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Journal of Photochemistry and Photobiology A: Chemistry 157 (2003) 257–267

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Kinetics and products of the reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol

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Received 30 May 2002; received in revised form 7 July 2002; accepted 8 July 2002

Abstract

Kinetics and products of the gas-phase reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol were investigated. Using a relative rate method, rate constants for the gas-phase reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol of $(7.93 \pm 0.58) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $(1.91 \pm 0.10) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, were measured at 298 ± 2 K, where the error limits are two standard deviations and do not include the uncertainty (estimated to be $\sim\pm10\%$) in the rate constant for the reference compound. Gas chromatographic analyses showed the formation of acetaldehyde, propanal, acetone and 2-pentanone from the 2-methyl-2-pentanol reaction in the presence of NO, with molar formation yields of 22 ± 3, 35 ± 4, 56 ± 6 and $5.4\pm1.1\%$, respectively. From the 4-methyl-2-pentanol reaction, gas chromatographic analyses showed the formation of acetaldehyde, acetone, 2-methyl-2-propanal and 4-methyl-2-pentanone, with molar formation yields of 37 ± 6, 26 ± 3, 11.1 ± 1.2 and $25 \pm 2\%$, respectively. In situ atmospheric pressure ionization mass spectrometry analyses showed the formation of molecular weight 163 and 179 nitrates (attributed to hydroxynitrates and dihydroxynitrates, respectively) from both reactions, and the sum of the hydroxynitrate and dihydroxynitrate yields were determined to be ~8% from the 2-methyl-2-pentanol reaction and ~7% from the 4-methyl-2-pentanol reaction. Reaction mechanisms leading to the observed products are discussed and presented.

Keywords: Hydroxyl radical; 2-Methyl-2-pentanol; 4-Methyl-2-pentanol; Reaction kinetics; Reaction products

1. Introduction

Volatile organic compounds (VOCs) emitted into the atmosphere can undergo photolysis and reaction with OH radicals, NO$_3$ radicals, and O$_3$ [1], with the OH radical reaction being an important, and often dominant, atmospheric loss process [1]. For saturated aliphatic compounds, such as alkanes, alcohols, and ethers, these OH radical-initiated reactions proceed by initial H-atom abstraction from the various C–H bonds and, to a much lesser extent, from the O–H bond(s) in alcohols [1]. The subsequent reactions involve the intermediary of organic peroxy (RO$_2^\bullet$) and alkoxy (RO$^\bullet$) radicals, with alkoxy radicals being the key intermediate species in the presence of sufficient NO that peroxy radicals react dominantly with NO rather than with HO$_2$ or organic peroxy radicals [1]. Under atmospheric conditions, alkoxy radicals decompose, isomerize (through a six-membered transition state) and/or react with O$_2$ [2–4]. To date, there have been relatively few absolute rate measurements of the rate constants for the reactions of alkoxy radicals with O$_2$ [5–11], or of alkoxy radical decomposition [5,6,9,12–15] or isomerization [7]. Additionally, these studies involve only $\leq$C$_5$ alkoxy radicals formed from alkanes, and several of the decomposition and isomerization rate constants are at 37.5 Torr total pressure [6,7,9] and because of falloff effects may not be applicable to atmospheric conditions. Furthermore, the measured room temperature rate constants for the reactions of O$_2$ with 2-butoxy [6,10] and 3-pentoxy [9,11] each disagree by a factor of ~2. Therefore, at present the database concerning alkoxy radical reactions consists largely of relative rate measurements obtained from product studies [2,3].

To obtain additional information concerning the reactions of alkoxy and substituted alkoxy radicals under atmospheric conditions, in this work we have investigated the OH radical-initiated reactions of 2-methyl-2-pentanol

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doi:10.1016/S1010-6030(03)00059-5

$[(CH_3)_2C(OH)CH_2CH_2CH_3]$ and 4-methyl-2-pentanol $[CH_3CH(OH)CH_2CH(CH_3)_2]$. Specifically, we used a relative rate method to measure rate constants for the gas-phase reactions of 2-methyl-2-pentanol and 4-methyl-2-pentanol with OH radicals at 298 ± 2 K, and investigated the products formed from these reactions using gas chromatography with flame ionization detection (GC–FID), combined gas chromatography–mass spectrometry (GC–MS), and in situ atmospheric pressure ionization mass spectrometry (API–MS). These VOCs were chosen because many of the products predicted to be formed from the reactions of the intermediate alkoxy radicals are commercially available and can be readily analyzed by gas chromatography, therefore allowing the relative importance of the various alkoxy radical reactions and the partial rate constants for H-atom abstraction by the OH radical from the various CH_3, CH_2 and CH groups to be determined.

2. Experimental

Experiments were carried out in 7500 l Teflon chambers, equipped with two parallel banks of blacklamps for irradiation, at 298 ± 2 K and 740 Torr total pressure of purified air at ∼5% relative humidity. Each chamber is fitted with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber.

2.1. Kinetic studies

Rate constants for the OH radical reactions were measured using a relative rate method in which the relative disappearance rates of the methylpentanols and a reference compound, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals [16]. Providing that the methylpentanols and the reference compound reacted only with OH radicals, then,

$$\ln\left(\frac{[\text{pentanol}]_{t_0}}{[\text{pentanol}]_t}\right) = \frac{k_1}{k_2}\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) \quad (1)$$

where $[\text{pentanol}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the methylpentanol and reference compound, respectively, at time t_0, $[\text{pentanol}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, and k_1 and k_2 are the rate constants for reactions (2) and (3), respectively.

$$\text{OH} + \text{methylpentanol} \rightarrow \text{products} \quad (2)$$

$$\text{OH} + \text{reference compound} \rightarrow \text{products} \quad (3)$$

OH radicals were generated by the photolysis of methyl nitrite (CH_3ONO) in air at wavelengths >300 nm [16], and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals. The initial reactant concentrations (in molecule cm^{-3} units) were: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; 2-methyl-2-pentanol $(2.18–3.06) \times 10^{13}$ [or 4-methyl-2-pentanol, $(2.44–2.56) \times 10^{13}$], and *n*-octane (the reference compound), $\sim 2.4 \times 10^{13}$. Irradiations were carried out for 10–45 min (2-methyl-2-pentanol) and 7–24 min (4-methyl-2-pentanol), resulting in up to 45 and 59% reaction of the initially present 2-methyl-2-pentanol and 4-methyl-2-pentanol, respectively.

The concentrations of 2- and 4-methylpentanol and *n*-octane were measured during the experiments by gas chromatography with flame ionization detection (GC–FID). For the analysis of 2- and 4-methylpentanol, their reaction products (see later), and *n*-octane, 100 cm^3 volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ∼250 °C onto a 30 m DB-1701 megabore column held at −40 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. Based on replicate analyses in the dark, the GC–FID measurement uncertainties for 2- and 4-methylpentanol and *n*-octane were ≤3%. GC–FID response factors for 2- and 4-methylpentanol and products were determined by introducing measured amounts of the chemicals into the 7500 l chamber and conducting several replicate GC–FID analyses [17]. On a relative basis, the measured GC–FID response factors agreed to within ±13% with those calculated using the effective carbon number concept [18]. NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments Inc., Model 42 chemiluminescent NO–NO_x analyzer.

2.2. Product studies

Products were identified and quantified from the reactions of the OH radical with 2- and 4-methylpentanol, both during the kinetic experiments (see earlier) and from additional irradiated CH_3ONO–NO–2-methyl-2-pentanol (or 4-methyl-2-pentanol)–air mixtures by GC–FID and GC–MS. The initial CH_3ONO and NO concentrations in the irradiated CH_3ONO–NO–methylpentanol–air mixtures and the GC–FID analysis procedures were similar to those employed in the kinetic experiments described earlier, and the initial 2-methyl-2-pentanol and 4-methyl-2-pentanol concentrations were in the range $(2.30–2.36) \times 10^{13}$ and $(2.32–2.56) \times 10^{13}$ molecule cm^{-3}, respectively. To verify the product identities, gas samples were collected onto Tenax-TA solid adsorbent for GC–MS analyses, with subsequent thermal desorption onto a 30 m DB-1701 fused silica capillary column in a HP 5890 GC interfaced to a HP 5971 Mass Selective Detector operated in the scanning mode. Additionally, for one 2-methyl-2-pentanol reaction, products were sampled onto a 65 μm PDMS/DVB solid phase microextraction (SPME) fiber coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride [19] to analyze for carbonyl products as their oxime derivatives. The fiber was thermally desorbed onto a 30 m DB-1701 fused silica capillary column in a Varian 2000 GC–MS operated in the chemical ionization (CI) mode with isobutane as the CI gas to provide molecular weight information on any carbonyl products.

CH_3ONO–NO–methylpentanol–air irradiations were also carried out 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). 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 previously [20,21]. 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 [20,21].

Both positive and negative ion modes were used in this work. In the positive ion mode, protonated water hydrates (H_3O^+ $(H_2O)_n$) generated by the corona discharge in the chamber diluent air were responsible for the protonation of analytes [20,21]. In the negative ion mode, adducts were formed between molecules and the negative ions generated by the negative corona around the discharge needle. 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, NO_2^- and NO_3^-, are formed through reactions between the primary reagent ions and neutral molecules, such as NO_2. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. In these experiments the API–MS instrument was operated under conditions that favored the formation of dimer ions in the ion source region [20,21]. 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 hetero-dimers [20,21] in the positive ion mode and mainly O_2^- or NO_2^- adducts in the negative ion mode [21]. Because NO_2 is generated from the oxidation of NO during the reactions (by HO_2 and organic peroxy radicals), it is preferable in the negative ion mode to measure the products as NO_2^- adducts [21]. Therefore, sufficient NO_2 was added to the chamber after the irradiations (with NO_2 concentrations $\geq(2\text{–}3)\times10^{13}$ molecule cm^{-3}) so that NO_2^- adducts of the hydroxycarbonyls and hydroxynitrates dominated over the corresponding O_2^- adducts [21]. The C_4-hydroxynitrate $CH_3CH(OH)CH(ONO_2)CH_3$ was formed in situ from the OH radical-initiated reaction of *cis*-2-butene [22,23] as an internal standard for the quantification of hydroxynitrates [21].

2.3. Chemicals

The chemicals used, and their stated purities, were: acetone (HPLC grade), Fisher Scientific; *n*-octane (>99%), acetaldehyde (>99.5%), 4-methyl-2-pentanone (>99%), 2-methylpropanal (>99%), 2-methyl-2-pentanol (99%), 4-methyl-2-pentanol (99%), propanal (>99%), 2-pentanone (>99%) and 4-hydroxy-4-methyl-2-pentanone (99%), Aldrich Chemical Company; and *cis*-2-butene (≥95%) and NO (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared as described previously [24] and stored at 77 K under vacuum.

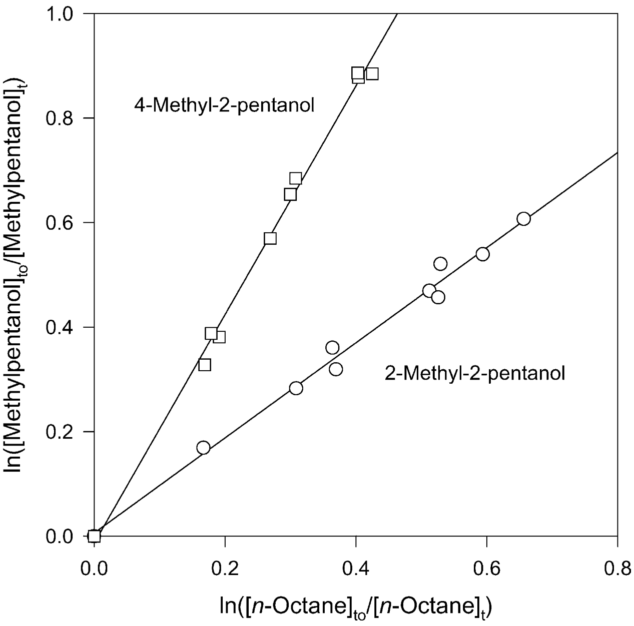


Fig. 1. Plots of Eq. (1) for the gas-phase reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol, with *n*-octane as the reference compound.

3. Results

3.1. OH radical reaction rate constants

A series of CH_3ONO–NO–2-methyl-2-pentanol (or 4-methyl-2-pentanol)–*n*-octane–air irradiations were carried out, and the data obtained are plotted in accordance with Eq. (1) in Fig. 1. Good straight-line plots are observed, and

Table 1
Rate constant ratios k_1/k_2 and rate constants k_1 for the gas-phase reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol at 298 ± 2 K

Alcohol	k_1/k_2 [a]	$10^{12} \times k_1$ (cm^3 $molecule^{-1}$ s^{-1}) [b]	
		This work	Estimated [c]
2-Methyl-2-pentanol	0.910 ± 0.066	7.93 ± 0.58	5.15
4-Methyl-2-pentanol	2.19 ± 0.11	19.1 ± 1.0	13.1

[a] *n*-Octane used as the reference compound. The indicated errors are two least-squares standard deviations.

[b] Placed on an absolute basis by use of a rate constant of k_2 (*n*-octane) $= 8.71\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K [3]. The indicated errors do not include the estimated overall uncertainty in the rate constant k_2 (estimated to be ~10%).

[c] Calculated using the estimation method of Kwok and Atkinson [30] as revised by Bethel et al. [16].

Table 2
Formation yields of selected products from the gas-phase reactions of the OH radical with 2-methyl-2-pentanol at 296 ± 2 K

Product	Molar yield[a]	Maximum value of factor F to account for reaction with OH radicals[b]	Maximum correction for secondary formation from other products[b] (%)
Acetaldehyde	0.22 ± 0.03	1.86	48
Propanal	0.35 ± 0.04	2.12	<1
Acetone	0.56 ± 0.06	1.01	[c]
2-Pentanone	0.054 ± 0.011	1.23	[c]
MW 163 hydroxynitrate	0.058[e]		
MW 179 hydroxynitrate	0.023[e]		
4-Hydroxy-4-methyl-2-pentanone	<0.04	1.19	[c]
4-Hydroxy-2-pentanone	Observed[d]		

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC–FID response factors for 2-methyl-2-pentanol and products of ±5% each.

[b] See text.

[c] No formation from other products.

[d] From GC–MS analysis of *O*-(2,3,4,5,6-pentafluoro)benzyl hydroxylamine coated SPME fiber (see text).

[e] Estimated to be uncertain to a factor of ∼2.

the rate constant ratios k_1/k_2 obtained from least-squares analyses of these data are given in Table 1. These rate constant ratios are placed on an absolute basis by use of a rate constant k_2 for reaction of the OH radical with *n*-octane at 298 K of 8.71×10^{-12} cm^3 molecule^{-1} s^{-1} [3], and the resulting rate constants k_1 are also given in Table 1.

3.2. OH radical reaction products; GC analyses

GC–MS and GC–FID analyses of irradiated CH$_3$ONO–NO–2-methyl-2-pentanol (or 4-methyl-2-pentanol)–air and CH$_3$ONO–NO–2-methyl-2-pentanol (or 4-methyl-2-pentanol)–*n*-octane–air mixtures showed the formation of several products from each alcohol. By comparison of the GC retention times and mass spectra with those of authentic standards, the products identified from 2-methyl-2-pentanol were acetaldehyde, propanal, acetone, 2-pentanone and 4-hydroxy-4-methyl-2-pentanone, and from 4-methyl-2-pentanol were acetaldehyde, acetone, 2-methylpropanal and 4-methyl-2-pentanone. These products also react with the OH radical, and their measured concentrations were corrected for secondary reactions with the OH radical as discussed previously [25], using the OH reaction rate constants measured here for the methylpentanols and those for the products recommended by Atkinson [26] of (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}): acetaldehyde, 15.8; propanal, 19.6; acetone, 0.219; 2-methylpropanal, 26.3; and 4-methyl-2-pentanone, 14.1. The multiplicative correction factors F to account for secondary reactions with the OH radical increase with increasing rate constant ratio $k(\mathrm{OH} + \mathrm{product})/k(\mathrm{OH} + \mathrm{methylpentanol})$ and with increasing extent of reaction [25], and the calculated maximum values of F are given in Tables 2 and 3. In addition to removal by secondary reaction with OH radicals, certain of the observed products are formed from other products in these secondary reactions. Thus, reaction of OH radicals with propanal leads to the formation of acetaldehyde [1,26] in 100% yield in the presence of sufficient NO that the $CH_3CH_2C(O)OO^\bullet$ radical reacts with NO rather than with NO$_2$; reaction of OH radicals with 2-pentanone leads to the formation of propanal (19%) and acetaldehyde (51%) [27]; reaction of OH radicals with 2-methylpropanal is assumed to lead to the formation of acetone in 100% yield [26]; and reaction of OH radicals with 4-methyl-2-pentanone leads

Table 3
Formation yields of selected products from the gas-phase reactions of the OH radical with 4-methyl-2-pentanol at 296 ± 2 K

Product	Molar yield[a]	Maximum value of factor F to account for reaction with OH radicals[b]	Maximum correction for secondary formation from other products (%)[b]
Acetaldehyde	0.37 ± 0.06	1.55	[c]
Acetone	0.26 ± 0.03	1.01	33
2-Methylpropanal	0.111 ± 0.012	2.02	5
4-Methyl-2-pentanone	0.25 ± 0.02	1.49	[c]
MW 163 hydroxynitrate	0.055[d]		
MW 179 hydroxynitrate	0.018[d]		

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC–FID response factors for 4-methyl-2-pentanol and products of ±5% each.

[b] See text.

[c] No formation from other products.

[d] Estimated to be uncertain to a factor of ∼2.

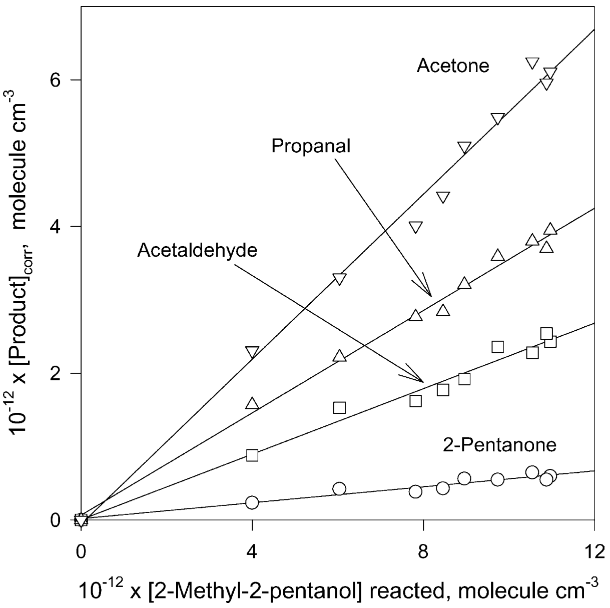


Fig. 2. Plots of the amounts of acetaldehyde, propanal, acetone and 2-pentanone formed, corrected for reaction with OH radicals, against the amounts of 2-methyl-2-pentanol reacted with the OH radical.

to the formation of acetone (78%) and 2-methylpropanal (7.1%) [28]. Therefore, in addition to correcting for losses of products by reaction with the OH radicals (note that photolysis of the products was of no importance for the light intensity and irradiation periods used here), corrections were also made for secondary formation from other products (Tables 2 and 3). As evident from Tables 2 and 3, the corrected data for the formation of acetaldehyde from the 2-methyl-2-pentanol reaction and of acetone from the 4-methyl-2-pentanol reaction are subject to significant uncertainties.

Plots of the amounts of products formed, corrected for reaction with the OH radical and for secondary formation from other products (when applicable; see earlier), against the amounts of 2-methyl-2-pentanol and 4-methyl-2-pentanol reacted are shown in Figs. 2 and 3, respectively. Reasonably good straight-line plots are observed, and the product formation yields obtained from least-squares analyses of these data are given in Table 2 (2-methyl-2-pentanol) and 3 (4-methyl-2-pentanol).

The GC–MS analysis of the *O*-(2,3,4,5,6-pentafluoro)-benzyl hydroxylamine coated SPME fiber exposed to the 2-methyl-2-pentanol reaction products showed a product peak whose mass spectrum corresponded to the oxime of a molecular weight 102 carbonyl product, which is attributed to the predicted 1,3-hydroxycarbonyl product $CH_3C(O)CH_2CH(OH)CH_3$ (Scheme 3). However, no peak attibutable to this product was observed in GC–MS analyses of gas samples collected onto Tenax solid adsorbent (note that 1,3-hydroxyketones appear to be amenable to gas chromatography without prior derivatization [16]), and hence this hydroxycarbonyl product could not be quantified.

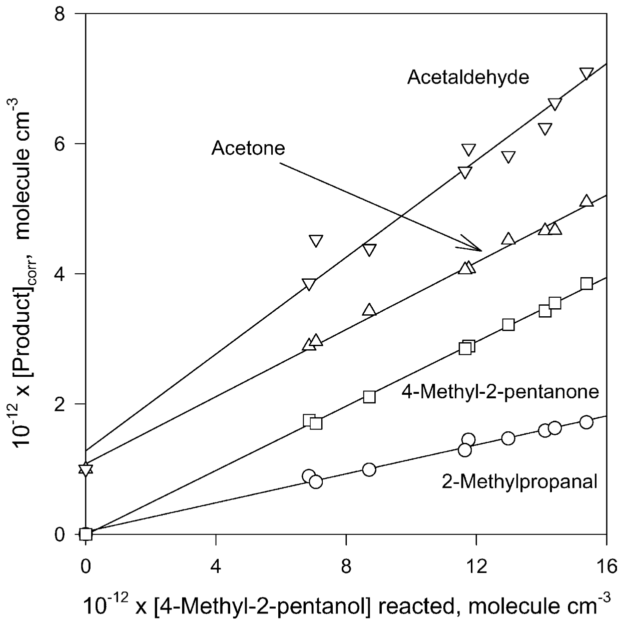


Fig. 3. Plots of the amounts of acetaldehyde, acetone, 2-methylpropanal and 4-methyl-2-pentanone formed, corrected for reaction with OH radicals, against the amounts of 4-methyl-2-pentanol reacted with the OH radical. The data for acetaldehyde and acetone have been displaced vertically by 1.0×10^{12} molecule cm^{-3} for clarity.

3.3. OH radical reaction products; API–MS analyses

Analyses of irradiated CH_3ONO–NO–2-methyl-2-pentanol (or 4-methyl-2-pentanol)–air mixtures were also carried out with in situ API–MS analyses. In the positive ion mode, using protonated water clusters as the reagent ion, API–MS and API–MS/MS analyses of the 2-methyl-2-pentanol reaction showed the presence of products of molecular weight 58 (attributed to propanal and/or acetone), 86 (attributed to 2-pentanone), 163 and 179 (note that the potential product $CH_3C(O)CH_2CH(OH)CH_3$ (see earlier and Section 4) has the same molecular weight as 2-methyl-2-pentanol and therefore could not be observed by these analyses). API–MS/MS "product ion" spectra of the protonated hetero-dimers of 2-methyl-2-pentanol with the molecular weight 163 and 179 products (i.e. of the ion peaks at 266 and 282 u, respectively) showed the presence of fragment ions at 46 u ($NO_2{}^+$). The products of molecular weight 163 and 179 are therefore identified as organic nitrates. Analogous analyses of the 4-methyl-2-pentanol reaction showed the presence of products of molecular weight 58 (attributed to acetone), 100 (attributed to 4-methyl-2-pentanone), 163 and 179, with the latter two products again being attributed to organic nitrates (as discussed below, to hydroxy- and dihydroxy-nitrates).

In the negative ion mode in the presence of $\sim 2.4 \times 10^{13}$ molecule cm^{-3} of NO_2, API–MS analyses of both the 2-methyl-2-pentanol and 4-methyl-2-pentanol reactions showed the presence of $NO_2{}^-$ adduct peaks at 209 and 225 u, as shown in Fig. 4 for experiments which included

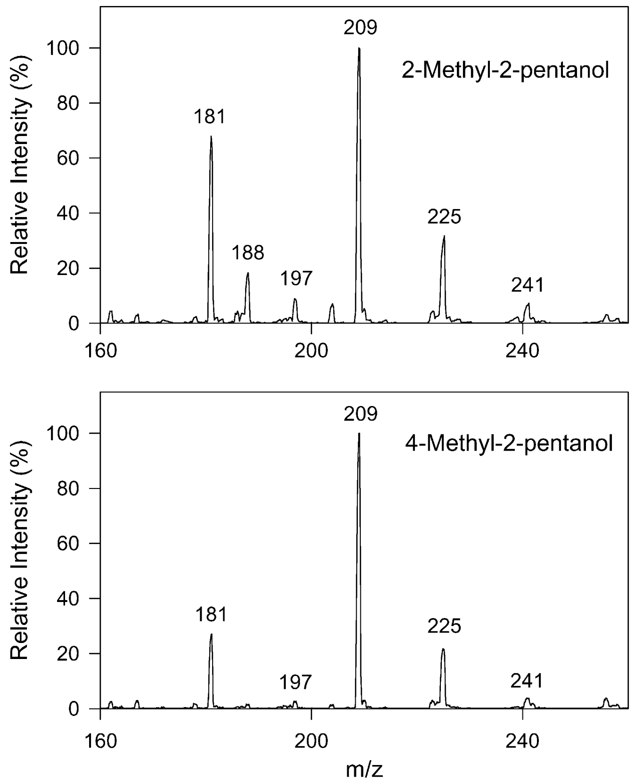


Fig. 4. API–MS negative ion spectra of irradiated CH_3ONO–NO–2-methyl-2-pentanol–air and CH_3ONO–NO–4-methyl-2-pentanol–air mixtures, using NO_2^- ions as the reagent ions.

cis-2-butene in the reactant mixture to form in situ the molecular weight 135 hydroxynitrate $CH_3CH(OH)CH(ONO_2)CH_3$ (seen as the NO_2^- adduct at 181 u in Fig. 4) as an internal standard [22,23]. As noted in Section 2, because NO_2 is present after reaction, and the hydroxynitrates will form O_2^-, NO_2^- (and smaller amounts of NO_3^-) adducts, additional NO_2 was added to minimize the O_2^- adducts, thus maximizing sensitivity and simplifying quantification.

As seen from Fig. 4, the major ion peaks observed are those at 181, 209 and 225 u, which are interpreted as the NO_2^- adducts of hydroxynitrates of molecular weight 135, 163 and 179. However, under our experimental conditions NO_3^- adducts of these products are also present (as evident from the 197 u ion peak for the molecular weight 135 hydroxynitrate $CH_3CH(OH)CH(ONO_2)CH_3$ seen in Fig. 4). Unfortunately, the NO_3^- adduct of the molecular weight 163 product cannot be differentiated from the NO_2^- adduct of the molecular weight 179 product, both being at 225 u. Therefore, a reacted mixture was diluted with purified air until the dominant ion peaks were the O_2^- adducts, i.e. until the molecular weight 135 hydroxynitrate appeared exclusively at 167 u. Then assuming that the signal intensities of the O_2^- adducts were proportional to the amounts of hydroxynitrates present, the ratios of the products were determined as the ratio of their O_2^- adducts. This ratio was then applied to the yield measurements obtained by summing the 209, 225 and 241 u ion peaks for the NO_2^- and NO_3^- adducts of the two organic nitrate products relative to the sum of the NO_2^- and NO_3^- adducts of the internal standard. Using a formation yield of $CH_3CH(OH)CH(ONO_2)CH_3$ from the OH radical-initiated reaction of *cis*-2-butene of 3.55% [22,23], the formation yields of the molecular weight 163 and 179 hydroxynitrates obtained from three experiments each for 2-methyl-2-pentanol and for 4-methyl-2-pentanol are listed in Tables 2 and 3. As in previous studies [21,29], these derived formation yields for the molecular weight 163 and 179 hydroxynitrates are estimated to be uncertain to a factor of ~2 (the individual measurements of the formation yields of the molecular weight 163 product from 2-methyl-2-pentanol were 8.1, 3.8 and 5.5%, and from 4-methyl-2-pentanol were 4.7, 7.4 and 4.6%).

In addition to these hydroxynitrates, ion peaks were also observed at 148 and 188 u. API–MS/MS "product ion" spectra showed the 148 u ion peak to be an NO_2^- adduct of a molecular weight 102 species (presumably the starting methylpentanols), with the 188 u ion peak being an adduct of a molecular weight 125 species observed in all reaction systems containing NO_2.

4. Discussion

These are the first measurements of rate constants for reaction of the OH radical with 2-methyl-2-pentanol and 4-methyl-2-pentanol. Room temperature rate constants calculated using the estimation method of Kwok and Atkinson [30], as revised by Bethel et al. [16] are compared with our measured values in Table 1. The estimated rate constants are seen to be a factor of ~1.5 lower than the measured values, this being considered to be reasonably good agreement [30]. The OH radical reactions with 2- and 4-methyl-2-pentanol proceed by H-atom abstraction from the various C–H bonds and, to a much lesser extent, from the O–H bond [1,26,30], and the estimation method of Kwok and Atkinson [30] (as revised by Bethel et al. [16]) can be used to calculate the fractions of the overall reaction occurring by H-atom abstraction from the various CH_3, CH_2, CH and OH groups. The resulting radicals (apart from α-hydroxyalkyl radicals; see later) then rapidly add O_2 to form organic peroxy radicals [1].

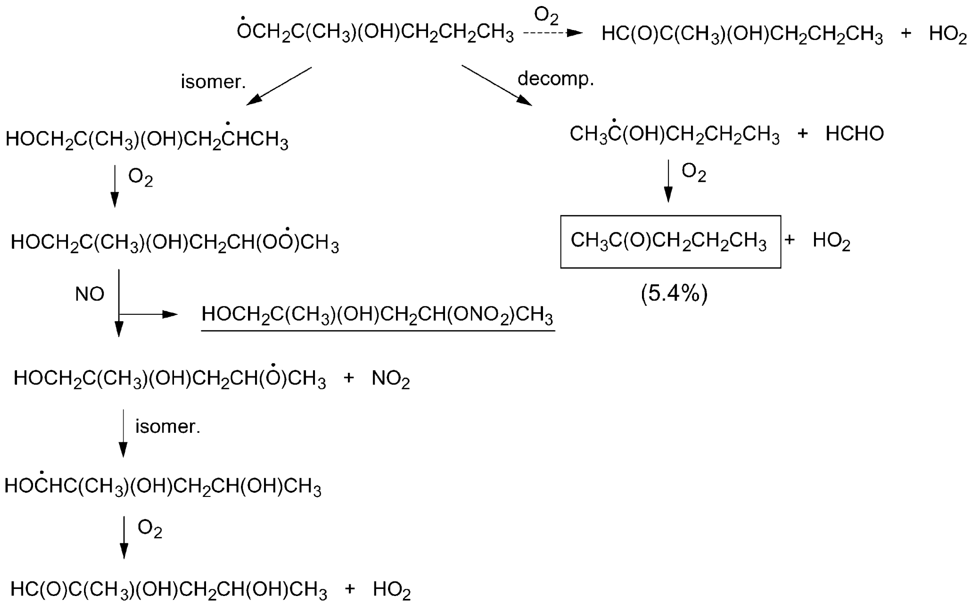
$$R^\bullet + O_2 \rightarrow ROO^\bullet \tag{4}$$

In the presence of NO, these organic peroxy radicals react with NO to form either an organic nitrate (a molecular weight 163 hydroxynitrate in this case) or a hydroxyalkoxy radical plus NO_2.

$$ROO^\bullet + NO \rightarrow RONO_2 \tag{5a}$$

$$ROO^\bullet + NO \rightarrow RO^\bullet + NO_2 \tag{5b}$$

Clearly, the molecular weight 163 nitrates observed in the API–MS analyses and quantified as their NO_2^- adducts are



Scheme 1.

the hydroxynitrates (for example, $(CH_3)_2C(OH)CH(ONO_2)CH_2CH_3$ and isomers formed from 2-methyl-2-pentanol and $CH_3CH(OH)CH(ONO_2)CH(CH_3)_2$ and isomers from 4-methyl-2-pentanol) formed from reaction (5a). Under atmospheric conditions, alkoxy radicals can react with O_2, decompose and isomerize through a six-membered transition state [2,3], noting that not all of these reaction pathways may be feasible for a given alkoxy radical.

Under atmospheric conditions, it appears that α-hydroxyalkyl radicals react rapidly, and solely, with O_2 to form a carbonyl plus HO_2 radical [26]; for example

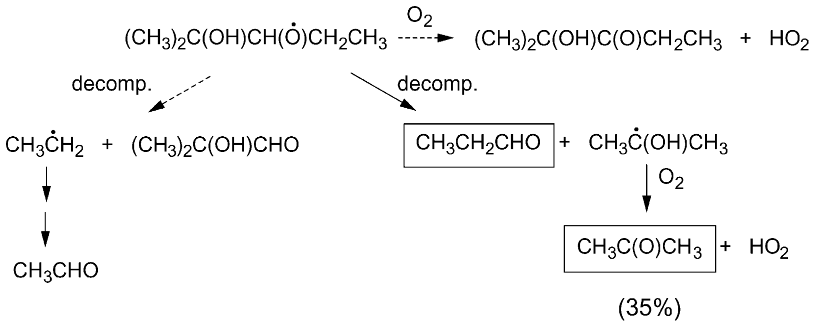
$$(CH_3)_2CHCH_2C^{\bullet}(OH)CH_3 + O_2 \rightarrow (CH_3)_2CHCH_2C(O)CH_3 + HO_2 \qquad (6)$$

In the following sections, the expected reactions of 2- and 4-methyl-2-pentanol are discussed, based on our current knowledge of the atmospheric chemistry of volatile organic compounds, and compared with the products identified and quantified here. Reaction rates of alkoxy radicals (by reaction with O_2, decomposition and isomerization) are estimated as described by Atkinson [2,3] and Aschmann and Atkinson [4].

4.1. 2-Methyl-2-pentanol

The percentage of the overall OH radical reaction occurring by H-atom abstraction from the C–H bonds at the various carbon atoms in $(CH_3)_2C(OH)CH_2CH_2CH_3$ are calculated [16,30] to be: from the two equivalent CH_3 groups at the 1-position, 14%; from the CH_2 group at the 3-position, 58%; from the CH_2 group at the 4-position, 22%; from the CH_3 group at the 5-position, 3%; and from the OH group, 3%. As noted above, the initially formed alkyl-type radicals add O_2 and then react with NO to form hydroxynitrates (mainly $(CH_3)_2C(OH)CH(ONO_2)CH_2CH_3$ and $(CH_3)_2C(OH)CH_2CH(ONO_2)CH_3$) of molecular weight 163. The expected reactions of the alkoxy radicals estimated to be formed in significant yield are shown in Schemes 1–3. In these reaction schemes, the intermediate alkyl and alkyl peroxy radicals are generally omitted for clarity. Based on the estimation method of Atkinson [2,3], as revised by Aschmann and Atkinson [4] and Bethel et al. [16] (see Supplementary material in Aschmann et al. [31]) and using thermochemical data from compilations [32,33] and the NIST estimation program [34], reaction pathways which are estimated to be of minor or negligible importance (<1% of the overall reaction rate) are denoted by dashed arrows, and if a reaction pathway is estimated to dominate over other pathways by a factor of >10, it is shown as a bold arrow. The observed products are shown in boxes and the possible structures for the molecular weight 179 dihydroxynitrates are shown underlined on the schemes. The detailed reactions of ethyl radicals, 1-propyl radicals and $(CH_3)_2C(OH)C^{\bullet}H_2$ radicals are not shown, because under atmospheric conditions these lead to the formation of acetaldehyde, propanal, and acetone + HCHO, respectively [2,3,26]. The alkoxy radical $(CH_3)_2C(O^{\bullet})CH_2CH_2CH_3$ formed after H-atom abstraction from the OH group is calculated [3] to mainly isomerize to ultimately form $(CH_3)_2C(OH)CH_2CH_2CHO$.

These predictions are in general accord with our product data (Table 2). The molecular weight 163 organic nitrates are the hydroxynitrates formed from the $ROO^{\bullet}$ + NO reactions, and the expected products from the alkoxy radicals are acetaldehyde + acetone from the $(CH_3)_2C(OH)CH_2CH(O^{\bullet})CH_3$ radical (Scheme 3), acetone + propanal from the $(CH_3)_2C(OH)CH(O^{\bullet})CH_2CH_3$ radical (Scheme 2), and 2-pentanone from the $^{\bullet}OCH_2C(CH_3)(OH)$-

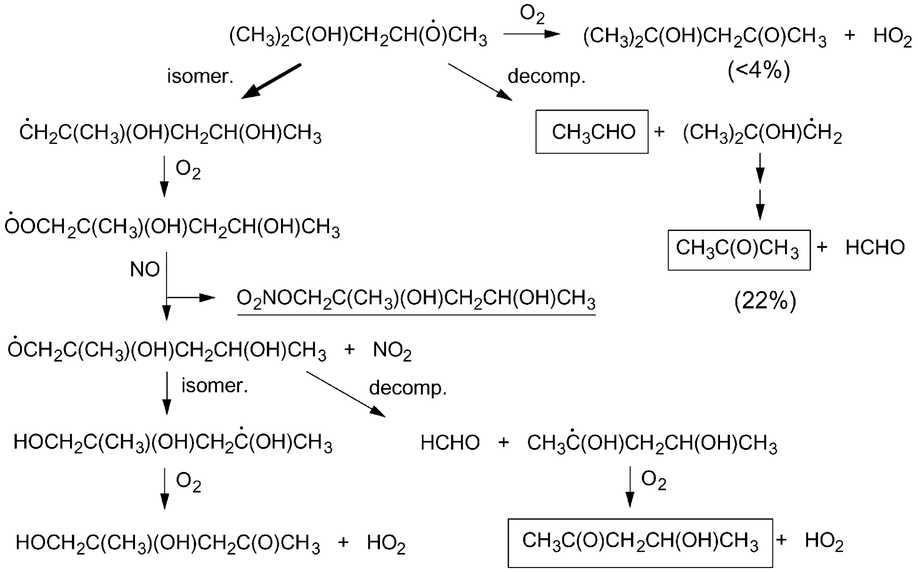


Scheme 2.

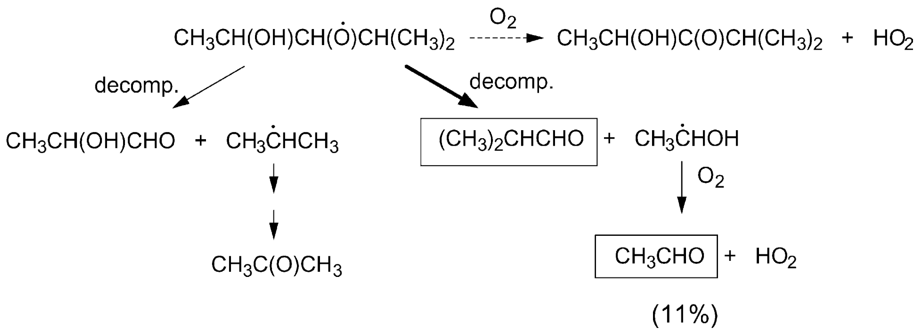
$CH_2CH_2CH_3$ radical (Scheme 1). The product yields given in Table 2 are in agreement with these expectations, in that the acetone yield (56 ± 6%) is equal to the sum of the formation yields of acetaldehyde plus propanal (57 ± 5%). Our product yield data indicate that the $(CH_3)_2C(OH)CH(O^\bullet)CH_2CH_3$ radical is formed in 35 ± 4% yield (from the propanal yield), significantly lower than predicted from the calculated percentage of H-atom abstraction from the 3-position CH_2 group (58%), noting that hydroxynitrate formation from the $(CH_3)_2C(OH)CH(OO^\bullet)CH_2CH_3$ radical occurs to a small extent. The observed lack of formation of 4-hydroxy-4-methyl-2-pentanone (<4% yield) is consistent with expectations (Scheme 3); however, the sum of the yields of acetaldehyde and acetone arising from reaction of the $(CH_3)_2C(OH)CH_2CH(O^\bullet)CH_3$ radical (22 ± 3%, based on the acetaldehyde yield), is higher than expected because the $(CH_3)_2C(OH)CH_2CH(O^\bullet)CH_3$ radical is estimated to dominantly isomerize rather than decompose or react with O_2 (Scheme 3) and the calculated percentage of H-atom abstraction at the 4-position CH_2 group is 22%. Our observation of a molecular weight 102 carbonyl, assumed to be 4-hydroxy-2-pentanone, indicates that the isomerization of the $(CH_3)_2C(OH)CH_2CH(O^\bullet)CH_3$ radical competes with decomposition. The presence of molecular weight 179 organic nitrates (predicted to be $O_2NOCH_2C(CH_3)(OH)CH_2CH(OH)CH_3$ and/or $HOCH_2C(CH_3)(OH)CH_2CH(ONO_2)CH_3$; see Schemes 1 and 3, respectively) also shows that isomerization of certain of the alkoxy radicals must occur.

4.2. 4-Methyl-2-pentanol

The percentage of the overall OH radical reaction occurring by H-atom abstraction from the C–H bonds at the various carbon atoms in $CH_3CH(OH)CH_2CH(CH_3)_2$ are calculated to be: from the CH_3 group at the 1-position, 3%; from the CH group at the 2-position, 53%; from the CH_2 group at the 3-position, 23%; from the CH group at the 4-position, 18%; from the two equivalent CH_3 groups at the 5-positions, 3%; and from the OH group, 1%. As for 2-methyl-2-pentanol, the initially-

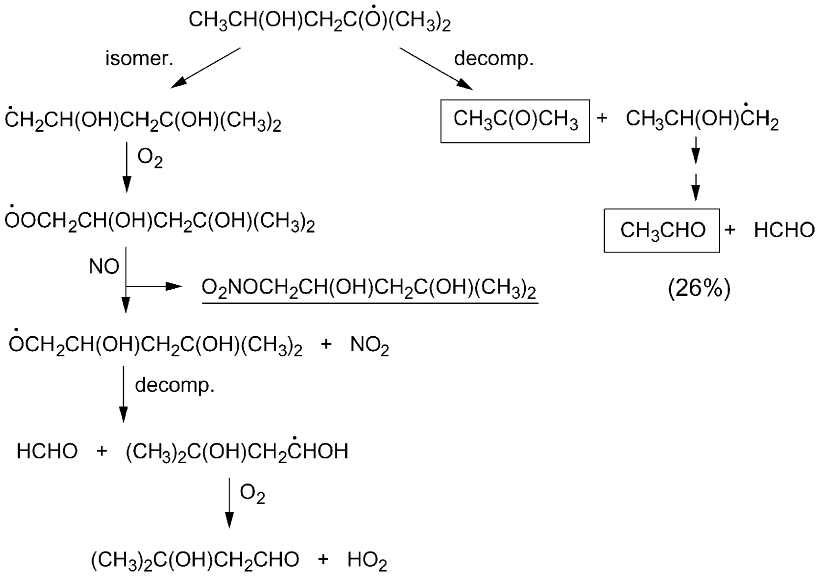


Scheme 3.



Scheme 4.

formed alkyl radicals will solely add O_2 (reaction (4)) and then react with NO (reactions (5a and 5b)) (apart from the $CH_3C^{\bullet}(OH)CH_2CH(CH_3)_2$ α-hydroxy radical which reacts with O_2 as shown in reaction (6) to form 4-methyl-2-pentanone). Schemes 4 and 5 show the expected reactions of the $CH_3CH(OH)CH(O^{\bullet})CH(CH_3)_2$ and $CH_3CH(OH)CH_2C(O^{\bullet})(CH_3)_2$ radicals, with the same format as mentioned above for 2-methyl-2-pentanol. In addition to the molecular weight 163 hydroxynitrates (primarily expected to be $CH_3CH(OH)CH(ONO_2)CH(CH_3)_2$ and $CH_3CH(OH)CH_2C(ONO_2)(CH_3)_2$), the expected products are 4-methyl-2-pentanone from the $CH_3C^{\bullet}(OH)CH_2CH(CH_3)_2$ radical, acetaldehyde plus 2-methylpropanal from the $CH_3CH(OH)CH(O^{\bullet})CH(CH_3)_2$ radical (Scheme 4), and acetaldehyde plus acetone from the $CH_3CH(OH)CH_2C(O^{\bullet})(CH_3)_2$ radical (Scheme 5). It should be noted that isomerization of this latter radical is predicted to dominate over the decomposition to form acetaldehyde plus acetone. The measured product yields are in semi-quantitative accord with these predictions, with the acetaldehyde yield (37 ± 6%) being equal to the sum of the acetone plus 2-methylpropanal yields (37 ± 4%). The measured formation yield of 4-methyl-2-pentanone of 25 ± 2% is a factor of 2 lower than the estimated fraction of the overall OH radical reaction proceeding by H-atom abstraction from the 2-position CH group (53%). Similarly, the 2-methylpropanal yield of 11.1±1.2% is a factor of 2 lower than the calculated percentage of the overall OH radical reaction proceeding by H-atom abstraction from the 3-position CH_2 group (23%), recognizing that some hydroxynitrate formation will occur from the $ROO^{\bullet} + NO$ reaction. The yield of acetaldehyde plus co-product acetone of 26 ± 3% (based on the acetone yield) is higher than anticipated because decomposition of the $CH_3CH(OH)CH_2C(O^{\bullet})(CH_3)_2$ radical to form acetone plus acetaldehyde is predicted to be somewhat less important than isomerization (by a factor of 2.5) and the percentage of H-atom abstraction from the 4-position CH groups is calculated to be 18%. Again, the presence of molecular weight 179 organic nitrates (predicted to be mainly $O_2NOCH_2CH(OH)CH_2C(OH)(CH_3)_2$; Scheme 5) shows that isomerization of certain of the alkoxy radicals must occur.



Scheme 5.

Table 4
Comparison of measured and calculated partial rate constants ($cm^3\ molecule^{-1}\ s^{-1}$) for H-atom abstraction by OH radicals from the various CH_3, CH_2 and CH groups

Methylpentanol and group	$10^{12} \times k_{exp}$	$10^{12} \times k_{calc}$[a]
2-Methyl-2-pentanol		
CH_3 at 1-position	≥0.214	0.354
CH_2 at 3-position	2.78	2.99
CH_2 at 4-position	>1.74	1.15
CH_3 at 5-position		0.167
4-Methyl-2-pentanol		
CH_3 at 1-position		0.354
CH at 2-position	4.78	6.92
CH_2 at 3-position	2.12	2.99
CH at 4-position	>4.97	2.39
CH_3 at 5-position		0.167

[a] Using the estimation method of Kwok and Atkinson [30] as revised by Bethel et al. [16].

5. Conclusions

Comparison of the experimental kinetic and product data obtained here for the reactions of OH radicals with 2-methyl-2-pentanol and 4-methyl-2-pentanol with predictions based on structure-reactivity relationships shows that we have a qualitative (or semi-quantitative) understanding of the initial rate of reaction and of the detailed subsequent reactions. For both reactions, we can account for ~70% of the reaction products and pathways. However, for both 2- and 4-methylpentanol, using the estimation method [16,30]to calculate the overall reaction rate constant and the partial rate constants (i.e. the rate constants for H-atom abstraction from the various CH, CH_2, CH_3 and OH groups) and hence the fraction of the overall OH radical reaction proceeding by H-atom abstraction from the various groups (Table 4), we overestimate the fraction of the overall reaction occurring from C–H bonds on the carbon atom adjacent to that to which the OH group is attached and, in the case of 4-methyl-2-pentanol, at the CH group to which the OH group is attached. In contrast, we appear to underestimate the fraction of the overall reaction occurring from C–H bonds on carbon atoms 2-removed from that to which the OH group is attached (i.e., the γ carbon). However, the calculated partial rate constants for H-atom abstraction from the C–H bond of the CH(OH) group (2-position in 4-methyl-2-pentanol) and of the CH_2 groups adjacent to the carbon to which the OH group is attached (the 3-position CH_2 group in both 2- and 4-methyl-2-pentanol) are in reasonable agreement with the values obtained from our product data (Table 4), as is the partial rate constant for H-atom abstraction from the 1-position CH_3 groups in 2-methyl-2-pentanol. However, the calculated partial rate constants for H-atom abstraction from the 4-position CH_2 or CH groups are much lower (by a factor of ~2 or more) than the values obtained from our product analyses. Clearly, the activating effects of the OH group are transmitted far down the carbon chain from the carbon atom to which the OH group is attached, as previously concluded by Wallington et al. [35] and Nelson et al. [36].

Acknowledgements

The authors gratefully thank the California Air Resources Board for supporting this research through Contract No. 99-306. While this research has been funded by the California Air Resources Board, the results and content of this publication do not necessarily reflect the views and opinions of the agency.

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