Reactions of Stabilized Criegee Intermediates from the Gas-Phase Reactions of O₃ with Selected Alkenes

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ABSTRACT: The gas-phase reactions of O₃ with 1-octene, trans-7-tetradecene, 1,2-dimethyl-1-cyclohexene, and α -pinene have been studied in the presence of an OH radical scavenger, primarily using in situ atmospheric pressure ionization tandem mass spectrometry (API-MS), to investigate the products formed from the reactions of the thermalized Criegee intermediates in the presence of water vapor and 2-butanol (1-octene and trans-7-tetradecene forming the same Criegee intermediate). With $H_3O^+(H_2O)_n$ as the reagent ions, ion peaks at 149 u $([M + H]^+)$ were observed in the API-MS analyses of the 1-octene and trans-7tetradecene reactions, which show a neutral loss of 34 μ (H₂O₂) and are attributed to the α -hydroxyhydroperoxide CH₃(CH₂)₅CH(OH)OOH, which must therefore have a lifetime with respect to decomposition of tens of minutes or more. No evidence for the presence of α -hydroxyhydroperoxides was obtained in the 1,2-dimethyl-1-cyclohexene or α -pinene reactions, although the smaller yields of thermalized Criegee intermediates in these reactions makes observation of α -hydroxyhydroperoxides from these reactions less likely than from the 1-octene and trans-7-tetradecene reactions. Quantifications of 2,7-octanedione from the 1,2dimethyl-1-cyclohexene reactions and of pinonaldehyde from the α -pinene reactions were made by gas chromatographic analyses during reactions with cyclohexane and with 2-butanol as the OH radical scavenger. The measured yields of 2,7-octanedione from 1,2-dimethyl-1cyclohexene and of pinonaldehyde from α -pinene were 0.110 \pm 0.020 and 0.164 \pm 0.029, respectively, and were independent of the OH radical scavenger used. Reaction mechanisms are presented and discussed. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 73-85, 2002

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INTRODUCTION

Gas-phase reactions with ozone are often an important atmospheric loss process for alkenes [1–3]. These O_3 -alkene reactions proceed by initial addition of O_3 across the C=C unsaturated bond to form an energyrich primary ozonide, which then decomposes to two sets of carbonyl ("primary" carbonyl) plus chemically activated "Criegee" intermediate [2,4–12], as shown in reaction (1).



(including
$$R_1CH_3$$
 if $R_2 = H$) (2c)



The sum of the formation yields of the primary carbonyls is therefore expected to be unity, in accord with experimental observations [1]. Theoretical calculations indicate that the Criegee intermediate is a carbonyl oxide [4–6], which (for mono-substituted intermediates) may be formed in either the syn or anti configuration.



The chemically activated carbonyl oxides are proposed to undergo collisional stabilization [reaction (2a)], isomerization to a "hot" hydroperoxide followed by breakage of the O–OH bond to form an OH radical plus a substituted alkyl radical [the "hydroperoxide channel," reaction (2b)] (see, for example, Refs. [1–3] and [10–12]), rearrangement to a "hot" ester with subsequent decomposition [the "ester channel," reaction (2c)], or elimination of an O(³P) atom [reaction (2d)]

$$\begin{split} [R_1CH_2C(R_2)OO]^* + M &\longrightarrow R_1CH_2C(R_2)OO + M \end{split} \eqno(2a) \\ & [R_1CH_2C(R_2)OO]^* &\longrightarrow [R_1CH=C(OOH)R_2]^* \\ & \longrightarrow R_1\dot{C}HC(O)R_2 + OH \end{split} \eqno(2b) \end{split}$$

 $[R_1CH_2C(R_2)OO]^* \longrightarrow R_1CH_2C(O)R_2 + O(^3P)$ (2d)

For monosubstituted carbonyl oxides (the carbonyl oxides are hereafter termed Criegee intermediates), formation of OH radicals through the hydroperoxide channel is anticipated to occur almost totally from the syn configuration [6,8,12].

While under atmospheric conditions $O(^{3}P)$ -atom elimination [reaction (2d)] is at most a minor pathway with an overall yield of <5% [1], the occurrence of the "ester channel" [reaction (2c)] has been observed through, for example, the formation of methane from the CH₃CHOO intermediate formed from the 2-butenes and of butanal, pentanal, and 2-hexanone from the Criegee intermediates formed from cyclopentene, cyclohexene, and 1-methyl-1-cyclohexene, respectively [1]. The formation of OH radicals from the ozonolysis of alkenes has been shown to be important [1,7-27], with OH radical formation yields approaching unity in several cases [1]. For the internally double-bonded cycloalkenes cyclopentene, cyclohexene, and 1-methyl-1-cyclohexene (where only Criegee intermediates are formed, with no primary carbonyl formation) the sum of the formation yield of the OH radical, the stabilization yield of the Criegee intermediate, and the yield of the "ester" channel (i.e., of butanal, pentanal, and 2hexanone, respectively) is unity within the (often significant) experimental uncertainties [1,20].

There is still uncertainty concerning the fate of the thermalized Criegee intermediate under atmospheric conditions [1,10,28]. Fenske et al. [10] have reported that thermalized CH₃CHOO intermediates formed from trans-2-butene undergo unimolecular decomposition and/or isomerization, presumed to be through the hydroperoxide channel, at a rate of $\sim 76 \text{ s}^{-1}$ at room temperature, and Kroll et al. [12] have observed the "slow" formation of OH radicals (on time scales of $\sim 0.1-1$ s under their experimental conditions of 10-100 Torr total pressure of N_2). The kinetic data reported by Fenske et al. [10] for decomposition of the CH₃CHOO intermediate and its reaction with CH₃CHO (1.0×10^{-12} cm³ molecule⁻¹ s^{-1}), combined with relative rate data for reactions of the CH₂OO intermediate with water vapor and HCHO ($\sim 1.8 \times 10^{-3}$: 1.0) [1] and assuming that all Criegee intermediates react similarly, suggests that in the troposphere the thermalized Criegee intermediates will react dominantly with water vapor. Moortgat and coworkers [29–31] have shown that R_1R_2COO intermediates react with water vapor to form α hydroxyhydroperoxides $R_1R_2C(OH)OOH$ [29,30] and that alcohols, R'OH, and carboxylic acids, R'C(O)OH, react with the Criegee intermediates to form α -oxyalkylhydroperoxides, $R_1R_2C(OR')OOH$, and α -oxyacylhydroperoxides, R₁R₂C(OC(O)R')OOH [31]. Neeb et al. [31] concluded that methanol is more reactive than is water vapor with respect to reaction with the CH₂OO intermediate, by \sim 2 orders of magnitude.

In this work, we have studied the gas-phase reactions of O₃ with 1,2-dimethyl-1-cyclohexene, α-pinene, 1octene, and trans-7-tetradecene, primarily using in situ atmospheric pressure ionization tandem mass spectrometry, to investigate the products formed from the reactions of the stabilized Criegee intermediates in the presence of water vapor and 2-butanol. 1-Octene and trans-7-tetradecene were chosen because they lead to the formation of the same Criegee intermediate, and the OH radical formation yield from 1-octene is in the range 0.10-0.18 [1,16,25], suggesting a high yield of thermalized Criegee intermediates. The reactions of O₃ with α -pinene and 1,2-dimethyl-1-cyclohexene form only Criegee intermediates (and only one in the case of 1,2-dimethyl-1-cyclohexene). Although the yields of stabilized Criegee intermediates are low because of the high formation yields of OH radicals from both of these cycloalkenes [1,14,17,18,20,24], it was also of interest to investigate the products formed from the organic radicals that are coproducts to the OH radical in the "hydroperoxide channel."

EXPERIMENTAL

Experiments were carried out at 296 ± 2 K and 740 Torr of purified air at typically $\sim 5\%$ relative humidity

(a water vapor concentration of $\sim 3.4 \times 10^{16}$ molecule cm^{-3}) in ~7000-1 Teflon chambers each equipped with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. One of the Teflon chambers was interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS). Experiments were carried out in the presence of sufficient cyclohexane or 2-butanol to scavenge >95% of the OH radicals formed from the O₃ reactions. The initial concentrations (in molecule cm^{-3}) were alkene, $\sim 2.4 \times 10^{13}$; cyclohexane, $\sim 7.5 \times 10^{15}$, or 2-butanol, $\sim 9.0 \times 10^{15}$; and 3 or 4 additions of O₃ in O₂ diluent (each O_3/O_2 addition corresponding to $\sim 6 \times 10^{12}$ molecule cm^{-3} of O₃ in the chamber) were made to the chamber during an experiment.

Analyses by Gas Chromatography

A series of experiments were carried out using gas chromatography with flame ionization detection (GC-FID) to quantify the formation of pinonaldehyde and 2, 7-octanedione from the O_3 reactions with α -pinene and 1,2-dimethyl-1-cyclohexene, respectively, in the presence of cyclohexane or 2-butanol. Gas samples of 100 cm³ volume were collected from the chamber onto Tenax-TA solid adsorbent for subsequent thermal desorption at ~250°C onto a 30 m DB-1701 megabore column held at 0°C and then temperature programmed at 8° C min⁻¹. The GC-FID response factors for α -pinene, 1,2-dimethyl-1-cyclohexene, and pinonaldehyde were measured by introducing measured amounts of the liquid compounds from a 1-liter Pyrex bulb by a stream of N₂ gas into the chamber and conducting several replicate GC-FID analyses (the chamber volume was determined by introducing a measured amount of trans-2-butene and analyzing its concentration using a precalibrated GC) [32]. Assuming that the synthesized pinonaldehyde sample [33] was 100% pure (the measured purity by GC was >90% [33]) and that all of the pinonaldehyde placed in the 1-l Pyrex bulb was transferred into the chamber, then the measured GC-FID response factors for pinonaldehyde and α -pinene from four independent GC-FID calibrations resulted in a measured Effective Carbon Number (ECN) [34] of pinonaldehyde, which was 0.90 ± 0.13 (two standard deviations) of the calculated [34] value. Since any impurities in the pinonaldehyde sample or incomplete transfer of pinonaldehyde from the bulb into the chamber would result in a lower measured (ECN) for pinonaldehyde, the agreement (within $\sim 10\%$) of the measured and calculated ECN factors was good. Therefore, the calculated ECNs of pinonaldehyde and α -pinene with the measured GC-FID response factor for α -pinene were used to obtain the GC-FID response factor for pinonaldehyde. The

GC-FID response factor for 2,7-octanedione relative to that for 1,2-dimethyl-1-cyclohexene was calculated from their respective ECNs [34].

In Situ Analyses by API-MS and API-MS/MS

In these experiments, the chamber contents were sampled through a 25 mm diameter ×75 cm length Pyrex tube at $\sim 20 \ 1 \ \text{min}^{-1}$ directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collisionally activated dissociation (CAD)] modes has been described elsewhere [35,36]. Use of the MS/MS mode with CAD allows the "product ion" or "precursor ion" spectrum of a given ion peak observed in the MS scanning mode to be obtained [35,36], as well as "common neutral loss" analysis where ion peaks having a characteristic fragmentation can be isolated. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain" gas). Both positive and negative ion modes were used in this work. In the positive ion mode, protonated water clusters, $H_3O^+(H_2O)_n$, formed from a corona discharge in the chamber diluent air (at \sim 5% relative humidity) are the reagent ions

$$H_3O^+ \cdot (H_2O)_n + M \rightarrow [(M+H)(H_2O)_m]^+$$
$$+ (n - m + 1)H_2O$$

which protonate a range of oxygenated species. As a result of the declustering action of the N₂ curtain gas, the analyzed ions are then mainly the protonated molecule, $[M + H]^+$, and protonated homo- and heterodimers [35,36]. Product peaks were identified based on the observation of homo- or heterodimers (for example, $[(M_{P1})_2 + H]^+$, $[(M_{P2})_2 + H]^+$ and $[M_{P1} + M_{P2} + H]^+$, where P1 and P2 are products) in the API-MS/MS "precursor ion" spectra, and consistency of the API-MS/MS "product ion" spectrum of a homo- or heterodimer ion with the "precursor ion" spectra of the $[M_P + H]^+$ ion peaks [35,36].

Observations made during an earlier API-MS study of the OH radical-initiated reactions of methylsubstituted ethenes in the absence of NO_x [37] indicated that product ions attributed to the protonated molecules from (CH₃)₂C(OOH)CH(OH)CH₃ and/or (CH₃)₂C(OH)CH(OOH)CH₃, (CH₃)₂C(OOH)CH₂OH and/or (CH₃)₂C(OH)CH₂OOH, and CH₃CH(OOH)-CH(OH)CH₃ show a loss of H₂O₂. Therefore, a neutral loss scan for 34 mass units was employed to identify peroxide products expected from reaction of the thermalized Criegee intermediates with water vapor in the experiments using cyclohexane as the OH scavenger. In contrast to cyclohexane, 2-butanol forms cluster ions and is readily detected by API-MS. When 2-butanol was used as the OH radical scavenger and to react with the thermalized Criegee intermediates, the MS/MS "product ion" spectra of the potential protonated α -oxybutylhydroperoxide ions showed fragment ions resulting from loss of 2-butanol and hence could not be distinguished from 2-butanol cluster ions. Therefore, definitive information could not be obtained as to whether or not the α -oxybutylhydroperoxides were present in the gas-phase in these experiments, and hence only limited discussion of these data are given.

In the negative ion mode, NO_2^- ions formed after addition of NO_2 to the chamber were used as the reagent ions [38]. Analytes were then detected as adducts formed between the neutral analyte (M) and the reagent ion NO_2^- ,

$$NO_2^- + M \rightarrow [NO_2 \cdot M]^-$$

Previous work in this laboratory indicates that the use of NO₂⁻ reagent ions allows primarily hydroxycompounds to be detected (for example, hydroxycarbonyls and hydroxynitrates) [38]. When NO₂⁻ was used as the reagent ion, quantification of hydroxycarbonyls from the α -pinene and 1-octene reactions (in the presence of cyclohexane) was carried out by adding a measured amount of 4-hydroxy-3-hexanone ($\sim 1 \times 10^{11}$ molecule cm⁻³) and NO₂ $(\sim 2.4 \times 10^{13} \text{ molecule cm}^{-3})$ to the chamber after the reaction, with the 4-hydroxy-3-hexanone being used as an internal standard and assuming that the intensities of the $[NO_2 \cdot M]^-$ ion peaks were proportional to the concentrations of the hydroxycarbonyls, M, present in the chamber [38]. The concentrations of alkene and 4-hydroxy-3-hexanone were measured by GC-FID as described above.

Chemicals

The chemicals used, and their stated purity levels, were cyclohexane (high purity solvent grade), American Burdick and Jackson; 2-butanol (99.5%), α -pinene (99+%), and *trans*-7-tetradecene (98%), Aldrich Chemical Company; 1-octene (99.9%), Chem Samples; 4-hydroxy-3-hexanone, TCI America; 1,2-dimethyl-1-cyclohexene (97%), Wiley Organics; pinonaldehyde (>90%) was a synthesized sample [33], with the impurities being tetrahydrofuran and methyl *tert*-butyl ether. O₃ in O₂ diluent was prepared as needed using a Welsbach T-408 ozone generator, and NO₂ was prepared just prior to use by reacting NO with an excess of O₂.

RESULTS AND DISCUSSION

API-MS and API-MS/MS analyses of the reactions of O₃ with α -pinene, 1,2-dimethyl-1-cyclohexene, 1-octene, and *trans*-7-tetradecene, and GC-FID analyses of the 1,2-dimethyl-1-cyclohexene and α -pinene reactions, were carried out in the presence of sufficient cyclohexane or 2-butanol to scavenge \geq 95% of the OH radicals formed. Based on the available literature data [1], it was expected that in our experiments the thermalized Criegee intermediates reacted with water vapor when cyclohexane was present as an OH radical scavenger, and (based on the data reported by Neeb et al. [31]) it was anticipated that they reacted primarily with 2-butanol when 2-butanol was present as an OH radical scavenger.

1-Octene and trans-7-Tetradecene Reactions

Scheme 1 shows the expected major reaction pathways and predicted products for the ozone reaction with



1-octene. The primary carbonyls formaldehyde and heptanal [Scheme 1, reaction (a)] are formed in very similar yields and the sum of their yields $(0.95 \pm 0.04$ [39] and 1.05 ± 0.09 [16]) is unity as expected [1]. As noted previously, the measured OH radical yield is in the range 0.10-0.18 [1,16,25] [Scheme 1, reaction (c)], making the 1-octene reaction a good candidate for observing hydroxyhydroperoxides from the stabilized Criegee intermediates [Scheme 1, reaction (b)]. Heptanal is one predicted product from the decomposition of the α -hydroxyhydroperoxide [(A) in Scheme 1], but the reported primary carbonyl yield data [16,39] suggest $\leq 14\%$ formation of heptanal via this pathway.

The result of a neutral loss scan for a loss of 34 u (H_2O_2) for the 1-octene reaction products is shown in Fig. 1A. A very similar neutral loss spectrum was obtained from the *trans*-7-tetradecene–O₃ reaction products (Fig. 1B). The expected α -hydroxyhydropero-xide CH₃(CH₂)₅CH(OH)OOH has a molecular weight of 148 and would, therefore, have an [M + H]⁺ at 149 u (MS/MS spectrum shown in Fig. 2A). Interestingly, the major peak observed to have a neutral loss of 34 u has an [M + H]⁺ of 147 u (MS/MS spectrum shown in Fig. 2B), which could be the hydroperoxide product of



Figure 1 API-MS/MS CAD "neutral loss" analysis for 34 u (H₂O₂) characteristic of hydroperoxides. (A) neutral loss scan from a reacted O₃-1-octene-air mixture in the presence of cyclohexane as an OH radical scavenger and (B) neutral loss scan from a reacted O₃-*trans*-7-tetradecene-air mixture in the presence of cyclohexane as an OH radical scavenger.



Figure 2 API-MS/MS CAD "product ion" spectra of (A) the 149 u ion peak, (B) the 147 u ion peak, and (C) the 131 u ion peak observed in the API-MS spectrum of a reacted O_3 -1-octene–air mixture in the presence of cyclohexane as an OH radical scavenger.

the alkyl radical with HO₂ [Scheme 1, product (C)]. In addition to heptanal and the presumed hydroperoxides, product(s) of molecular weight 130 were observed, presumably $CH_3(CH_2)_5C(O)OH$ formed by decomposition of the α -hydroxyhydroperoxide [Scheme 1, product (B)] and/or $CH_3(CH_2)_4CH(OH)CHO$ formed by an RO₂' + RO₂' reaction [Scheme 1, product (D)] (MS/MS spectrum shown in Fig. 2C).

In the presence of 2-butanol, the α -oxybutylhydroperoxide formed from reaction of the Criegee intermediate with 2-butanol, CH₃(CH₂)₅CH(OC₄H₉)OOH, has a molecular weight of 204. The API-MS/MS "product ion" spectrum of the 205 u ion peak, ([M + H]⁺), observed in the presence of 2-butanol showed a loss of 74 (2-butanol) and a further fragment ion spectrum similar to that of the 131 u ion, and therefore, could be solely a butanol adduct of the 130 u product or could include the α -oxybutylhydroperoxide. It is concluded that the products formed from reaction of O₃ with 1-octene include heptanal and products of molecular weight 130, 146, and 148, with the latter two being hydroperoxides. The results of a limited study of the reaction of O₃ with *trans*-7-tetradecene showed similar products. Our API-MS analyses of the 1-octene and *trans*-7-tetradecene reactions indicate that the α -hydroxyhydroperoxide CH₃(CH₂)₅CH(OH)OOH is present and therefore that it must be stable with respect to decomposition on a time scale of tens of minutes or longer. The other products observed are consistent with the expectations of the reactions of the CH₃CH₂CH₂CH₂CH₂C⁺HCHO radical formed as a coproduct to the OH radical in the hydroperoxide channel [Scheme 1, reaction (c)].

The API-MS was also used in the negative ion mode with NO₂⁻ as the reagent ion and 4-hydroxy-3hexanone (molecular weight 116) as the internal standard to identify and quantify hydroxy-compounds [38]. The major [NO₂·M]⁻ ion attributed to a product of the 1-octene reaction was at 176 u, corresponding to the molecular weight 130 product observed using positive ion API-MS and API-MS/MS (see above). Three experiments gave a molar yield of this product of 0.27, 0.10, and 0.12. Given the uncertainties associated with using a 1,2-hydroxycarbonyl for the hydroxycarbonyl anticipated to be formed from 1-octene (of structure CH₃(CH₂)₄CH(OH)CHO, see Scheme 1), we cite a formation yield of the molecular weight 130 hydroxydicarbonyl of 16^{+16}_{-8} %. It should be recognized that there may be a contribution to this molecular weight 130 hydroxy-compound from products(s) formed from the OH radical with cyclohexane. This hydroxycarbonyl yield of 16^{+16}_{-8} % is of the same magnitude as the OH radical yield from the 1-octene reaction [1,16,25].

1,2-Dimethyl-1-cyclohexene

A single Criegee intermediate is formed from the reaction of 1,2-dimethyl-1-cyclohexene with O_3 , as shown in Scheme 2. The OH radical yield formed from the O_3 reaction with 1,2-dimethyl-1-cyclohexene has been measured as 1.02 ± 0.16 [20], showing that pathway (b) in Scheme 2 dominates. The expected products of the alkyl radicals formed as coproducts with the OH radical are shown and include compounds of molecular weights 114, 156, and 158 and a peroxide of molecular weight 174. The product of reaction of the stabilized Criegee intermediate with H₂O [Scheme 2, product (A)] would be an α -hydroxyhydroperoxide of molecular weight 176. A neutral loss scan for a 34 u loss



was conducted on the products of the 1,2-dimethyl-1cyclohexene-O3 reaction, and no hydroperoxides were detected. Small ion peaks at 175 and 177 u were observed in the API-MS scan, but MS/MS scans revealed that these were protonated water clusters of the molecular weight 156 and 158 products. The API-MS/MS "product ion" spectra of the 177 and 159 u ion peaks are shown in Fig. 3. Figure 3A clearly shows that the 177 u ion peak has fragment ions resulting from losses of H₂O and 2H₂O, and the fragment ions are similar to those in the 159 u ion spectrum shown in Fig. 3B. In particular, no fragment ion at 143 u resulting from loss of H₂O₂ was observed in the API-MS/MS "product ion" spectrum of the 177 u ion peak (Fig. 3A), and the 177 u ion is therefore attributed to $[158 + H + H_2O]^+$. The API-MS/MS "product ion" spectrum of the 233 u ion peak observed in the reaction conducted in the presence of 2-butanol showed a loss of 2-butanol and the remaining spectrum was again very similar to that of the 159 u ion peak.

The Criegee intermediate formed from 1,2dimethyl-1-cyclohexene is disubstituted and decomposition of the α -hydroxyhydroperoxide (A) can only occur to give 2,7-octanedione and H₂O₂ [Scheme 2, pathway (a)]. 2,7-Octanedione was also seen in the reaction conducted in the presence of 2-butanol, and the API-MS/MS "product ion" spectrum of the 143 u $([M+H]^+)$ ion peak was identical in the presence of cyclohexane or 2-butanol. The concentrations of 2,7-octanedione and 1,2-dimethyl-1-cyclohexene were measured by GC-FID during a series of O₃-1,2-dimethyl-1-cyclohexene-cyclohexane (in excess)air and O₃-1,2-dimethyl-1-cyclohexene-2-butanol (in excess)-air reactions, with the concentrations of cyclohexane or 2-butanol being sufficient to scavenge $\geq 95\%$ of the OH radicals formed from the O3 reactions. Figure 4 shows a plot of the amounts of 2,7-octanedione formed against the amounts of 1,2dimethyl-1-cyclohexene reacted. The 2,7-octanedione formation yields are independent of the OH radical scavenger used, and a least-squares analysis results in a 2,7-octanedione formation yield of 0.115 \pm 0.020, where the indicated error is two least-squares standard deviations combined with an estimated overall uncertainty of the 2,7-octanedione GC-FID response factor relative to that for 1,2-dimethyl-1-cyclohexene of $\pm 15\%$. Our present formation yield of 2,7-octanedione of 0.115 ± 0.020 is somewhat higher than our previous measurement of 0.07 ± 0.02 [20] obtained under conditions similar to those used here.



Figure 3 API-MS/MS CAD "product ion" spectra of (A) the 177 u ion peak and (B) the 159 u ion peak observed in the API-MS spectrum of a reacted O_3 -1,2-dimethyl-1-cyclohexene–air mixture in the presence of cyclohexane as an OH radical scavenger.



Figure 4 Plots of the amounts of pinonaldehyde and 2,7octanedione formed against the amounts of α -pinene and 1,2dimethyl-1-cyclohexene, respectively, reacted with O₃ in the presence of sufficient cyclohexane (\circ ,•) or 2-butanol (\Box) to scavenge \geq 95% of the OH radicals formed in the O₃ reactions. Water vapor concentrations were: \circ , $\Box \sim 3.4 \times 10^{16}$ molecule cm⁻³; • \sim 3.4 × 10¹⁷ molecule cm⁻³. The data for pinonaldehyde have been displaced vertically by 8.0 × 10¹¹ molecule cm⁻³ for clarity.

Our API-MS and API-MS/MS analyses show no evidence for the presence of the α -hydroxyhydroperoxide CH₃C(O)CH₂CH₂CH₂CH₂C(OH)(CH₃)OOH, and indicate that this α -hydroxyhydroperoxide decomposes within a time-scale of minutes or less to 2,7-octanedione plus H_2O_2 . The measured 2,7-octanedione yield should therefore be the same as the yield of the stabilized Criegee intermediate CH₃C(O)CH₂CH₂CH₂- $CH_2C(OO)CH_3$, and the sum of the yield of the stabilized Criegee intermediate (0.115 \pm 0.020) plus that of OH radicals formed via the "hydroperoxide" channel (1.02 \pm 0.16 [20]), plus a small amount of 1,2-dimethyl-1-cyclohexene oxide formed directly $(0.020 \pm 0.006 \ [20])$, account for $115 \pm 17\%$ of the reaction pathways. The products observed by API-MS and GC agree with those of our previous study[20], and include 5-oxopentanal ([CH₃C(O)CH₂CH₂CH₂-CHO]) [20], CH₃C(O)CH₂CH₂CH₂C(O)C(O)CH₃-(or isomer), and CH₃C(O)CH₂CH₂CH₂CH(OH)C(O)-CH₃ (or isomer). Combining our present measurements of the formation yield of 2,7-octanedione with our previously measured yields of 5-oxopentanal (0.19 \pm 0.05 [20]) and of the tentatively identified ketone CH₃C(O)CH₂CH₂CH₂CH₂C(O)C(O)CH₃, (~0.07 [20]), we can account for ~40% of the reaction products.

α -Pinene

Schemes 3 and 4 show products expected from the two Criegee intermediates formed from the reaction of α -pinene with O₃, as each intermediate is either stabilized and reacts with water or follows the hydroperoxide channel leading to OH and an alkyl radical, which further reacts with HO₂radicals or with RO₂ • radicals. The yield of OH radicals from the α -pinene–O₃ reaction has been measured as 0.76 ± 0.11 [17], 0.70 ± 0.17 [18], and 0.83 ± 0.21 [24] suggesting that <40% of the Criegee intermediates are stabilized. API-MS spectra (positive ion mode) of the reaction of O₃ with α -pinene in the presence of cyclohexane showed





prominent ion peaks attributed to reaction products of molecular weights 154, 156, 168, and 184 u and additional minor product ion peaks corresponding to products of molecular weight 152 and 200 u. It should be noted that the only possible pathways for formation of pinonaldehyde (168 u) are from the stabilized Criegee intermediates (see Schemes 3 and 4).

A "neutral loss" scan for 34 u showed no evidence for hydroperoxide products. An API-MS/MS "product ion" spectrum of the very weak 203 u ion peak in the reaction conducted in the presence of cyclohexane (which could potentially be the protonated α -hydroxyhydroperoxide (A) in Schemes 3 and 4) showed losses of H2O and 2H2O and no evidence for loss of H_2O_2 and was, therefore, attributed to a water cluster of the 185 u ion peak. The API-MS/MS "product ion" spectrum of the 185 u ion peak is shown in Fig. 5A. In the presence of 2-butanol, the API-MS/MS "product ion" spectrum of the 259 u ion (Fig. 5B), which would correspond to an α -oxybutylhydroperoxide, showed a fragment ion corresponding to loss of 2-butanol and the remaining fragment ions were similar to those of the 185 u ion peak.

For each of the 169 and 185 u ion peaks, the API-MS/MS "product ion" spectra in the presence of cyclohexane or 2-butanol were identical and the 169 u product ion spectra matched that of an authentic standard of pinonaldehyde. The API-MS/MS "product ion" spectra of the 185 u ion peak (Fig. 5A) was very similar to that of protonated cis-pinonic acid (Fig. 5C). While some *cis*-pinonic acid may be formed from the alternate decomposition of one of the two α hydroxyhydroperoxides (see Scheme 4), the majority of the molecular weight 184 product(s) are expected to arise from reaction of the alkyl radical coproduct to the OH radical with RO_2^{\bullet} radicals (Schemes 3 and 4). The similarity of the API-MS/MS "product ion" spectra of the 185 u ion peak from the α -pinene–O₃ reaction with the spectra of cis-pinonic acid does not rule out the spectrum shown in Fig. 5A being either a mixture of isomers or even mainly the hydroxydicarbonyl(s) formed in the "hydroperoxide" channel.

In the negative ion mode with NO_2^- as the reagent ion, the major $[NO_2 \cdot M]^-$ ion attributed to a product of the α -pinene reaction was at 230 u, corresponding to the molecular weight 184 product identified as discussed



Figure 5 API-MS/MS CAD "product ion" spectra of (A) the 185 u ion peak observed in the API-MS spectrum of a reacted $O_3-\alpha$ -pinene—air mixture in the presence of cyclohexane as an OH radical scavenger, (B) the 259 u ion peak observed in an API-MS spectrum of a reacted $O_3-\alpha$ -pinene—air mixture in the presence of 2-butanol as an OH radical scavenger and (C) the $[M + H]^+$ ion peak of authentic *cis*-pinonic acid.

above. Two experiments using 4-hydroxy-3-hexanone as an internal standard gave a molar yield of this product of 0.081 and 0.082. Noting again the uncertainties associated with using a 1,2-hydroxycarbonyl for the hydroxy-dicarbonyl anticipated to be formed from α -pinene (of structure CH₃C(O)(C₆H₁₀)CH(OH)-CHO, $HOCH_2C(O)(C_6H_{10})CH_2CHO and/or CH_3C(O)$ C(O H)(C₅H₉)CH₂CHO; see Schemes 3 and 4), a formation yield of the molecular weight 184 hydroxydicarbonyl of 8^{+8}_{-4} % is cited. As noted above, the pathways forming pinonaldehyde are from reaction of the thermalized Criegee intermediates with water vapor followed by decomposition of the intermediate α -hydroxyhydroperoxide (A) in Schemes 3 and 4. The concentrations of pinonaldehyde and α -pinene were measured by GC-FID during a series of O₃-alkenecyclohexane (in excess)-air and O₃-alkene-2-butanol (in excess)-air reactions, with the concentrations of cyclohexane or 2-butanol being sufficient to scavenge >95% of the OH radicals formed from the O₃ reactions. Figure 4 shows a plot of the amounts of pinonaldehyde formed against the amounts of α -pinene reacted, and it is clear that the pinonaldehyde formation yields in the presence of cyclohexane or 2-butanol are identical. Furthermore, the pinonaldehyde formation yield appears independent of the water vapor concentration over the range \sim (3.4–34) \times 10¹⁶ molecule cm⁻³ (\sim 5–50% relative humidity), indicating that the thermalized Criegee intermediates are reacting dominantly with water vapor. Losses of gas-phase pinonaldehyde to the chamber walls were shown to be of no importance during the experiments by monitoring the pinonaldehyde and α -pinene concentrations at the end of an experiment for up to 4 h; the measured pinonaldehyde concentration decreased by <4% during this 4-h period while the α -pinene concentration decreased by 8% due to a small amount of continuing reaction with O3. Losses of pinonaldehyde to particles formed during the experiments potentially could have occurred. However, it should be noted that since particles were not filtered out prior to our Tenax sampling, as long as pinonaldehyde desorbed from the collected particles, particle-bound pinonaldehyde would also be measured.

Our observation of the formation of pinonaldehyde under conditions where OH radicals are scavenged is consistent with previous studies of Hakola et al. [40] and Alvarado et al. [20] using gas chromatography, Ruppert et al. [41] using in situ Fourier transform infrared absorption spectroscopy, and Yu et al. [42] using derivatization methods coupled to combined gas chromatography-mass spectrometry. Our present pinonaldehyde formation yield of $0.164 \pm$ 0.029 (where the indicated error is two least-squares standard deviations combined with an estimated overall uncertainty of the pinonaldehyde GC response factor relative to that for α -pinene of $\pm 15\%$), is in good agreement with the previous values of Hakola et al. [40] (0.19 \pm 0.04) and Alvarado et al. [20] (0.143 \pm 0.024). Ruppert et al. [41] reported that the pinonaldehyde yield decreased with extent of the reaction; from an initial value of 0.48 ± 0.05 to a final value of $0.19 \pm$ 0.07, with their yield being a factor of \sim 3 higher than ours (as is also the case for their measured pinonaldehyde yield from the OH radical reaction with α -pinene in the presence of NO [43,44]). Yu et al. [42] obtained a total (gas-phase plus aerosol-phase) pinonaldehyde yield of 6–19% for initial α -pinene concentrations of $(1.4-2.6) \times 10^{12}$ molecule cm⁻³, with 2-butanol as an OH radical scavenger and in the presence of seed particles, in reasonable agreement with our present yield, with 5-8% of the total (gas- plus aerosol-phase)

pinonaldehyde being in the aerosol phase under their experimental conditions [42].

Based on the literature data for the reactions of O_3 with acyclic alkenes [1], we expect that the dominant Criegee intermediate formed is disubstituted $[CH_3C(OO)(C_6H_{10})CH_2CHO]^*$ (see Scheme 3). Our API-MS data show no evidence for the presence of the α -hydroxyhydroperoxide(s) formed from reaction of the thermalized Criegee intermediates with water vapor, suggesting that the α -hydroxyhydroperoxide(s) decompose on a time-scale of a few minutes or less to form pinonaldehyde plus H₂O₂ (or for the CH₃C(O)(C₆H₁₀)CH₂CHOO intermediate, also possibly to cis-pinonic acid plus H₂O). The pinonaldehyde yield should therefore be the yield (or lower limit thereof) of stabilized Criegee intermediates, and our pinonaldehyde formation yield of 0.164 ± 0.029 is indeed in reasonable agreement with the yield of stabilized Criegee intermediate of 0.125 ± 0.040 reported by Hatakeyama et al. [45]. Our API-MS and GC data are in general agreement with the extensive product analysis study of Yu et al. [42], in which the yields of hydroxypinonaldehydes (MW 184), pinonic acid (MW 184), and norpinonaldehyde (MW 154) were measured to be 1.9-11.2%, 2.2-7.9%, and 1.2-2.6%, respectively. The yield of the MW 184 product(s) (assumed to be hydroxypinonaldehydes) of 8% by API-MS in this work is therefore consistent with the data of Yu et al. [42].

The sum of the stabilized Criegee intermediate (0.16) plus that of the OH radical formed via the "hydroperoxide" channel (0.70–0.83 [17,18,24]), plus the small amount of α -pinene oxide formed directly (0.021±0.007 [20]), account for ~94±11% of the reaction pathways.

CONCLUSIONS

Our present investigation of the products formed from the reactions of O₃ with 1,2-dimethyl-1-cyclohexene, α -pinene, 1-octene, and (to a more limited extent) trans-7-tetradecene indicate that the basic details of the reactions are understood [1,4–12], as shown in Schemes 1-4. The API-MS and API-MS/MS spectra showed clear evidence for the presence of the α -hydroxyhydroperoxide CH₃(CH₂)₅-CH(OH)OOH in the 1-octene and trans-7-tetradecene reactions, but no evidence for the presence of α hydroxyhydroperoxides in the 1,2-dimethyl-1-cyclohexene or α -pinene reactions. Based on the measured OH radical yield [1,16,25], the 1-octene reaction has a large yield of stabilized Criegee intermediates (\sim 80–90%) while the 1,2-dimethyl-1-cyclohexene and a-pinene reactions lead to only low amounts of stabilized Criegee intermediates (\sim 11% and \sim 16%, respectively, based on our measured 2,7-octanedione and pinonaldehyde yields), and these differences will be reflected in the ease of observing α -hydro-xyhydroperoxides.

Rate constants for the gas-phase reactions of 1octene, 1,2-dimethyl-1-cyclohexene and α -pinene at room temperature are 1.4×10^{-17} cm³ molecule⁻¹ s⁻¹, $2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $8.7 \times 10^{-17} \text{ cm}^3$ molecule⁻¹ s⁻¹, respectively [1], and that for *trans*-7-tetradecene is expected to be similar to those for trans-4-octene and trans-5-decene $(1.4 \times 10^{-16} \text{ cm}^3)$ molecule⁻¹ s⁻¹ and $\geq 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively [1]). Hence under the experimental conditions employed the O₃ lifetimes in the presence of 1×10^{13} molecule cm⁻³ of alkene were ~120 min for the 1-octene reaction and \sim 8–20 min for the trans-7tetradecene, α-pinene and 1,2-dimethyl-1-cyclohexene reactions. Therefore, the observation of an α -hydroxyhydroperoxide from the trans-7-tetradecene reaction over time-periods of several tens of minutes after the reactions were initiated (in these API-MS experiments the O_3/O_2 additions were made over a 10-15-min time-span) shows that the lifetimes of the a-hydroxyhydroperoxides from 1-octene and trans-7-tetradecene must be tens of minutes or greater. Therefore, our data suggest that mono-alkyl-substituted Criegee intermediates, RCHOO, form ahydroxyhydroperoxides which have lifetimes with respect to decomposition of tens of minutes or more and, which may therefore play a role in the formation of secondary organic aerosol from the O₃ reactions with alkenes [46] and other organics containing C=C bonds.

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