Alkoxy Radical Isomerization Products from the Gas-Phase OH Radical-Initiated Reactions of 2,4-Dimethyl-2-pentanol and 3,5-Dimethyl-3-hexanol
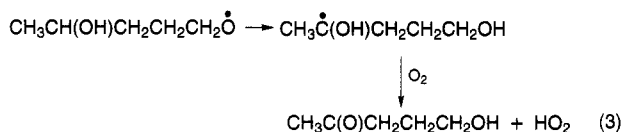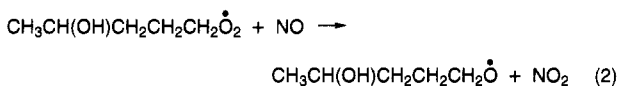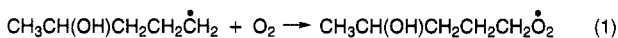
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The products of the gas-phase reactions of the OH radical with 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol in the presence of NO_x have been determined at atmospheric pressure of air and 296 ± 2 K to assess the occurrence and importance of alkoxy radical isomerization. The products identified and quantified and their formation yields were as follows: from 2,4-dimethyl-2-pentanol: acetone, 0.92 $\pm$ 0.15; 2-methylpropanal, 0.209 $\pm$ 0.022; 4-methyl-2-pentanone, 0.046 $\pm$ 0.008; and 4-hydroxy-4-methyl-2-pentanone, 0.116 $\pm$ 0.018; from 3,5-dimethyl-3-hexanol: acetone, 0.120 $\pm$ 0.029; 2-butanone, 0.275 $\pm$ 0.021; 2-methylpropanal, 0.169 $\pm$ 0.016; 4-methyl-2-pentanone, 0.161 $\pm$ 0.012; and 4-hydroxy-4-methyl-2-pentanone, 0.250 $\pm$ 0.023. The observed formation of 4-hydroxy-4-methyl-2-pentanone provides conclusive evidence for the occurrence of isomerization of the alkoxy radicals $(CH_3)_2C(OH)CH_2C(\dot{O})(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH_2C(\dot{O})(CH_3)_2$ via 1,5-H shifts. The reaction mechanisms are discussed, and isomerization rate constants for 1,5-H-atom abstraction from the $-CH_3$ and $-CH_2-$ groups in the $RCH_2C(CH_3)(OH)$-$CH_2C(\dot{O})(CH_3)_2$ alkoxy radicals (R = H and CH_3) are derived.

Introduction

The atmospheric degradation reactions of organic compounds which proceed by H-atom abstraction from C-H bonds (for example, for alkanes, ketones, ethers, and alcohols) and OH radical addition to carbon–carbon double bonds (for example, for alkenes and α,β-unsaturated carbonyls) involve the intermediary of alkyl ($\dot{R}$), alkyl peroxy ($R\dot{O}_2$), and alkoxy ($R\dot{O}$) radicals (1). A major uncertainty in these degradation schemes, which affects the products formed, concerns the reactions of the alkoxy radicals and especially the relative importance of their thermal decomposition, isomerization, and reaction with O_2 (1, 2). For example, the reactions for the 2-pentoxy radical are as shown in Scheme 1, with the isomerization reaction proceeding by a 1,5-hydrogen shift via a six-membered transition state (3, 4). The alkoxy radical formed as a result of the initial isomerization, through reactions 1 and 2, [CH_3-$CH(OH)CH_2CH_2CH_2\dot{O}$ for the 2-pentoxy radical example shown in Scheme 1] may undergo a second isomerization [reaction 3] to form δ-hydroxycarbonyls [$CH_3C(O)CH_2CH_2$-CH_2OH for the 2-pentoxy radical shown in Scheme 1] (1).

$$CH_3CH(OH)CH_2CH_2\dot{C}H_2 + O_2 \rightarrow CH_3CH(OH)CH_2CH_2CH_2\dot{O}_2 \quad (1)$$

$$CH_3CH(OH)CH_2CH_2CH_2\dot{O}_2 + NO \rightarrow$$

$$CH_3CH(OH)CH_2CH_2CH_2\dot{O} + NO_2 \quad (2)$$

$$CH_3CH(OH)CH_2CH_2CH_2\dot{O} \rightarrow CH_3\dot{C}(OH)CH_2CH_2CH_2OH$$

$$\downarrow O_2$$

$$CH_3C(O)CH_2CH_2CH_2OH + HO_2 \quad (3)$$

Apart from the studies of Dóbé et al. (5), in which the CH_3-$CH(OH)CH_2CH_2\dot{C}H_2$ radical resulting from isomerization of the 2-pentoxy radical at 279–385 K was trapped by methyl radicals to form 2-hexanol, and Eberhard et al. (6), in which 2-hydroxy-5-hexanone formed from the 2-hexoxy radical was detected as the 2,4-dinitrodiphenylhydrazone derivative, the occurrence of the isomerization reaction at room temperature has been inferred by the lack of the products expected from the competing alkoxy radical decomposition and reaction with O_2 (3, 7–9).
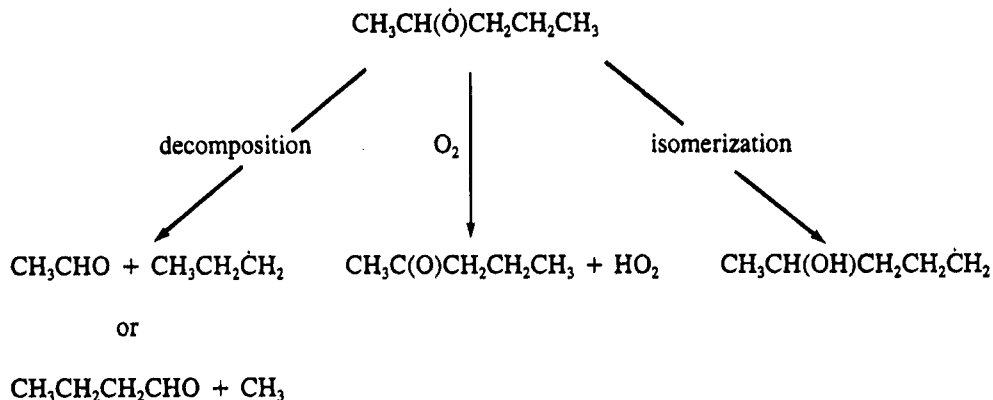
Therefore, a reactant molecule has been sought for which the alkoxy radical resulting from the initial isomerization decomposes to form commercially available and readily identifiable products. In this work, we have investigated the formation of selected products from the OH radical reactions with 2,4-dimethyl-2-pentanol [$(CH_3)_2C(OH)CH_2$-$CH(CH_3)_2$] and 3,5-dimethyl-3-hexanol [$CH_3CH_2C(CH_3)$-$(OH)CH_2CH(CH_3)_2$] in the presence of NO. For both of these alcohols, it is expected that a significant fraction of the OH radical reaction occurs by H-atom abstraction from the tertiary >CH- bond (10), with the resulting alkoxy radical either undergoing decomposition to form either acetone or acetone and 2-butanone or undergoing isomerization to yield 4-hydroxy-4-methyl-2-pentanone (1) (Scheme 2).

To allow the occurrence of secondary reactions of OH radicals with the products to be taken into account (11),
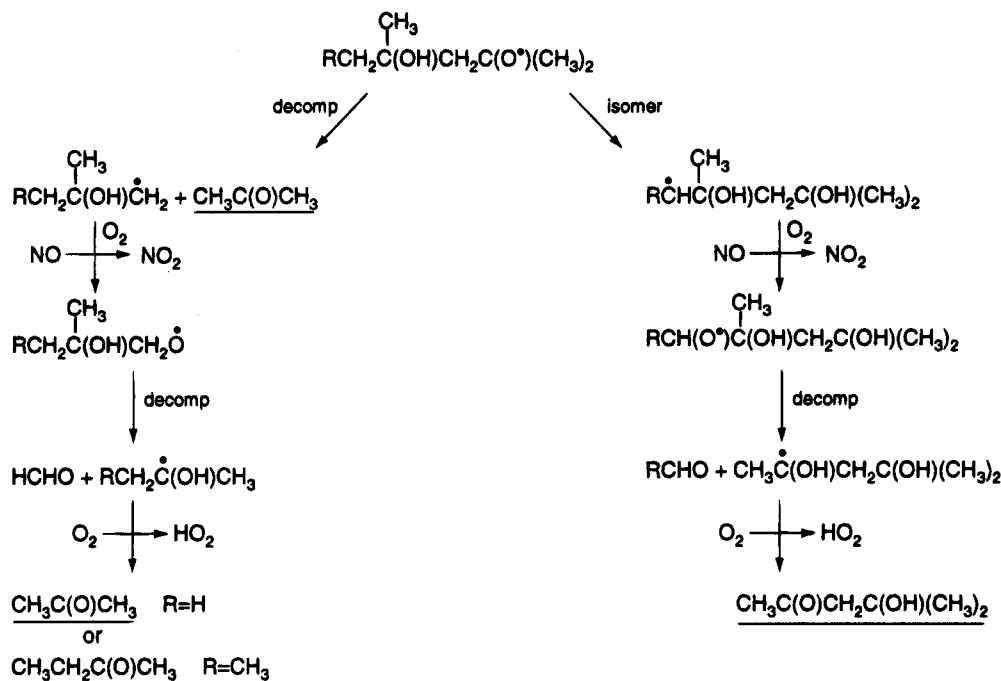

SCHEME 1

$$CH_3CH(\dot{O})CH_2CH_2CH_3$$

decomposition O_2 isomerization

$$CH_3CHO + CH_3CH_2\dot{C}H_2 \qquad CH_3C(O)CH_2CH_2CH_3 + HO_2 \qquad CH_3CH(OH)CH_2CH_2\dot{C}H_2$$

or

$$CH_3CH_2CH_2CHO + CH_3$$

SCHEME 2

$$\underset{|}{\overset{CH_3}{\underset{RCH_2C(OH)CH_2C(O^\bullet)(CH_3)_2}{}}}$$

decomp   isomer

$$\underset{|}{\overset{CH_3}{RCH_2C(OH)\dot{C}H_2}} + CH_3C(O)CH_3 \qquad\qquad \overset{CH_3}{\underset{|}{R\dot{C}HC(OH)CH_2C(OH)(CH_3)_2}}$$

NO $\xrightarrow{\quad O_2 \quad}$ NO$_2$ NO $\xrightarrow{\quad O_2 \quad}$ NO$_2$

$$\underset{|}{\overset{CH_3}{RCH_2C(OH)CH_2\dot{O}}} \qquad\qquad \underset{|}{\overset{CH_3}{RCH(O^\bullet)C(OH)CH_2C(OH)(CH_3)_2}}$$

decomp   decomp

$$HCHO + RCH_2\dot{C}(OH)CH_3 \qquad\qquad RCHO + CH_3\dot{C}(OH)CH_2C(OH)(CH_3)_2$$

$$O_2 \xrightarrow{\quad} HO_2 \qquad\qquad O_2 \xrightarrow{\quad} HO_2$$

$$\underline{CH_3C(O)CH_3} \quad R{=}H \qquad\qquad \underline{CH_3C(O)CH_2C(OH)(CH_3)_2}$$
or
$$\underline{CH_3CH_2C(O)CH_3} \quad R{=}CH_3$$

rate constants for the gas-phase reactions of the OH radical with 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol, and 4-hydroxy-4-methyl-2-pentanone were also determined using a relative rate method.

Experimental Section

Experiments were carried out at 296 ± 2 K and 740 Torr total pressure of purified air (~5% relative humidity) in a 7900-L all-Teflon chamber equipped with two parallel banks of blacklamps. Hydroxyl radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm (12). NO was included in the reactant mixtures to convert peroxy radicals to alkoxy radicals and to suppress the formation of O_3 and, hence, of NO_3 radicals.

OH Radical Reaction Rate Constant Measurements. Rate constants for the gas-phase reactions of the OH radical with 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol, and 4-hydroxy-4-methyl-2-pentanone were determined using a relative rate method (12) in which the decays of the reactants and a reference organic were measured in the presence of OH radicals.

$$OH + \text{oxygenate} \rightarrow \text{products} \tag{4}$$

$$OH + \text{reference organic} \rightarrow \text{products} \tag{5}$$
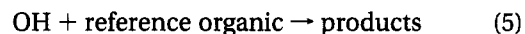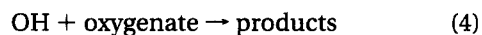
Providing that the oxygenated reactant and the reference organic are removed only by reaction with the OH radical, then

$$\ln\left\{\frac{[\text{oxygenate}]_{t_0}}{[\text{oxygenate}]_t}\right\} = \frac{k_4}{k_5}\ln\left\{\frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t}\right\} \tag{I}$$

where $[\text{oxygenate}]_{t_0}$ and $[\text{reference organic}]_{t_0}$ are the concentrations of the oxygenated reactant and reference organic, respectively, at time t_0; $[\text{oxygenate}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time t; and k_4 and k_5 are the rate constants for reactions 4 and 5, respectively. n-Hexane was used as the reference organic for the experiments with 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol, while n-butane was used as the reference organic for the experiments with 4-hydroxy-4-methyl-2-pentanone. The initial reactant concentrations (in molecule cm^{-3} units) were as follows: CH_3ONO, (2.0–2.3) x 10^{14}; NO, (1.9–2.1) x 10^{14}; 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol, or 4-hydroxy-4-methyl-2-pentanone, ~2.2 x 10^{13}; and n-butane or n-hexane, ~2.4 x 10^{13}. Irradiations were carried out at 20% of the maximum

light intensity for 8−30 min (2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol) or 12−45 min (4-hydroxy-4-methyl-2-pentanone).

The oxygenated reactants and n-butane and n-hexane reference organics were analyzed during the experiments by gas chromatography with flame ionization detection (GC−FID). For the analyses of 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol and 4-hydroxy-4-methyl-2-pentanone, 100 cm³ volume samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~250 °C onto a 30-m DB-5.625 megabore column in a Hewlett Packard (HP) 5710 GC, initially held at 0 °C and then temperature programmed to 200 °C at 8 °C min⁻¹. For the analyses of n-butane and n-hexane, gas samples were collected from the chamber in 100 cm³ all-glass, gas-tight syringes and introduced via a 1-cm³ gas sampling loop onto a 30-m DB-5 megabore column in a HP 5890 GC, initially held at −25 °C and then temperature programmed to 200 °C at 8 °C min⁻¹.

Products of OH Radical Reactions with Alcohols. Irradiations of CH₃ONO−NO−alcohol−air mixtures were carried out at 20% of the maximum light intensity for 8−30 min (2,4-dimethyl-2-pentanol) or 6−24 min (3,5-dimethyl-3-hexanol). The initial reactant concentrations (in molecule cm⁻³ units) were as follows: CH₃ONO, (2.0−2.2) × 10¹⁴; NO, (2.1−2.2) x 10¹⁴, 2,4-dimethyl-2-pentanol, (2.30−2.76) × 10¹³, or 3,5-dimethyl-3-hexanol, (2.17−2.26) × 10¹³. The reactant alcohols, acetone, 2-butanone, 2-methylpropanal, 4-methyl-2-pentanone, and 4-hydroxy-4-methyl-2-pentanone were analyzed by GC−FID with the thermal desorption system as described above. The GC−FID response factors for the alcohol reactants and products were determined by introducing known amounts of these compounds and *trans*-2-butene into the 7900-L chamber and determining the chamber volume from the *trans*-2-butene concentration as measured using a precalibrated HP 5890 GC/loop injection system. For 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol, 4-hydroxy-4-methyl-2-pentanone, acetone, and 2-methylpropanal (isobutyraldehyde), partial pressures were measured with an MKS Baratron 0−100 Torr sensor in a 2.03-L Pyrex bulb, and the contents of the bulb were flushed into the chamber with a stream of N₂ gas. For 2-butanone and 4-methyl-2-pentanone, measured volumes of the liquids were introduced into a 1-L Pyrex bulb, the contents of which were flushed into the chamber as described above. On a relative basis, the GC−FID response factors agreed with the equivalent carbon numbers, as calculated by Scanlon and Willis (*13*), to within ±9%, giving confidence that the calibration factors were accurate and that the sample collection and thermal desorption procedures were quantitative.

Gas samples were also collected onto Tenax-TA solid adsorbent for subsequent thermal desorption and analysis by combined gas chromatography−mass spectrometry (GC−MS), using a 60-m DB-5MS fused silica capillary column, temperature programmed from −80 to 200 °C at 10 °C min⁻¹, in a HP 5890 GC interfaced to a HP 5970 mass selective detector operated in the scanning mode. The NO concentrations and initial NO₂ concentrations were monitored during these experiments using a Thermo Environmental Instruments, Inc., Model 42 chemiluminescence NO−NO₂−NO$_x$ analyzer.

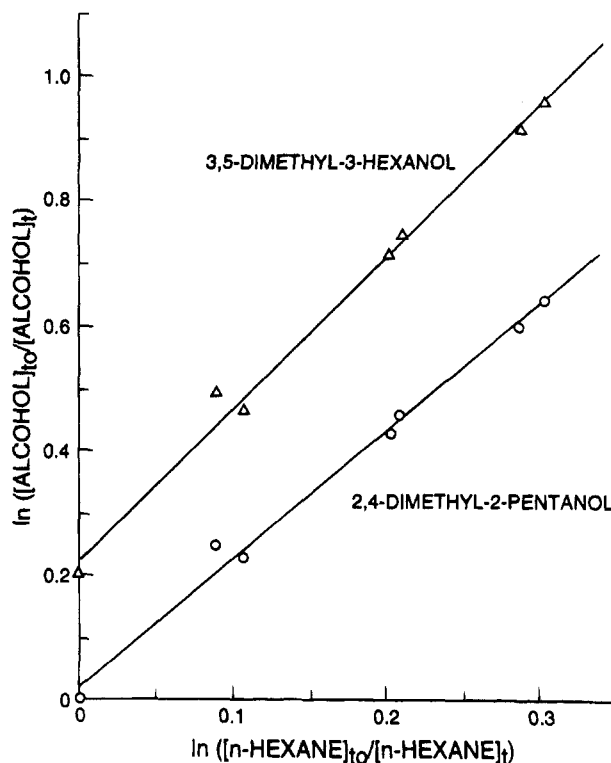The chemicals used and their stated purities were as follows: acetone (>99.6%), Fisher Scientific; 2-butanone

FIGURE 1. Plots of eq I for the gas-phase reactions of the OH radical with 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol, with n-hexane as the reference organic. The data for 3,5-dimethyl-3-hexanol have been displaced vertically by 0.2 unit for clarity.

(99+%), n-hexane (99+%), 4-hydroxy-4-methyl-2-pentanone (99%), 4-methyl-2-pentanone (99+%), and 2-methylpropanal [isobutyraldehyde] (99+%), Aldrich Chemical Company; 2,4-dimethyl-2-pentanol, ICN Biomedicals; 3,5-dimethyl-3-hexanol, Pfaltz and Bauer; n-butane (≥99.5%) and NO (≥99.0%), Matheson Gas Products; and *trans*-2-butene (CP grade), Linde. Methyl nitrite was prepared and stored as described previously (*12*).

Results

OH Radical Reaction Rate Constant Measurements. Two irradiations each of CH₃ONO−NO−2,4-dimethyl-2-pentanol−3,5-dimethyl-3-hexanol−n-hexane−air and CH₃-ONO−NO−4-hydroxy-4-methyl-2-pentanone−n-butane−air mixtures were carried out at 296 ± 2 K and 740 Torr total pressure of air. The experimental data for 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol are plotted in accordance with eq I in Figure 1, and the rate constant ratios k_4/k_5 obtained by least-squares analyses of the experimental data are given in Table 1. These rate constant ratios can be placed on an absolute basis by use of rate constants k_5 for the reactions of the OH radical with n-butane and n-hexane of 2.51 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (±20%) and 5.57 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ (±25%) at 296 K, respectively (*1, 14*), and the resulting rate constants k_4 are also given in Table 1. These measured rate constants for 2,4-dimethyl-2-pentanol, 3,5-dimethyl-3-hexanol, and 4-hydroxy-4-methyl-2-pentanone are uniformly higher, by factors of 2.3−3.1, than those calculated from the estimation method of Atkinson (*10, 15*), presumably indicating that the -OH substituent group has a significant effect on the β-CH₃ and -CH₂ groups, which is not accounted for in the present estimation method (*10, 15*).

Products of OH Radical Reactions with Alcohols. GC−FID and GC−MS analyses of irradiated CH₃ONO−NO−

TABLE 1

Rate Constant Ratios k_4/k_5 and Rate Constants k_4 for Gas-Phase Reactions of the OH Radical with 2,4-Dimethyl-2-pentanol, 3,5-Dimethyl-3-hexanol, and 4-Hydroxy-4-methyl-2-pentanone at 296 ± 2 K

oxygenate	reference organic	k_4/k_5[a]	$10^{12} \times k_4$ (cm^3 molecule^{-1} s^{-1})[b]
2,4-dimethyl-2-pentanol	n-hexane	2.05 ± 0.18	11.4 ± 3.0
3,5-dimethyl-3-hexanol	n-hexane	2.45 ± 0.20	13.6 ± 3.6
4-hydroxy-4-methyl-2-pentanone	n-butane	1.60 ± 0.34	4.0 ± 1.2

[a] Indicated errors are 2 least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants k_5 at 296 K (1, 14) of k_5(n-butane) = 2.51 × 10^{-12} cm^3 molecule^{-1} s^{-1} (±20%) and k_5(n-hexane) = 5.57 × 10^{-12} cm^3 molecule^{-1} s^{-1} (±25%). The indicated errors include the estimated overall uncertainties in the rate constants k_5.

2,4-dimethyl-2-pentanol—air and CH$_3$ONO—NO—3,5-di-methyl-3-hexanol—air mixtures showed the formation of acetone, 2-methylpropanal, 4-methyl-2-pentanone, and 4-hydroxy-4-methyl-2-pentanone from the 2,4-dimethyl-2-pentanol reaction and acetone, 2-butanone, 2-methyl-propanal, 4-methyl-2-pentanone, and 4-hydroxy-4-methyl-2-pentanone from the 3,5-dimethyl-3-hexanol reaction. Since these products react with the OH radical (1, 14), their measured concentrations were corrected to take into account their reactions with OH radicals (11), using the rate constants determined here for 2,4-dimethyl-2-pen-tanol, 3,5-dimethyl-3-hexanol, and 4-hydroxy-4-methyl-2-pentanone and the recommended literature rate con-stants at 296 K for the OH radical reactions with acetone, 2-butanone, 2-methylpropanal, and 4-methyl-2-pentanone (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}) of acetone, 0.215 (1); 2-butanone, 1.15 (14); 2-methylpropanal, 26.5 (1, 14); and 4-methyl-2-pentanone, 14.1 (1, 14). The multiplicative factors, F, to account for reactions of the products with OH radicals during the reactions increase with the extent of reaction and depend on the rate constant ratio k(OH + product)/k(OH + alcohol reactant) (11). Using the rate constants measured here for the alcohol reactants and 4-hydroxy-4-methyl-2-pentanone and the recommended rate constants (1, 14) for the other carbonyl products, these multiplicative factors, F, were <1.01 for acetone, <1.04 for 2-butanone, ≤2.25 for 2-methylpropanal, ≤1.59 for 4-meth-yl-2-pentanone, and <1.15 for 4-hydroxy-4-methyl-2-pentanone. For the formation of acetone, 2-butanone, and 4-hydroxy-4-methyl-2-pentanone, the estimated overall uncertainties in the rate constants k_4 for the alcohol reactants and 4-hydroxy-4-methyl-2-pentanone and in the recommended rate constants for the reactions of the OH radical with acetone (±35%) (1) and 2-butanone (±30%) (14) lead to <1, <2, and <6% uncertainties in the values of F(acetone), F(2-butanone), and F(4-hydroxy-4-methyl-2-pentanone), respectively. However, because of the higher rate constants for the reactions of 2-methylpropanal and 4-methyl-2-pentanone with the OH radical (1, 14), the estimated overall uncertainties in the rate constants for these reactions [of ±30% each (1, 14)] correspond to significant uncertainties in the values of F(2-methylpro-panal) and F(4-methyl-2-pentanone). For example, com-bining the estimated overall uncertainties in the rate constants k_4 for the alcohols (Table 1) with those for the OH radical reaction rate constants for 2-methylpropanal and 4-methyl-2-pentanone results in maximum values of the correction factors F in the range 1.67—2.93 for 2-meth-
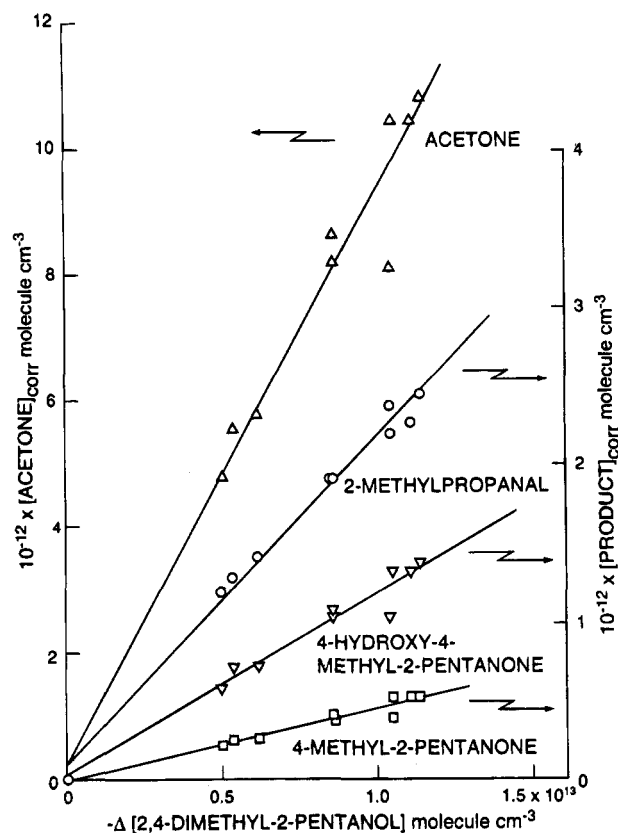

FIGURE 2. Plots of the amounts of acetone, 2-methylpropanal, 4-hydroxy-4-methyl-2-pentanone and 4-methyl-2-pentanone formed, corrected for reaction with the OH radical and (for acetone) for formation from 2-methylpropanal (see text), against the amounts of 2,4-dimethyl-2-propanol reacted with the OH radical.

ylpropanal and in the range 1.33—1.87 for 4-methyl-2-pentanone. As indicated below, our experimental data are consistent with the recommended rate constants for 2-methylpropanal and 4-methyl-2-pentanone (1, 14). The data shown in Figures 2—4 and Table 2 and discussed below are obtained using our measured (Table 1) and the recommended (1, 14) rate constants; the effects of the cited estimated overall uncertainties in these rate constants on the product yields derived are briefly noted in the footnotes to Table 3. Photolysis of the carbonyl products was negligible because of the low light intensities (relative to the ambient atmosphere) and short irradiation times used.

The amounts of 2-methylpropanal, 4-methyl-2-pen-tanone, and 4-hydroxy-4-methyl-2-pentanone formed from three separate OH radical-initiated reactions of 2,4-di-methyl-2-pentanol, corrected for reaction with the OH radical, are plotted against the amounts of 2,4-dimethyl-2-pentanol reacted in Figure 2. Similarly, the amounts of 2-butanone, 2-methylpropanal, 4-methyl-2-pentanone, and 4-hydroxy-4-methyl-2-pentanone formed from three cor-responding 3,5-dimethyl-3-hexanol reactions, corrected for reaction with the OH radical, are plotted against the amounts of 3,5-dimethyl-3-hexanol reacted in Figures 3 (2-butanone and 2-methylpropanal) and 4 (4-methyl-2-pentanone and 4-hydroxy-4-methyl-2-pentanone). Good straight line plots are observed, and least-squares analyses of these data lead to the product formation yields given in Table 2. Using the highest and lowest rate constant ratios k(OH + product)/k(OH + alcohol) allowed by the estimated overall uncertainties in the rate constants (Table 1 and refs 1 and 14), the corresponding plots for the formation of
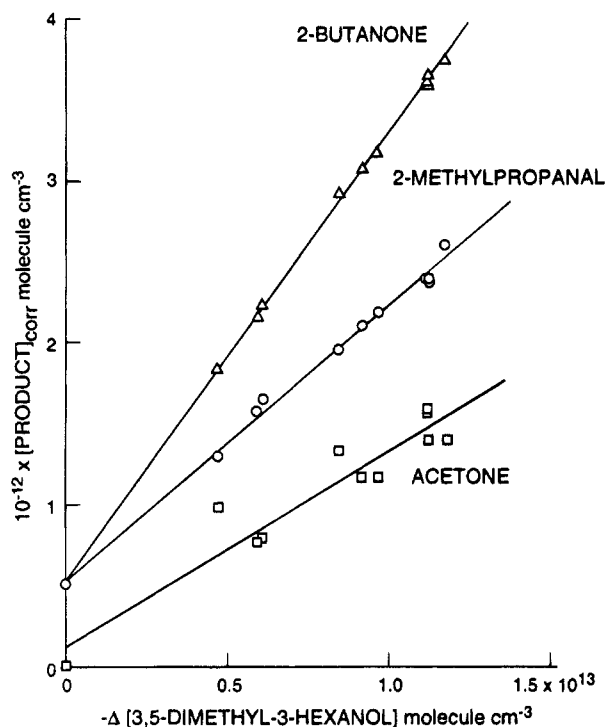
FIGURE 3. Plots of the amounts of acetone, 2-methylpropanal, and 2-butanone formed, corrected for reaction with the OH radical and (for acetone) for formation from secondary reactions of 2-methylpropanal and 4-methyl-2-pentanone (see text), against the amounts of 3,5-dimethyl-3-hexanol reacted with the OH radical. The data for 2-methylpropanal and 2-butanone have been displaced vertically by 5 × 10¹¹ molecule cm⁻³ for clarity.
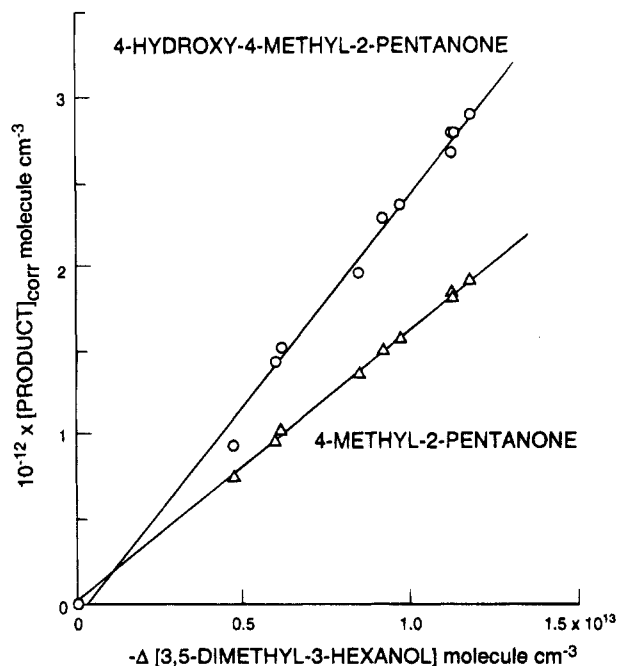

FIGURE 4. Plots of the amounts of 4-methyl-2-pentanone and 4-hydroxy-4-methyl-2-pentanone formed, corrected for reaction with the OH radical (see text), against the amounts of 3,5-dimethyl-3-hexanol reacted with the OH radical.

2-methylpropanal from both 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol and of 4-methyl-2-pentanone from 3,5-dimethyl-3-hexanol are positively and negatively curved, respectively, indicating that the recommended rate constants for 2-methylpropanal and 4-methyl-2-pentanone (1, 14) are most consistent with our experimental data.

In addition to being a potential "first-generation" product of the reactions of the OH radical with 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol in the presence of NO, acetone is formed (or expected to be formed) as a product of the OH radical reactions with 4-methyl-2-pentanone (16), 2-methylpropanal (1), and 4-hydroxy-4-methyl-2-pentanone (1), with measured or expected yields of 0.78 ± 0.06 (16), ~1.0 (1), and ~0.6 (1, 10, 15), respectively. For the 2,4-dimethyl-2-pentanol reaction and using the measured (Table 1) and recommended (1, 14) OH radical reaction rate constants, the calculated formation of acetone from the reactions of 4-methyl-2-pentanone and 4-hydroxy-4-methyl-2-pentanone with the OH radical accounted for <2 and <1% of the observed acetone, respectively, while acetone formation from 2-methylpropanal increased with the extent of reaction and accounted for 6–13% of the measured acetone concentrations. For the 3,5-dimethyl-3-hexanol reaction, the calculated formation of acetone from the OH radical reactions with 2-methylpropanal and 4-methyl-2-pentanone increased with the extent of reaction and accounted for 14–34 and 6–17%, respectively, of the measured acetone concentrations, with acetone formation from 4-hydroxy-4-methyl-2-pentanone accounting for <7% of the observed acetone. The amounts of acetone formed, corrected for reaction with the OH radical (a <1% correction) and for formation from 2-methylpropanal and (for the 3,5-dimethyl-3-hexanol reaction) 4-methyl-2-pentanone, are plotted against the amounts of the alcohols reacted in Figures 2 (2,4-dimethyl-2-pentanol reaction) and 3 (3,5-dimethyl-3-hexanol reaction), and the acetone formation yields obtained from least-squares analyses of these data are given in Table 2.

In addition to the above identified and quantified products, a small product peak was observed in the GC–FID analyses of each reaction system which eluted slightly later than the reactant alcohol. The mass spectrum of this peak from the 3,5-dimethyl-3-hexanol reaction was consistent with 3,5-dimethyl-4-hexen-3-ol formed from the tertiary nitrate CH$_3$CH$_2$C(CH$_3$)(OH)CH$_2$C(ONO$_2$)(CH$_3$)$_2$ during the thermal desorption process. Using GC–FID response factors for these products identical to those for the parent reactant alcohol (13) and assuming quantitative formation of these observed products from their precursors,

TABLE 3

Expected Products of OH Radical-Initiated Reactions of 2,4-Dimethyl-2-pentanol and 3,5-Dimethyl-3-hexanol ($RCH_2C(CH_3)(OH)CH_2CH(CH_3)_2$) and Observed Product Formation Yields

H-atom abstraction from	product	alkoxy radical reaction	observed yield[a]
	2,4-Dimethyl-2-pentanol		
R-CH₂- -CH₂-CH<	4-methyl-2-pentanone	decomposition	0.046 ± 0.008
	acetone		(0.209)[b,c]
	+	decomposition	
	2-methylpropanal		0.209 ± 0.022[c]
-CH<	2 acetone	decomposition	0.355 ± 0.076[c]
	or		
	4-hydroxy-4-methyl-2-pentanone	isomerization	0.116 ± 0.018
		total	0.73 ± 0.09[d]
	3,5-Dimethyl-3-hexanol		
R-CH₂- -CH₂-CH<	4-methyl-2-pentanone	decomposition	0.161 ± 0.012
	2-butanone		(0.169)[b,e]
	+	decomposition	
	2-methylpropanal		0.169 ± 0.016[e]
-CH<	acetone		0.120 ± 0.029[e]
	+	decomposition	
	2-butanone		0.106 ± 0.027[e]
	4-hydroxy-4-methyl-2-pentanone	isomerization	0.250 ± 0.023
		total	0.69 ± 0.05[d]

[a] Indicated errors are as defined in footnote a of Table 2. [b] Assumed equal to yield of expected and observed 2-methylpropanal co-product. [c] Use of the lowest and highest rate constant ratios k(OH + 2-methylpropanal)/k(OH + 2,4-dimethyl-2-pentanol), respectively, allowed within the uncertainties in the rate constants leads to yields of (acetone + 2-methylpropanal) from decomposition of the -CH₂-CH< moiety, 0.150 ± 0.026 and 0.277 ± 0.025, respectively; and (2 acetone) from decomposition of the -CH< group, 0.415 ± 0.072 and 0.288 ± 0.067, respectively. [d] Total is sum of reaction pathways. [e] Use of the lowest and highest rate constant ratios k(OH + 2-methylpropanal)/k(OH + 3,5-dimethyl-3-hexanol) and k(OH + 4-methyl-2-pentanone)/k(OH + 3,5-dimethyl-3-hexanol), respectively, allowed within the uncertainties in the rate constants leads to yields of 4-methyl-2-pentanone from decomposition of the R-CH₂- moiety, 0.135 ± 0.012 and 0.191 ± 0.016, respectively; (2-butanone + 2-methylpropanal) from decomposition of the -CH₂-CH< moiety, 0.123 ± 0.018 and 0.221 ± 0.020, respectively; acetone from decomposition of the -CH< group, 0.186 ± 0.030 and 0.044 ± 0.036, respectively; and 2-butanone from decomposition of the -CH< group, 0.152 ± 0.028 and 0.054 ± 0.029, respectively.
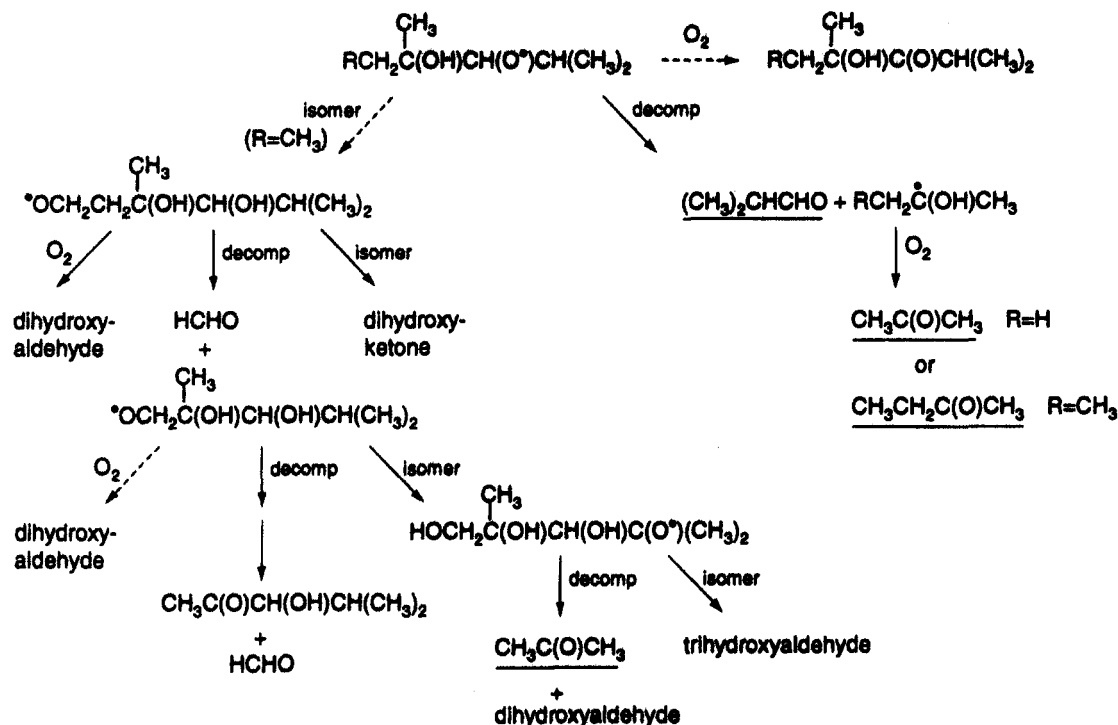
SCHEME 3
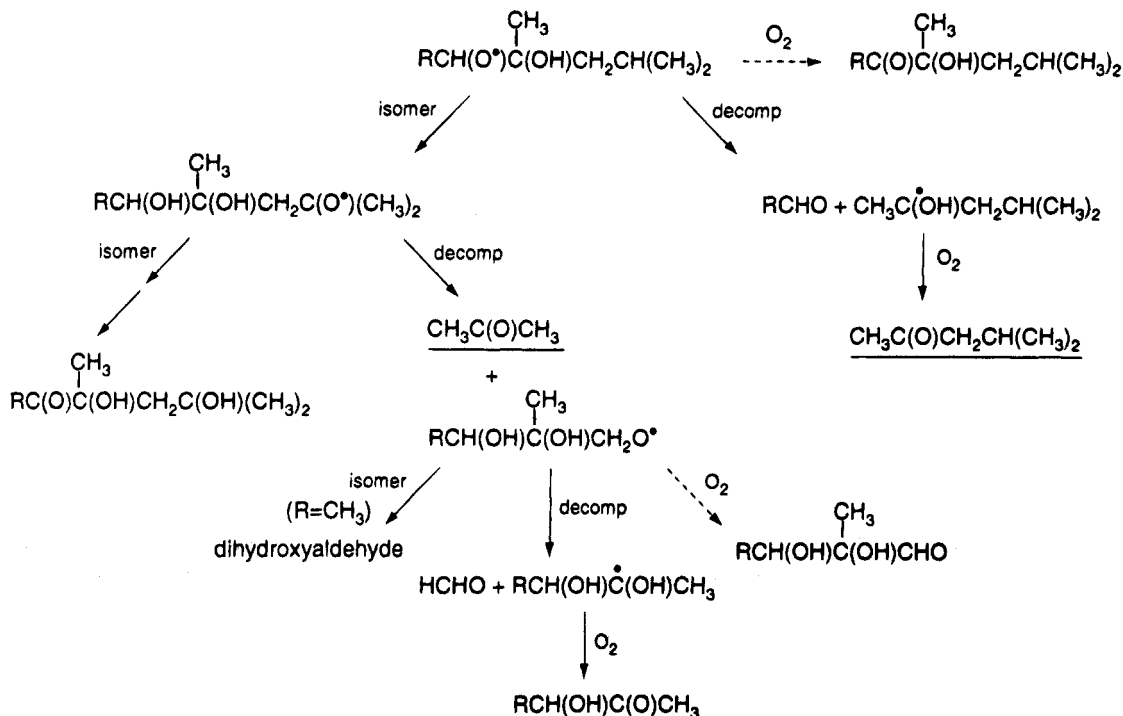
the formation yields of these minor products attributed to a tertiary nitrate were ~0.04 ± 0.01 for each alcohol reaction system.
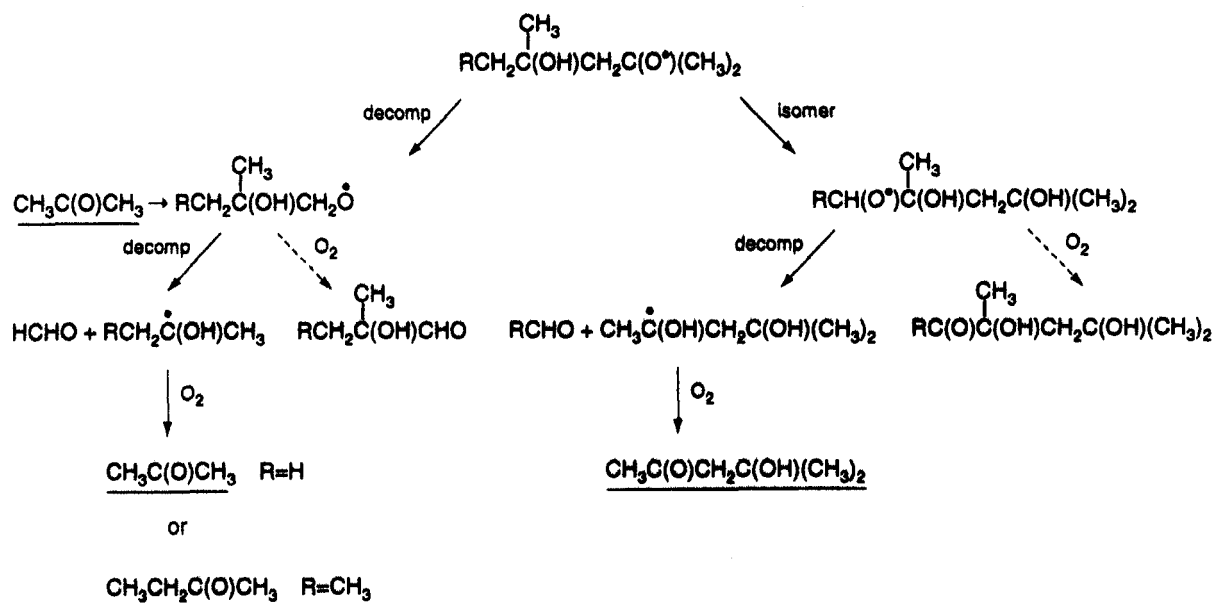
Discussion

Reaction Schemes 3–5 show the reaction sequences expected after H-atom abstraction at the -CH₂- and >CH- groups in the alcohols RCH₂C(CH₃)(OH)CH₂CH(CH₃)₂, with

R = H for 2,4-dimethyl-2-pentanol and R = CH₃ for 3,5-dimethyl-3-hexanol. In these reaction schemes, the alkyl and alkyl peroxy radicals have generally been omitted for clarity, and in most cases only the alkoxy radicals involved are shown. Furthermore, organic nitrate formation has been neglected, and complex reaction sequences leading to multifunctional products not observed (and probably not observable with the present analytical methods) are

SCHEME 4

$$CH_3$$
$$RCH_2C(OH)CH(O^\bullet)CH(CH_3)_2 \quad \xrightarrow{O_2} \quad RCH_2C(OH)C(O)CH(CH_3)_2$$
$$CH_3$$

isomer (R=CH$_3$) / decomp

$$CH_3$$
$$^\bullet OCH_2CH_2C(OH)CH(OH)CH(CH_3)_2$$

$$(CH_3)_2CHCHO + RCH_2\overset{\bullet}{C}(OH)CH_3$$

O$_2$ / | decomp \ isomer

| O$_2$

dihydroxy-aldehyde & HCHO & dihydroxy-ketone

$$CH_3C(O)CH_3 \quad R=H$$

or

$$CH_3CH_2C(O)CH_3 \quad R=CH_3$$

$$CH_3$$
$$^\bullet OCH_2C(OH)CH(OH)CH(CH_3)_2$$

O$_2$ / | decomp \ isomer

$$CH_3$$
$$HOCH_2C(OH)CH(OH)C(O^\bullet)(CH_3)_2$$

dihydroxy-aldehyde

| decomp \ isomer

$$CH_3C(O)CH(OH)CH(CH_3)_2$$
+
HCHO

$$CH_3C(O)CH_3 \quad trihydroxyaldehyde$$
+
dihydroxyaldehyde

SCHEME 5

$$CH_3$$
$$RCH_2C(OH)CH_2C(O^\bullet)(CH_3)_2$$

decomp /   \ isomer

$$CH_3$$
$$CH_3C(O)CH_3 \rightarrow RCH_2C(OH)CH_2\overset{\bullet}{O}$$

$$CH_3$$
$$RCH(O^\bullet)C(OH)CH_2C(OH)(CH_3)_2$$

decomp / \ O$_2$

decomp / \ O$_2$

$$CH_3$$
$$HCHO + RCH_2\overset{\bullet}{C}(OH)CH_3 \quad RCH_2\overset{\bullet}{C}(OH)CHO$$

$$RCHO + CH_3\overset{\bullet}{C}(OH)CH_2C(OH)(CH_3)_2 \quad RC(O)\overset{\bullet}{C}(OH)CH_2C(OH)(CH_3)_2$$

| O$_2$

| O$_2$

$$CH_3C(O)CH_3 \quad R=H$$

$$CH_3C(O)CH_2C(OH)(CH_3)_2$$

or

$$CH_3CH_2C(O)CH_3 \quad R=CH_3$$

omitted [but with the expected product class (for example, dihydroxyaldehyde) being noted]. In several cases, the reaction of an alkoxy radical with O$_2$ is expected to be of minor importance relative to decomposition (1), and these are indicated by an arrow with a dashed line. In Scheme 4, the decomposition of the CH$_3$CH$_2$C(CH$_3$)(OH)CH(Ȯ)-CH(CH$_3$)$_2$ alkoxy radical is exothermic (17–19), and the isomerization reaction involves H-atom abstraction from a -CH$_3$ group; hence, the isomerization reaction is also expected to be minor relative to decomposition (1), and this is also noted by an arrow with a dashed line. These estimates for the relative importance of alkoxy radical reactions with O$_2$ and decomposition used thermochemical data from the NIST thermochemical data computer program (19), which for molecules for which experimental data

are not available uses the group additivity method of Benson (17) and the empirical assessment approach of Atkinson (1).

The formation routes to the observed products after H-atom abstraction from the -CH$_2$- and >CH-groups are given in Table 3, based on Schemes 3–5 [note that while formation of 4-methyl-2-pentanone from 2,4-dimethyl-2-pentanol arises after H-atom abstraction from the 1- and 2-position -CH$_3$ groups, these can be viewed as R-CH$_2$ groups with R = H]. Table 3 also gives the fractions of the overall OH radical reactions which proceed by these reaction pathways, based on the product yield data given in Table 2. The fractions of the overall OH radical reactions proceeding from these groups in 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol are expected to be >85% (10,

15). As noted in Schemes 3 and 4, acetone could also be formed after the isomerization reaction of the $RCH(\dot{O})C$-$(CH_3)(OH)CH_2CH(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH(\dot{O})$-$CH(CH_3)_2$ alkoxy radicals followed by decomposition of the subsequently formed alkoxy radical. However, these acetone formation pathways are not expected to be important (*1*). For the 3,5-dimethyl-3-hexanol reaction system, if acetone is not formed from these $CH_3CH(\dot{O})C$-$(CH_3)(OH)CH_2CH(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH(\dot{O})$-$CH(CH_3)_2$ isomerization reactions, the formation yield of 2-butanone should be equal to the sum of the formation yields of 2-methylpropanal and acetone. As shown in Table 2, the 2-butanone formation yield from 3,5-dimethyl-3-hexanol of 0.275 ± 0.021 is in excellent agreement with the sum of the 2-methylpropanal and acetone formation yields (0.289 ± 0.034), indicating that acetone formation following isomerization of the $RCH(\dot{O})C(CH_3)(OH)CH_2CH(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH(\dot{O})CH(CH_3)_2$ alkoxy radicals is indeed negligible.

The carbonyl and hydroxycarbonyl products observed and quantified in this work (Tables 2 and 3) account for $73 \pm 9\%$ of the overall OH radical reaction with 2,4-dimethyl-2-pentanol and $69 \pm 5\%$ of the overall OH radical reaction with 3,5-dimethyl-3-hexanol, with the minor GC−FID peak ascribed to a nitrate adding a further $4 \pm 1\%$ for each reaction system. As noted above, uncertainties in the rate constant ratios $k(OH + 2\text{-methylpropanal})/k(OH + alcohol)$ and $k(OH + 4\text{-methyl-2-pentanone})/k(OH + alcohol)$ lead to corresponding uncertainties in the multiplicative correction factors F. For example, increases in the rate constant ratios $k(OH + 2\text{-methylpropanal})/k(OH + alcohol)$ and $k(OH + 4\text{-methyl-2-pentanone})/k(OH + alcohol)$ increase the calculated 2-methylpropanal and 4-methyl-2-pentanone formation yields and also increase the amounts of acetone formed from the secondary reactions of 2-methylpropanal and 4-methyl-2-pentanone with the OH radical, thus decreasing the primary formation yields of acetone from the alcohols. In fact, the total yields of the observed products (Table 3) are essentially invariant of uncertainties in the rate constants for the reactions of the OH radical with the reactant alcohols and the products. The effects of varying the rate constant ratios $k(OH + 2\text{-methylpropanal})/k(OH + alcohol)$ and $k(OH + 4\text{-methyl-2-pentanone})/k(OH + alcohol)$ over the maximum ranges allowed from the cited overall uncertainties in the rate constants (Table 1 and refs 1 and 14) on the individual product formation yields are noted in footnotes c and e in Table 3.

Thus, the majority of the reaction pathways and products are accounted for, and the remainder presumably involve H-atom abstraction from the $-CH_3$ groups of the $-CH(CH_3)_2$ moiety and isomerization and/or O_2 reaction of the $RCH(\dot{O})C(CH_3)(OH)CH_2CH(CH_3)_2$ and $CH_3CH_2C(CH_3)$-$(OH)CH(\dot{O})CH(CH_3)_2$ alkoxy radicals (Schemes 3 and 4). The ratios of the product formation yields observed after H-atom abstraction from the $-CH_2-$ and $>CH-$ groups in the $-CH_2CH(CH_3)_2$ moiety of 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol are similar with, for example, respective values of 0.44 ± 0.09 and 0.47 ± 0.07 (Table 3) using our measured (Table 1) and the recommended (*1, 14*) OH radical reaction rate constants. This is expected (*1, 10, 15*) since the only difference between the two alcohols $RCH_2C(CH_3)(OH)CH_2CH(CH_3)_2$ is R = H or CH_3, relatively distant from the $-CH_2CH(CH_3)_2$ moiety.

With the product yields given in Table 3 for the reactions subsequent to H-atom abstraction from the $>CH-$ groups

in 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol [using the measured (Table 1) and recommended (*1, 14*) OH radical reaction rate constants], measured rate constant ratios for the overall isomerization (k_i) and decomposition (k_d) reactions of the alkoxy radicals $(CH_3)_2C(OH)CH_2C(\dot{O})$-$(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH_2C(\dot{O})(CH_3)_2$ are obtained of $k_i/k_d = 0.33 \pm 0.09$ for the $(CH_3)_2C(OH)CH_2C(\dot{O})(CH_3)_2$ radical and $k_i/k_d = 2.2 \pm 0.6$ for the $CH_3CH_2C(CH_3)(OH)$-$CH_2C(\dot{O})(CH_3)_2$ radical. Since isomerization of the $(CH_3)_2C$-$(OH)CH_2C(\dot{O})(CH_3)_2$ radical by a 1,5-H shift occurs from two equivalent $-CH_3$ groups, a rate constant ratio of k_i-$(CH_3)/k_d = 0.16 \pm 0.05$ for 1,5-H shift abstraction from a $-CH_3$ group in the $(CH_3)_2C(OH)CH_2C(\dot{O})(CH_3)_2$ radical is obtained. Isomerization of the $CH_3CH_2C(CH_3)(OH)CH_2C$-$(\dot{O})(CH_3)_2$ radical occurs from one $-CH_3$ group and one $-CH_2-$ group and with the value of $k_i(CH_3)/k_d = 0.16 \pm 0.05$ obtained above, a rate constant ratio of $k_i(CH_2)/k_d = 2.0 \pm 0.6$ for 1,5-H shift abstraction from the $-CH_2-$ group in the $CH_3CH_2C(CH_3)(OH)CH_2C(\dot{O})(CH_3)_2$ radical is obtained. The decomposition rate constant k_d is expected to be essentially identical for these two alkoxy radicals (*1*), and an increase in the isomerization rate constant for H-atom abstraction from a $-CH_2-$ group compared to a $-CH_3$ group is expected (*1*) because of the lower C-H bond dissociation energy for a $-CH_2-$ group compared to a $-CH_3$ group (*18*). It should be noted, however, that the observed increase in $k_i(CH_2)/k_i(CH_3)$ of a factor of 12.5 ± 5.5 for H-atom abstraction from a $-CH_2-$ group compared to a $-CH_3$ group is lower than the factor of ~ 100 predicted for isomerizations of alkoxy radicals formed from alkanes (*1*). [Allowing the rate constant ratios $k(OH + 2\text{-methylpropanal})/k(OH + alcohol)$ and $k(OH + 4\text{-methyl-2-pentanone})/k(OH + alcohol)$ to vary within their allowable limits (see above and Table 3, footnotes c and e) leads to values of $k_i(CH_2)/k_i(CH_3)$ in the range 6−34.]

The decomposition rate constants k_d, of the RCH_2C-$(CH_3)(OH)CH_2C(\dot{O})(CH_3)_2$ alkoxy radicals can be estimated to be $k_d \sim 8 \times 10^5 \text{ s}^{-1}$ at 296 K (*1*), based on the calculated heats of reaction of $\Delta H_d = 0.1-0.4$ kcal mol^{-1} (*18, 19*). The rate constants for isomerization are then $\sim 1.3 \times 10^5 \text{ s}^{-1}$ for H-atom abstraction from the $-CH_3$ groups and $\sim 1.6 \times 10^6$ s^{-1} for H-atom abstraction from the $-CH_2-$ group in the $(CH_3)_2C(OH)CH_2C(\dot{O})(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)CH_2C$-$(\dot{O})(CH_3)_2$ radicals. These isomerization rate constants can be compared to those involving H-atom abstraction from $-CH_3$ and $-CH_2-$ groups in the alkoxy radicals formed from the alkanes of 7×10^4 and 8×10^6 s^{-1}, respectively (*1*), with the isomerization rate constant for H-atom abstraction from a $-CH_3$ group being based on the data of Carter *et al.* (*7*), Niki *et al.* (*8*), and Cox *et al.* (*9*) for the 1-butoxy radical relative to reaction of the 1-butoxy radical with O_2 (*1*). Despite significant uncertainties, the 296 K rate constants derived in this work for the 1,5-H shift isomerizations of the $(CH_3)_2C(OH)CH_2C(\dot{O})(CH_3)_2$ and $CH_3CH_2C(CH_3)(OH)$-$CH_2C(\dot{O})(CH_3)_2$ radicals are reasonably consistent with previous literature estimates for the alkanes (*1*), although the present rate constant for isomerization via H-atom abstraction from a $-CH_2-$ group is somewhat lower than previous estimations (*1*) of 1,5- H shift isomerization rates from alkane $-CH_2-$ groups.

Conclusions

The product data obtained in this work provide conclusive evidence for the occurrence of the alkoxy radical isomerization reaction via a 1,5-H shift at room temperature, with

the isomerization rate constants derived being reasonably consistent with previous estimates. Our product data also provide a fairly complete understanding of the reaction pathways involved in the OH radical reactions with 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol and of the products formed in the presence of NO_x.

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