Products and Mechanism of the Reaction of OH Radicals with 2,3,4-Trimethylpentane in the Presence of NO

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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. Using a relative rate method, a rate constant for the reaction of OH radicals with 2,3,4-trimethylpentane of $(6.84 \pm 0.12) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \pm 2 \text{ K}$ was measured, where the indicated error is two leastsquares standard deviations and does not include the uncertainty in the rate constant for the *n*-octane reference compound. Products of the gas-phase reaction of OH radicals with 2,3,4-trimethylpentane in the presence of NO at 298 \pm 2 K and atmospheric pressure of air have been investigated using gas chromatography with flame ionization detection (GC-FID), combined gas chromatographymass spectrometry (GC-MS), and in situ atmospheric pressure ionization tandem mass spectrometry (API-MS). Products identified and quantified by GC-FID and GC-MS were (molar yields given in parentheses): acetaldehyde $(47 \pm 6\%)$, acetone (76 \pm 11%), 3-methyl-2-butanone (41 \pm 5%), 3-methyl-2-butyl nitrate (1.6 \pm 0.2%), and 2-propyl nitrate (6.2 \pm 0.8%). These compounds account for 69 \pm 6% of the reaction products, as carbon. Additional products observed by API-MS analyses using positive and negative ion modes were C5- and C8-hydroxynitrates and a C8hydroxycarbonyl, which, together with the predicted formation of octyl nitrates, account for some or all of the remaining products. The product distribution is compared to those for the linear and branched C₈-alkanes n-octane and 2,2,4trimethylpentane.

Introduction

Alkanes are important constituents of gasoline fuel (1) and vehicle exhaust (1), and account for \sim 50% of the nonmethane organic compounds observed in urban atmospheres (2, 3). In the troposphere, alkanes react mainly with the OH radical (4), initiating a series of reactions which, in the presence of NO, lead to formation of alkoxy radicals and alkyl nitrates (4, 5):

$$OH + RH \rightarrow H_2O + R^{\bullet}$$
(1)

$$\mathbf{R}^{\bullet} + \mathbf{O}_2 \to \mathbf{RO}_2^{\bullet} \tag{2}$$

$$\operatorname{RO}_{2}^{\bullet} + \operatorname{NO}(+ M) \rightarrow \operatorname{RONO}_{2}(+ M)$$
 (3a)

$$\mathrm{RO}_{2}^{\bullet} + \mathrm{NO} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{NO}_{2}$$
 (3b)

The alkoxy radicals formed in reaction 3b then react with O_2 , decompose by C–C bond scission, or isomerize through a six-membered ring transition state (4, 5). The isomerization reaction results in formation of a 1,4-hydroxyalkyl radical. After reactions analogous to reactions 2 and 3a, the 1,4-hydroxyalkyl radicals lead to 1,4-hydroxynitrates and, after reactions analogous to reactions 2 and 3b followed by reaction with O_2 , to 1,4-hydroxycarbonyls (4–11).

Rate constants for the reactions of the OH radical with a number of alkanes have been measured (4, 12). While there have been a number of studies of the products formed from the OH radical-initiated reactions of alkanes (6-11, 13-23), most of these have concerned *n*-alkanes (6-11, 15, 16, 19)and cycloalkanes (10, 14, 20-22); several were concerned solely with alkyl nitrate formation (15-19). Branched alkanes account for \sim 30–50% of the alkanes other than methane in urban areas (2, 3), and comprehensive product studies have only been reported for 2,2,4-trimethylpentane (23) and 3,4diethylhexane (10). In this work, we have investigated the kinetics and products of the OH radical-initiated reaction of 2,3,4-trimethylpentane [(CH₃)₂CHCH(CH₃)CH(CH₃)₂] in the presence of NO. The products of this reaction and the relative importance of the three potential reactions (decomposition, isomerization, and reaction with O_2) of the intermediate alkoxy radicals are then compared to those for the corresponding *n*-octane (9, 11) and 2,2,4-trimethylpentane (23) reactions.

Experimental Methods

Experiments were carried out at 298 ± 2 K and 740 Torr total pressure of air at ~5% relative humidity in a ~7500 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 black lamps, and in a ~7500 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 black lamps. 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 (9-11, 23), and NO was added to the reactant mixtures to suppress the formation of O₃ and hence of NO₃ radicals.

Kinetic Studies. The rate constant for the reaction of OH radicals with 2,3,4-trimethylpentane was measured using a relative rate method, in which the relative decay rates of 2,3,4-trimethylpentane and a reference compound, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals (*10*). Providing that 2,3,4-trimethylpentane and the reference compound (*n*-

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octane in this case) were removed only by reaction with OH radicals, then

$$\ln\left(\frac{[2,3,4-\text{TMP}]_{t_o}}{[2,3,4-\text{TMP}]_t}\right) = \frac{k_1}{k_4}\ln\left(\frac{[n-\text{octane}]_{t_o}}{[n-\text{octane}]_t}\right) \tag{I}$$

where $[2,3,4-\text{TMP}]_{t_0}$ and $[n\text{-octane}]_{t_0}$ are the concentrations of 2,3,4-trimethylpentane and *n*-octane at time t_0 , respectively; $[2,3,4-\text{TMP}]_t$ and $[n\text{-octane}]_t$ are the corresponding concentrations at time t; and k_1 and k_4 are the rate constants for reactions 1 and 4, respectively:

$$OH + 2,3,4$$
-trimethylpentane \rightarrow products (1)

$$OH + n$$
-octane \rightarrow products (4)

Hence a plot of $\ln([2,3,4-\text{trimethylpentane}]_{t_0}/[2,3,4-\text{trimethylpentane}]_{t_0}$ against $\ln([n-\text{octane}]_{t_0}/[n-\text{octane}]_{t_0})$ should be a straight line of slope k_1/k_4 and zero intercept.

A series of $CH_3ONO-NO-2,3,4$ -trimethylpentane-noctane-air irradiations were carried out, with initial concentrations (molecule cm⁻³) of CH₃ONO, \sim 2.4 × 10¹⁴; NO, \sim 2.4 \times 10¹⁴; and 2,3,4-trimethylpentane and *n*-octane, \sim 2.4 \times 10^{13} each. Irradiations were carried out at 20% of the maximum light intensity for 15-65 min. 2,3,4-Trimethylpentane and *n*-octane were analyzed by GC-FID, using two different procedures. In one procedure, gas samples of 100 cm³ volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at \sim 250 °C onto a 30 m DB-5MS megabore column, initially held at -40 °C and then temperature programmed to 200 °C at 8 °C min⁻¹. In the second procedure, gas samples were collected from the chamber into 100 cm³ volume gastight, all-glass syringe and transferred via a 1 cm³ gas sampling valve onto a 30 m DB-5 megabore column, initially held at -25 °C and then temperature programmed to 200 °C at 8 °C \min^{-1} .

Product Studies. (a) Analyses by GC-FID and GC-MS. Products were investigated from a series of CH₃ONO-NO-2,3,4-trimethylpentane-air irradiations, with initial reactant concentrations (molecule cm⁻³) of CH₃ONO, $\sim 2.4 \times 10^{14}$; NO, \sim 2.4 \times 10¹⁴; and 2,3,4-trimethylpentane, (2.69–2.93) \times 10¹³. Irradiations were carried out at 20% of the maximum light intensity for 10-60 min, resulting in up to 50% reaction of the initially present 2,3,4-trimethylpentane. The concentrations of 2,3,4-trimethylpentane and reaction products were measured during the experiments by GC-FID, using the solid adsorbent/thermal desorption procedure described above. 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 5971 mass selective detector operating in the scanning mode. GC-FID response factors were determined as described previously (24). NO and initial NO₂ concentrations were measured using a Thermo Environmental Instruments, Inc., model 42 NO-NO₂-NO_x chemiluminescence analyzer.

(b) 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 \sim 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 (9, 20). 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 (9, 20). Both positive and negative ion modes were used in this work.

In the positive ion mode, protonated water clusters, H_3O^+ - $(H_2O)_n$, formed from a corona discharge in the chamber



FIGURE 1. Plot of eq I for the reaction of OH radicals with 2,3,4-trimethylpentane, with *n*-octane as the reference compound. (\bigcirc) Syringe collection/gas sampling loop procedure; (\Box) Tenax solid adsorbent/thermal desorption procedure.

diluent air (at \sim 5% relative humidity) are the reagent ion and a range of oxygenated species can be observed in this mode of operation (9, 20). In the negative ion mode, the superoxide ion (O_2^{-}) , its hydrates $[O_2(H_2O)_n]^{-}$, and O_2 clusters $[O_2(O_2)_n]^-$ 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 neutral molecules such as NO2, and instrument tuning and operation were designed to induce cluster formation. NO2⁻ present in the irradiated CH3ONO-NO-2,3,4-trimethylpentane-air mixtures was used as the reagent ion in the negative ion mode analyses (9). Analytes were then detected as adducts, [NO2·M]-, formed between the neutral analyte (M) and NO_2^- (9, 10). Previous work in this laboratory (9) indicates that the use of NO₂⁻ reagent ions allows primarily hydroxy compounds to be detected (for example, hydroxycarbonyls and hydroxynitrates).

In the positive or negative ion modes, ions are then 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). The initial concentrations of CH₃-ONO, NO, and 2,3,4-trimethylpentane were ~ 2.4×10^{13} molecule cm⁻³ each, and irradiations were carried out at 20% of the maximum light intensity for 10 min.

Chemicals. The chemicals used (and their stated purities) were as follows: acetaldehyde (99.5+%), 3-methyl-2-butanone (99%), *n*-octane (99+%), and 2,3,4-trimethylpentane (98%), Aldrich Chemical Co.; acetone (HPLC grade), Fisher Scientific; 2-propyl nitrate, Eastman Chemical Company; 3-methyl-2-butyl nitrate and 3-octyl nitrate, Fluorochem, Inc.; and NO (\geq 99.0%), Matheson Gas Products. Methyl nitrite was prepared as described by Taylor et al. (*25*) and stored at 77 K under vacuum.

Results

Kinetics. The data obtained from a series of CH₃ONO–NO– 2,3,4-trimethylpentane–*n*-octane–air irradiations are plotted in accordance with eq I in Figure 1. Independent sets of experiments were carried out using (a) collection of gas samples in gastight syringes with transfer to the DB-5 column through a gas sampling valve and (b) collection of gas samples



FIGURE 2. Plots of the amounts of acetaldehyde, acetone, and 3-methyl-2-butanone formed, corrected for reaction with the OH radical (see text), against the amounts of 2,3,4-trimethylpentane reacted. The data for acetaldehyde and acetone have been displaced vertically by 2.0 \times 10^{12} molecule cm $^{-3}$ for clarity.

onto Tenax solid adsorbent with thermal desorption onto a DB-5MS column. As evident from Figure 1, the agreement between these data sets is excellent, and a least-squares analysis of the entire data set leads to a rate constant ratio of $k_1/k_4 = 0.844 \pm 0.014$, where the indicated error is two least-squares standard deviations. This rate constant ratio can be placed on an absolute basis by use of a rate constant for the reaction of OH radicals with *n*-octane of $k_4 = 8.11 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K (4, 12), leading to $k_1 = (6.84 \pm 0.12) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 ± 2 K where the indicated error does not include the uncertainty in the rate constant k_4 (which is expected (12) to be ~±10%).

Products. (a) GC-FID and GC–MS Analyses. GC-FID and GC–MS analyses of irradiated CH₃ONO–NO–2,3,4-trimethylpentane–air mixtures showed the formation of acetaldehyde, acetone, 3-methyl-2-butanone [CH₃C(O)CH-(CH₃)₂], 2-propyl nitrate, 3-methyl-2-butyl nitrate, and a nitrate that eluted at around the same time as 3-octyl nitrate and, hence, is presumed to be a C₈ alkyl nitrate.

Secondary reactions of acetaldehyde, acetone, 3-methyl-2-butanone, 2-propyl nitrate, 3-methyl-2-butyl nitrate, and the C₈-nitrate with the OH radical during these experiments were taken into account as described previously (15) using rate constants for reactions of the OH radical (in units of 10^{-12} cm³ molecule⁻¹ s⁻¹) of 2,3,4-trimethylpentane, 6.84 (this work); acetaldehyde, 15 (26); acetone, 0.17 (26); 3-methyl-2-butanone, 2.87 (27); 2-propyl nitrate, 0.29 (26); 3-methyl-2-butyl nitrate, 1.6 (17) [re-evaluated to be consistent with the most recent rate constant (4, 12) for the n-butane reference compound]; and C₈-nitrate, \sim 3.6 [estimated (28)]. 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 (15), and the maximum values of F were 1.01 for acetone, 2.10 for acetaldehyde, 1.17 for 3-methyl-2-butanone, 1.02 for 2-propyl nitrate, 1.09 for 3-methyl-2-butyl nitrate, and 1.22 for the C₈-nitrate. Plots of the amounts of products formed, corrected for secondary reactions, against the amounts of 2,3,4trimethylpentane reacted are shown in Figure 2 for acetaldehyde, acetone, and 3-methyl-2-butanone and in Figure 3 for 2-propyl nitrate and 3-methyl-2-butyl nitrate. The forma-



FIGURE 3. Plots of the amounts of 2-propyl nitrate and 3-methyl-2-butyl nitrate formed, corrected for reaction with the OH radical (see text), against the amounts of 2,3,4-trimethylpentane reacted.

tion yields of these products obtained by least-squares analyses of the data are given in Table 1. Note that the GC-FID analyses are relatively insensitive to acetaldehyde and 2-propyl nitrate because of their low GC-FID response factors; hence, only small GC peaks were observed for these products, especially for 2-propyl nitrate given its low formation yield.

(b) API-MS Analyses. Analyses of an irradiated CH₃ONO-NO-2,3,4-trimethylpentane-air mixture were carried out using in situ API-MS in both positive and negative ion mode. In the positive ion mode, API-MS/MS "product ion" and "precursor ion" spectra were obtained for ion peaks observed in the API-MS analyses. Product peaks were identified based on the observation of homo- or heterodimers (for example, $[(M_{P1})_2 + H]^+$, $[(M_{P2})_2 + H]^+$, and $[M_{P1} + M_{P2} + H]^+$, where P1 and P2 are products) in the API-MS/MS precursor ion spectra and consistency of the API-MS/MS product ion spectrum of a homo- or heterodimer ion with the precursor ion spectra of the $[M_P + H]^+$ ion peaks (9, 20). Water cluster ion peaks of the product ions, $[M + H + H_2O]^+$, were also occasionally observed. The products observed from the OH radical-initiated reaction of 2,3,4-trimethylpentane in the presence of NO are listed in Table 1. The positive ion API-MS and API-MS/MS analyses indicate the formation of products of molecular weight 58 and 86, attributed to acetone and 3-methyl-2-butanone, respectively, both of which were also identified and quantified by GC-FID. A product of molecular weight 191 and a product of molecular weight 144 were also observed and, as discussed below, are attributed to a C8hydroxynitrate and a C₈-hydroxycarbonyl, respectively.

The product of molecular weight 191 was present in the API-MS spectra as its protonated heterodimers with acetone and 3-methyl-2-butanone at 250 and 278 u, respectively, and the API-MS/MS product ion spectra of these ion peaks showed the presence of a 46 u fragment ion, attributed to NO_2^+ . Hence the molecular weight 191 product is attributed to an organic nitrate. The evidence for the presence of the molecular weight 144 product was less direct, because the API-MS/MS product ion spectra of the 145 u ion peak observed in the API-MS spectra showed no appreciable fragment ion due to expected loss of H_2O from the $[M + H]^+$ ion of the hydroxycarbonyl; rather, the fragment ions were those expected for a protonated heterodimer of acetone and 3-methyl-2-butanone. However, 127 and 143 u ion peaks were present in the API-MS spectra (the 127 u ion peak being

TABLE 1. Products Observed and Their Molar Formation Yields from OH Radical-Initiated Reaction of 2,3,4-Trimethylpentane in the Presence of NO and the Predicted Product Distribution (in %) from Radicals Shown in Schemes 1-3

			70 yields for predicted product distributions						
			Scheme 1 ^b		Scheme 2 ^c		Scheme 3 ^d	net	
product	GC-FID ^a	API-MS	30%	25%	10%	15%	40%	Ae	B ^f
acetaldehyde	0.47 ± 0.06		33.3	27.8	8.3	12.5		42	40
acetone	0.76 ± 0.11	observed ^g	18.3	15.3	18.0	27.0	38.4	75	81
3-methyl-2-butanone	0.41 ± 0.05	observed ^g			0.35	0.53	40.0	40	41
2-propyl nitrate	0.062 ± 0.008				0.32	0.48	1.56	1.9	2.0
3-methyl-2-butyl nitrate	0.016 ± 0.002				1.34	2.01		1.3	2.0
C ₈ –alkyl nitrate	~0.02								
MW 144 product (C ₈ -hydroxycarbonyl)		tentatively observed ^{g,h}							
MW 149 product (C ₅ -hydroxynitrate)		observed ^h							
MW 191 product (C ₈ -hydroxynitrate)		observed ^{g,h}							

^{*a*} Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for 2,3,4-trimethylpentane and products of ±5% each. ^{*b*} Product yields predicted for 30% and 25% formation of the (CH₃)₂CHCH(CH₃)CH(CH₃)CH₂O⁺ radical (Scheme 1). ^{*c*} Product yields predicted for 10% and 15% formation of the (CH₃)₂C(O')CH(CH₃)CH(CH₃)₂CHC(HCH₃)CH(CH₃)CH(CH₃)₂ radical (Scheme 2). ^{*d*} Product yields predicted for 40% formation of the (CH₃)₂CHC(CH₃)(O')CH(CH₃)₂ radical (Scheme 3). ^{*e*} Net A: with yields of radicals shown in Schemes 1–3 as follows: Scheme 1, 20%; Scheme 2, 10%; and Scheme 3, 40%. ^{*f*} Net B: with yields of radicals shown in Schemes 1–3 as follows: Scheme 1, 25%; Scheme 2, 15%; and Scheme 3, 40%. ^{*g*} In positive-ion mode. ^{*h*} In negative-ion mode, as NO₂⁻⁻ adduct.

more intense than the 143 u ion peak), with these being attributed (8) to the $[M + H - H_2O]^+$ and $[M + H - H_2]^+$ fragments of a M = 144 u hydroxycarbonyl product. Also, an ion peak observed at 201 u, which showed a loss of 58 in the product ion spectra, is attributed to a fragment of the hetero-dimer of acetone (P1) and the hydroxycarbonyl (P2) (i.e., $[M_{P1} + M_{P2} + H - H_2]^+$).

In the negative ion mode, the dominant ion peak was that at 237 u, which was shown from API-MS/MS product ion and precursor ion spectra to be the NO_2^- adduct of a molecular weight 191 species. An order of magnitude weaker ion peak in the API-MS spectrum at 195 u was shown to be an NO_2^- adduct of a molecular weight 149 species. Because of their odd masses, these molecular weight 149 and 191 products are attributed to organic nitrates. A weak ion peak at 190 u is attributed to the NO_2^- adduct of the molecular weight 144 hydroxycarbonyl.

Discussion

The rate constant k_1 measured here of $(6.84 \pm 0.12) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 ± 2 K is in good agreement with the rate constant of $k_1 = (6.46 \pm 0.21) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 295 K (*12*) obtained from the only other reported study of this reaction, by Harris and Kerr (*19*) in which rate constants were measured relative to those for reaction of OH radicals with *n*-hexane over the temperature range 243–313 K. The 298 K rate constant calculated using the empirical estimation method of Kwok and Atkinson (*29*) is 8.54 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, in reasonable agreement with the measured rate constants (note that the rate constants predicted from the Kwok and Atkinson (*29*) estimation method are 5–7% too high because of changes in the recommended rate constants for the reactions of OH radicals with alkanes (*12*) since the time of the Kwok and Atkinson (*29*) study).

The product data given in Table 1 show that, with the five products quantified by GC-FID, we have accounted for 69 \pm 6% of the products (as carbon), and the GC and API-MS data allow the reaction pathways to be delineated. OH radicals can react with 2,3,4-trimethylpentane at four positions; the four equivalent CH₃ groups attached to the 2- and 4-carbons (8% total), the CH₃ group attached to the 3-position carbon (2%), the two equivalent tertiary CH groups at the 2- and 4-positions (56% total), and the CH group at the 3-position (34%), where the numbers in parentheses are the percentages of the four reaction pathways calculated using the estimation method of Kwok and Atkinson (29). Note that even if the overall reaction rate constant is well-predicted, these calculated percentages of reaction occurring at the various CH

and CH₃ groups may be subject to significant uncertainties (7, 23), and, as noted above, the overall rate constant for 2,3,4-trimethylpentane is overpredicted by 20-25%.

% violds for product distributions

After H-atom abstraction from these various C–H bonds, the resulting alkyl radicals add O₂ to form alkyl peroxy radicals which, under our experimental conditions, then react with NO to form the corresponding alkoxy radical ($C_8H_{17}O^{+}$) plus NO₂ or the alkyl nitrate ($C_8H_{17}ONO_2$, of molecular weight 175), as shown in reactions 1–3 in the Introduction. As also noted in the Introduction, the four $C_8H_{17}O^{+}$ alkoxy radicals can react with O₂, unimolecularly decompose by C–C bond scission or isomerize through a six-membered ring transition state to form a 1,4-hydroxyalkyl radical (4, 5), with not all of these reaction pathways being possible for all four alkoxy radicals initially formed from 2,3,4-trimethylpentane.

Schemes 1-3 show the potential reactions of the three C₈H₁₇O[•] alkoxy radicals predicted to be most important, leading to first-generation products. In these reaction schemes, detailed reactions are omitted for the CH₃C•HCH₃ radical, which is known to react in the atmosphere to form $CH_3C(O)CH_3$ and 2-propyl nitrate (5, 30). The rates of the decomposition, isomerization, and reaction with O₂ of the various alkoxy and hydroxyalkoxy radicals involved in Schemes 1-3 were calculated using the estimation methods described by Atkinson (5), as revised by Aschmann and Atkinson (31) [see also Supporting Information in Aschmann et al. (32). The calculated rates of these reactions are not shown in Schemes 1-3, 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 <10% of the overall reaction rate of the alkoxy radical. In these schemes, the products identified by gas chromatography are shown in boxes, and those consistent with the API-MS analyses are underlined (note that certain products are produced by multiple pathways). The reactions of the four initially formed C₈H₁₇O[•] radicals are discussed below and compared with the products observed. It should be noted that the four C₈H₁₇ONO₂ nitrates expected to be formed from the reactions of the four C₈H₁₇O₂. radicals with NO [reaction 3a] were not identified by API-MS analyses (which has low sensitivity for simple nitrates) and only one of these nitrates was observed by GC-FID and GC MS, due in large part to a lack of authentic standards.

(CH₃)₂CHCH(CH₃)CH(CH₃)CH₂O[•] Radical (Scheme 1). 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 4.7×10^4 , 6.5×10^4 , and 5×10^6 s⁻¹, respectively (5, 31, 32). Decomposition of the SCHEME 1



(CH₃)₂C(O[•])CH(CH₃)CH(CH₃)CH₂OH radical formed after the first isomerization is predicted to dominate over isomerization by a factor of \sim 1.6, and the resulting alkoxy radical CH₃CH(O[•])CH(CH₃)CH₂OH is predicted to decompose a factor of 10 faster than its reaction rate with O2. The predicted products from the (CH₃)₂CHCH(CH₃)CH(CH₃)CH₂O[•] radical are then acetone (61%), acetaldehyde (111%), and HCHO (56%) [where the percentages are the predicted molar yields from the precursor (CH₃)₂CHCH(CH₃)CH(CH₃)CH₂O• alkoxy radical], together with the molecular weight 191 hydroxynitrate (CH₃)₂C(ONO₂)CH(CH₃)CH(CH₃)CH₂OH, the molecular weight 144 hydroxycarbonyl (CH₃)₂C(OH)CH(CH₃)CH(CH₃)-CHO, and the molecular weight 149 hydroxynitrate CH₃CH-(ONO₂)CH(CH₃)CH₂OH. Our observation by API-MS of molecular weight 149 and 191 organic nitrates and the molecular weight 144 hydroxycarbonyl is consistent with these predictions. The molecular weight 149 and 191 organic nitrates can be attributed to the predicted C5- and C8hydroxynitrates, respectively (see Scheme 1).

(CH₃)₂C(O[•])CH(CH₃)₂CH(CH₃)₂Radical (Scheme 2). Scheme 2 shows that this alkoxy radical can only decompose or isomerize with calculated reaction rates at 298 K of 1.3×10^7 and 4×10^5 s⁻¹, respectively (*5*, *31*, *32*). The CH₃CH(O[•])CH-(CH₃)₂ alkoxy radical formed after the decomposition is predicted to dominantly decompose (1.1×10^6 s⁻¹) rather than react with O₂ (4.7×10^4 s⁻¹). Neglecting the minor isomerization channel, the major products are predicted to be acetone (180%), 3-methyl-2-butyl nitrate (13.4%), 3-methyl-2-butyl nitrate (3.5%), acetaldehyde (83%), and 2-propyl nitrate

(3.2%), where the percentages are the predicted molar yields from the precursor (CH₃)₂C(O[•])CH(CH₃)CH(CH₃)₂ alkoxy radical. These yields are calculated using the previously measured yields of 3-methyl-2-butyl nitrate from the CH₃-CH(OO[•])CH(CH₃)₂ + NO reaction of 13.4% [data of ref *17* reevaluated using more up-to-date estimates of the partial rate constants for initial H-atom abstraction from the various C-H bonds in 2-methylbutane (*29*)] and of 2-propyl nitrate from the CH₃CH(OO[•])CH₃ + NO reaction of 3.9% (*9*).

(CH₃)₂CHC(CH₃)(O')CH(CH₃)₂ Radical (Scheme 3). As shown in Scheme 3, decomposition is the only process which can occur. The decomposition to CH₃C(O)CH(CH₃)₂ + CH₃C[•]-HCH₃ is predicted to dominate, by a factor of $\sim 2 \times 10^4$, over decomposition to 'CH₃ + (CH₃)₂CHC(O)CH(CH₃)₂ (*5*, *31*, *32*). Using the 2-propyl nitrate from the CH₃CH(OO')CH₃ + NO reaction of 3.9% (*9*), the predicted products are therefore 3-methyl-2-butanone (100%), acetone (96.1%), and 2-propyl nitrate (3.9%), where the percentages are the predicted molar yields from the precursor (CH₃)₂CHC(CH₃)(O')CH(CH₃)₂ alkoxy radical.

 $(CH_3)_2$ CHCH (CH_2O) CH $(CH_3)_2$ Radical. The precursor alkyl (and peroxy) radical is predicted to account for only 2% of the overall reaction (29); hence, no reaction scheme is shown for this alkoxy radical. Isomerization is predicted to dominate over decomposition and reaction with O₂, leading to the molecular weight 191 hydroxynitrate $(CH_3)_2$ CHCH- (CH_2OH) CH (CH_3) CH $_2$ ONO₂, the molecular weight 144 hydroxycarbonyl (CH₃)₂CHCH(CHO)CH (CH_3) CH $_2OH$, and other products. SCHEME 3



Delineating the Product Distribution. Formation of 3-methyl-2-butanone is predicted to occur almost entirely from the $(CH_3)_2CHC(CH_3)(O^{\circ})CH(CH_3)_2$ radical (see Scheme 3). The other potential source of 3-methyl-2-butanone is from reaction of the $(CH_3)_2C(O^{\circ})CH(CH_3)CH(CH_3)_2$ radical (see Scheme 2). However, the measured low yield of 3-methyl-2-butyl nitrate (1.6%), which is predicted to arise only from the $(CH_3)_2C(O^{\circ})CH(CH_3)CH(CH_3)_2$ radical with a yield from this alkoxy radical of 13.4% (Scheme 2), implies that the yield of the $(CH_3)_2C(O^{\circ})CH(CH_3)CH(CH_3)_2$ radical from 2,3,4-trimethylpentane is significantly less than the 56% predicted using the Kwok and Atkinson (*29*) estimation method. Furthermore, the pathway leading to 3-methyl-2-butanone

from the (CH₃)₂C(O[•])CH(CH₃)CH(CH₃)₂ radical (Scheme 2) is predicted to be minor. Therefore, the measured yield of 3-methyl-2-butanone (41 ± 5%) corresponds to the formation yield of the (CH₃)₂CHC(CH₃)(O[•])CH(CH₃)₂ radical from 2,3,4-trimethylpentane. Accounting for some formation of the C₈-alkyl nitrate (CH₃)₂CHC(CH₃)(ONO₂)CH(CH₃)₂ from the RO₂[•] + NO reaction, H-atom abstraction from the 3-position CH group must account for ~45% and at a minimum for 40 ± 5% of the overall OH radical reaction. This is somewhat higher than the predicted importance of H-atom abstraction from the 3-position CH group (34%).

Delineation of the remaining pathways is rendered difficult because the same major observed products (acetone

and acetaldehyde) are formed from both the (CH₃)₂CHCH-(CH₃)CH(CH₃)CH₂O[•] radical (Scheme 1) and the (CH₃)₂C-(O[•])CH(CH₃)CH(CH₃)₂ radical (Scheme 2). Summing the formation yields of 2-propyl nitrate and acetone (because the CH₃CH(OO[•])CH₃ radical forms either acetone or 2-propyl nitrate), then our observed products arising from the (CH₃)₂-CHCH(CH₃)CH(CH₃)CH₂O[•] (Scheme 1), (CH₃)₂C(O[•])CH(CH₃)-CH(CH₃)₂ (Scheme 2), and (CH₃)₂CHCH(CH₂O[•])CH(CH₃)₂ (no Scheme shown) radicals are: acetone + 2-propyl nitrate (41) \pm 13%, after subtracting the 41% attributed to the coproducts of 3-methyl-2-butanone in Scheme 3), 3-methyl-2-butyl nitrate (1.6 \pm 0.2%), and acetaldehyde (47 \pm 6%). These correspond to 28% (as carbon) of the reaction products. While some C₈-alkyl nitrate will be formed from the (CH₃)₂C(OO[•])-CH(CH₃)CH(CH₃)₂ + NO reaction, this 41 \pm 13% yield of acetone plus 2-propyl nitrate (i.e., other than that formed as a coproduct to 3-methyl-2-butanone) indicates that H-atom abstraction from the 2- and 4-position CH groups cannot account for more than 25-30% of the overall reaction, significantly less than the predicted value of 56% (29) and consistent with the above-noted low yield of 3-methyl-2butyl nitrate (see Scheme 2).

A plausible range of product distributions is shown in Table 1, assuming the $(CH_3)_2CHC(CH_3)(O^{\bullet})CH(CH_3)_2$ radical shown in Scheme 3 is formed in 40% yield (see above) and considering two possible formation yields of the $(CH_3)_2$ -CHCH $(CH_3)CH(CH_3)CH_2O^{\bullet}$ and $(CH_3)_2C(O^{\bullet})CH(CH_3)CH_{-}(CH_3)_2$ radicals shown in Schemes 1 and 2, respectively. The distribution of the products for the individual radicals are those given above for the individual alkoxy radicals and were predicted using the methods described by Atkinson (*5*), as revised by Aschmann and Atkinson (*31*) [see also Supporting Information in Aschmann et al. (*32*)].

The predicted product yields are consistent with our measured values, except that our measured 2-propyl nitrate yield is a factor of 3 higher than that predicted. For the predicted product distributions shown in Table 1, H-atom abstraction from the CH groups at the 2- and 4-positions accounts for 10-15% plus the percentage formation of the C₈-alkyl nitrate (CH₃)₂C(ONO₂)CH(CH₃)CH(CH₃)₂; hence expected (33) to be $\leq 20\%$ and a factor of ~ 3 lower than predicted from the Kwok and Atkinson (29) estimation method. This discrepancy can be attributed to steric hindrance at the 2- and 4-position CH groups toward OH radical reaction, similar to the conclusion drawn for reaction of OH radicals with 2,2,4-trimethylpentane (23). An alternative explanation, but thought to be less likely, is that isomerization of the (CH₃)₂C(O[•])CH(CH₃)CH(CH₃)₂ radical (Scheme 2) is much more important than predicted and accounts for $\sim 30-$ 35% of the overall reaction, leading to hydroxycarbonyl and hydroxynitrate products that were not quantified. Note that the formation of the observed C5- and C8-hydroxynitrates of molecular weight 149 and 191, respectively, is predicted (see Scheme 1). Additionally, based on data for alkanes, including branched alkanes (33), \sim 15% of C₈-alkyl nitrates are expected to be formed from the reactions of the various octyl peroxy radicals with NO. The octyl nitrate, C5- and C8-hydroxynitrates, and C₈-hydroxycarbonyl products combined with those quantified (Table 1) and with the HCHO anticipated as a coproduct to the acetaldehyde formed from the (CH₃)₂-CHCH(CH₃)CH(CH₃)CH₂O[•] radical (Scheme 1) may well account for all of the reaction products.

The reaction of OH radicals with 2,3,4-trimethylpentane therefore leads to \sim 50–55% of the product carbon being formed from first-generation alkoxy radical decomposition reactions. This can be compared to the 2,2,4trimethylpentane reaction (*23*), where 40±5% of the products were readily observed by GC methods and attributed to decomposition of the first-generation alkoxy radicals and to the *n*-octane reaction (9), where none of the products formed arose from alkoxy radical decomposition (rather all of the first-generation alkoxy radicals appeared to undergo isomerization to form hydroxycarbonyls and hydroxynitrates, in addition to the octyl nitrates formed from the RO_2 • + NO reactions). Clearly, the higher the degree of branching, the greater the importance of alkoxy radical decomposition and the higher the yields of carbonyl compounds with less carbon atoms than the parent alkane. This may have implications for secondary organic aerosol formation from alkane atmospheric photooxidations, with branched alkanes leading to a higher fraction of products containing fewer carbon atoms than their precursor alkane and thus potentially forming less aerosol than the corresponding *n*-alkane of the same carbon number.

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Literature Cited

- (1) Hoekman, S. K. Environ. Sci. Technol. 1992, 26, 1206.
- (2) Lurmann, F. W.; Main, H. H. Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study; Final Report to California Air Resources Board Contract A832-130, Sacramento, CA, February 1992.
- (3) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*, Oxford University Press: New York, 2002.
- (4) Atkinson, R.; Arey, J. Chem. Rev. 2003, 103, 4605.
- (5) Atkinson, R. J. Phys. Chem. Ref. Data 1997, 26, 215.
- (6) Eberhard, J.; Müller, C.; Stocker, D. W.; Kerr, J. A. Environ. Sci. Technol. 1995, 29, 232.
- (7) Atkinson, R.; Kwok, E. S. C.; Arey, J.; Aschmann, S. M. Faraday Discuss. 1995, 100, 23.
- (8) Kwok, E. S. C.; Arey, J.; Atkinson, R. J. Phys. Chem. 1996, 100, 214.
- (9) Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. J. Phys. Chem. A 2001, 105, 1020.
- (10) Aschmann, S. M.; Arey, J.; Atkinson, R. J. Phys. Chem. A 2001, 105, 7598.
- (11) Reisen, F.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* (to be submitted for publication).
- (12) Atkinson, R. Atmos. Chem. Phys. 2003, 3, 2233.
- (13) Cox, R. A.; Derwent, R. G.; Williams, M. R. Environ. Sci. Technol. 1980, 14, 57.
- (14) Takagi, H.; Washida, N.; Bandow, H.; Akimoto, H.; Okuda, M. J. Phys. Chem. 1981, 85, 2701.
- (15) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. J. Phys. Chem. **1982**, 86, 4563.
- (16) Atkinson, R.; Carter, W. P. L.; Winer, A. M. J. Phys. Chem. 1983, 87, 2012.
- (17) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. Int. J. Chem. Kinet. **1984**, *16*, 1085.
- (18) Atkinson, R.; Aschmann, S. M.; Winer, A. M. J. Atmos. Chem. **1987**, *5*, 91.
- (19) Harris, S. J.; Kerr, J. A. Int. J. Chem. Kinet. 1989, 21, 207.
- (20) Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. J. Phys. Chem. A 1997, 101, 8042.
- (21) Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. J. Phys. Chem. A 1999, 103, 2688.
- (22) Orlando, J. J.; Iraci, L. T.; Tyndall, G. S. J. Phys. Chem. A 2000, 104, 5072.
- (23) Aschmann, S. M.; Arey, J.; Atkinson, R. Environ. Sci. Technol. 2002, 36, 625.
- (24) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. Environ. Sci. Technol. 1995, 29, 1674.
- (25) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. Int. J. Chem. Kinet. 1980, 12, 231.

- (26) IUPAC. http://www.iupac-kinetic.ch.cam.ac.uk/; 2004.
- (27) Le Calvé, S.; Hitier, D.; Le Bras, G.; Mellouki, A. J. Phys. Chem. A **1998**, *102*, 4579.
- (28) Atkinson, R. Atmospheric oxidation. In *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*; Boethling, R. S., Mackay, D., Eds.; Lewis Publishers: Boca Raton, FL, 2000; pp 335–354.
- (29) Kwok, E. S. C.; Atkinson, R. Atmos. Environ. 1995, 29, 1685.
- (30) Atkinson, R. J. Phys. Chem. Ref. Data 1994, Monograph 2, 1.
- (31) Aschmann, S. M.; Atkinson, R. Int. J. Chem. Kinet. 1999, 31, 501.
- (32) Aschmann, S. M.; Martin, P.; Tuazon, E. C.; Arey, J.; Atkinson, R. *Environ. Sci. Technol.* **2001**, *35*, 4080.
- (33) Carter, W. P. L.; Atkinson, R. J. Atmos. Chem. 1989, 8, 165.

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