

Products and Mechanism of the Reaction of OH Radicals with 2,2,4-Trimethylpentane in the Presence of NO

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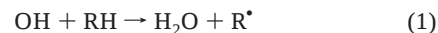
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Alkanes are important constituents of gasoline fuel and vehicle exhaust, with branched alkanes comprising a significant fraction of the total alkanes observed in urban areas. Products of the gas-phase reactions of OH radicals with 2,2,4-trimethylpentane and 2,2,4-trimethylpentane-*d*₁₈ in the presence of NO at 298 ± 2 K and atmospheric pressure of air have been investigated using gas chromatography with flame ionization detection (GC-FID), combined gas chromatography–mass spectrometry (GC–MS), and in situ atmospheric pressure ionization tandem mass spectrometry (API–MS). Acetone, 2-methylpropanal, and 4-hydroxy-4-methyl-2-pentanone were identified and quantified by GC-FID from 2,2,4-trimethylpentane with molar formation yields of 54 ± 7%, 26 ± 3%, and 5.1 ± 0.6%, respectively; upper limits to the formation yields of acetaldehyde, 2,2-dimethylpropanal, and 4,4-dimethyl-2-pentanone were obtained. Additional products observed from 2,2,4-trimethylpentane by API–MS and API–MS/MS analyses using positive and negative ion modes were hydroxy products of molecular weight 130 and 144, a product of molecular weight 128 (attributed to a C₈-carbonyl), and hydroxynitrates of molecular weight 135, 177, and 191 (attributed to HOC₄H₈ONO₂, HOC₇H₁₄ONO₂, and HOC₈H₁₆ONO₂, respectively). Formation of HOC₈H₁₆ONO₂ and HOC₇H₁₄ONO₂ is consistent with the observation of products of molecular weight 207 (HOC₈D₁₆ONO₂) and 191 (HOC₇D₁₄ONO₂), respectively, in the API–MS analyses of the 2,2,4-trimethylpentane-*d*₁₈ reaction (–OD groups rapidly exchange to –OH groups under our experimental conditions). These product data allow the reaction pathways to be delineated to a reasonable extent, and the reaction mechanism is discussed.

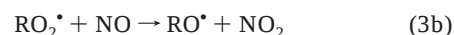
Introduction

Alkanes are important constituents of gasoline fuel and vehicle exhaust (1) and account for ~50% of the non-methane

organic compounds measured in ambient air in urban areas (2, 3). In the troposphere, alkanes present in the gas phase react mainly with the OH radical (4) to form alkyl radicals, which react rapidly with O₂ to form alkyl peroxy (RO₂•) radicals (4):



In urban areas in the presence of sufficiently high concentrations of NO, alkyl peroxy radicals react with NO to form the alkyl nitrate, RONO₂, or the corresponding alkoxy radical plus NO₂ (4):



The alkoxy radicals formed in reaction 3b then react with O₂, decompose by C–C bond scission, or isomerize through a six-membered ring transition state (4). The isomerization reaction, which can occur for ≥C₄ alkanes, forms a 1,4-hydroxyalkyl radical that adds O₂, giving a 1,4-hydroxyalkyl peroxy radical. The 1,4-hydroxyalkyl peroxy radical then reacts further by reactions analogous to reactions 3a and 3b and leads to the formation of hydroxycarbonyls and hydroxynitrates (4–8).

While rate constants for the reactions of the OH radical with a large number of alkanes have been measured (4), the products and mechanisms of the OH radical-initiated reactions of alkanes have received less attention. Most of the more recent and comprehensive studies of the products and mechanisms of the OH radical reactions of alkanes have involved *n*-alkanes and cycloalkanes (4–10), with the exception of a recent study that included 3,4-diethylhexane (10). However, branched alkanes are important, accounting for ~30–50% of the alkanes other than methane in urban areas (1, 2). Accordingly, in this work we have investigated the products and mechanism of the OH radical-initiated reaction of 2,2,4-trimethylpentane (isooctane) in the presence of NO. In addition to the use of gas chromatography for product analyses, we have used atmospheric pressure ionization tandem mass spectrometry to identify reaction products not amenable to gas chromatography. 2,2,4-Trimethylpentane-*d*₁₈ was also used in the experiments with API–MS analyses to aid in the interpretation of the API–MS spectra.

Experimental Methods

Experiments were carried out at 298 ± 2 K and 740 Torr total pressure of air (at ~5% relative humidity, RH) in a 7900-L Teflon chamber with analysis by gas chromatography with flame ionization detection (GC-FID) and combined gas chromatography–mass spectrometry (GC–MS), with irradiation provided by two parallel banks of blacklamps, and in a 7300-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. Both 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 in air at wavelengths >300 nm (6–10), and NO was added to the reactant mixtures to suppress the formation of O₃ and hence of NO₃ radicals.

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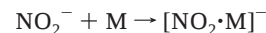
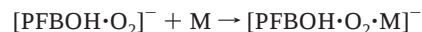
Analyses by GC-FID and GC-MS. For the reactions carried out in the 7900-L Teflon chamber (at ~5% RH), the initial reactant concentrations (in molecule cm^{-3} units) were as follows: CH_3ONO , $(2.2\text{--}2.4) \times 10^{14}$; NO , $(1.9\text{--}2.2) \times 10^{14}$; and 2,2,4-trimethylpentane, $(2.24\text{--}3.02) \times 10^{13}$. Irradiations were carried out at 20% of the maximum light intensity for 10–45 min, resulting in up to 23% reaction of the initially present 2,2,4-trimethylpentane. The concentrations of 2,2,4-trimethylpentane and reaction products were measured during the experiments by GC-FID. Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~250 °C onto a DB-1701 megabore column in a Hewlett-Packard (HP) 5710 GC, initially held at -40 °C and then temperature programmed to 200 °C at 8 °C min^{-1} . In addition, gas samples were collected onto Tenax-TA solid adsorbent for GC-MS analyses, with thermal desorption onto a 60-m HP-5 fused silica capillary column in an HP 5890 GC interfaced to a HP 5970 mass selective detector operating in the scanning mode. GC-FID response factors were determined as described previously (11). NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., model 42 $\text{NO-NO}_2\text{-NO}_x$ chemiluminescence analyzer.

Analyses by API-MS. In the experiments with API-MS analyses, the chamber contents were sampled through a 25 mm diameter $\times$ 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 (6–10). 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 (6–10). Both positive and negative ion modes were used in this work.

In the positive ion mode, protonated water clusters, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, formed from a corona discharge in the chamber diluent air (at ~5% RH) are the reagent ions, and a range of oxygenated species can be observed in this mode of operation (6–9). 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), 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 molecules ($[\text{M} + \text{H}]^+$) and their protonated homo- and heterodimers. Product peaks were identified based on the observation of homo- or heterodimers (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 mode in precursor ion spectra of the $[\text{M}_{\text{P}} + \text{H}]^+$ ion peaks and confirmed by consistency of the API-MS/MS product ion spectrum of a homo- or heterodimer ion with the precursor ion spectra (9).

In the negative ion mode, negative ions were generated by the negative corona around the discharge needle. The superoxide ion (O_2^-), its hydrates $[\text{O}_2(\text{H}_2\text{O})_n]^-$, and O_2 clusters $[\text{O}_2(\text{O}_2)_n]^-$ are the major reagent negative ions in the chamber pure air. Other reagent ions, for example, NO_2^- and NO_3^- , are formed through reactions between the primary reagent ions and the neutral molecules such as NO_2 . Instrument tuning and operation were designed to induce adduct formation. Two species served as reagent ions in this work; NO_2^- present in the irradiated $\text{CH}_3\text{ONO-NO-2,2,4-trimethylpentane}$ air mixtures and $[\text{PFBOH}\cdot\text{O}_2]^-$ (where PFBOH = pentafluorobenzyl alcohol, $\text{C}_6\text{F}_5\text{CH}_2\text{OH}$) generated by addition of pentafluorobenzyl alcohol to the sampled airstream from the chamber by diffusion through a pinhole in a covered, heated vial containing PFBOH (8). Analytes were then detected as adducts formed between the neutral analyte

(M) and the reagent ion (NO_2^- or $[\text{PFBOH}\cdot\text{O}_2]^-$), where M can also be PFBOH when PFBOH was added to the sampled airstream:



Previous work in this laboratory (8, 10) indicated that the use of NO_2^- or $[\text{PFBOH}\cdot\text{O}_2]^-$ reagent ions allows primarily hydroxy compounds to be detected (for example, hydroxycarbonyls and hydroxynitrates). When NO_2^- was used as the reagent ion, quantification of hydroxycarbonyls was carried out (8) by adding a measured amount of 5-hydroxy-2-pentanone to the chamber after the irradiation as an internal standard and assuming that the intensities of the $[\text{NO}_2\cdot\text{M}]^-$ ion peaks were proportional to the concentrations of the hydroxycarbonyls, M, present in the chamber (8).

The initial concentrations of CH_3ONO , NO , and 2,2,4-trimethylpentane (or 2,2,4-trimethylpentane- d_{18}) were $\sim(2.4\text{--}4.8) \times 10^{13}$ molecule cm^{-3} each, and irradiations were carried out at the maximum light intensity for 1–3 min (resulting in up to ~15% reaction of the initially present 2,2,4-trimethylpentane).

Chemicals. The chemicals used and their stated purities were as follows: 4,4-dimethyl-2-pentanone (99%), 2,2-dimethylpropanal (97%), 4-hydroxy-4-methyl-2-pentanone (99%), 2-methylpropanal (99+%), octanal (99%), pentafluorobenzyl alcohol (98%), and 2,2,4-trimethylpentanone (99%), Aldrich Chemical Co.; 5-hydroxy-2-pentanone, TCI America; 2,2,4-trimethylpentane- d_{18} (98% atom D), C/D/N Isotopes, Inc.; 3-octyl nitrate, Fluorochem, Inc.; and NO ($\geq 99.0\%$), Matheson Gas Products. Methyl nitrite was prepared as described previously (12) and stored at 77 K under vacuum.

Results

GC-FID and GC-MS Analyses. GC-FID and GC-MS analyses of irradiated $\text{CH}_3\text{ONO-NO-2,2,4-trimethylpentane}$ air mixtures showed the formation of acetone, 2-methylpropanal, and 4-hydroxy-4-methyl-2-pentanone. As discussed below, consideration of the potential reactions involved indicated that a number of other product species that can be observed by gas chromatography could be formed, including acetaldehyde, 2,2-dimethylpropanal, and 4,4-dimethyl-2-pentanone. However, GC-FID analyses showed no evidence for the formation of these three potential products, and upper limits to their concentrations were obtained. Secondary reactions of acetone, 2-methylpropanal, and 4-hydroxy-4-methyl-2-pentanone (and of the potential products acetaldehyde, 2,2-dimethylpropanal, and 4,4-dimethyl-2-pentanone) with the OH radical during these experiments were taken into account as described previously (13) using rate constants for reactions of the OH radical (in units of 10^{-12} cm^3 molecule $^{-1}$ s $^{-1}$) of 2,2,4-trimethylpentane, 3.57 (4); acetaldehyde, 15.8 (14); acetone, 0.219 (14); 2-methylpropanal, 26.3 (14); 4-hydroxy-4-methyl-2-pentanone, 4.0 (15); 2,2-dimethylpropanal, 26.5 (14); and 4,4-dimethyl-2-pentanone, 1.47 [estimated (16)]. The multiplicative factors F to take into account the secondary reactions of OH radicals with the products increase with the rate constant ratio $k(\text{OH} + \text{product})/k(\text{OH} + 2,2,4\text{-trimethylpentane})$ and with the extent of reaction (13), and the maximum values of F were 1.01 for acetone, 1.74 for acetaldehyde, 2.38 for 2-methylpropanal and 2,2-dimethylpropanal, 1.16 for 4-hydroxy-4-methyl-2-pentanone, and 1.06 for 4,4-dimethyl-2-pentanone. The formation yields (or upper limits thereof) of these products obtained by least-squares analyses of the data

TABLE 1. Products Observed and Their Molar Formation Yields, from the OH Radical-Initiated Reactions of 2,2,4-Trimethylpentane (TMP) and 2,2,4-Trimethylpentane-*d*₁₈ (TMP-*d*₁₈) in the Presence of NO

product	GC-FID ^a	API-MS			
		positive ion mode		TMP negative ion mode	
		TMP	TMP- <i>d</i> ₁₈	PFB OH addition	NO ₂ ⁻ adduct
acetone	0.58 ± 0.13 ^b 0.53 ± 0.07 ^b 0.54 ± 0.07^c	obsd	obsd	nd	nd
2-methylpropanal	0.28 ± 0.05 ^b 0.25 ± 0.03 ^b 0.26 ± 0.03^c	obsd	obsd	nd	nd
4-hydroxy-4-methyl-2-pentanone (MW 116)	0.051 ± 0.006	obsd	obsd	obsd	obsd, yield ~0.08
MW 128 product (CH ₃) ₃ CCH ₂ CH(CH ₃)CHO ^d		obsd	obsd	nd	nd
MW 130 product HOCH ₂ C(CH ₃) ₂ CH ₂ C(O)CH ₃ ^d		obsd	obsd	obsd	obsd, yield ~0.03
MW 135 product C ₄ -hydroxyalkyl nitrate ^d		nd	nd	obsd	obsd
MW 144 product (CH ₃) ₂ C(OH)CH ₂ C(CH ₃) ₂ CHO ^d		obsd	obsd	obsd (weak)	obsd, yield ~0.03
MW 177 product C ₇ -hydroxyalkyl nitrate ^d		obsd	obsd ^e	obsd	obsd
MW 191 product C ₈ -hydroxyalkyl nitrate ^d		obsd	obsd ^e	obsd	obsd
potential product					
acetaldehyde	<0.04				
2,2-dimethylpropanal	<0.013				
4,4-dimethyl-2-pentanone	<0.004				

^a Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for 2,2,4-trimethylpentane and products of ±5% each. obsd = observed. nd = not detected. ^b Independent determinations. ^c Weighted average. ^d Attributed, see text and Table 2. ^e Observed as dimers with acetone-*d*₆.

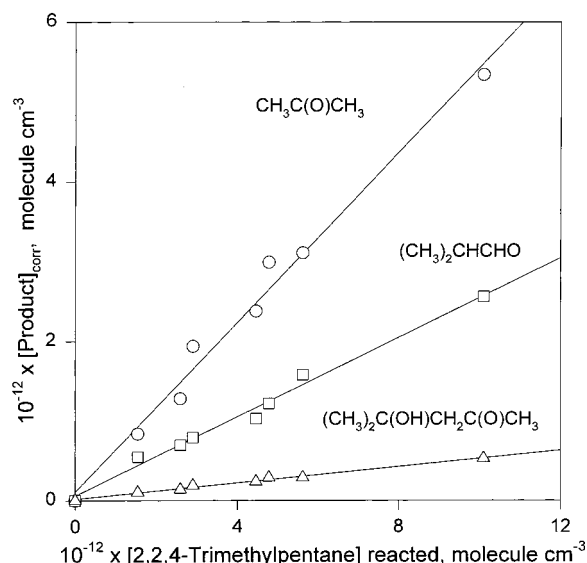


FIGURE 1. Plots of the amounts of acetone, 2-methylpropanal, and 4-hydroxy-4-methyl-2-pentanone formed, corrected for reaction with OH radicals (see text), against the amounts of 2,2,4-trimethylpentane reacted. Quantification by GC-FID.

(Figure 1) are given in Table 1. While no obvious GC peaks were observed in the GC-FID analyses that could be attributed to C₈-carbonyls or to C₈-nitrates, GC-MS analysis of an irradiated CH₃ONO-NO-2,2,4-trimethylpentane-air mixture showed the presence of two closely eluting peaks with high-mass ions at *m/z* 128 [and more intense fragments at *m/z* 127, 109 (-HCO), and 43] and of three peaks with fragment ions at 46 u (interpreted as organic nitrates). However, no isomer-specific identifications could be made, and no obvious corresponding peaks were observed in the GC-FID analyses and hence no quantifications could be made.

API-MS Analyses. A series of CH₃ONO-NO-2,2,4-trimethylpentane (or 2,2,4-trimethylpentane-*d*₁₈)-air irradiations were carried out with analyses using in situ API-MS. In these analyses, the API-MS was operated in the positive ion mode, or in negative ion mode with NO₂⁻ or [PFB OH·O₂]⁻ ions as the ionizing species.

Positive Ion Mode. API-MS/MS product ion and precursor ion spectra were obtained for ion peaks observed in the API-MS analyses of the products of the reactions of OH radicals with 2,2,4-trimethylpentane and 2,2,4-trimethylpentane-*d*₁₈. As noted above, product peaks were observed as protonated molecules and homo- and/or heterodimers. Using the API-MS/MS mode, products were identified based on the consistency of the API-MS/MS product ion spectrum of a protonated homo- or hetero-dimer with the precursor ion spectra of the [M_p + H]⁺ ion peaks (9). The products observed from the OH radical-initiated reaction of 2,2,4-trimethylpentane in the presence of NO and their suggested structures or empirical formulas (see Discussion for reaction schemes leading to these products) are shown in Table 1. The positive ion API-MS and API-MS/MS analyses indicated the formation of products of molecular weight 58 (assumed to be acetone, quantified by GC-FID), 72 (assumed to be 2-methylpropanal, quantified by GC-FID), 116 (assumed to be 4-hydroxy-4-methyl-2-pentanone, quantified by GC-FID), 128, 130, 144, 177, and 191. As expected from their odd molecular weights, API-MS/MS product ion analyses of the [M + H]⁺ ion peaks of the two products of molecular weight 177 and 191 showed the presence of fragment ions at 46 u (NO₂⁺), and these are therefore attributed to organic nitrates. As discussed below, additional evidence of these organic nitrates as well as of a C₄-hydroxyalkyl nitrate of molecular weight 135 was obtained in the negative ion mode.

The low reactivity of 2,2,4-trimethylpentane-*d*₁₈ (17) limited the extent of reaction achieved and the amount of deuterated products formed. However, as noted in Table 1, the API-MS and API-MS/MS analyses of an irradiated CH₃ONO-NO-2,2,4-trimethylpentane-*d*₁₈-air mixture showed evidence for each of the corresponding deuterated products and provided additional structural information. It has previously been observed that an alcohol -OD group, if present, will rapidly exchange to an -OH group (6, 7). Therefore, the fact that the protonated molecule of the following products were fully deuterated (i.e., no exchangeable hydrogens were present) is consistent with their structures being carbonyls or aldehydes: acetone-*d*₆, 2-methylpropanal-*d*₈, and a C₈D₁₆O aldehyde/carbonyl (corresponding to the molecular weight 128 product in Table 1). The API-MS/MS product ion spectra of the 145 u ion peak

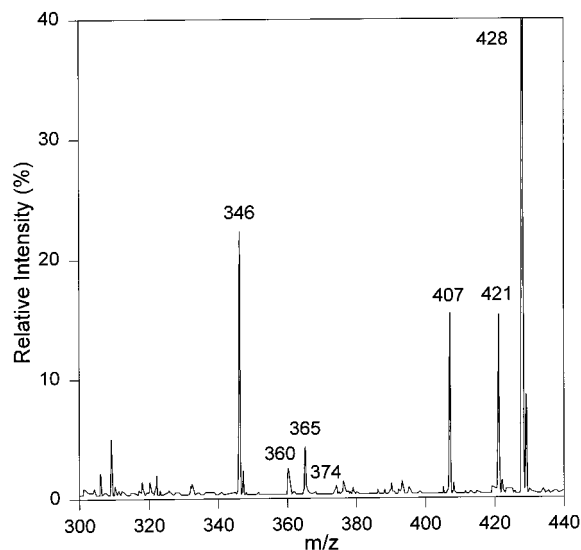


FIGURE 2. API-MS/MS CAD "precursor ion" spectrum (negative ion mode) of the $[\text{PFBOH}\cdot\text{O}_2]^-$ reagent ion in an irradiated $\text{CH}_3\text{ONO}-\text{NO}-2,2,4\text{-trimethylpentane}$ -air mixture. The peaks at 365, 407, and 421 u are tentatively identified as adducts of hydroxynitrates of molecular weight 135, 177, and 191 u, respectively. The peaks at 346, 360, and 374 u are tentatively identified as adducts of hydroxycarbonyls of molecular weight 116 (4-hydroxy-4-methyl-2-pentanone), 130, and 144 u, respectively.

$([\text{M} + \text{H}]^+ \text{ of the } \text{C}_8\text{D}_{16}\text{O product})$ showed losses of HDO and D_2O (but not H_2O), confirming that no -OH group was present in this compound.

Consistent with their assignment as substituted alcohols, the following hydroxycarbonyls/aldehydes were observed as protonated molecules exhibiting an exchange of -OD/-OH: 4-hydroxy-4-methyl-2-pentanone- d_{11} , $\text{C}_7\text{D}_{13}\text{O}(\text{OH})$, and $\text{C}_8\text{D}_{15}\text{O}(\text{OH})$, corresponding to the molecular weight 116, 130, and 144 products in Table 1, respectively. Consistent with their assignment as hydroxynitrates, the deuterated products corresponding to the C_7 - and C_8 -hydroxyalkyl nitrates also exhibited -OD/-OH exchange. API-MS/MS product ion spectra were obtained for the deuterated products corresponding to the molecular weight 144 hydroxycarbonyl and the molecular weight 177 and 191 hydroxynitrate products listed in Table 1, and in each case the CAD product spectrum showed losses including H_2O , indicative of -OD/-OH exchange.

Negative Ion Mode. As noted in the Experimental Section above, the negative ion mode is very sensitive to hydroxy compounds, and the hydroxycarbonyls and hydroxynitrates observed in this mode are listed in Table 1. PFBOH forms adducts with O_2 and certain species M, forming $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$ ions that can be readily fragmented by MS/MS with CAD to give $[\text{PFBOH}\cdot\text{O}_2]^-$. Thus the difference in mass of the precursor $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$ ion and the 230 u $[\text{PFBOH}\cdot\text{O}_2]^-$ product ion is the molecular weight of the product M (8). API-MS and API-MS/MS analyses of irradiated $\text{CH}_3\text{ONO}-\text{NO}-2,2,4\text{-trimethylpentane}$ -air mixtures were carried out in the negative ion mode with PFBOH added to the sampled gas stream. API-MS/MS precursor ion spectra of the 230 u $[\text{PFBOH}\cdot\text{O}_2]^-$ ion showed ion peaks at 346, 360, 365, 374 (weak), 407, 421, and 428 ($[(\text{PFBOH})_2\cdot\text{O}_2]^-$) (Figure 2). Reflecting the high sensitivity for hydroxynitrates and the significant yield of 4-hydroxy-4-methyl-2-pentanone, it was possible to obtain API-MS/MS CAD product ion spectra of the ion peaks at 346, 365, 407, and 421 u. The product ion spectra were consistent with these ion peaks being $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$ ions, confirming molecular weight 116 (4-hydroxy-4-methyl-2-pentanone), 135, 177, and 191 hydroxy-substituted products.

Using NO_2^- as the ionizing agent, $[\text{NO}_2\cdot\text{M}]^-$ adduct ions were observed at 162, 181, 223, and 237 u, corresponding to products of molecular weight 116, 135, 177, and 191. A number of weaker ion peaks were also observed, including peaks corresponding to molecular weight 130 and 144 products. Using 5-hydroxy-2-pentanone as an internal standard added after irradiation of a $\text{CH}_3\text{ONO}-\text{NO}-2,2,4\text{-trimethylpentane}$ -air mixture allowed approximate quantification of presumed hydroxycarbonyl products of molecular weight 116, 130, and 144 with formation yields of ~8%, ~3%, and ~3%, respectively, after correction for secondary reactions using the measured (15) or estimated (16) OH radical reaction rate constants for the products of these molecular weights predicted from the reaction mechanisms [corrections for secondary reactions were only significant for the molecular weight 144 product attributed to $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{CH}_3)_2\text{CHO}$, with an estimated multiplicative correction factor of 1.76]. Thus, the negative ion mode analyses confirmed the formation of the molecular weight 116, 130, 144, 177, and 191 products observed in the positive ion mode analyses and suggested that the molecular weight 116, 130, and 144 products are hydroxycarbonyls (with the molecular weight 116 product being 4-hydroxy-4-methyl-2-pentanone) and that the molecular weight 177 and 191 products are hydroxynitrates. Additionally, the high sensitivity of the negative ion mode allowed detection of a C_4 -hydroxynitrate of molecular weight 135.

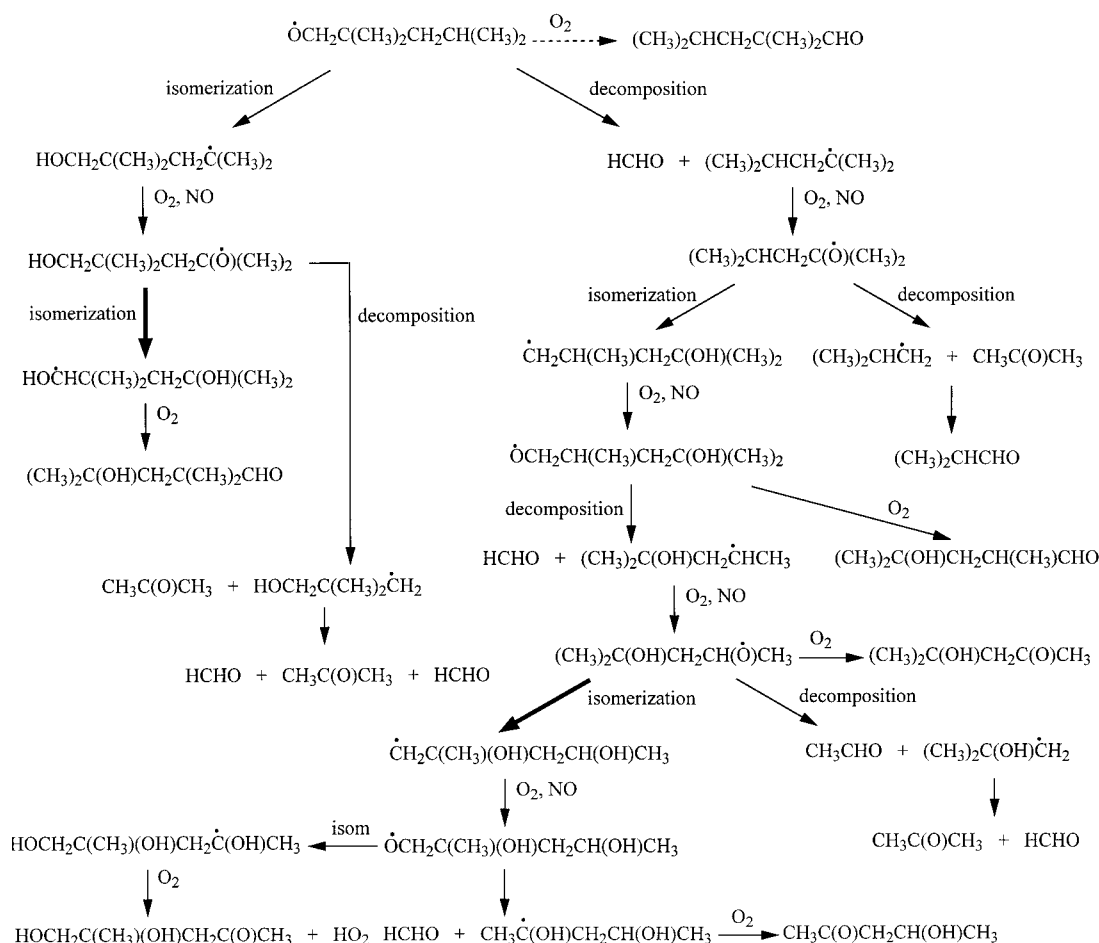
Discussion

The product data given in Table 1 allow the reaction pathways to be delineated to a reasonable extent. OH radicals can react with 2,2,4-trimethylpentane at four positions; the three equivalent CH_3 groups attached to the 2-carbon (11%), the secondary CH_2 group at the 3-position (30%), the tertiary CH group at the 4-position (52%), and the two equivalent CH_3 groups attached to the 4-carbon (7%), where the numbers in parentheses are the percentages of the four reaction pathways calculated using the estimation method of Kwok and Atkinson (16). These calculated percentages may be subject to significant uncertainties, especially because the total rate constant for 2,2,4-trimethylpentane is overpredicted by 30%. In particular, it is likely that the fraction of the overall reaction proceeding by H-atom abstraction from the tertiary C-H bond at the 4-position is overestimated (due to steric hindrance), while the fractions of the overall reaction proceeding by H-atom abstraction from the other C-H bonds are underestimated.

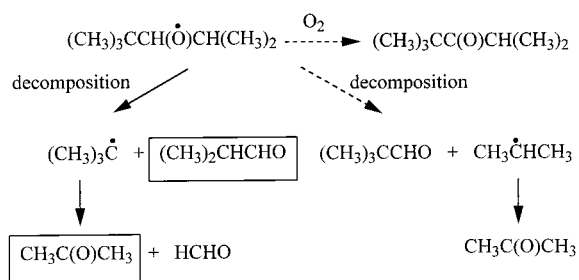
After H-atom abstraction from these various C-H bonds, the resulting alkyl radicals add O_2 to form alkyl peroxy radicals, which under our experimental conditions then react with NO to form the corresponding alkoxy radical ($\text{C}_8\text{H}_{17}\text{O}\cdot$) plus NO_2 or the alkyl nitrate $\text{C}_8\text{H}_{17}\text{ONO}_2$ (of molecular weight 175), as shown in reactions 1-3 in the Introduction. It should be noted that the lack of authentic standards for the four expected $\text{C}_8\text{H}_{17}\text{ONO}_2$ nitrates precluded their identification by gas chromatographic or GC-MS analyses, and under our experimental conditions, API-MS is rather insensitive to alkyl nitrates (8).

As noted in the Introduction, the four $\text{C}_8\text{H}_{17}\text{O}\cdot$ alkoxy radicals can react with O_2 , unimolecularly decompose by C-C bond scission, or isomerize through a six-membered ring transition state to form a 1,4-hydroxyalkyl radical (4, 14, 18), with not all of these reaction pathways being possible for all four alkoxy radicals initially formed from 2,2,4-trimethylpentane. Schemes 1-4 show the potential reactions of the four $\text{C}_8\text{H}_{17}\text{O}\cdot$ alkoxy radicals leading to first-generation products. In these reaction schemes, detailed reactions are omitted for $\text{CH}_3\text{C}\cdot\text{HCH}_3$, $(\text{CH}_3)_3\text{C}\cdot$, $(\text{CH}_3)_2\text{CHC}\cdot\text{H}_2$, and $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\cdot\text{H}_2$ radicals, which are known to react in the atmosphere to form $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, $\text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{HCHO}$, $(\text{CH}_3)_2\text{C}$ -

SCHEME 1



SCHEME 2



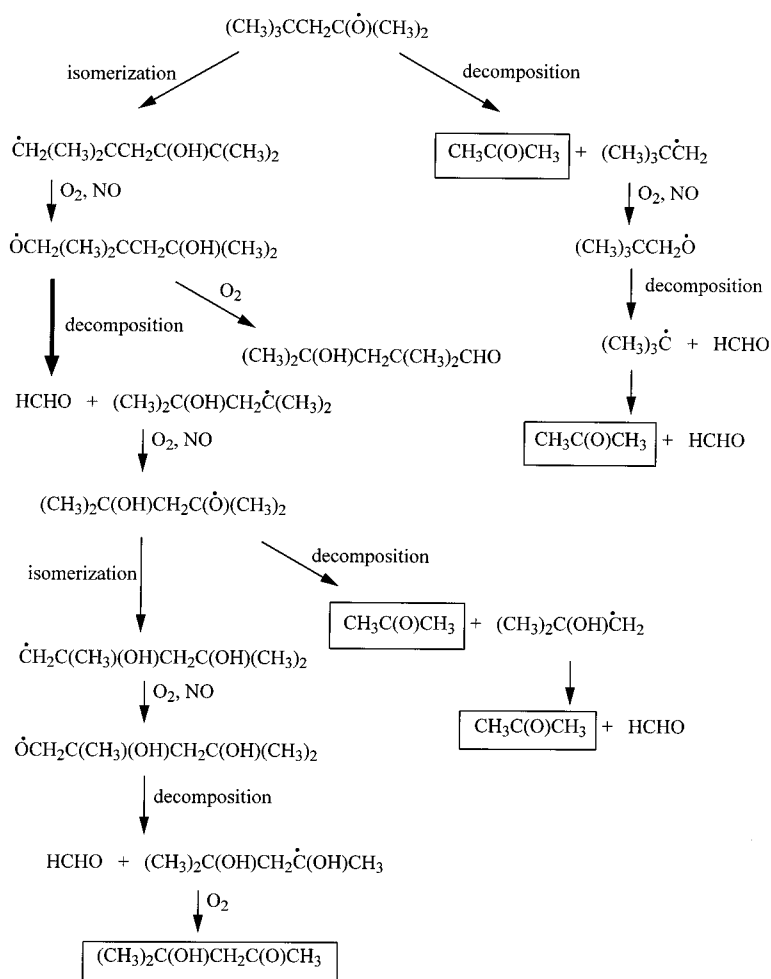
CHCHO , and $\text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{HCHO}$, respectively (4, 14, 18), and decomposition or isomerization of 1,2-hydroxyalkoxy radicals is assumed to dominate over their reaction with O_2 (4, 14, 18–20). The rates of the decomposition, isomerization, and reaction with O_2 of the various alkoxy and hydroxyalkoxy radicals involved in Schemes 1–4 were calculated using the estimation methods described by Atkinson (4, 18), as revised by Aschmann and Atkinson (21). The calculated rates of these reactions are not shown in Schemes 1–4, rather the relative importance of the various reactions of a given alkoxy radical are denoted by the arrows: a dashed arrow indicates that the reaction pathway is estimated to account for $\leq 1\%$ of the overall reaction rate of the alkoxy radical, and a large, boldface, arrow indicates that the reaction pathway is estimated to dominate over the other(s) by a factor of ≥ 10 . The reactions of the four initially formed $\text{C}_8\text{H}_{17}\text{O}\cdot$ radicals are discussed below and compared with the products observed. Considering the product yields (Table 1) and the yields of the precursor alkoxy radicals, the boxes shown in Schemes 2 and 3 indicate how all, or most, of the acetone,

2-methylpropanal, and 4-hydroxy-4-methyl-2-pentanone observed and quantified by GC-FID analyses must originate.

$\text{O}\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ Radical (11% Estimated Yield of Precursor Peroxy Radical). Scheme 1 shows that this alkoxy radical can react with O_2 , decompose, or isomerize with predicted reaction rates at 298 K and atmospheric pressure of air of 4.9×10^4 , 1.1×10^6 , and $5 \times 10^6 \text{ s}^{-1}$, respectively (4, 18, 21). Because isomerization of the $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{O}\cdot)(\text{CH}_3)_2$ radical is predicted to dominate over decomposition by a factor of ~ 20 (4, 18, 21, 22), the dominant predicted product from the $\text{O}\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ radical is the molecular weight 144 compound $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{CH}_3)_2\text{CHO}$ (consistent with our API-MS analyses, including API-MS analyses of the 2,2,4-trimethylpentane-*d*₁₈ reaction where a corresponding product of molecular weight 159 was observed). In addition, acetone + 2-methylpropanal, the molecular weight 130 compound $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$, and the C_8 -hydroxynitrate $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{ONO}_2)(\text{CH}_3)_2$ (products consistent with our GC and API-MS analyses) are predicted to be formed from more minor pathways.

$(\text{CH}_3)_3\text{CCH}(\text{O}\cdot)\text{CH}(\text{CH}_3)_2$ Radical (30% Estimated Yield of Precursor Peroxy Radical). Scheme 2 shows that this alkoxy radical can react with O_2 , decompose to $(\text{CH}_3)_3\text{CCHO} + \text{CH}_3\dot{\text{C}}\text{HCH}_3$, or decompose to $(\text{CH}_3)_2\text{CHCHO} + (\text{CH}_3)_3\text{C}\cdot$ with predicted reaction rates at 298 K and atmospheric pressure of air of 4.1×10^4 , 5.4×10^5 , and $2.4 \times 10^7 \text{ s}^{-1}$, respectively (4, 18, 21). The formation of acetone and 2-methylpropanal as coproducts is therefore anticipated to be essentially the only process for the $(\text{CH}_3)_3\text{CCH}(\text{O}\cdot)\text{CH}(\text{CH}_3)_2$ radical, and our measured formation yield of 2-methylpropanal of $26 \pm 3\%$ is consistent with this expectation

SCHEME 3



(with most or all of the 2-methylpropanal arising from this alkoxy radical decomposition). Furthermore, our lack of observation of 2,2-dimethylpropanal (with a formation yield of $<1.3\%$) confirms the prediction that decomposition of the $(\text{CH}_3)_3\text{CCH}(\text{O}^\bullet)\text{CH}(\text{CH}_3)_2$ radical to $(\text{CH}_3)_3\text{CCHO} + \text{CH}_3\text{C}^\bullet\text{HCH}_3$ is of no importance. Of the $54 \pm 7\%$ molar yield of acetone observed, $26 \pm 3\%$ is presumably associated with 2-methylpropanal, leaving $28 \pm 8\%$ acetone (molar) to be formed via other pathways.

(CH₃)₃CCH₂C(O[•])(CH₃)₂ Radical (52% Estimated Yield of Precursor Peroxy Radical). Scheme 3 shows that this alkoxy radical can decompose or isomerize (but not react with O₂ because of the lack of an abstractable α-H atom). The decomposition and isomerization rates are calculated to be equal at $6 \times 10^5 \text{ s}^{-1}$ (4, 18, 21). The O[•]CH₂C(CH₃)₂-CH₂C(OH)(CH₃)₂ radical formed after the isomerization reaction cannot isomerize and is calculated (4, 18, 21) to dominantly decompose rather than react with O₂. The anticipated major products from the (CH₃)₃CCH₂C(O[•])(CH₃)₂ radical are therefore acetone (with two molecules of acetone formed per molecule of 2,2,4-trimethylpentane reacting) or 4-hydroxy-4-methyl-2-pentanone [(CH₃)₂C(OH)CH₂C(O)-CH₃] (plus 2HCHO) from its isomerization reaction. The reactions of the various hydroxyalkylperoxy radicals formed after the initial isomerization are predicted to form C₈-, C₇-, and C₄-hydroxynitrates, all observed in the API-MS analyses. The predicted dominant decomposition of the (CH₃)₃CCH₂C(O[•])(CH₃)₂ radical [formed by decomposition of the (CH₃)₃CCH₂C(OO[•])(CH₃)₂ radical] is consistent with the observed lack of formation of its O₂ reaction product 2,2-dimethylpropanal (Table 1). Our API-MS and GC data are therefore qualitatively

consistent with predictions, although the sum of the formation yields of acetone plus acetone and of 4-hydroxy-4-methyl-2-pentanone ($19 \pm 5\%$) is significantly lower than the predicted importance of H-atom abstraction from the 4-position (16).

(CH₃)₃CCH₂CH(CH₃)CH₂O[•] Radical (7% Estimated Yield of Precursor Peroxy Radical). Scheme 4 shows that this alkoxy radical can decompose or react with O₂, and the reaction rates of these two processes are predicted to be essentially identical at (5–6) × 10⁴ s^{−1} (4, 18, 21). The (CH₃)₃CCH₂CH(O[•])CH₃ radical formed after the decomposition reaction can react with O₂, decompose or isomerize with estimated rates of 4.1 × 10⁴, 6.9 × 10⁴, and 6 × 10⁵ s^{−1}, respectively (4, 18, 21). Neither 4,4-dimethyl-2-pentanone (which would be the product of the O₂ reaction) nor CH₃CHO (a product of the decomposition reaction), with formation yields of <0.4% and <4%, respectively, were observed, indicating that reaction of the (CH₃)₃CCH₂CH(O[•])CH₃ radical with O₂ is of no importance and that the decomposition of this alkoxy radical probably is not dominant. The O[•]CH₂C-(CH₃)₂CH₂CH(OH)CH₃ radical formed after isomerization of the (CH₃)₃CCH₂CH(O[•])CH₃ radical is predicted to primarily isomerize. Scheme 4 therefore predicts that the major products formed from the (CH₃)₃CCH₂CH(CH₃)CH₂O[•] radical are the molecular weight 128 aldehyde (CH₃)₃CCH₂CH(CH₃)-CHO and the molecular weight 130 hydroxycarbonyl HOCH₂C(CH₃)₂CH₂C(O)CH₃, consistent with our API-MS data. In addition, formation of the C₇-hydroxynitrate CH₃CH(OH)CH₂C(CH₃)₂CH₂ONO₂ is anticipated following isomerization of the (CH₃)₃CCH₂CH(O[•])CH₃ radical.

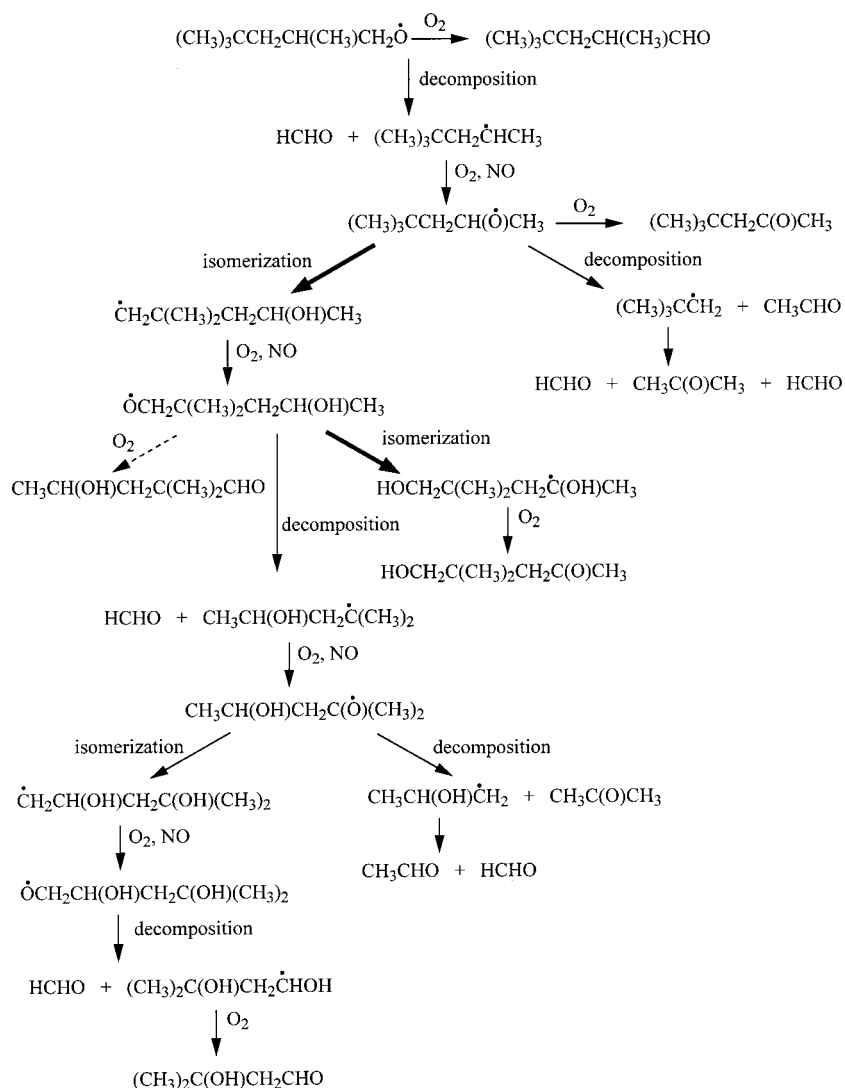
SCHEME 4


TABLE 2. Initially Formed Peroxy Radicals from OH Radical-Initiated Reaction of 2,2,4-Trimethylpentane in the Presence of NO and Observed Products Arising from Their Subsequent Reactions

peroxy radical	estd yield (%)	products formed and yield (%)	observed by
$\text{O}\cdot\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	11	$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{CH}_3)_2\text{CHO}$ (MW 144) (~3%)	API-MS
$(\text{CH}_3)_3\text{CCH}(\text{OO}\cdot)\text{CH}(\text{CH}_3)_2$	30	$\text{HOC}_8\text{H}_{16}\text{ONO}_2$	API-MS
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{OO}\cdot)(\text{CH}_3)_2$	52	$\text{CH}_3\text{C}(\text{O})\text{CH}_3 + (\text{CH}_3)_2\text{CHCHO}$ (26 ± 3%)	GC, API-MS
		2 $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (14 ± 4%)	GC, API-MS
		$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$ (MW 116) (5.1 ± 0.6%)	GC, API-MS
		$\text{HOC}_8\text{H}_{16}\text{ONO}_2$	API-MS
		$\text{HOC}_7\text{H}_{14}\text{ONO}_2$	API-MS
		$\text{HOC}_4\text{H}_8\text{ONO}_2$	API-MS
$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OO}\cdot$	7	$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CHO}$ (MW 128)	API-MS
		$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{CH}_3$ (MW 130) (~3%)	API-MS
		$\text{HOC}_7\text{H}_{14}\text{ONO}_2$	API-MS

Table 2 shows the initially formed peroxy radicals, their predicted formation yields, and the assignment of observed products. The products quantified by GC-FID and those for which approximate [to within a factor of ~2 (8)] formation yields were obtained by API-MS analyses account for 51 ± 10% of the overall products and reaction pathways, with the remainder including alkyl nitrates, hydroxynitrates, and the aldehyde $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CHO}$. In agreement with previous studies of the $\geq \text{C}_4$ alkanes (4–10), our product data show the importance of alkoxy radical isomerization reactions leading to hydroxycarbonyls and hydroxynitrates.

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