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

SARA M. ASCHMANN, JANET AREY, AND ROGER ATKINSON
Air Pollution Research Center, University of California, Riverside, California 92521

Introduction

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-d18 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-methylpropanol, 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 51 ± 0.6%, respectively; upper limits to the formation yields of acetaldehyde, 2,2-dimethylpropanol, 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 C6-carbonyl), and hydroxynitrates of molecular weight 135, 177, and 191 (attributed to HOC4H8ONO2, HOC7H14ONO2, and HOC 8H16ONO2, respectively). Formation of HOC8H16ONO2 and HOC7H14ONO2, respectively, in the API–MS analyses of the 2,2,4-trimethylpentane-d18 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.

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):

\[
\text{RO}^+ + \text{O}_2 \rightarrow \text{RO}_2^+ \quad (1)
\]

\[
\text{R}^+ + \text{O}_2 \rightarrow \text{RO}_2^+ \quad (2)
\]

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 alkyl radical plus NO2 (4):

\[
\text{RO}_2^+ + \text{NO} \rightarrow \text{RONO}_2 \quad (3a)
\]

\[
\text{RO}_2^+ + \text{NO} \rightarrow \text{RO}^+ + \text{NO}_2 \quad (3b)
\]

The alkoxo 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 pathway is invoked for C4 alkanes, forms a 1,4-hydroxylalkyl radical that adds O2, giving a 1,4-hydroxylalkyl peroxy radical. The 1,4-hydroxylalkyl 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-d18 was also used in the experiments with API–MS analyses to aid in the interpretation of the API–MS spectra.
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: CH₂ONO, (2.2–2.4) × 10¹⁶; NO, (1.9–2.2) × 10¹⁴; and 2,2,4-trimethylpentane, (2.24–3.02) × 10¹³. 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 cm³ 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 NO₂ concentrations were measured using a Thermo Environmental Instruments, Inc., model 42 NO–NO₂–NO, chemiluminescence analyzer.

Analyses 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 (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, H₂O+(H₂O)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 ([M + H⁺]) and their protonated homo- and heterodimers. Product peaks were identified based on the observation of homo- or heterodimers (for example, [M₁₂₂ + H⁺], ([M₂₂₂ + H⁺], and [M₃₂₂ + H⁺]), where P1 and P2 are products) in the API–MS/MS mode in precursor ion spectra of the [M + H⁺] ion peaks and confirmed by consistency of the API–MS/MS product ion spectra 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 (O₂⁻), its hydrates [O₂(H₂O)ₙ]⁻, and O₂ clusters [O₂(O₂)n]⁻ are the major reagent negative ions in the chamber pure air. Other reagent ions, for example, NO₂⁻ and NO₃⁻, are formed through reactions between the primary reagent ions and the neutral molecules such as NO. Instrument tuning and operation were designed to induce adduct formation. Two species served as reagent ions in this work; NO₂⁻ present in the irradiated CH₂ONO–NO₂–2,2,4-trimethylpentane–air mixtures and [PFBOH-O₂⁻]⁻ (where PFBOH = pentafluorobenzyl alcohol; C₆F₅CH₂OH) 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 (NO₂⁻ or [PFBOH-O₂⁻]⁻), where M can also be PFBOH when PFBOH was added to the sampled airstream:

\[
\text{[PFBOH-O}_2\text{]}^{-} + M \rightarrow \text{[PFBOH-O}_2\text{]M}^{-}
\]

\[
\text{NO}_2^{-} + M \rightarrow \text{[NO}_2\text{]M}^{-}
\]

Previous work in this laboratory (8, 10) indicated that the use of NO₂⁻ or [PFBOH-O₂⁻]⁻ reagent ions allows primarily hydroxyl compounds to be detected (for example, hydroxycarbonyls and hydroxynitrates). When NO₂⁻ 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 [NO₂⁻ M]⁻ ion peaks were proportional to the concentrations of the hydroxycarbonyls, M, present in the chamber (8).

The initial concentrations of CH₂ONO, NO, and 2,2,4-trimethylpentane (or 2,2,4-trimethylpentane-d₈) were (∼2.4–4.8) × 10¹⁶ 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 (99%), 4-hydroxy-4-methyl-2-pentanone (99%), 2-methylpropanal (99.1%), octanal (99%), pentafluorobenzyl alcohol (98%), and 2,2,4-trimethylpentane (99%), Aldrich Chemical Co.; 5-hydroxy-2-pentanone, TCI America; 2,2,4-trimethylpentane-d₈ (98% atom D), C/D/N Isotopes, Inc.; 3-oxyl nitrate, Fluorochem, Inc.; and NO (≥ 99.0%), Matheson Gas Products. Methyl nitrate 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 CH₂ONO–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 acetalddehyde, 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 acetalddehyde, 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 cm³ molecule⁻¹ s⁻¹) of 2,2,4-trimethylpentane, 3.57 (4); acetaldheyde, 15.8 (14), aceton, 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(OH + product)/k(OH + 2,2,4-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-d18 (TMP-d18) in the Presence of NO

<table>
<thead>
<tr>
<th>Product</th>
<th>GC-FID</th>
<th>Positive ion mode</th>
<th>Negative ion mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TMP</td>
<td>TMP-d18</td>
</tr>
<tr>
<td>acetone</td>
<td>0.58 ± 0.13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>2-methylpropanal</td>
<td>0.53 ± 0.07&lt;sup&gt;b&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>4-hydroxy-4-methyl-2-pentanone (MW 116)</td>
<td>0.54 ± 0.07&lt;sup&gt;c&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>MW 128 product (CH3)2CCH2CH(CH3)CHO&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.28 ± 0.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>MW 130 product HOCH2C(CH3)2CH2C(O)CH3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.25 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>MW 135 product C4-hydroxyalkyl nitrate&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.26 ± 0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>MW 144 product (CH3)2C(OH)CH2C(CH3)2CHO&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.051 ± 0.006</td>
<td>obsd</td>
<td>nd</td>
</tr>
<tr>
<td>MW 177 product C4-hydroxyalkyl nitrate&lt;sup&gt;d&lt;/sup&gt;</td>
<td>obsd</td>
<td>obsd</td>
<td>obsd, yield ~0.03</td>
</tr>
<tr>
<td>MW 191 product C4-hydroxyalkyl nitrate&lt;sup&gt;d&lt;/sup&gt;</td>
<td>obsd</td>
<td>obsd</td>
<td>obsd</td>
</tr>
</tbody>
</table>

<sup>a</sup> 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. <sup>b</sup> Independent determinations. <sup>c</sup> Weighted average. <sup>d</sup> Attributed, see text and Table 2. 

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 C4-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-d18)—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 [PFBOH-O2]<sup>−</sup> 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-d18. 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 + H]<sup>+</sup> 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]<sup>+</sup> ion peaks of the two products of molecular weight 177 and 191 showed the presence of fragment ions at 46 u (NO2<sup>−</sup>), 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-d18 (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-d18—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-d6, 2-methylpropanal-d6, and a C4H9O 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...
Using NO$_3^-$ as the ionizing agent, [NO$_2^-$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 CH$_3$ONO–NO–2,2,4-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 (CH$_3$)$_2$C(OH)CH$_2$C(CH$_3$)$_2$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$_6$ hydroxynitrinate 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 alky radicals add O$_2$ to form alkyl peroxy radicals, which under our experimental conditions then react with NO to form the corresponding alkoxy radical (C$_3$H$_7$O$_2^-$) plus NO$_2$, or the alkoxy nitrate C$_3$H$_7$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 C$_3$H$_7$ONO$_2$ nitrates precluded their identification by gas chromatographic or GC–MS analyses, and under our experimental conditions, API–MS is rather insensitive to alkoxy nitrates (8).

As noted in the Introduction, the four C$_3$H$_7$O$_2$ 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 C$_3$H$_7$O$_2$ alkoxy radicals leading to first-generation products. In these reaction schemes, detailed reactions are omitted for CH$_2$CH$_2$CHO, CH$_3$CHO, and CH$_3$C(=O)CH$_2$ radicals, which are known to react in the atmosphere to form CH$_3$C(O)CH$_3$, CH$_3$C(O)CH$_3$ + HCHO, (CH$_3$)$_2$C(=O)CH$_2$CH$_3$, and (CH$_3$)$_2$C(=O)CH$_2$C(=O)CH$_3$. Schemes 1 and 2 show the reaction of 1,4-hydroxyalkyl radicals with NO; the peroxyalkyl radicals formed (C$_3$H$_7$O$_3^-$) react with water to form hydroxynitrate ions (C$_3$H$_7$ONOOH$^-$), which in turn react with NO to form alkoxy nitrate ions. In scheme 3, the 1,4-hydroxyalkyl radical is oxidized directly to the peroxyalkyl radical; in scheme 3, the peroxyalkyl radical is oxidized directly to the peroxyalkyl radical.
CHCHO, and CH₃C(O)CH₃ + HCHO, respectively (4, 14, 18), and decomposition or isomerization of 1,2-hydroxyalkoxy radicals is assumed to dominate over their reaction with O₂ (4, 14, 18–20). The rates of the decomposition, isomerization, and reaction with O₂ 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 ≤ 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 C₆H₅O⁺ 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.

O’C₆H₅C(CH₃)₂CH₂CH(CH₃)₂ Radical (11% Estimated Yield of Precursor Peroxy Radical). Scheme 1 shows that this alkoxy radical can react with O₂, decompose, or isomerize with predicted reaction rates at 298 K and atmospheric pressure of air of 4.9 × 10⁴, 1.1 × 10⁶, and 5 × 10⁶ s⁻¹, respectively (4, 18, 21). Because isomerization of the HOCH₂C(CH₃)₂CH₂CH(OH)CH₃ radical is predicted to dominate over decomposition by a factor of ~20 (4, 18, 21, 22), the dominant predicted product from the O’C₆H₅C(CH₃)₂CH₂CH(OH)CH₃ radical is the molecular weight 144 compound (CH₃)₂C(OH)CH₂CH₂CH(CH₃)₂CHO (consistent with our API–MS analyses, including API–MS analyses of the 2,2,4-trimethylpentane-d₁₈ reaction where a corresponding product of molecular weight 159 was observed). In addition, acetone + 2-methylpropanal, the molecular weight 130 compound (CH₃)₂C(OH)CH₂CH₂CH(CH₃)₂CHO, and the C₆-hydroxynitrate HOCH₂C(CH₃)₂CH₃C(ONO₂)(CH₃)₂ (products consistent with our GC and API–MS analyses) are predicted to be formed from more minor pathways.

(2CH₃)₃CC(O’CH₃)CH(CH₃)₂ Radical (30% Estimated Yield of Precursor Peroxy Radical). Scheme 2 shows that this alkoxy radical can react with O₂, decompose to (CH₃)₂CC(O)CH(CH₃)₂, or decompose to (CH₃)₂CHCHO + (CH₃)₂C³⁻ with predicted reaction rates at 298 K and atmospheric pressure of air of 4.1 × 10⁴, 5.4 × 10⁵, and 2.4 × 10⁷ 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 (CH₃)₂CC(O’CH₃)CH(CH₃)₂ radical, and our measured formation yield of 2-methylpropanal of 26 ± 3% is consistent with this expectation.
(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 \((\text{CH}_3)_3\text{CCH(O)}\cdot\text{CH}_2\text{C}(-\text{H})\cdot\text{CH}_3\) radical to \((\text{CH}_3)_3\text{CCHO} + \text{CH}_3\text{C}(-\text{H})\cdot\text{HCH}_3\) is of no importance. Of the 54 ± 7 molar yield of acetone observed, 26 ± 3% is presumably associated with 2-methylpropanal, leaving 28 ± 8% acetone (molar) to be formed via other pathways.

\((\text{CH}_3)_2\text{CCH}_2\text{C}(-\text{O})\cdot\text{CH}_3\) Radical (52% Estimated Yield of Precursor Peroxy Radical). Scheme 3 shows that this alkoxy radical can decompose or isomerize (but not react with \(\text{O}_2\) because of the lack of an abstractable \(\alpha\)-H atom). The decomposition and isomerization rates are calculated to be equal at \(6 \times 10^5\) s\(^{-1}\) (4, 18, 21). The \((\text{CH}_3)_3\text{CCH(O)}\cdot\text{CH}_3\) radical formed after the isomerization reaction cannot isomerize and is calculated (4, 18, 21) to dominantly decompose rather than react with \(\text{O}_2\). The anticipated major products from the \((\text{CH}_3)_3\text{CCH}_2\text{C}(-\text{O})\cdot\text{CH}_3\) 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 \([(\text{CH}_3)_2\text{C(OH)}\cdot\text{CH}_2\text{C(O)}\cdot\text{CH}_3\) plus 2HCHO] from its isomerization reaction. The reactions of the various hydroxalkyloxy radicals formed after the initial isomerization are predicted to form \(\text{C}_9\), \(\text{C}_7\), and \(\text{C}_4\) hydroxynitrates, all observed in the API-MS analyses. The predicted dominant decomposition of the \((\text{CH}_3)_3\text{CCH}_2\text{O}^\cdot\text{CH}_3\) radical [formed by decomposition of the \((\text{CH}_3)_3\text{CCH}_2\text{O}^\cdot\text{CH}_3\) radical] is consistent with the observed lack of formation of its \(\text{O}_2\) 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 ± 5\%) is significantly lower than the predicted importance of H-atom abstraction from the 4-position (16).

\((\text{CH}_3)_3\text{CCH}_2\text{CH(\text{O})\cdot\text{CH}_3}\) Radical (7% Estimated Yield of Precursor Peroxy Radical). Scheme 4 shows that this alkoxy radical can decompose or react with \(\text{O}_2\), and the reaction rates of these two processes are predicted to be essentially identical at \((5-6) \times 10^5\) s\(^{-1}\) (4, 18, 21). The \((\text{CH}_3)_3\text{CCH}_2\text{CH(O)}\cdot\text{CH}_3\) radical formed after the decomposition reaction can react with \(\text{O}_2\), decompose or isomerize with estimated rates of \(4.1 \times 10^5\), \(6.9 \times 10^4\), and \(6 \times 10^3\) s\(^{-1}\), respectively (4, 18, 21). Neither 4,4-dimethyl-2-pentanone (which would be the product of the \(\text{O}_2\) reaction) nor \(\text{CH}_3\text{CHO}\) (a product of the decomposition reaction), with formation yields of \(<0.4\%\) and \(<4\%\), respectively, were observed, indicating that reaction of the \((\text{CH}_3)_3\text{CCH}_2\text{CH(O)}\cdot\text{CH}_3\) radical with \(\text{O}_2\) is of no importance and that the decomposition of this alkoxy radical probably is not dominant. The \((\text{CH}_3)_3\text{CCH}_2\text{CH(\text{O})\cdot\text{CH}_3}\) radical is predicted to primarily isomerize. Scheme 4 therefore predicts that the major products formed from the \((\text{CH}_3)_3\text{CCH}_2\text{CH(\text{O})\cdot\text{CH}_3}\) radical are the molecular weight 128 aldehyde \((\text{CH}_3)_3\text{CCH}_2\text{CHO}\) and the molecular weight 130 hydroxycarbonyl \(\text{HOCH}_2\text{C(CH}_3)_2\text{CH}_2\text{C(O)}\cdot\text{CH}_3\) consistent with our API-MS data. In addition, formation of the \(\text{C}_7\) hydroxynitrile \(\text{CH}_3\text{CH(OH)}\cdot\text{CH}_2\text{C(CH}_3)_2\text{CH}_2\text{ONO}_2\) is anticipated following isomerization of the \((\text{CH}_3)_3\text{CCH}_2\text{CH(O)}\cdot\text{CH}_3\) radical.
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 formation yields were obtained by API-MS analyses account for 51% of the overall products and reaction pathways, with the remainder including alkyl nitrates, hydroxynitrates, and the aldehyde (CH₃)₃CCH₂CH(CH₃)CHO. In agreement with previous studies of the C₄ alkanes (4-10), our product data show the importance of alkoxy radical isomerization reactions leading to hydroxycarbonyls and hydroxynitrates.

Acknowledgments
The authors thank the U.S. Environmental Protection Agency, National Center for Environmental Research and Quality Assurance (Grant R-825252-01-0) and the California Air Resources Board (Contract 99-330) for supporting this research. The statements and conclusions are those of the authors and not necessarily those of the funding Agencies.

Literature Cited


Received for review July 13, 2001. Revised manuscript received October 23, 2001. Accepted October 29, 2001.

ES011134V