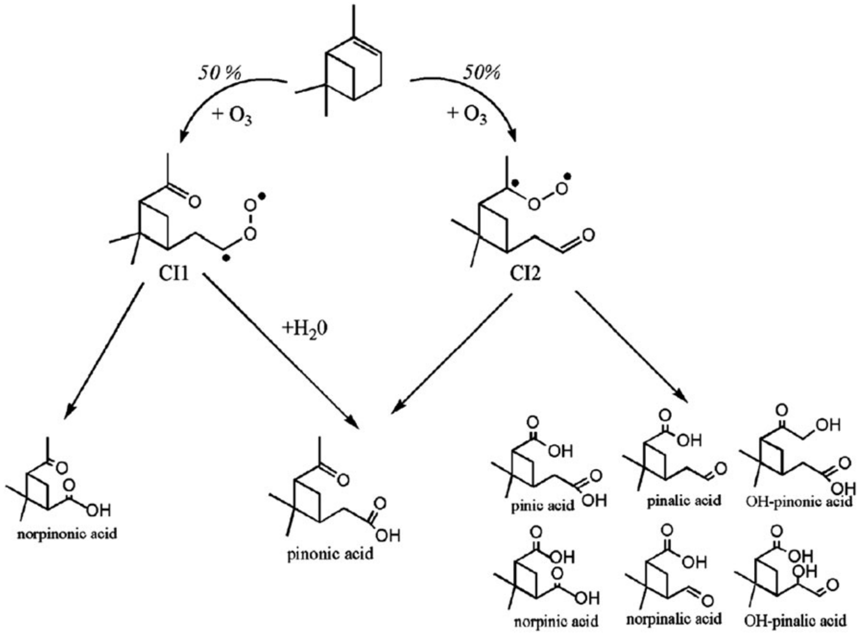
Scheme 10

The yield of pinonic acid from α-pinene shows a component that is RH independent and a component that is RH dependent. Ozonolysis of the enal (B) shows that this RH-independent part can be attributed predominantly to formation through CI2, while ozonolysis of the enone (A) indicates a small yield that is RH independent, but a larger RH dependent yield. It is possible to write mechanisms for these various processes. Mechanisms for the formation of pinonic acid from CI1 *via* an RH-dependent mechanism and the ester channel are based on well established chemistry. On the other hand, CI2 is expected to fall apart virtually exclusively to give $^{\bullet}OH$ *via* the hydroperoxide channel, as already discussed. It is possible, however, that CI2 could decompose to produce $^{\bullet}OH$ in a different process, as illustrated in Scheme 10(b); the mechanisms for formation of pinonic acid are summarised in Schemes 10(a) and (b).

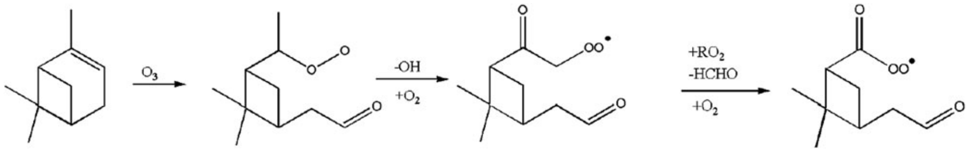
What can be seen from Fig. 12(a) is that the total yield of pinonic acid from α-pinene ozonolysis is approximately equal to the sum of the yields from the ozonolyses of the enone and enal. This observation implies that the branching ratios for the formation of the two CIs are the same. Fig. 12(b) shows this a little more clearly for norpinonic acid. In this case, the CI leading to norpinonic acid formation from α-pinene is the less-substituted of the two, while from the enone, it is the more-substituted (the less-substituted CI being $^{\bullet}CH_2OO^{\bullet}$). That the yields of the acid from α-pinene and the enone are identical implies that the CI yields are identical for both ozonolysis reactions and the most logical explanation is that the branching ratios are each 0.5. The overall results are summarised in Scheme 11.

The exact details of subsequent steps leading to the individual products are by no means certain. Some progress can be made by invoking known chemistry supported by experimental evidence combined with novel steps supported by theoretical calculations. For example, Jenkin *et al.*[39] and Koch *et al.*[40] have proposed mechanisms for the formation of pinic acid that involve a number of common steps, as illustrated in Scheme 12, but differ in subsequent steps, as shown in Schemes 13(a) and (b).

The mechanism of Jenkin *et al.* is supported by theoretical calculations which indicate that occurrence of the key intramolecular isomerisation reaction is kinetically feasible. Furthermore, studies in this laboratory[41] have shown that the yield of pinic acid is greater when cyclohexane is used as the $^{\bullet}OH$ scavenger than when methanol is employed. As represented in Scheme 3, cyclohexane reacts with $^{\bullet}OH$ (then



Scheme 11



Scheme 12

O_2) to give a C-centred peroxyl radical ($RO_2^\bullet$), while methanol reacts with $^\bullet OH$ (and then O_2) to give $HO_2^\bullet$. If the mechanism of Koch *et al.* were correct, the presence of additional $HO_2^\bullet$ would enhance pinic acid formation, whereas in the mechanism of Jenkin *et al.*, it would promote termination of radical chains. Thus, the experiments provide further support for the mechanism proposed by Jenkin *et al.*

While it is clear that organic acids comprise part of the observed SOA, it is not clear that they lead to particle nucleation. Bonn *et al.*[42] have studied the impact of water vapour on the ozonolysis of α-pinene and discovered that increased relative humidity decreases particle density. As pinic acid formation is not expected to be (significantly) affected by relative humidity, this appears to exclude this compound as the nucleating source. These authors suggest that the SCI is implicated as the source *via* the formation of SOZs. As already discussed, water reacts with SCIs, and is thus expected to reduce particle formation if the SCI is involved in such chemistry. However, a more recent study from Jonsson *et al.*[43] found that increased relative humidity *increased* the number of particles formed in the ozonolysis of α-pinene and some other terpenes, indicating that SCIs are not directly linked to particle formation.

At this time it is clear that there are a large number of uncertainties in current understanding of the detailed reaction mechanism for α-pinene ozonolysis (and similarly for the reactions of ozone with other terpenes). Some progress has been made in recent years in elucidating some aspects of the mechanisms, but there is still a long way to go. Similarly, the exact nature of the compounds leading to particle nucleation is not yet known.

4 Atmospheric significance of ozone–alkene reactions

Free radical budgets and tropospheric ozone photochemistry

There exists in the literature a growing number of studies in which the atmospheric significance of direct radical production from gas-phase ozone–alkene reactions has been discussed. Such chemistry is often considered in order to explain initially surprising atmospheric observations for polluted urban and remote continental atmospheres, both during the night-time and the daytime. For example, detailed box modelling revealed that during both summer and winter, the majority of $^\bullet OH$ measured in the PUMA campaign (Pollution in the Urban Midlands Atmosphere) resulted from ozonolysis reactions.[44] For the purposes of the present article, one case study, pertinent to the chemistry of the UK urban environment, will briefly be discussed.

As already mentioned, $^\bullet OH$ is the most important initiator of oxidation chemistry for the majority of VOCs and, hence, it is sometimes referred to as the "detergent" of the troposphere. The major source of $^\bullet OH$ in this region of the atmosphere is usually assumed to be the gas-phase reaction of excited oxygen atoms ($O^*(^1D)$) with water (*e.g.*, see ref. 10).

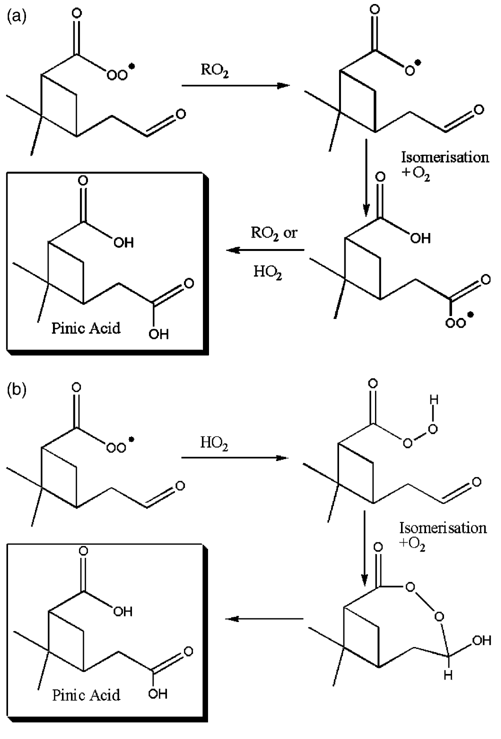
$$O_3 + h\nu\,(\lambda \leq 336\text{ nm}) \rightarrow O^*(^1D) + O_2^* \qquad \text{(R8)}$$

$$O^*(^1D) + H_2O \rightarrow {}^\bullet OH + {}^\bullet OH \qquad \text{(R9)}$$

$$O^*(^1D) + M\,(N_2, O_2) \rightarrow O(^3P) + M \qquad \text{(R10)}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{(R11)}$$

Here, M is a third body which serves to collisionally stabilise nascent adduct species, and, due to the composition of the atmosphere, it is either a molecule of O_2 or N_2. Under typical European atmospheric conditions, about 10% of any $O^*(^1D)$ are converted to $^\bullet OH$ radicals.[45] Thus, $^\bullet OH$ production rates are expected to vary diurnally and seasonally (*i.e.*, with the availability of photons) and to drop to zero during the night-time. Other tropospheric sources of $^\bullet OH$ include the photolysis of nitrous acid (HONO) and (indirectly) formaldehyde, and the reactions of ozone with alkenes. Ozonolysis



Scheme 13

reactions are thus believed to be an important night-time source of $^{\bullet}OH$.[10]

$$HONO + h\nu\,(\lambda \le 400\text{ nm}) \rightarrow {}^{\bullet}OH + NO \qquad (R12)$$

$$HC(O)H + h\nu\,(\lambda \le 338\text{ nm}) \rightarrow H^{\bullet} + HC(O)^{\bullet} \qquad (R13)$$

$$HC(O)^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + CO \qquad (R14)$$

$$H^{\bullet} + O_2 + M \rightarrow HO_2^{\bullet} \qquad (R15)$$

$$HO_2^{\bullet} + NO \rightarrow {}^{\bullet}OH + NO_2 \qquad (R16)$$

Photochemical ozone formation is mediated by chains and cycles of free radical reactions, key amongst which is the conversion of NO to NO_2 by reaction with peroxyl radicals ($RO_2^{\bullet}$ and $HO_2^{\bullet}$). NO_2 is photolabile in the troposphere and, hence, provides the source of O atoms required for *in situ* ozone production.

$$RO_2^{\bullet}\,(HO_2^{\bullet}) + NO \rightarrow RO^{\bullet}\,({}^{\bullet}OH) + NO_2 \qquad (R17)$$

$$NO_2 + h\nu\,(\lambda \le 400\text{ nm}) \rightarrow NO + O(^3P) \qquad (R18)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (R11)$$

From the earlier discussions of the mechanism of ozone–alkene reactions, it can be appreciated that they have the potential to produce significant amounts of HO_x species (HO_x = $^{\bullet}OH$, $HO_2^{\bullet}$, $RO_2^{\bullet}$) in the atmosphere and, hence, lead to a net positive rate of *in situ* ozone production.

Following the example of an earlier study, which calculated HO_x production rates from measured ambient non-methane hydrocarbon (NMHC), NO_x and O_3 data,[46] the contribution made by ozone–alkene reactions to local radical production rates can be simply estimated, for example, for the centre of the city of Birmingham (a background urban location in the UK) during early summer 1998 (a period for which speciated O_3, NMHC and NO_x data are available). This can then be compared to the rate of radical production from the photolysis of O_3 and subsequent reaction of $O(^1D)$ with water. For the present study, production rates have been calculated using expressions (E2) and (E3), for ozone–alkene reactions and ozone photolysis, respectively:

$$\frac{d[HO_x]}{dt} = 2 \times \sum_{i=1}^{8} ([\text{alkene}]_i \times [\text{ozone}] \times k_i \times Y_{OH_i}) \qquad (E2)$$

$$\frac{d[OH]}{dt} = 2 \times [\text{ozone}] \times J_{O(1D)} \times f_{OH} \qquad (E3)$$

For a given alkene, i, k_i is the (298 K) rate coefficients for reaction with O_3, Y_{OH_i} is the measured $^{\bullet}OH$ yield for that reaction, $J_{O(1D)}$ is the photolysis rate coefficient for reaction (R8), and f_{OH} is the fraction of $O(^1D)$ that reacts with water vapour as opposed to being collisionally quenched (*i.e.*, reaction (R9) *vs.* (R10)). For simplicity, this latter was assumed to be 0.10, appropriate to temperatures and relative humidities representative of Northern Europe. The eight alkenes for which measured concentration data were available[¶] are: ethene, propene, 1-butene, *Z*- and *E*-2-butene, *Z*- and *E*-2-pentene, and isoprene (2-methyl-1,3-butadiene). The factor of 2 in eqn (E2) and (E3) reflects the fact that two radicals are produced both from the decomposition of a vinylhydroperoxide (lower panel of Scheme 2) and from reaction (R9). The diurnal variation of $J_{O(1D)}$ was estimated for Birmingham (52.5° N) for the beginning of July using calculated actinic flux data (*i.e.*, the total flux of photons available to initiate photochemistry), measured absorption cross sections for O_3 and measured photolysis quantum yields (*i.e.*, what is the proportional yield of $O(^1D)$ following the absorption of a photon, of a given wavelength, by a molecule of O_3). Absolute values of $J_{O(1D)}$ were estimated for different solar zenith angles (and, hence, different times of the day) by scaling the estimated relative photolysis rate coefficients to give a maximum value of $1.5 \times 10^{-5}\ s^{-1}$.[‖] The results of these simple calculations are summarised in Fig. 13.

What can be seen from these data is that the formation of HO_x species from ozone–alkene reactions is significant throughout the whole of the five day period both during the daytime and the night-time. Additionally, the maximum magnitude of HO_x production from ozone–alkene reactions ranges, for a given 24 h period, from being significantly greater than the source due to O_3 photolysis, roughly equal in magnitude to this source, and down to a third of its value. By comparing the magnitude of night-time HO_x production due to ozone–alkene chemistry to the strength of the ozone-photolysis source of $^{\bullet}OH$ for the first 24 h period, clear indirect evidence is seen for a very significant amount of $^{\bullet}OH$-initiated oxidation chemistry occurring throughout the hours of darkness. Percent contributions to the total rate of HO_x production, due to ozone–alkene reactions, are represented for each individual ozonolysis reaction in Fig. 14.

Despite their relatively low measured atmospheric concentrations, the reactions of ozone with internally unsaturated alkenes are clearly seen to be the dominant source of HO_x from this class of reactions in the urban setting of Birmingham—this is a consequence of their relatively high reactivity towards ozone and $^{\bullet}OH$ yields. Finally, it should be mentioned that the rate of HO_x production from the photolysis of aldehyde species was not considered in this exercise due to the absence of any coincident measured carbonyl data. The photolysis of aldehydes can provide a significant additional source of radical species in the atmosphere, and the reactions of ozone with alkenes can constitute a significant *in situ* source of aldehyde species. Thus, the full significance of ozone reactions to the boundary layer radical pool may not be fully suggested by, for example, Fig. 13.

5 Conclusions, uncertainties and suggested future studies

The material presented throughout this article hopefully indicates that a great deal of progress has been made in recent years in understanding the kinetics and mechanisms of the gas-phase reactions of ozone with unsaturated compounds. This understanding concerns not only details of the physical chem-

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[¶] These are the alkene species that appear in the table of the 50 most significant NMVOC species, on a mass emission basis, of the UK National Atmospheric Emissions Inventory (http://www.airquality.co.uk/)

[‖] Maximal photolysis rate coefficients of this magnitude have been measured and reported for the centre of Birmingham at this time of year—see data in ref. 47.

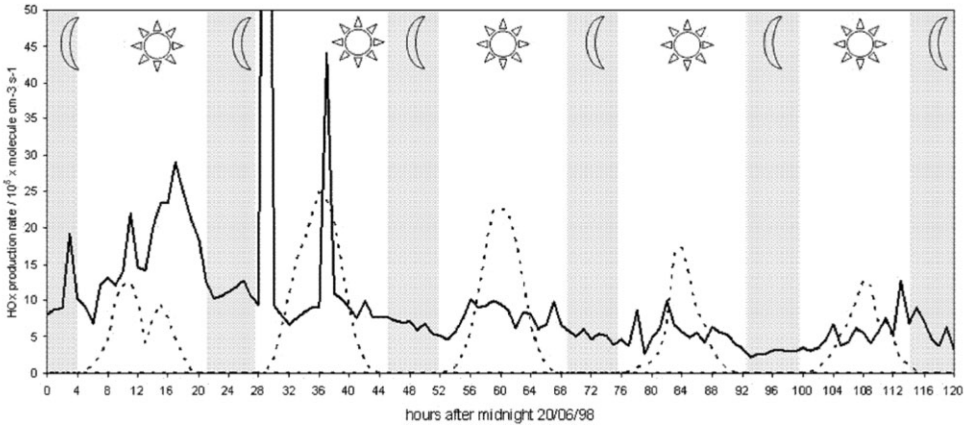

Fig. 13 Calculated HO_x production rates for central Birmingham during the period 20–24 June 1998.

istry involved but also the potential atmospheric impacts that such reactions can have. Broadly speaking, the accumulated body of experimental results confirms the applicability of the Criegee mechanism in describing gas-phase ozonolysis reactions, and there is much indirect evidence for the intermediacy of Criegee intermediates themselves in these processes. To date, no Criegee intermediate has been observed in any gas-phase study of ozone–alkene chemistry. The unimolecular chemistry of Criegee intermediates has the potential to be very important to the chemistry of the Earth's troposphere as a whole, being widely regarded as a significant source of new radical species affecting, for example, the *in situ* formation of important secondary pollutants. The details of such chemistry have become somewhat clearer in recent years as a result of the first time-resolved measurements of $^{\bullet}OH$ formation. Similarly, the bimolecular chemistry of Criegee intermediates has the potential to impact atmospheric trace composition and yet to date only one direct kinetic investigation has been reported for the reaction of a Criegee intermediate with a reaction partner. $^{\bullet}OH$-tracer studies carried out in the presence of high concentrations of Criegee intermediate-scavenger species suggest that the $^{\bullet}OH$-forming chemistry occurs at a fast enough rate to preclude the possibility of bimolecular chemistry—in both the experiments and, hence, the atmosphere. One key question for atmospheric chemistry remains unanswered here: what are the rates of CI reactions with NO_x compared to the rates of their unimolecular chemistry? From a viewpoint more centred on physical chemistry, it would be extremely desirable for experiments to reveal more about the nature of the Criegee intermediate, their unimolecular chemistry (*e.g.*, precisely how is $^{\bullet}OH$ formed), their bimolecular chemistry (time-resolved reaction rate and product studies), and, again, whether these latter have the potential to compete with various unimolecular processes.

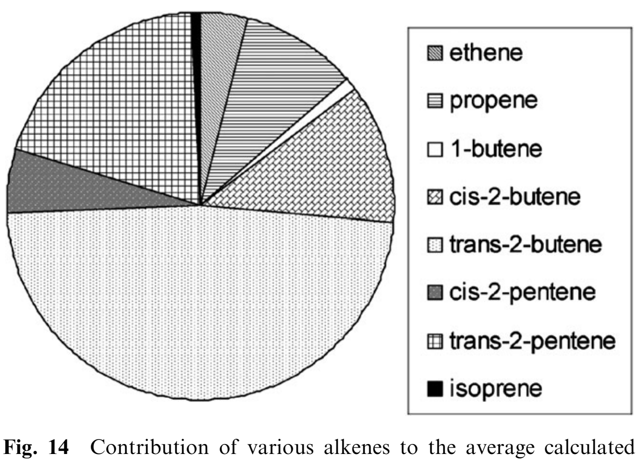

Fig. 14 Contribution of various alkenes to the average calculated total HO_x production rate from ozone–alkene reactions for the period 20–24 June 1998.

In terms of SOA formation from ozone–alkene chemistry there is relatively much more still to find out. By better understanding the chemical nature and (unimolecular and bimolecular) chemistry of CIs it should be easier to propose mechanisms for the formation of non-volatile oxidation products which are key to the formation and growth of SOA material. The results of studies such as those detailed above for acid production from the ozonolysis of α-pinene will greatly aid in this endeavour, as will the results of well designed electronic structure calculations. To take a step backwards, there is still a vast amount to be understood about the complex composition of SOA, including the identification of species which nucleate new particle formation and species which promote aerosol growth (*e.g.*, through their participation in molecular-weight growing accretion reactions within the particle). As a final example of uncertainty, evidence is emerging for the importance of O_3–sesquiterpene** chemistry.[48] By virtue of their molecular size and structure, sesquiterpenes have the potential to be very efficient SOA precursors in the atmosphere and to exhibit high reactivity towards atmospheric oxidants. This latter means that their atmospheric lifetimes are expected to be short and their spatial distribution will be associated with the forest canopies from which they are emitted. Careful flux measurements are required to quantitatively estimate the extent and rate of their emission to the Earth's atmosphere.

Acknowledgements

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** A sesquiterpene is a $C_{15}H_{24}$ biogenic, cyclic, unsaturated hydrocarbon.

C518230/1). G. M. wishes to thank NERC for support through the COSMAS Programme (NER/T/S/2000/01083).

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