

Products of the Gas-Phase Reactions of a Series of Methyl-Substituted Ethenes with the OH Radical

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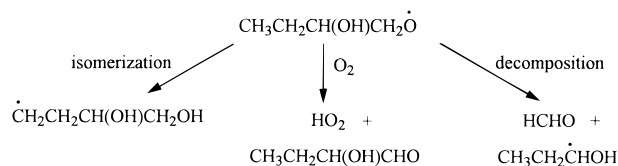
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Alkenes are a significant component of ambient air in urban areas, and in the atmosphere they react with OH radicals, NO₃ radicals, and O₃, with the OH radical reaction often dominating as the tropospheric removal process. Products of the gas-phase reactions of the OH radical with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the presence of NO have been investigated at room temperature and 740 Torr total pressure of air by gas chromatography with flame ionization detection, in situ Fourier transform infrared absorption spectroscopy, and in situ atmospheric pressure ionization tandem mass spectrometry (API-MS). For all four alkenes, hydroxynitrate formation from the β -hydroxyalkyl peroxy radical plus NO reaction accounted for ~10% of the overall products observed, with decomposition of the intermediate β -hydroxyalkoxy radical dominating over the alternative reaction with O₂ (isomerization via a six-member transition state is not possible for any of the intermediate β -hydroxyalkoxy radicals formed in these reactions) and leading to the formation of the carbonyls expected from >C=C< bond cleavage in ~90% yield each. These data are consistent with estimates of the rates of the various reactions of β -hydroxyalkoxy radicals under atmospheric conditions. API-MS analyses of the OH radical-initiated reactions of propene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the absence of NO indicated the formation of the hydroxyhydroperoxides, dihydroxyalkanes, and hydroxycarbonyls expected from the reactions of intermediate β -hydroxyalkyl peroxy radicals with HO₂ and organic peroxy radicals, in addition to the carbonyl compounds formed from decomposition of the β -hydroxyalkoxy radicals also formed from the peroxy plus peroxy radical reactions.

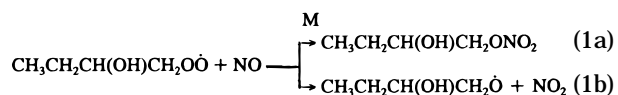
Introduction

Alkenes are a significant component of ambient air in urban areas (1–3), and in the atmosphere they react with OH radicals, NO₃ radicals, and O₃ (4, 5) with the daytime OH radical reaction often dominating as the tropospheric removal process (6, 7). The kinetics and products of the gas-phase

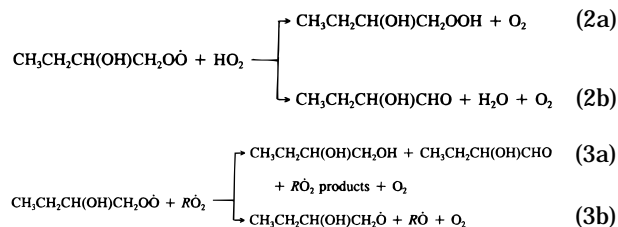
SCHEME 1



reactions of the OH radical with alkenes have been studied previously (4, 5, 8). While the kinetics of these OH radical reactions are now reasonably well understood for a large number of alkenes (4, 5, 8), for acyclic alkenes product studies have only been carried out for a few simple compounds at room temperature and atmospheric pressure of air (5, 9–20). The gas-phase reactions of the OH radical with alkenes proceed mainly by initial addition of the OH radical to the >C=C< bond(s) to form β -hydroxyalkyl radicals (5), which in the troposphere rapidly add O₂ to form the corresponding β -hydroxyalkyl peroxy radicals (5). In the presence of NO, β -hydroxyalkyl peroxy radicals react to form either the β -hydroxynitrate or the β -hydroxyalkoxy radical plus NO₂ (5). For example, for the β -hydroxybutyl peroxy radical formed after internal OH radical addition to 1-butene:



At low NO concentrations or in the absence of NO, the β -hydroxyalkyl peroxy radicals are expected to react with HO₂ radicals and organic peroxy radicals (including the self-reaction) (5).



The β -hydroxyalkoxy radicals formed from the reactions of the β -hydroxyalkyl peroxy radicals with NO (reaction 1b) and with RO₂ radicals (reaction 3b) then react with O₂, decompose, or isomerize via a six-member transition state (5, 18, 20, 21). These alkoxy radical reactions are illustrated in Scheme 1 for the CH₃CH₂CH(OH)CH₂˙O radical formed after internal OH radical addition to 1-butene (note that the CH₃CH₂CH(˙O)CH₂OH radical formed after terminal OH radical addition to 1-butene cannot undergo isomerization via a six-member transition state). The α -hydroxyalkyl radicals formed in the decomposition pathway react rapidly with O₂ to form the corresponding carbonyl compound (4, 5), as shown for the CH₃CH₂˙CHOH radical formed in Scheme 1.



The alkoxy radical ˙CH₂CH₂CH(OH)CH₂OH formed after the isomerization reaction in Scheme 1 is predicted to undergo a further isomerization, eventually leading to the dihydroxycarbonyl product HOCH₂CH₂CH(OH)CHO (5, 20, 21).

Previous studies have shown that, at room temperature and atmospheric pressure of air containing NO, the HOCH₂-

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CH₂Ö radical formed from OH radical addition to ethene reacts with O₂ and decomposes (10), while the β -hydroxyalkoxy radicals formed from propene, 1-butene, and *trans*-2-butene predominantly decompose (9, 11). However, the carbonyl products observed and quantified from the OH radical reactions with isoprene (13, 14, 17) and 1-butene through 1-octene (15, 18) suggest that decomposition of the intermediate β -hydroxyalkoxy radicals is not the sole process and that other reaction pathways, including isomerization (20, 21), must be occurring. Indeed, Kwok et al. (20), employing atmospheric pressure ionization mass spectrometry to study the products of the OH radical-initiated reactions of 1-butene through 1-octene, observed the formation of C_n-dihydroxycarbonyls from the C_n-1-alkene reactions and hence obtained direct evidence for isomerization of the β -hydroxyalkoxy radicals involved. Atkinson (21) has used the literature product data for the alkanes and alkenes to propose methods to calculate the reaction rates of alkoxy and β -hydroxyalkoxy radicals under tropospheric conditions, and these estimation methods predict that decomposition of the β -hydroxyalkoxy radicals will dominate over their reaction with O₂ at around room temperature and atmospheric pressure of air (21).

In this work, we have used gas chromatography with flame ionization detection (GC-FID), in situ Fourier transform infrared (FT-IR) absorption spectroscopy, and in situ atmospheric pressure ionization tandem mass spectrometry (API-MS) to investigate the products formed from the reactions of the OH radical with the methyl-substituted ethenes propene, 2-methylpropene, *cis*- and *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene at 297 ± 2 K and 740 Torr total pressure of air.

Experimental Section

Experiments were carried out in a 5800 L evacuable, Teflon-coated chamber containing an in situ multiple reflection optical system interfaced to a Nicolet 7199 Fourier transform infrared (FT-IR) absorption spectrometer and with irradiation provided by a 24 kW xenon arc filtered through a 0.25 in. thick Pyrex pane (to remove wavelengths <300 nm); in a 7900 L Teflon chamber with analysis by GC-FID and irradiation provided by two parallel banks of blacklamps; and in a 6500 L Teflon chamber interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS), again with irradiation provided by two parallel banks of blacklamps. All three chambers are fitted with Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber.

Hydroxyl radicals were generated in the presence of NO by the photolysis of methyl nitrite (CH₃ONO) or ethyl nitrite (C₂H₅ONO) in air at wavelengths >300 nm (13, 18, 22):



where R = H or CH₃. NO was added to the reactant mixtures to suppress the formation of O₃ and hence of NO₃ radicals (22). Experiments were carried out in the 7900 L Teflon chamber for GC-FID measurements of the formation yields of carbonyls other than HCHO (18, 23) and in the 5800 L evacuable, Teflon-coated chamber for FT-IR absorption spectroscopic determination of the HCHO (and other carbonyl) formation yields (18, 23). Because HCHO is the primary photolytic product of methyl nitrite (see above), the photolysis of ethyl nitrite in air was used as the OH radical source for the determination of HCHO formation yields in

the 5800 L evacuable chamber (13, 18). In the 6500 and 7900 L Teflon chambers with analyses by GC-FID and API-MS, OH radicals were generated by the photolysis of CH₃ONO in air. Additional experiments were carried out in the 6500 L Teflon chamber with API-MS analyses in which OH radicals were generated in the absence of NO from the reaction of O₃ with the alkene being studied (24).

Teflon Chamber with Analysis by GC-FID. For the experiments carried out in the 7900 L Teflon chamber, the initial reactant concentrations (in molecules per cubic centimeter units) were CH₃ONO, (1.85–2.25) × 10¹⁴; NO, (1.95–2.30) × 10¹⁴; and alkene, (2.28–2.50) × 10¹³. Irradiations were carried out at 20% of the maximum light intensity for 1–6 min. The concentrations of the alkenes and the carbonyl (apart from HCHO) products were measured during the experiments by GC-FID as described previously (23).

Evacuatable Chamber with Analysis by FT-IR Absorption Spectroscopy. The initial concentrations of the alkenes, methyl or ethyl nitrite, and NO in the experiments with FT-IR absorption spectroscopic analyses in the 5800 L evacuable chamber were (2.4–4.8) × 10¹⁴ molecule cm⁻³, 2.4 × 10¹⁴ molecule cm⁻³, and (1.8–2.4) × 10¹⁴ molecule cm⁻³, respectively. Intermittent irradiations of 0.5–1.0 min duration were carried out with analysis by FT-IR spectroscopy during the dark periods, with 64 coadded interferograms (scans)/spectrum (1.8 min measurement time) recorded with a full width at half-maximum (fwhm) resolution of 0.7 cm⁻¹ and a path length of 62.9 m (23). FT-IR absorptions of the alkenes were obtained by measuring known partial pressures of the gaseous compound into a 5.25 L Pyrex bulb with an MKS Baratron 0–100 Torr sensor and flushing the contents of the bulb into the 5800 L chamber with FT-IR detection of the authentic compound. IR reference spectra of the products measured were available from previous IR calibrations in this laboratory (23).

Teflon Chamber with Analysis by API-MS. In the experiments with API-MS analyses, the chamber contents were sampled through a 25 mm diameter × 75 cm length Pyrex tube at ~20 L min⁻¹ directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision activated dissociation (CAD)] modes has been described elsewhere (19, 20, 25). Use of the MS/MS mode with CAD allows the “daughter ion” or “parent ion” spectrum of a given ion peak observed in the MS scanning mode to be obtained (19, 20, 25). The positive ion mode was used in these API-MS and API-MS/MS analyses, with protonated water hydrates [H₃O⁺·(H₂O)_n] generated by the corona discharge in the chamber diluent gas being responsible for the protonation of analytes.



Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. For these experiments, the API-MS instrument was operated under conditions that favored the formation of dimer ions in the ion source region (25). Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen (“curtain” gas), and as a result of the declustering action of the curtain gas on the hydrated ions, the ions that are mass analyzed are mainly protonated molecular ions ([M + H]⁺) and their protonated homo- and heterodimers (25).

For the reactions of 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene carried out in the presence of NO, OH radicals were generated by the photolysis of methyl nitrite. The initial concentrations of CH₃ONO, NO, and alkene were ~4.8 × 10¹³ molecule cm⁻³ each, and irradiations were carried out for 1–2 min at 20% of the maximum light intensity. For reactions carried out in

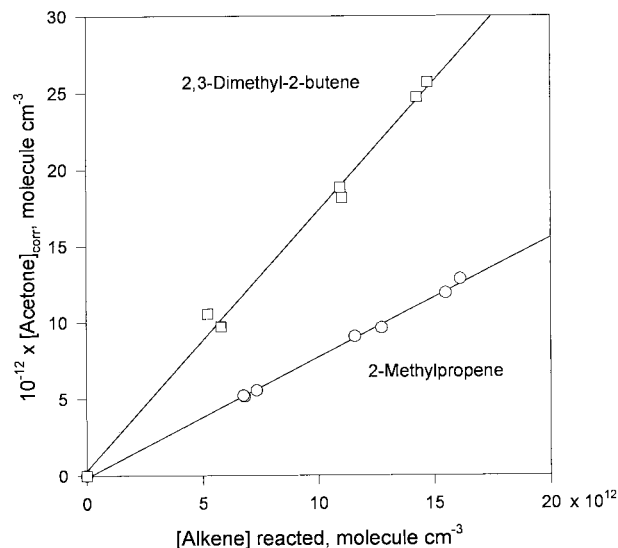


FIGURE 1. Plots of the amounts of acetone formed, corrected for reaction with the OH radical, against the amounts of 2-methylpropene and 2,3-dimethyl-2-butene reacted with the OH radical in the presence of NO, with analyses by GC-FID.

the absence of NO, OH radicals were generated by the dark reaction of O_3 with the alkene (24), with the initial concentration of the alkene being $\sim 4.8 \times 10^{13}$ molecule cm^{-3} and with two additions of 50 cm^3 volume of O_3 in O_2 diluent (each addition corresponding to an initial concentration of O_3 in the chamber of $\sim 6 \times 10^{12}$ molecule cm^{-3}) being made to the chamber during an experiment. The alkenes studied in the experiments in the absence of NO also included propene and *trans*-2-butene.

Chemicals. The chemicals used (acetaldehyde, acetone, *cis*-2-butene, *trans*-2-butene, 2,3-dimethyl-2-butene, 2-methyl-2-butene, 2-methylpropene, propene, and NO) were all of $\geq 99.0\%$ stated purity. Methyl nitrite was prepared as described by Taylor et al. (26), and ethyl nitrite was distilled from a commercial 15% (by weight) solution of C_2H_5ONO in ethanol (Aldrich Chemical Co.), and both nitrites were stored at 77 K under vacuum. O_3 in O_2 diluent was prepared as needed using a Welsbach T-408 ozone generator.

Results

Reactions in the Presence of NO. Teflon Chamber with GC-FID Analyses. GC-FID analyses showed the formation of acetone from the OH radical-initiated reactions of 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene and of acetaldehyde from the reactions of *cis*-2-butene and 2-methyl-2-butene. Because the carbonyl products react with the OH radical (4, 8), secondary reactions of the products with the OH radical were taken into account as described previously (27), using the recommended OH radical reaction rate constants for the alkenes and carbonyl products (4, 5, 8). Corrections to the measured carbonyl compound concentrations to take into account secondary reactions were $<15\%$ for acetaldehyde and $<0.03\%$ for acetone. Figure 1 shows representative plots of the amounts of acetone formed against the amounts of 2-methylpropene and 2,3-dimethyl-2-butene reacted, and the carbonyl formation yields obtained from least-squares analyses of the data obtained are given in Table 1. Two independent sets of experiments were carried out to measure the acetone formation yield from the 2-methyl-2-butene reaction and, as shown in Table 1, the agreement between the two measured acetone formation yields is excellent.

(b) Evacuatable Chamber with Analyses by FT-IR Spectroscopy. Products from the gas-phase reactions of the OH

TABLE 1. Products and Their Formation Yields Observed from the Reactions of the OH Radical with Alkenes in the Presence of NO at 296 ± 2 K and 740 Torr Total Pressure of Air

alkene	product	formation yield	
		GC-FID ^a	FT-IR ^b
2-methylpropene	acetone	0.78 ± 0.06	0.90 ± 0.07
	formaldehyde		0.92 ± 0.08
	hydroxynitrate		$\sim 0.09^c$
<i>cis</i> -2-butene	acetaldehyde	1.85 ± 0.25	1.58 ± 0.12
	hydroxynitrate		$\sim 0.06^c$
2-methyl-2-butene	acetaldehyde	0.98 ± 0.10	0.84 ± 0.10
	acetone	0.92 ± 0.09^d	0.81 ± 0.08
		0.88 ± 0.07^d	
		0.90 ± 0.08^e	
2,3-dimethyl-2-butene	hydroxynitrate		$\sim 0.13^c$
	acetone	1.70 ± 0.17	1.60 ± 0.15
	hydroxynitrate		$\sim 0.07^c$

^a Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the alkene and carbonyl products of $\pm 5\%$ each. ^b Indicated errors are two least-squares standard deviations combined with the errors arising from FT-IR measurement uncertainties due to errors in calibrations and in the subtractive method of spectral analysis of $\pm 4\%$ each for the products and alkenes, except for 2-methyl-2-butene which has an estimated $\pm 6\%$ uncertainty. ^c The hydroxynitrate yields have estimated uncertainties of $\pm 35\%$ (see text). ^d Independent sets of experiments, each with separately measured GC-FID calibration factors. ^e For combined data sets.

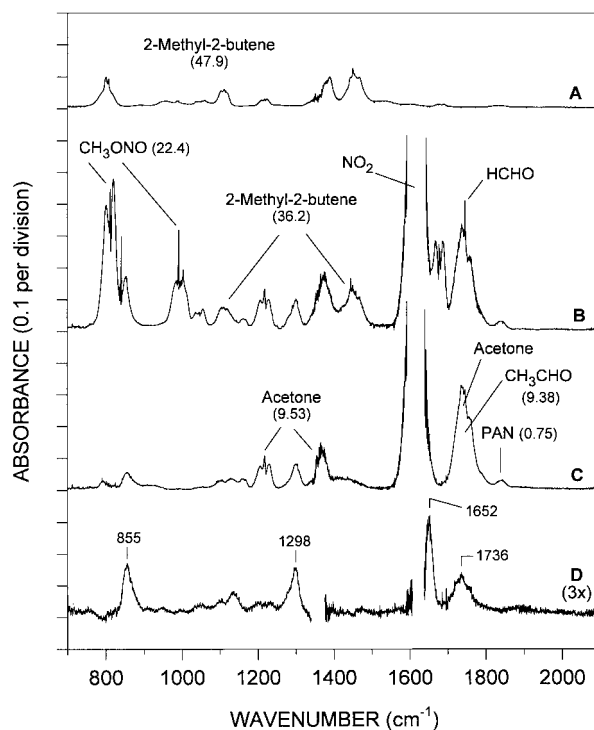


FIGURE 2. Infrared spectra from a CH_3ONO -NO-2-methyl-2-butene-air irradiation. (A) Initial alkene. (B) Mixture after 3.0 min of irradiation. (C) Product spectrum from panel B. (D) Residual spectrum ($3\times$ absorbance). Gaps in the ~ 1625 and ~ 1350 cm^{-1} regions are due to distortions by the strong absorptions, respectively, of the NO_2 formed and the NO_3^- accumulated on the KBr window. Values in parentheses are concentrations in units of 10^{13} molecule cm^{-3} . The HCHO observed arises from photolysis of the methyl nitrite used as the OH radical precursor (see text).

radical with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the presence of NO were identified and quantified by in situ FT-IR absorption spectroscopy. Figure 2 shows, for example, the FT-IR spectra

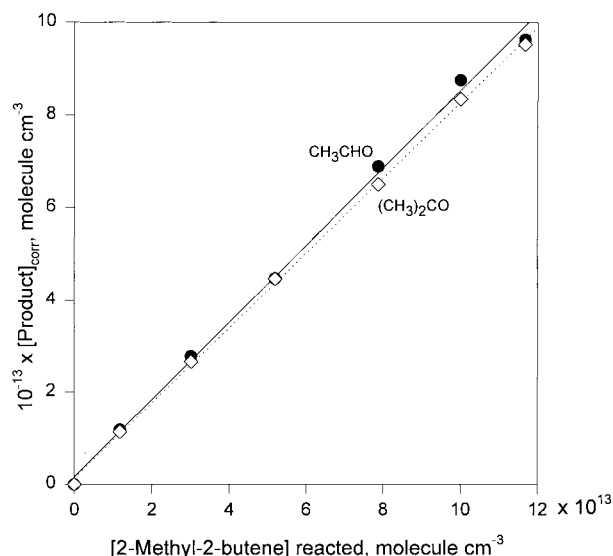


FIGURE 3. Plots of the amounts of acetaldehyde and acetone formed, corrected for reaction with the OH radical, against the amounts of 2-methyl-2-butene reacted with the OH radical in an irradiated $\text{CH}_3\text{ONO}-\text{NO}-2\text{-methyl-2-butene}-\text{air}$ mixture. Analyses were by in situ FT-IR absorption spectroscopy.

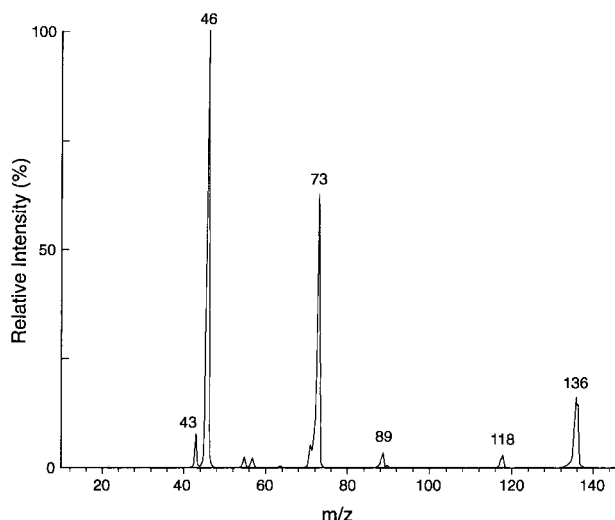


FIGURE 4. API-MS/MS CAD "daughter ion" spectrum of the 136 u ion peak observed in the API-MS spectrum of an irradiated $\text{CH}_3\text{ONO}-\text{NO}-\text{cis-2-butene}-\text{air}$ mixture, showing a loss of HNO_3 at 73 u and the presence of an NO_2^+ fragment at 46 u.

of reactants and products from an irradiated $\text{CH}_3\text{ONO}-\text{NO}-2\text{-methyl-2-butene}-\text{air}$ irradiation [note that the HCHO observed arises from the photolysis of methyl nitrite (reactions 5 and 6)]. The products observed and their measured formation yields from these FT-IR absorption spectroscopic analyses are given in Table 1, where the measured concentrations of HCHO, CH_3CHO , and $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ are again corrected for secondary reactions (see above) and the HCHO yields were determined from experiments utilizing the photolysis of ethyl nitrite as the OH radical precursor. The corrections for secondary reactions were $<5\%$ for HCHO and CH_3CHO and were negligible for acetone. Representative plots of the amounts of CH_3CHO and $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ formed, corrected for secondary reactions, against the amounts of 2-methyl-2-butene reacted with the OH radical are shown in Figure 3. We have previously shown that any contribution to HCHO formation from secondary reactions of CH_3CHO generated from the photolysis of ethyl nitrite is minor ($<4\%$ formation yield) in irradiated $\text{C}_2\text{H}_5\text{ONO}-\text{NO}-1\text{-alkene}-\text{air}$

mixtures (18), and the formation of HCHO from ethyl nitrite chemistry in the present experiments would be even less because of the higher reactivity of the alkenes studied here.

The residual spectra after subtraction of known components, illustrated in Figure 2 for the 2-methyl-2-butene reaction, showed weak but distinct sets of absorption bands near 855, 1300, and 1650 cm^{-1} which are characteristic of the $-\text{ONO}_2$ group. These bands are assigned to hydroxynitrates, although the low signal-to-noise ratio in the 3600 cm^{-1} region did not allow O-H stretch absorption bands to be observed. These hydroxynitrates are expected to be formed during the reactions of the β -hydroxyalkyl peroxy radicals with NO (reaction 1a) (4, 5). Approximate yields of the hydroxynitrates (Table 1) were calculated using an average absorption coefficient for the $-\text{ONO}_2$ absorption band at $\sim 1300\text{ cm}^{-1}$ previously derived for analogous compounds (13). On the basis of the range of absorption coefficients observed for these organic nitrates (13) and the uncertainties in integrated band area obtained from the residual spectra, it is estimated that the hydroxynitrate yields reported in Table 1 are accurate to within $\pm 35\%$. For the 2-methyl-2-butene reaction, the formation of a minor carbonyl product (other than acetone or acetaldehyde) is also indicated by the occurrence of an absorption band at 1736 cm^{-1} (Figure 2D). Similarly, in the 2,3-dimethyl-2-butene reaction, weak absorptions by a minor unidentified product, which include a band(s) near 1730 cm^{-1} , were also observed.

(c) Teflon Chamber with Analyses by API-MS. Experiments were carried out using API-MS for analysis of the products formed from the reactions of the OH radical with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the presence and absence of NO. The reactions of the OH radical with propene and *trans*-2-butene in the absence of NO were also investigated.

API-MS/MS "daughter ion" and "parent ion" spectra were obtained for ion peaks observed in the API-MS analyses. Product ion peaks were identified based on the observation of homo- or heterodimer (and, in certain cases, trimer) ions (for example, $[(\text{M}_{\text{P1}})_2 + \text{H}]^+$, $[(\text{M}_{\text{P2}})_2 + \text{H}]^+$, and $[\text{M}_{\text{P1}} + \text{M}_{\text{P2}} + \text{H}]^+$, where P1 and P2 are products) in the API-MS/MS "parent ion" spectra and consistency of the API-MS/MS "daughter ion" spectrum of a homo- or heterodimer ion with the "parent ion" spectra of the various $[\text{M} + \text{H}]^+$ ion peaks. Water cluster ion peaks of the product ions, $[\text{M} + \text{H} + \text{H}_2\text{O}]^+$, were also occasionally observed. The products observed are listed in Table 2 and the evidence for the formation of the products, in the form of API-MS and API-MS/MS data of molecular ions, dominant fragment ions, and the presence of homo- and heterodimers formed in the API-MS under the experimental conditions employed, is also summarized in Table 2.

For the reactions carried out in the presence of NO, the products observed by API-MS and API-MS/MS analyses are consistent with the GC-FID and FT-IR spectroscopic identifications given in Table 1. The API-MS and API-MS/MS spectra provided definitive evidence for the formation of hydroxynitrates, thus supporting the assignments based on FT-IR spectroscopic data (see above). For example, Figure 4 shows the API-MS/MS "daughter ion" spectrum of the 136 u ion peak in the *cis*-2-butene reaction, attributed to the $[\text{M} + \text{H}]^+$ ion of the β -hydroxynitrate $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_3$. Note that the spectrum exhibits a loss of HNO_3 from the protonated molecular ion and the presence of a prominent NO_2^+ fragment ion peak. Consistent with our GC-FID and FT-IR data which show an essentially 100% carbon balance, our API-MS and API-MS/MS spectra show no evidence for the formation of the hydroxycarbonyls arising from reaction of the intermediate β -hydroxyalkoxy radicals with O_2 (Scheme 1). While the 103 u ion peak observed in the OH radical-initiated reaction of 2-methyl-2-butene in

TABLE 2. Products Formed from the Gas-Phase Reactions of the OH Radical with Methyl-Substituted Ethenes in the Presence of NO, as Observed by API-MS and API-MS/MS Analyses

product		API-MS data	other evidence
2-methylpropene			
CH ₃ C(O)CH ₃	M ₁ (MW 58)	M ₁ + H = 59 M ₁ + M ₁ + H = 117 M ₁ + M ₁ + M ₁ + H + H ₂ O = 193	identified and quantified by GC-FID and FT-IR (Table 1). MS/MS of 117 and 193 u ion peaks
(CH ₃) ₂ C(ONO ₂)CH ₂ OH and/or (CH ₃) ₂ C(OH)CH ₂ ONO ₂	M ₂ (MW 135)	M ₂ + M ₁ + H = 194	MS/MS of 194 u ion peak, showing [M ₂ +H] and [M ₁ +H] ions, a loss of HNO ₃ , and the presence of NO ₂ ⁺ fragment
cis-2-Butene			
CH ₃ CHO	M ₁ (MW 44)	M ₁ + H = 45 M ₁ + M ₁ + H = 89	identified and quantified by GC-FID and FT-IR (Table 1). MS/MS of 89 u ion peak. Parents of 45 u ion observed at 89 and 180 [M ₁ + M ₂ + H] u
CH ₃ CH(OH)CH(ONO ₂)CH ₃	M ₂ (MW 135)	M ₂ + H = 136 M ₂ + M ₁ + H = 180 M ₂ + M ₁ + H + H ₂ O = 198	MS/MS of 136 u ion showing loss of HNO ₃ and presence of NO ₂ ⁺ fragment (Figure 4). MS/MS of 180, 190 [M ₂ +H+3H ₂ O] and 198 u ion peaks showing presence of [M ₂ +H] ion and its fragments. Parents of 136 u ion peak at 154 [M ₂ + H + H ₂ O], 172 [M ₂ + H + 2H ₂ O], 180, 190 and 198 u
2-Methyl-2-butene			
CH ₃ CHO	M ₁ (MW 44)	M ₁ + M ₂ + H = 103	identified and quantified by GC-FID and FT-IR (see Table 1). MS/MS of 103 u ion peak
CH ₃ C(O)CH ₃	M ₂ (MW 58)	M ₂ + H = 59 M ₂ + M ₁ + H = 103 M ₂ + M ₂ + H = 117	identified and quantified by GC-FID and FT-IR (Table 1). MS/MS of 103 and 117 u ion peaks. Parents of 59 u ion at 103, 117, and 208 [M ₂ + M ₃ + H] u
(CH ₃) ₂ C(OH)CH(ONO ₂)CH ₃ and/or (CH ₃) ₂ C(ONO ₂)CH(OH)CH ₃	M ₃ (MW 149)	M ₃ + H - HNO ₃ = 87 M ₃ + M ₂ + H = 208 M ₃ + M ₃ + H = 299	MS/MS of 208 u ion peak showing loss of HNO ₃ and presence of [M ₂ + H] and [M ₃ + H - HNO ₃] ions. MS/MS of 299 u ion peak showing losses of HNO ₃ and 2 HNO ₃ and presence of [M ₃ + H - HNO ₃] ion
2,3-Dimethyl-2-butene			
CH ₃ C(O)CH ₃	M ₁ (MW 58)	M ₁ + H = 59 M ₁ + M ₁ + H = 117	identified and quantified by GC-FID and FT-IR (Table 1). MS/MS of 117 u ion peak
(CH ₃) ₂ C(OH)C(ONO ₂)(CH ₃) ₂	M ₂ (MW 163)	M ₂ + H - HNO ₃ = 101 M ₂ + M ₂ + H = 327	MS/MS of 327 u ion peak, showing presence of intense 101 u fragment ion

the presence of NO could be the [M + H]⁺ ion of the hydroxycarbonyl (CH₃)₂C(OH)C(O)CH₃, its API-MS/MS spectrum suggested that this ion peak was the protonated heterodimer of CH₃CHO and CH₃C(O)CH₃ (Table 2).

Reactions in the Absence of NO. Experiments to investigate the products of the reactions of the OH radical with propene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the absence of NO were carried out with API-MS analyses, with OH radicals being produced from the reactions of O₃ with the alkenes being studied (24). In these reaction systems, the expected products of the OH radical-initiated reactions then arise from peroxy radical plus HO₂ radical and peroxy radical plus peroxy radical reactions (reactions 2 and 3). Product ions were identified as described above and these products are listed in Table 3 together with the API-MS and API-MS/MS evidence. As an example of the spectra obtained, Figure 5 shows the API-MS/MS "parent ion" spectrum of the 121 u ion peak observed in the OH radical-initiated reaction of 2-methyl-2-butene. It should be recognized that the O₃ reactions with the alkenes form the primary carbonyls HCHO + CH₃CHO from propene, HCHO + CH₃C(O)CH₃ from 2-methylpropene, CH₃CHO from *cis*- and *trans*-2-butene, CH₃CHO + CH₃C(O)CH₃ from 2-methyl-2-butene, and CH₃C(O)CH₃ from 2,3-dimethyl-2-butene (5, 23). Hence, these carbonyl products cannot be ascribed solely to being products of the OH radical-initiated reactions.

Discussion

Reactions in the Presence of NO. The GC-FID and FT-IR spectroscopy product formation yield data given in Table 1 and the qualitative API-MS data all show that the dominant products of the gas-phase reactions of the OH radical with 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene in the presence of NO are the two carbonyls arising from decomposition of the intermediate

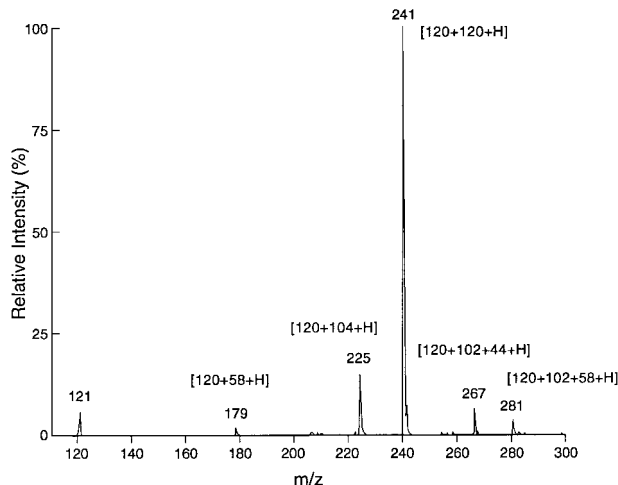


FIGURE 5. API-MS/MS CAD "parent ion" spectrum of the 121 u ion peak observed in the API-MS spectrum of a reacted O₃-2-methyl-2-butene-air mixture.

β -hydroxyalkoxy radical(s) and β -hydroxynitrates formed in the reaction of the β -hydroxyalkyl peroxy radicals with NO. Our API-MS analyses showed no evidence for the formation of the hydroxycarbonyls which would be formed from reaction of the intermediate β -hydroxyalkoxy radicals with O₂ (Scheme 1), and it was not established in the present work using FT-IR absorption spectroscopy whether the minor reaction product observed from the 2-methyl-2-butene reaction and containing a 1736 cm⁻¹ absorption band (Figure 2D) was the hydroxyketone (CH₃)₂C(OH)C(O)CH₃, or not.

Formation of organic nitrates from the reactions of the OH radical with *cis*-2-butene and 2,3-dimethyl-2-butene in the presence of NO has been reported previously by Muthuramu et al. (16) and Niki et al. (12), respectively.

TABLE 3. Products Formed from the Gas-Phase Reactions of the OH Radical with Methyl-Substituted Ethenes in the Absence of NO, as Observed by API-MS and API-MS/MS Analyses

product		API-MS data	evidence from API-MS and API-MS spectra
Propene			
CH ₃ CHO ^a	M ₁ (MW 44)	M ₁ + H = 45	parents of 75 u ion at 119 [M ₂ + M ₁ + H], 149 [M ₂ + M ₂ + H], 151 [M ₂ + M ₃ + H] and 167 [M ₂ + M ₄ + H] u. MS/MS of 149 u ion peak
CH ₃ C(O)CH ₂ OH and/or CH ₃ CH(OH)CHO	M ₂ (MW 74)	M ₂ + H = 75 M ₂ + M ₂ + H = 149	
CH ₃ CH(OH)CH ₂ OH	M ₃ (MW 76)	M ₃ + H = 77	
CH ₃ CH(OOH)CH ₂ OH and/or CH ₃ CH(OH)CH ₂ OOH	M ₄ (MW 92)	M ₄ + H = 93 M ₄ + H + H ₂ O = 111 M ₄ + M ₄ + M ₄ + H = 277	parents of 77 u ion at 151 [M ₃ + M ₂ + H], 153 [M ₃ + M ₃ + H] and 169 [M ₃ + M ₄ + H] u parents of 93 u ion at 169 [M ₄ + M ₃ + H], 185 [M ₄ + M ₄ + H] and 277 [M ₄ + M ₄ + M ₄ + H] u. MS/MS of 277 u ion peak
2-Methylpropene			
CH ₃ C(O)CH ₃ ^a	M ₁ (MW 58)	M ₁ + H = 59 M ₁ + M ₁ + H = 117	parents of 59 u ion at 117, 147 [M ₁ + M ₂ + H], 149 [M ₁ + M ₃ + H], and 165 [M ₁ + M ₄ + H] u
(CH ₃) ₂ C(OH)CHO	M ₂ (MW 88)	M ₂ + H = 89	parent of 89 u ion at 179 [M ₂ + M ₃ + H] u
(CH ₃) ₂ C(OH)CH ₂ OH	M ₃ (MW 90)	M ₃ + H = 91	parents of 91 u ion at 163 [M ₃ + M ₃ + H - H ₂ O], 181 [M ₃ + M ₃ + H] and 197 [M ₃ + M ₄ + H] u
(CH ₃) ₂ C(OOH)CH ₂ OH and/or (CH ₃) ₂ C(OH)CH ₂ OOH	M ₄ (MW 106)	M ₄ + H = 107	parents of 107 u ion at 165 [M ₄ + M ₁ + H], 197 [M ₄ + M ₃ + H] and 213 [M ₄ + M ₄ + H] u
cis-2-Butene, trans-2-Butene			
CH ₃ CHO ^a	M ₁ (MW 44)	M ₁ + H = 45	parents of 45 u ion at 89 [M ₁ + M ₁ + H] and 133 [M ₁ + M ₂ + H] and/or [M ₁ + M ₁ + M ₁ + H] u
CH ₃ C(O)CH(OH)CH ₃	M ₂ (MW 88)	M ₂ + H = 89 M ₂ + M ₃ + H = 179 M ₂ + M ₄ + H = 195	parents of 89 u ion at 133 [M ₂ + M ₁ + H], 177 [M ₂ + M ₂ + H] and 179 [M ₂ + M ₃ + H] u
CH ₃ CH(OH)CH(OH)CH ₃	M ₃ (MW 90)	M ₃ + H = 91 M ₃ + M ₂ + H = 179 M ₃ + M ₄ + H = 197	parents of 91 u ion at 135 [M ₃ + M ₁ + H], 181 [M ₃ + M ₃ + H] and 197 [M ₃ + M ₄ + H] u
CH ₃ CH(OOH)CH(OH)CH ₃	M ₄ (MW 106)	M ₄ + H = 107 M ₄ + M ₂ + H = 195 M ₄ + M ₄ + H = 213	parents of 107 u ion at 151 [M ₄ + M ₁ + H], 195 [M ₄ + M ₂ + H], 197 [M ₄ + M ₃ + H] and 213 [M ₄ + M ₄ + H] u. MS/MS of 195 u ion peak
2-Methyl-2-butene			
CH ₃ CHO ^a	M ₁ (MW 44)	M ₁ + H = 45	parents of 103 u ion at 147 [M ₃ + M ₁ + H] and 161 [M ₃ + M ₂ + H] u
CH ₃ C(O)CH ₃ ^a	M ₂ (MW 58)	M ₂ + H = 59 M ₂ + M ₂ + H = 117	
(CH ₃) ₂ C(OH)C(O)CH ₃	M ₃ (MW 102)	M ₃ + H = 103	
(CH ₃) ₂ C(OH)CH(OH)CH ₃	M ₄ (MW 104)	M ₄ + H = 105	parents of 105 u ion at 163 [M ₄ + M ₂ + H], 209 [M ₄ + M ₄ + H] and 225 [M ₄ + M ₅ + H] u
(CH ₃) ₂ C(OOH)CH(OH)CH ₃ and/or (CH ₃) ₂ C(OH)CH(OOH)CH ₃	M ₅ (MW 120)	M ₅ + H = 121	parents of 121 u ion at 179 [M ₅ + M ₂ + H], 225 [M ₅ + M ₄ + H], 241 [M ₅ + M ₅ + H], 267 [M ₅ + M ₃ + M ₁ + H] and 281 [M ₅ + M ₃ + M ₂ + H] u (see Figure 5)
2,3-Dimethyl-2-butene			
CH ₃ C(O)CH ₃ ^a	M ₁ (MW 58)	M ₁ + H = 59 M ₁ + M ₁ + H = 117 M ₁ + M ₃ + H = 193	parents of 119 u ion at 237 [M ₂ + M ₂ + H] and 253 [M ₂ + M ₃ + H] u. MS/MS of 253 u ion peak
(CH ₃) ₂ C(OH)C(OH)(CH ₃) ₂	M ₂ (MW 118)	M ₂ + M ₃ + H = 253	
(CH ₃) ₂ C(OOH)C(OH)(CH ₃) ₂	M ₃ (MW 134)	M ₃ + M ₃ + H = 269 M ₃ + M ₂ + H = 253 M ₃ + M ₁ + H = 193	

^a Because OH radicals were produced from the reaction of O₃ with the alkene, these carbonyls are also formed from the O₃ reaction (5, 23).

Muthuramu *et al.* (16) reported the formation of the β -hydroxynitrate CH₃CH(OH)CH(ONO₂)CH₃ from the reaction of the CH₃CH(OH)CH(OO)CH₃ radical with NO in 3.7 \pm 0.9% yield, while Niki *et al.* (12) reported a yield of an organic nitrate, attributed to (CH₃)₂C(OH)C(ONO₂)(CH₃)₂, of 15% from the OH radical-initiated reaction of 2,3-dimethyl-2-butene in the presence of NO. Our present semiquantitative FT-IR data for the formation of hydroxynitrates from the *cis*-2-butene and 2,3-dimethyl-2-butene reactions (Table 1) are reasonably consistent with these previous literature data (12, 16). Of the alkenes studied here, only for the 2,3-dimethyl-2-butene reaction have product yields been previously obtained (12), and Niki *et al.* (12) reported an acetone yield of 1.7 \pm 0.1 for this reaction, in excellent agreement with both our GC-FID and FT-IR data (Table 1).

In all cases, the formation yields measured using both GC-FID and FT-IR spectroscopic analyses agree within the

combined overall errors. For all four reactions, hydroxynitrate formation from the reaction of the β -hydroxyalkyl peroxy radical with NO accounts for \sim 10% of the overall products observed, with decomposition of the β -hydroxyalkoxy radical dominating over the alternative isomerization and O₂ reaction and leading to the formation of the carbonyls expected from >C=C< bond cleavage in \sim 90% yield each (note that isomerization via a six-member transition state is not possible for any of the intermediate β -hydroxyalkoxy radicals formed in these reactions). These experimental data are consistent with the estimated rates of decomposition and reaction with O₂ of the intermediate β -hydroxyalkoxy radicals (21).

However, it should be noted that the reactions of alkyl peroxy and β -hydroxyalkyl peroxy radicals with NO are exothermic by \sim 10 kcal mol⁻¹ (28), and Orlando *et al.* (29) have recently shown that 25% of the HOCH₂CH₂O radicals formed after OH radical addition to ethene in the presence

of NO are chemically activated and rapidly decompose. The remaining 75% of the HOCH₂CH₂O radicals are thermalized and undergo competitive reaction with O₂ and decomposition. The results reported here concern β -hydroxyalkoxy radicals formed from the exothermic reactions of β -hydroxyalkyl peroxy radicals with NO. Hence, depending on the fractions of chemically activated β -hydroxyalkoxy radicals formed from these reactions and which presumably rapidly decompose, our data may overestimate the extent of decomposition of thermalized β -hydroxyalkoxy radicals formed from less exothermic reactions, including from the slightly endothermic (28) reaction pathway (3b).

Reactions in the Absence of NO. The products suggested by the API-MS and API-MS/MS analyses (Table 3) are those expected from reactions 2 and 3 and Scheme 1, leading to the formation of hydroxycarbonyls, dihydroxyalkanes (diols), and hydroxyhydroperoxides.

The product data obtained from this study of the reactions of the OH radical with methyl-substituted ethenes in the absence (and presence) of NO confirm reaction schemes previously proposed for these alkenes (5). In the troposphere, it is likely that the major products arising from the reactions of the OH radical with alkenes in the absence of NO will be the hydroxyhydroperoxides formed in reaction 2. This needs to be confirmed by ambient atmospheric analyses, and the atmospheric chemistry of this class of organic compounds studied.

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