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Branching Ratios and Rate Constants for Decomposition and Isomerization of β-Hydroxyalkoxy Radicals Formed from OH Radical-Initiated Reactions of C_6−C_{13} 2-Methyl-1-Alkenes in the Presence of NO_x

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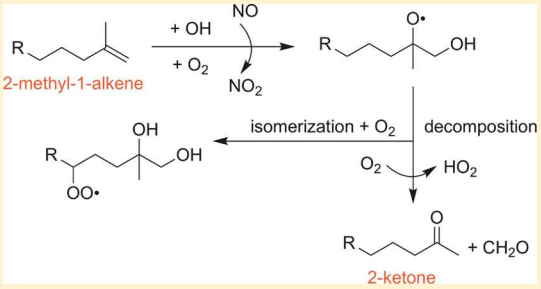
Supporting Information

ABSTRACT: A series of C_6−C_{13} 2-methyl-1-alkenes were reacted with OH radicals in the presence of NO_x in a Teflon environmental chamber, and molar yields of the 2-ketone products were measured using gas chromatography. Yields were corrected for secondary reactions with OH radicals and for gas-wall partitioning of the 2-methyl-1-alkene and 2-ketone, with the latter correction being determined from measurements of gas-wall partitioning of 2-ketone standards. Molar yields of 2-ketones decreased with increasing 2-methyl-1-alkene carbon number from a maximum of 0.82 for C_6 to a minimum of 0.34 ± 0.02 for C_9−C_{13}, which after normalization for the fraction of reaction that occurred by OH radical addition to the C═C double bond (with the rest occurring by H atom abstraction) were 0.86 and 0.39 ± 0.01. These yields were combined with branching ratios determined previously for site-specific OH radical addition to the C═C double bond and for formation of β-hydroxynitrates to determine branching ratios for decomposition and isomerization of β-hydroxyalkoxy radicals. Branching ratios for decomposition decreased with increasing 2-methyl-1-alkene carbon number from a maximum of 0.97 for C_6 to a minimum of 0.49 ± 0.01 for C_9−C_{13}, while the corresponding values for isomerization increased from 0.03 to 0.51 ± 0.01. The results were used to estimate absolute rate constants and activation energies for decomposition and isomerization and were also combined with previously measured yields of β-hydroxynitrates, dihydroxynitrates, trihydroxynitrates, and H atom abstraction products to obtain yields of ∼75% for the C_9−C_{13} reaction products, with the remainder likely being mostly dihydroxycarbonyls and trihydroxycarbonyls.



INTRODUCTION

Alkenes are the dominant component of biogenic nonmethane volatile organic compound (VOC) emissions, with isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$) comprising approximately 50, 15, and 3% of the estimated annual global budget of 1000 Tg.[1] In the atmosphere, these compounds react primarily with OH radicals, O_3, and NO_3 radicals to form oxygenated products, some of which have sufficiently low vapor pressure or high water solubility to condense into particles where they can react further.[2−7] These reactions influence O_3 formation,[8] the cycling of radicals,[9] and the formation of secondary organic aerosol (SOA),[10] which impact climate, human health, and the fate of organic compounds.[11] Although the products and mechanisms of the reactions of isoprene are reasonably well (but by no means fully) understood,[2] much less is known about the reactions of other terpenes.[3−5] This is due in large part to the complexity and diversity of molecular structures, which typically contain varying numbers of C═C double bonds, alkyl group branches, and rings.[12]

Simple linear and branched monoalkenes are also emitted from vegetation and from anthropogenic sources,[1,13] but because of their less complex structures, their reactions form fewer products that tend to be more amenable to identification and quantitation. This is especially the case for reactions with OH radicals conducted under "high NO_x" conditions, which are characteristic of polluted environments, and where products mostly consist of monofunctional carbonyls and multifunctional compounds containing various combinations of hydroxyl, carbonyl, and nitrate groups.[14−19] Knowledge gained from studies of the reactions of simple alkenes can be useful for understanding reactions of more complex VOCs, which often have similar structural features. In the study presented here, we measured the yields of 2-ketones formed from the reactions of C_6−C_{13} 2-methyl-1-alkenes with OH radicals in the presence of NO_x. We then used the results to quantify the branching ratios and rate constants for the decomposition and isomerization of β-hydroxyalkoxy radicals, which are key reaction intermediates. The results are compared with those obtained previously for other alkenes and with predictions of structure−activity relationships (SARs), and yield insights into the effects of molecular structure on reaction

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mechanisms. The results should also be applicable to other reactions and therefore are useful for improving mechanisms of oxidation and SOA formation for VOCs in addition to 2-methyl-1-alkenes.

EXPERIMENTAL SECTION

Chemicals. The following chemicals, with purities and suppliers, were used without further purification: 2-pentanone (>99%), 2-hexanone (>99%), 2-heptanone (99%), 2-octanone (98%), 2-nonanone (>99%), 2-decanone (98%), 2-undecanone (99%), 2-dodecanone (98%), 2-methyl-1-heptene (99%), 2-methyl-1-nonene (97%), and 2-methyl-1-undecene (97%) from Sigma-Aldrich; 2-methyl-1-pentene (99+%) and 2-methyl-1-hexene (96%) from Aldrich; 2-methyl-1-octene (97%) from ChemSampCo; 2-methyl-1-decene (97%) and 2-methyl-1-dodecene (>97%) from Rieke Metals; and NO from Matheson Tri Gas. Methyl nitrite was synthesized[20] and stored on a gas manifold in liquid nitrogen until used.

Environmental Chamber Method. Reactions of C_6-C_{13} 2-methyl-1-alkenes with OH radicals in the presence of NO_x were performed at room temperature (~25 °C) and atmospheric pressure (~740 Torr) in an 8.2 m^3 FEP Teflon environmental chamber whose volume was calibrated as described previously.[21] The chamber was filled with clean, dry air (<5 ppbv hydrocarbons, <1% RH) from an Aadco clean air system and has blacklights covering two walls. In each experiment, 1 ppmv each of three or four 2-methyl-1-alkenes was added to the chamber from a glass bulb (heated when necessary) by flushing it with ultrahigh purity N_2.[22] This particular mixture of compounds was selected so that peaks from neither these nor the 2-ketone reaction products overlapped in gas chromatograms. Then 10 ppmv each of methyl nitrite and NO were prepared on a gas manifold and flushed into the chamber in a similar manner. The NO concentrations were sufficiently high to prevent O_3 and NO_3 radical formation and guarantee that all alkylperoxy radicals reacted with NO. The chamber was mixed for 1 min with a Teflon-coated fan, Tenax samples were taken as described below, and then reactions were initiated by turning on the blacklights to form OH radicals by methyl nitrite photolysis.[23] After 6 min, the blacklights were turned off and more Tenax samples were taken. Typically, ~40−50% of the 2-methyl-1-alkenes reacted. The average OH radical concentration estimated from the amount of 2-methyl-1-alkene reacted and its OH radical rate constant[24] was ~3×10^7 cm^{-3}. The NO and NO_x concentrations were monitored using a Thermo Environmental Instruments Inc. 42C NO−NO_2−NO_x analyzer, and particle mass concentration was measured using a scanning mobility particle sizer.[25]

Measurement of 2-Ketone Yields. Concentrations of 2-methyl-1-alkenes and 2-ketones were measured before and after reaction by collecting three replicate ~1100 cm^3 samples (flow rate ~240 cm^3 min^{-1} for ~4.5 min) on the Tenax solid adsorbent. The 12 cm long, 0.635 cm OD stainless-steel sampling line was flushed with chamber air for 20 min prior to collecting the first sample. The sampling line was then flushed continuously to allow the walls to maintain equilibrium,[22,26] and samples were collected again at 50 and 80 min. Samples were then analyzed by gas chromatography with flame ionization detection (GC/FID) using an Agilent 6890 GC equipped with an Agilent DB-1701 column. Analyses of 2-methyl-1-alkenes in the three replicate samples collected at 30 min intervals were within ±5%, and FID signals measured before reaction were within ±5% of values expected for 1 ppmv chamber concentrations based on calibration curves prepared from solution measurements. This indicated that the 2-methyl-1-alkenes were added quantitatively to the chamber and did not partition to the walls, but even if a small fraction of the largest ones did partition to the walls,[22] the constant concentrations measured over more than an hour indicated that partitioning equilibrium was achieved before and after reaction. We have shown previously[21] that in either case, the concentration of 2-methyl-1-alkene reacted is $[2M1A]_{reacted} = [2M1A]_{T,i}\ (1 - FID_f/FID_i)$, where $[2M1A]_{T,i}$ is the moles of 2-methyl-1-alkene added to the chamber divided by the chamber volume, and FID_i and FID_f are the GC/FID signals measured before and after reaction per volume of air sampled.

Analyses of the 2-ketone products indicated that they had reached gas-wall partitioning equilibrium within 60 min, similar to the behavior observed for 2-ketone standards that were added to the chamber before the first and after the last 2-methyl-1-alkene chamber experiments. Using the same methods described above for 2-methyl-1-alkenes, 300 ppbv each of the C_5-C_{12} 2-ketones were added to the chamber, the chamber was mixed for 1 min, the sampling line was flushed for 20 min, and then a ~500 cm^3 sample was collected on Tenax and analyzed by GC/FID. The first sample was collected 20 min after mixing the chamber, and then at 60 and 100 min. The extent of gas-wall partitioning was within ±5% at the beginning and end of the study.

No attempt was made to detect β-hydroxynitrates using GC/FID analysis. The C_6-C_{13} β-hydroxynitrates formed here will quickly partition to the Teflon chamber walls, as we have observed for 1,2-diols.[27] Also any β-hydroxynitrates that were collected would likely not be detected, either because they did not desorb from the Tenax or the column, or because they decomposed at the high temperatures encountered in the injector and on the column.[28] Instead, in the data analysis discussed below, we used results from previous studies[16,19] in which we quantified β-hydroxynitrates $\geq C_{14}$ that were present entirely in particles using high-performance liquid chromatography with UV/vis detection.

RESULTS AND DISCUSSION

Reaction Mechanism. The mechanism of reaction of 2-methyl-1-alkenes with OH radicals in air in the presence of NO is shown in Scheme 1, where R corresponds to an alkyl group.[19] Branching ratios for individual reaction pathways are designated by α_i and are equal to the fraction of a particular species that reacts by this pathway. The reaction begins either by abstraction of an H atom from the carbon chain to form H_2O and a series of alkyl radical isomers (α_{abs}) or by addition of an OH radical to either of the C atoms in the C=C double bond (α_{add}) to form a pair of β-hydroxyalkyl radicals. In air, these radicals react solely with O_2 to form the corresponding alkylperoxy and 1-hydroxy-2-peroxy (α_1) and 1-peroxy-2-hydroxy (α_2) radicals, respectively. The products formed from subsequent reactions of alkylperoxy radicals are the same as those formed from reactions of *n*-alkanes (but with C=C double bonds) and for carbon numbers larger than 6 include only alkyl nitrates, 1,4-hydroxynitrates, and 1,4-hydroxycarbonyls.[29] The two β-hydroxyperoxy radical isomers react with NO by addition to form the corresponding β-hydroxynitrate isomers, 1-hydroxy-2-nitrooxyalkane (α_3) and 1-nitrooxy-2-hydroxyalkane (α_4), which are designated as 1H2N and 1N2H in Scheme 1, or they react with NO by O-atom abstraction to

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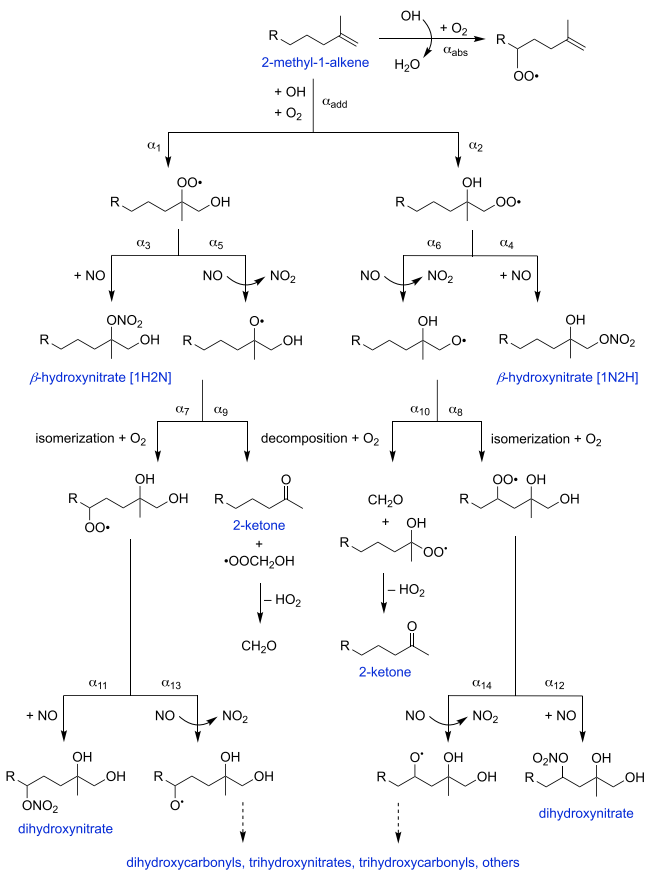
Scheme 1. Mechanism of Reaction of 2-Methyl-1-alkenes with OH Radicals in the Presence of NO_x



form the corresponding 1-hydroxy-2-alkoxy (α_5) and 2-hydroxy-1-alkoxy (α_6) radicals and NO_2. The two β-hydroxyalkoxy radical isomers can isomerize via a six-member ring transition state and then add O_2 to form a pair of 1,2-dihydroxyperoxy radicals (α_7, α_8) that differ only in the position of the peroxy radical group or they can decompose. Reaction with O_2 to form carbonyls is too slow to compete with isomerization and decomposition.[18] The 1,2-dihydroxyperoxy radicals react with NO by pathways similar to those of β-hydroxyperoxy radicals to form dihydroxynitrates and dihydroxyalkoxy radicals, which can then react further to form dihydroxycarbonyls, trihydroxynitrates, and other products. Decomposition of the 1-hydroxy-2-alkoxy radical (α_9) forms a 2-ketone and $\bullet CH_2OH$, which adds O_2 to form $\bullet OOCH_2OH$. Decomposition of the 2-hydroxy-1-alkoxy radical (α_{10}) forms formaldehyde and a α-hydroxyalkyl radical, which adds O_2 to form a α-hydroxyperoxy radical. The α-hydroxyperoxy radical and $\bullet OOCH_2OH$ primarily decompose by the loss of HO_2 to form the same 2-ketone and formaldehyde, but in the presence of high NO concentrations can also react with NO by a minor pathway to form the corresponding alkoxy radicals. Although this reaction will slightly reduce the yield of 2-ketones, studies of reactions of 1-octene and 7-tetradecene by Aschmann et al.[18] under conditions similar to those used here indicate that the reduction should be ~5% or less and so is not considered here.

2-Ketone Yields. The measured molar yields of 2-ketones (moles of 2-ketone formed/moles of 2-methyl-1-alkene reacted) corrected for secondary reactions with OH radicals and gas-wall partitioning are shown in Figure 1A and in Figure 1B after normalization for the fraction of the OH reaction that occurred by addition to the C=C double bond (with the rest occurring by H atom abstraction). Error bars were calculated using a relative standard deviation of 8%, which was the maximum value measured in duplicate experiments conducted for the C_8 and C_{10}–C_{13} 2-methyl-1-alkenes (Table S1). The yields decreased with increasing 2-methyl-1-alkene carbon number from a maximum of 0.82 for C_6 to a minimum of 0.34 ± 0.02 for C_9–C_{13} and after normalization were 0.86 and 0.39 ± 0.01. Uncorrected and corrected values without and with normalization are given in Table S1 in the Supporting Information. This trend is similar to that reported by Kwok et al.,[30] where the yields of aldehydes formed from similar reactions of C_4–C_8 1-alkenes decreased from 0.94 to 0.21 with increasing carbon number.

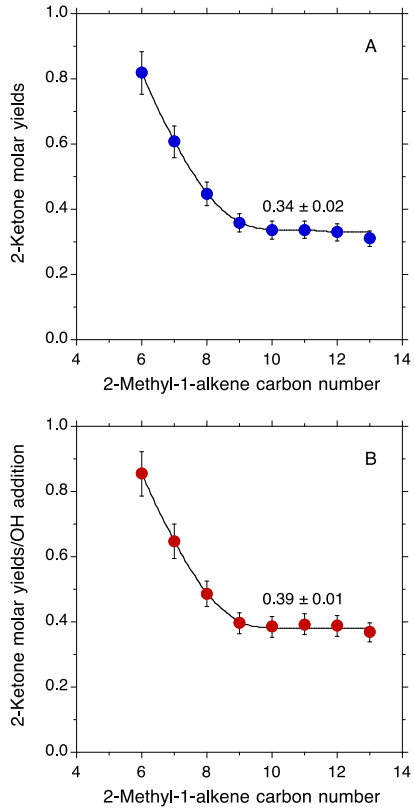


Figure 1. Molar yields of 2-ketones formed from the reactions of C_6–C_{13} 2-methyl-1-alkenes with OH radicals in the presence of NO_x (A) without and (B) with normalization for the fraction of the OH reaction that occurred by addition to the C=C double bond. Error bars are standard deviations calculated using a relative standard deviation of 8%, and the average ± standard deviation shown in the figures was calculated from the C_9–C_{13} values.

Yields were corrected for secondary reactions with OH radicals by multiplying by the factor $1 + F_{OH}$, where F_{OH} is the fraction of 2-ketone product that reacted with OH radicals. Values of F_{OH} were calculated using consecutive reaction rate theory as presented by Atkinson et al.,[31] with rate constants for 2-methyl-1-alkenes calculated according to Nishino et al.[24] and those for 2-ketones calculated from SARs.[7] The yields were also corrected for gas-wall partitioning by multiplying by the factor F_{wall}, the inverse of the fraction of 2-ketone in the gas phase at gas-wall partitioning equilibrium. Values of F_{wall} were measured as described above by adding 2-ketone standards to the chamber and measuring the fraction in the gas phase at

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equilibrium.[22] The combined correction ($[1 + F_{OH}] \times F_{wall}$) increased nearly monotonically from 1.03 to 1.21 for the C_6−C_{13} 2-methyl-1-alkenes (Table S1). Yields were normalized for the fraction of the OH reaction that occurred by addition to the C=C double bond using branching ratios for OH radical addition and abstraction calculated according to Nishino et al.[24] This fraction decreases from 0.96 to 0.84 for the C_6−C_{13} 2-methyl-1-alkenes because of the increasing number of CH_2 groups from which H atoms can be abstracted, thus increasing the normalized yields by 4−19%. Although the method used to sample 2-ketones captures both gases and particles, estimates based on gas-particle partitioning theory,[32] calculated 2-ketone vapor pressures,[33] and measured aerosol mass concentrations of ∼1 mg m^{-3} indicated that <1% of any 2-ketone was present in the particles. For this reason, the yields were not corrected for particle deposition to the walls, for which loss rates were ∼15% h^{-1}.

Branching Ratios and Rate Constants for Decomposition and Isomerization of β-Hydroxyalkoxy Radicals. Because the yield of a reaction product is equal to the product of the branching ratios along the pathway by which it is formed, it can be seen from Scheme 1 that the molar yield of a 2-ketone, Y_{ket}, is equal to the sum of the yields formed following OH radical addition to the 1 and 2 carbon atoms, respectively, and thus given by the equation $Y_{ket} = (\alpha_{add} \times \alpha_1 \times \alpha_5 \times \alpha_9) + (\alpha_{add} \times \alpha_2 \times \alpha_6 \times \alpha_{10})$. Because these two pathways form the same 2-ketone product, it is not possible to determine the individual branching ratios for decomposition of the 1-hydroxy-2-alkoxy and 2-hydroxy-1-alkoxy radicals from the available information. We therefore assume that these two radicals have the same branching ratio for decomposition, α_{dec}, and thus that $\alpha_{dec} = \alpha_9 = \alpha_{10}$. The consequences of this assumption will be discussed below. Combining these equations and rearranging, we obtain $\alpha_{dec} = Y_{ket}/[(\alpha_{add} \times \alpha_1 \times \alpha_5) + (\alpha_{add} \times \alpha_2 \times \alpha_6)]$. Similarly, we assume that these two radicals have the same branching ratio for isomerization, α_{isom}, and thus that $\alpha_{isom} = \alpha_7 = \alpha_8$. Also, because $\alpha_{dec} + \alpha_{isom} = 1$, $\alpha_{isom} = 1 - \alpha_{dec}$.

The α values needed to calculate α_{dec} were obtained from the literature, with corrections for the carbon number as necessary. Values of α_{add} were calculated from the equations $\alpha_{add} = k_{add}/(k_{add} + k_{abs})$, $k_{abs} = 2.6 + 1.4 \times (C_n - 6)$, and $k_{add} = 51 + 16 \times [1 - \exp(-0.35 \times (C_n - 3))]$, where C_n is the 2-methyl-1-alkene carbon number, developed by Nishino et al.[24] from results of kinetics experiments on the reactions of OH radicals with a homologous series of 2-methyl-1-alkenes. Values of $\alpha_1 = 0.81$ and $\alpha_2 = 0.19$ for the formation of tertiary and primary β-hydroxyalkyl radical isomers were taken from Matsunaga and Ziemann and are not expected to depend on the carbon number.[19] Values of α_3 and α_4 for the formation of tertiary and primary β-hydroxynitrate isomers were obtained using the plateau values of 0.25 and 0.12 (reached at $C_n \geq 14$) taken from Matsunaga and Ziemann[19] and the model of Arey et al.[34] to correct for the carbon number. The plateau values of α_1−α_4 taken from Matsunaga and Ziemann[19] were determined from measured yields of β-hydroxynitrate isomers formed in reactions of OH radicals with homologous series of internal alkenes, 1-alkenes, and 2-methyl-1-alkenes, and values of α_{add} calculated as described above. Values of α_5 and α_6 were calculated as $1 - \alpha_3$ and $1 - \alpha_4$. Values of α_{add}, α_{abs}, α_1, α_2, α_3, α_4, α_5, α_6, α_{dec}, and α_{isom} are given in Table S2 as a function of the 2-methyl-1-alkene carbon number.

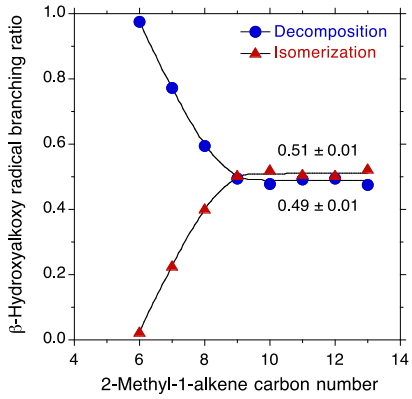

Figure 2. Branching ratios for decomposition and isomerization of β-hydroxyalkoxy radicals formed from the reactions of C_6−C_{13} 2-methyl-1-alkenes with OH radicals in the presence of NO_x. The average ± standard deviation shown for each curve was calculated from the C_9−C_{13} values.

The calculated branching ratios for decomposition and isomerization of C_6−C_{13} β-hydroxyalkoxy radicals are shown in Figure 2, where the plots are essentially mirror images of each other because $\alpha_{dec} + \alpha_{isom} = 1$ and both branching ratios approach 0.5 at large carbon numbers. Values for decomposition decreased with increasing 2-methyl-1-alkene carbon number from 0.97 at C_6 to an average of 0.49 ± 0.01 for C_9−C_{13}, whereas corresponding values for isomerization increased from 0.03 to 0.51 ± 0.01.

The branching ratios of 0.49 and 0.51 determined for the C_9−C_{13} 2-methyl-1-alkenes are similar to those measured previously for decomposition and isomerization of β-hydroxyalkoxy radicals formed from the reactions of 1-octene (0.42 and 0.58) and 7-tetradecene (0.65 and 0.35).[18] These values can be used to estimate the rate constants and activation energies for decomposition of β-hydroxyalkoxy radicals formed from reactions of 1-alkenes, 2-methyl-alkenes, and internal alkenes that have at least one alkyl group ≥C_4 attached to the C=C double bond (and thus allows isomerization to occur via abstraction of a secondary H atom). Because the ratios of the rate constants for decomposition/isomerization, k_{dec}/k_{isom}, are equal to the ratios of the corresponding branching ratios, $\alpha_{dec}/\alpha_{isom}$, then for 1-alkenes, 2-methyl-alkenes, and internal alkenes the ratio $k_{dec}/k_{isom} = 0.72$, 0.96, and 1.86, respectively. Multiplying these values by $k_{isom} = 3.9 \times 10^6$ s^{-1} (the sum of values for 1,5- and 1,6-H-shifts,[35] which for internal alkenes is multiplied by 2 to account for isomerization in both directions) gives k_{dec}, and the activation energy for decomposition, E_{dec}, can then be calculated at 298 K from the equation $k_{dec} = 1.8 \times 10^{13} \exp(-E_{dec}/RT)$.[36] Values of α_{dec}, k_{dec}, and E_{dec} calculated from experimental results are given in Table 1 along with values predicted using the SARs of Vereecken and Peeters.[35,36] The SAR values are weighted according to the fractions of 1-hydroxy-2-alkoxy and 2-hydroxy-1-alkoxy radicals formed in each reaction (0.62 and 0.38 for 1-alkenes, 0.78 and 0.22 for 2-methyl-1-alkenes, and 0.50 and 0.50 for internal alkenes), which were calculated using Scheme 1 and branching ratios for α_{add}, α_1, α_2, α_5, and α_6 given in Table S2. For comparison, we also include values for reactions of 1-alkenes with NO_3 radicals calculated using the ratio $k_{dec}/k_{isom} = 2.57$ and branching ratios for other pathways taken from our previous study of the reaction of 1-pentadecene.[37] If one makes the reasonable assumption

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Table 1. Branching Ratios, Rate Constants, and Activation Energies for Decomposition of β-Hydroxyalkoxy Radicals Formed from the Reactions of 1-Alkenes, 2-Methyl-1-alkenes, and Internal Alkenes with OH Radicals in the Presence of NO_x or with NO_3 Radicals, Determined from Experimental Results and Structure−Activity Relationships

alkene + oxidant	α_{dec}		k_{dec} ($\times 10^6$ s^{-1})		E_{dec} (kcal mol^{-1})	
	exp.	SAR[e]	exp.[f]	SAR[e]	exp.[g]	SAR[e]
1-alkenes + OH/NO_x	0.42[a]	0.94	2.8	60	9.3	7.5
2-methyl-1-alkenes + OH/NO_x	0.49[b]	1.00	3.7	4000	9.1	5.0
internal alkenes + OH/NO_x	0.65[c]	1.00	15	4000	8.3	5.0
1-alkenes + NO_3	0.72[d]	0.00	10	0.01	8.5	12.6

[a]Aschmann et al.[18] for 1-octene. [b]This study for C_9−C_{13} 2-methyl-1-alkenes. [c]Aschmann et al.[18] for 7-tetradecene. [d]Yeh et al.[37] for 1-pentadecene. [e]Calculated using the methods of Vereecken and Peeters.[35,36] [f]Calculated as $k_{dec} = (\alpha_{dec}/1 - \alpha_{dec})k_{isom} = (\alpha_{dec}/1 - \alpha_{dec})(3.9 \times 10^6)$ using exp. α_{dec} values and k_{isom} from Vereecken and Peeters.[35] [g]Calculated as $E_{dec} = RT \ln(1.8 \times 10^{13}/k_{dec})$ using exp. k_{dec} values and equation from Vereecken and Peeters.[36]

(based on reported values[16,19,24]) that the relative standard deviations in each of the quantities used to calculate $\alpha_{dec}/\alpha_{isom}$, and therefore k_{dec}/k_{isom}, are ∼10%, then from a propagation of uncertainty, the relative standard deviation of k_{dec} is ∼35%.

The results in Table 1 show that the measured range of branching ratios (0.42−0.72), rate constants (2.8 to 15 × 10^6 s^{-1}), and activation energies (8.3−9.3 kcal mol^{-1}) for the decomposition of β-hydroxyalkoxy and β-nitrooxyalkoxy radicals (all with carbon numbers in the range C_8−C_{15}) is much narrower than the corresponding values calculated with the SAR (0−1; 0.01 to 4000 × 10^6 s^{-1}; 5.0−12.6 kcal mol^{-1}). For the OH radical reactions, the branching ratios for decomposition increase in the order 1-alkenes < 2-methyl-1-alkenes < internal alkenes because of a lowering of the activation energy by added alkyl groups,[36,38] but only by a factor of ∼1.5. Also, the average branching ratio of 0.52 indicates that decomposition and isomerization are both important pathways, whereas the SAR predicts nearly complete decomposition.

It is also worth exploring possible reasons for the change in the ratio $\alpha_{dec}/\alpha_{isom}$ (equal to k_{dec}/k_{isom}) as the 2-methyl-1-alkene carbon number decreases from C_9 to C_6. Using values from Table S2, $\alpha_{dec}/\alpha_{isom}$ increases from 0.96 for the C_9−C_{13} plateau to 1.5, 3.4, and 37 for C_8 to C_6. If k_{dec} is not influenced by the length of the alkyl chain and thus has the same value as that calculated for the C_9−C_{13} plateau (k_{dec} = 3.7 × 10^6 s^{-1}), then k_{isom} = 3.7 × 10^6 s^{-1} × $\alpha_{isom}/\alpha_{dec}$ and is equal to 3.9, 2.5, 1.1, and 0.1 (× 10^6 s^{-1}) for C_9 to C_6, respectively, with estimated uncertainties similar to those of k_{dec} of ∼35%. At least part of the decrease in k_{isom} values can be explained by an increase in the strength of the C−H bond involved in the 1,5-H-shift reactions, which for C_9 to C_6 1-hydroxy-2-alkoxy radicals (the dominant β-hydroxyalkoxy radical) will involve H atom abstraction at the following locations along the alkyl chain: $-\underline{CH_2}CH_2CH_2CH_3$, $-CH_2\underline{CH_2}CH_2CH_3$, $-CH_2CH_2\underline{CH_2}CH_3$, and $-CH_2CH_2CH_2\underline{CH_3}$. For comparison, using measurements of absolute rate constants for isomerization of 1-butoxy, 2-pentoxy, and 1-pentoxy radicals, Atkinson[38] estimated that the rate constants for the 1,5-H-shift reactions at $-CH_2CH_2\underline{CH_2}CH_3$ and $-CH_2CH_2CH_2\underline{CH_3}$ are 3.3 × 10^6 s^{-1} and 3.2 × 10^5 s^{-1}, respectively, although based on the value for the 1-butoxy radical (1.8 × 10^5 s^{-1}), the latter value may be lower. The difference of a factor or ∼10−40 in the rate constants calculated above for isomerization involving abstraction of secondary (C_9 to C_7) and primary (C_6) H atoms is therefore roughly consistent with measurements of absolute rate constants, although it was not expected that a significant change would be observed from C_9 to C_7. Some of this discrepancy might be due to "prompt" decomposition of β-hydroxyalkoxy radicals, which is not accounted for in the Arrhenius equation used here to describe the kinetics. As discussed by Calvert et al.,[39] because of the significant exothermicity of this reaction, chemically activated β-hydroxyalkoxy radicals can be formed and then undergo prompt decomposition before they can be thermalized by collisions. For example, it has been estimated that prompt decomposition is responsible for ∼25% of the decomposition of β-hydroxyalkoxy radicals formed in the reaction of ethene.[40] For carbon numbers larger than ∼C_6, the lifetimes of chemically activated β-hydroxyperoxy radical−NO complexes likely become sufficiently long (due to the greater number of vibrational modes available for energy redistribution) such that collisional stabilization competes with prompt decomposition, thus reducing its importance. This process might help to explain some of the decrease in the calculated values of k_{isom} from C_9 to C_6, because if k_{dec} increases with decreasing carbon number (instead of being constant at 3.7 × 10^6 s^{-1}) the values of k_{isom} calculated using the equation $k_{isom} = k_{dec} \times \alpha_{isom}/\alpha_{dec}$ will not decrease as rapidly with decreasing carbon number.

Product Yield Balance. The molar yields of all the products in Scheme 1 that have been measured or can be accurately calculated from available information, normalized for the fraction of the OH reaction that occurred by addition to the C=C double bond, are shown in Figure 3. Values for β-hydroxynitrates were calculated as ($\alpha_1 \times \alpha_3$) + ($\alpha_2 \times \alpha_4$), where values for α_1−α_4 were the same as those used above for the calculation of α_{dec} as a function of carbon number; values for 2-ketones are the same as those shown in Figure 1B, and the dashed lines are values measured previously for C_{14} and C_{15} dihydroxynitrates and C_{14} trihydroxynitrates, which should be similar to those in the C_9−C_{13} range.

The value of 0.98 for the sum of the β-hydroxynitrate and 2-ketone yields for 2-methyl-1-pentene is consistent with a branching ratio of 0.97 for decomposition of the C_6 β-hydroxyalkoxy radicals, and thus only these two products and formaldehyde are formed, which is a coproduct of 2-ketone formation. This result also supports our assumption that α-hydroxyperoxy radicals primarily decompose to form a 2-ketone and HO_2 rather than forming other products via reaction with NO. We also note that from this figure and Scheme 1, the branching ratio for the formation of dihydroxynitrates from the reaction of dihydroxyperoxy radicals and NO (α_{11} + α_{12}) is equal to the yield of dihydroxynitrates/yield of dihydroxyperoxy radicals = 0.06/(1 − 0.60) = 0.15. This value agrees well with branching ratios of 0.15 and 0.18 that we determined previously for organic

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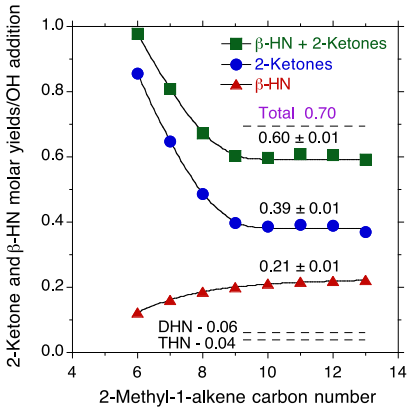

Figure 3. Molar yields of products formed from the reactions of C_6−C_{13} 2-methyl-1-alkenes with OH radicals in the presence of NO_x, normalized for the fraction of the OH reaction that occurred by addition to the C=C double bond. The average ± standard deviation is for the C_9−C_{13} values. Values for β-hydroxynitrates are based on previous measurements.[9] Dashed lines correspond to values measured previously[9] for the C_{14} and C_{15} DHN and C_{14} THN and the total of β-HN + 2-ketones + DHN + THN.

nitrate formation from the reactions of secondary 1,2- and 1,4-hydroxyperoxy radicals.[19,41] In the C_9−C_{13} region, where the sum of the yields of the quantified products is 0.70, the other 0.30 should be primarily dihydroxycarbonyls and trihydroxycarbonyls. On an absolute yield basis, these values should be approximately 0.61 and 0.26, respectively, with the other 0.13 being products of H atom abstraction. Based on studies of the products of similar reactions of *n*-alkanes,[21,29,41] in the absence of secondary reactions, the H atom abstraction products should be unsaturated alkyl nitrates, 1,4-hydroxynitrates, and 1,4-hydroxycarbonyls with yields of approximately 0.04, 0.02, and 0.07. In particles, 1,4-hydroxycarbonyls, dihydroxycarbonyls, and trihydroxycarbonyls can cyclize or form dimers, which in the presence of the HNO_3 (formed from the OH + NO_2 reaction) can dehydrate.[17,42]

CONCLUSIONS

Alkoxy radicals are key intermediates in VOC oxidation mechanisms because their reactions have a major influence on the volatility and therefore atmospheric fate of reaction products. Although alkoxy radical isomerization leads to the addition of multiple functional groups, thus enhancing the tendency of products to partition into SOA, decomposition cleaves C−C bonds to form more volatile products. The branching between decomposition and isomerization is influenced by neighboring functional groups and by the length of the alkyl chain on which isomerization occurs. In general, functional groups located on the same (α-) or an adjacent (β-) carbon relative to the alkoxy group will enhance rates of decomposition, whereas longer alkyl chains (up to a point) enhance rates of isomerization. Because of the very limited experimental data available on the effects of molecular structure on the rates of these reactions, they are usually estimated using SARs. The most commonly used of these was developed by Vereecken and Peeters[35,36] using computational quantum chemistry.

In this study, we measured the yields of 2-ketones formed from the OH radical-initiated reactions of the C_6−C_{13} 2-methyl-1-alkenes in the presence of NO_x, and combined these with results from previous studies to calculate the branching ratios for decomposition and isomerization of the β-hydroxyalkoxy radicals from which they are formed. These values were then used to estimate rate constants and activation energies for decomposition, which were compared with predictions based on SARs and with experimental results from studies of similar reactions of other alkenes. The branching ratios for decomposition and isomerization of C_9−C_{13} β-hydroxyalkoxy radicals were essentially constant at 0.49:0.51, similar to previously measured[18] values of 0.42:0.58 for a 1-alkene (1-octene) and 0.65:0.35 for an internal alkene (7-tetradecene). The slight differences are due to a lowering of the activation energy for decomposition by the added alkyl groups,[36,38] but overall it is clear that decomposition and isomerization are both important pathways in all cases. On the other hand, the SARs predict nearly complete decomposition. As the carbon number of the 2-methyl-1-alkene decreases from C_9 to C_6, the ratio of the branching ratios (equal to the ratio of the rate constants) for decomposition and isomerization increases from 0.96 for the C_9−C_{13} plateau to 1.5, 3.4, and 37 for C_8, C_7, and C_6, respectively. This is likely due at least in part to decreasing rates of isomerization (caused by increasing strength of the C−H bond involved in the 1,5-H-shift reaction),[38] but prompt decomposition (caused by chemical activation)[39] may also play a role. If the first of these is the dominant cause, and the rate constant for decomposition is assumed to be constant at the C_9−C_{13} plateau value, then the rate constants for isomerization are 3.9, 2.5, 1.1, and 0.1 ($\times 10^6$ s^{-1}) for the C_9 to C_6 β-hydroxyalkoxy radicals. This is an interesting trend that is worthy of further investigation. In spite of these discrepancies, the branching ratios and rate constants determined here are likely applicable to other systems and should be useful for evaluating and improving SARs that are widely employed in oxidation mechanisms used to predict the fate of the enormous variety of VOCs that are present in the atmosphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b06218.

Table of molar yields of 2-ketones with corrections for secondary OH reactions and gas-wall partitioning, table of branching ratios for pathways involved in the formation of 2-ketones, and table of molar yields of β-hydroxynitrates and 2-ketones and branching ratios for decomposition and isomerization of β-hydroxyalkoxy radicals (PDF)

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Notes

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Supporting Information

Branching Ratios and Rate Constants for Decomposition and Isomerization of β-Hydroxyalkoxy Radicals Formed from OH Radical-Initiated Reactions of C_6–C_{13} 2-Methyl-1-Alkenes in the Presence of NO_x

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Table S1. Molar Yields of 2-Ketones Formed from the OH Radical-Initiated Reactions of 2-Methyl-1-Alkenes in Air in the Presence of NO_x, with Corrections for Secondary OH Reactions and Gas-Wall Partitioning.

alkene C_n	correction factors[a]			2-ketone molar yields[b,c]			
	$1 + F_{OH}$	F_{wall}	$(1 + F_{OH}) \times F_{wall}$	uncorrected	OH corrected	OH + wall loss corrected	OH + wall loss corrected/OH addition
6	1.03	1.00	1.03	0.795	0.819	0.819	0.855
7	1.05	1.00	1.05	0.579	0.608	0.608	0.647
8	1.04	1.00	1.04	0.430 ± 0.04	0.447 ± 0.04	0.447 ± 0.04	0.485 ± 0.04
9	1.03	1.00	1.03	0.348	0.358	0.358	0.396
10	1.06	1.00	1.06	0.317 ± 0.03	0.336 ± 0.03	0.336 ± 0.03	0.385 ± 0.03
11	1.06	1.06	1.12	0.300 ± 0.00	0.318 ± 0.00	0.337 ± 0.00	0.393 ± 0.00
12	1.07	1.07	1.14	0.289 ± 0.03	0.309 ± 0.03	0.331 ± 0.03	0.388 ± 0.03
13	1.08	1.12	1.21	0.257 ± 0.01	0.278 ± 0.01	0.311 ± 0.01	0.369 ± 0.03

[a]F_{OH} is the fraction of 2-ketone product that subsequently reacted further with OH radicals, whereas F_{wall} is the inverse of the fraction of 2-ketone product that remained in the gas phase and thus was not lost to the chamber walls by gas-wall partitioning. Values of F_{OH} were calculated using the method of Atkinson et al.,[1] whereas values of $F_{wall\ loss}$ were measured by adding 2-ketone standards to the chamber and measuring the fraction present in the gas phase after gas-wall partitioning equilibrium was attained.

[b]Molar yields of 2-ketones were corrected for secondary reactions with OH radicals by multiplying the uncorrected molar yields by the factor $1 + F_{OH}$, whereas molar yields of 2-ketones were corrected for secondary reactions with OH radicals and gas-wall partitioning by multiplying the uncorrected molar yields by the factor $(1 + F_{OH}) \times F_{wall}$.

[c]Standard deviations were calculated from duplicate experiments conducted for the C_8 and C_{10}–C_{13} 2-methyl-1-alkenes.

Table S2. Branching Ratios for Pathways Involved in the Formation of 2-Ketones from the OH Radical-Initiated Reaction of 2-Methyl-1-Alkenes in Air in the Presence of NO.

alkene C_n	branching ratios[a]									
	α_{add}	α_{abs}	α_1	α_2	α_3	α_4	α_5	α_6	α_{dec}	α_{isom}
6	0.959	0.041	0.81	0.19	0.137	0.066	0.863	0.934	0.974	0.026
7	0.940	0.060	0.81	0.19	0.180	0.086	0.820	0.914	0.772	0.228
8	0.922	0.078	0.81	0.19	0.207	0.100	0.793	0.900	0.596	0.404
9	0.905	0.095	0.81	0.19	0.224	0.107	0.776	0.893	0.495	0.505
10	0.889	0.111	0.81	0.19	0.234	0.112	0.766	0.888	0.479	0.521
11	0.873	0.127	0.81	0.19	0.240	0.115	0.760	0.885	0.493	0.508
12	0.858	0.142	0.81	0.19	0.244	0.117	0.756	0.883	0.495	0.505
13	0.843	0.157	0.81	0.19	0.246	0.118	0.754	0.882	0.474	0.526

[a]Values were obtained as follows: (1) $\alpha_{add} = k_{add}/(k_{add} + k_{abs})$, with $k_{abs} = 2.6 + 1.4 \times (C_n - 6)$ and $k_{add} = 51 + 16 \times [1 - \exp(-0.35 \times (C_n - 3))]$, where C_n is the 2-methyl-1-alkene carbon number;[2] (2) $\alpha_{abs} = 1 - \alpha_{add}$; (3) $\alpha_1 = 0.81$ and $\alpha_2 = 0.19$ were from Matsunaga and Ziemann;[3] (3) α_3 and α_4 values were calculated as a function of carbon number using the model of Arey et al.[4] and corresponding plateau values (reached at $C_n \geq 14$) of 0.25 and 0.12 from Matsunaga and Ziemann;[3] (4) $\alpha_5 = 1 - \alpha_3$ and $\alpha_6 = 1 - \alpha_4$; (5) $\alpha_{dec} = Y_{ket}/((\alpha_{add} \times \alpha_1 \times \alpha_5) + (\alpha_{add} \times \alpha_2 \times \alpha_6))$, where Y_{ket} is the 2-ketone yield corrected for secondary reactions with OH radicals and gas-wall partitioning from Table S1; and $\alpha_{isom} = 1 - \alpha_{dec}$.

Table S3. Molar Yields of β-Hydroxynitrates and 2-Ketones and Branching Ratios for Decomposition and Isomerization of β-Hydroxyalkoxy Radicals Formed from the OH Radical-Initiated Reaction of 2-Methyl-1-Alkenes in Air in the Presence of NO.

alkene C_n	product molar yields per OH addition		
	β-HN[a]	2-ketone[b]	β-HN + 2-ketone
6	0.123	0.855	0.978
7	0.162	0.647	0.809
8	0.187	0.485	0.672
9	0.201	0.396	0.602
10	0.210	0.385	0.597
11	0.216	0.393	0.609
12	0.219	0.388	0.607
13	0.222	0.369	0.591

[a]Calculated by dividing the molar yields of β-hydroxynitrates (β-HN) by the values of α_{add} given in Table S1. Molar yields of β-HN were calculated as the sum of the molar yields of the 1H2N and 1N2H isomers according to the following equation: β-HN molar yield = ($\alpha_1 \times \alpha_3$) + ($\alpha_2 \times \alpha_4$), which was obtained from the reaction mechanism in Scheme 1. Values for α_1, α_2, α_3, and α_4 were taken from Table S2.

[b]Calculated by dividing the molar yields of 2-ketones corrected for OH and wall-loss from Table S1 by the value of α_{add} given in Table S2.

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