Rate Constants for the Gas-Phase Reactions of OH Radicals with a Series of C_6-C_{14} Alkenes at 299 ± 2 K

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Rate constants for the gas-phase reactions of OH radicals with the C_6-C_{14} 2-methyl-1-alkenes and the C_6-C_{10} *trans*-2-alkenes have been measured at 299 ± 2 K and atmospheric pressure of air using a relative rate technique. The rate constants obtained (in units of 10^{-11} cm^3 molecule^{-1} s^{-1}) were as follows: 2-methyl-1-pentene, 5.67 ± 0.21; 2-methyl-1-hexene, 6.50 ± 0.11; 2-methyl-1-heptene, 6.71 ± 0.21; 2-methyl-1-octene, 7.02 ± 0.16; 2-methyl-1-nonene, 7.28 ± 0.21; 2-methyl-1-decene, 7.85 ± 0.26; 2-methyl-1-undecene, 7.85 ± 0.21; 2-methyl-1-dodecene, 7.96 ± 0.26; 2-methyl-1-tridecene, 8.06 ± 0.37; *trans*-2-hexene, 6.08 ± 0.26; *trans*-2-heptene, 6.76 ± 0.32; *trans*-2-octene, 7.23 ± 0.21; *trans*-2-nonene, 7.54 ± 0.16; and *trans*-2-decene, 7.80 ± 0.26, where the indicated errors are two least-squares standard deviations and do not include the uncertainty associated with the rate constant for the reference compound α-pinene. Our data show that the rate constants for the reactions of OH radicals with 2-methyl-1-alkenes and *trans*-2-alkenes increase with increasing carbon number, suggesting that this is in part due to H-atom abstraction from the C−H bonds of the alkyl substituent groups. Combined with previous literature data for the reactions of OH radicals with a series of 1-alkenes, we propose that the increase in rate constant with increasing carbon number is due to H-atom abstraction from the C−H bonds of the alkyl substituent groups and to enhancement of the rate constant for OH radical addition to the C═C bond, which increases with carbon number of a C_n-alkyl substituent group up to a maximum at ~C_8.

Introduction

Alkenes are emitted into the atmosphere from biogenic[1] and anthropogenic[2,3] sources, with emissions from vegetation dominating worldwide.[1] In ambient air in urban areas, alkenes comprise ~10% of nonmethane volatile organic compounds.[4] In the troposphere, alkenes react with OH radicals, NO_3 radicals, and O_3, with the daytime reaction with OH radicals being an important, and sometimes dominant, loss process.[5,6] The OH radical reactions with alkenes proceed by initial addition to C═C bonds and by H-atom abstraction from C−H bonds of the substituent alkyl group(s), but not from vinylic C−H bonds,[5−7] with the addition pathway dominating for small acyclic alkenes.[8,9] The rate constants for the reactions of OH radicals with $\geqslant C_4$ alkenes are at the high-pressure limit at total pressures greater than a few Torr at room temperature and below,[7,10] and for small acyclic alkenes the limiting high-pressure rate constants have measured Arrhenius activation energies of $E/R \sim -500$ K.[6]

Product studies of 1-butene[11] and 3-methyl-1-butene[12] indicate that H-atom abstraction accounts for <10% and 5−10%, respectively, of the overall OH radical reactions at room temperature. Kinetic studies of the reaction of OH radicals with C_4-C_{14} 1-alkenes show that the measured room temperature rate constants increase essentially linearly with carbon number,[9,13] suggesting that H-atom abstraction is responsible for this linear increase and that for 1-tetradecene H-atom abstraction accounts for ~40% of the overall rate constant.[9] These rate data for the 1-alkenes[9,13] show that the increase in rate constant per additional CH_2 group is a factor of ~1.4−1.5 higher than that observed in the *n*-alkanes.[9] Room-temperature rate constants measured for *trans*-7-tetradecene and 2-methyl-1-tridecene were consistent with this conclusion based on the 1-alkene reactions.[9] Since H-atom abstraction appears to be relatively minor in the 1-alkenes, estimates of its importance in the more reactive 2-methyl-1-alkenes, $CH_2{=}C(CH_3)R$, and 2-alkenes, $CH_3CH{=}CHR$ (where R is alkyl), are more uncertain because they are derived from subtraction of an assumed rate constant for OH radical addition from the total measured rate constant, and further assume that OH radical addition is not affected by an increase in carbon number.[9,14]

To investigate the kinetics of the reactions of OH radicals with alkenes other than the 1-alkenes and to further assess the importance of H-atom abstraction, in this work we have extended previous studies of 1-alkene reactions[9,13] to measure rate constants for the gas-phase reactions of OH radicals with the C_6-C_{14} 2-methyl-1-alkenes and the C_6-C_{10} *trans*-2-alkenes at 299 ± 2 K (unfortunately, *trans*-2-alkenes with higher carbon number than C_{10} were not commercially available).

Experimental Methods

Experiments were carried out in a ~7500 L Teflon chamber at 299 ± 2 K and 735 Torr total pressure of dry purified air. The chamber is equipped with a Teflon-coated fan for rapid mixing of chemicals and two parallel banks of blacklamps (λ > 300 nm) for irradiation. Rate constants for the reactions of OH radicals with the alkenes were measured by a relative rate method in which the concentrations of the alkene and a reference compound (whose OH radical reaction rate constant is reliably known) were measured in the presence of OH radicals:[9,13]

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$$\mathrm{OH} + \text{alkene} \rightarrow \text{products} \qquad (1)$$

$$\mathrm{OH} + \text{reference compound} \rightarrow \text{products} \qquad (2)$$

Providing that the alkenes and the reference compound reacted only with OH radicals, then,[9]

$$\ln\left(\frac{[\text{alkene}]_{t_0}}{[\text{alkene}]_t}\right) = \frac{k_1}{k_2} \ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) \qquad (\mathrm{I})$$

where $[\text{alkene}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the alkene and reference compound, respectively, at time t_0, $[\text{alkene}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

OH radicals were generated from the photolysis of CH_3ONO at wavelengths > 300 nm, and NO was included in the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals. The initial reactant concentrations (molecules cm^{-3}) were as follows: CH_3ONO and NO, $\sim 2.4 \times 10^{14}$ each; and alkene and reference compound, $\sim 2.4 \times 10^{13}$ each. α-Pinene was chosen as the reference compound except for experiments with 2-methyl-1-dodecene, where an α-pinene reaction product interfered with the gas chromatographic analysis of 2-methyl-1-dodecene. The rate constant for the OH radical-initiated reaction of α-pinene is well-established and is similar to those of the alkenes studied,[6] and α-pinene and the alkenes studied could be analyzed using the same sample collection procedure and gas chromatographic column (see below). 2-Methyl-1-octene was employed as the reference compound for the experiments involving 2-methyl-1-dodecene. Irradiations were carried out at 20% of the maximum light intensity for up to 15 min, resulting in up to 76−85% of the initially present alkenes being consumed by reaction.

The concentrations of the alkenes and α-pinene were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA adsorbent, with subsequent thermal desorption at ~250 °C onto a 30 m DB-5 and/or 30 m DB-1701 megabore column. For both columns, the initial temperature was held for 2 min at −40, −20, or 0 °C (for experiments with C_6-C_7, C_6-C_{10}, and C_8-C_{14} alkenes, respectively), and then temperature programmed to 250 °C at 8 °C min^{-1}. For 2-methyl-1-pentene, GC-FID analyses were also carried out in selected experiments by collection of gas samples into a 100 cm^3 volume all-glass, gastight syringe, with direct injection of the gas sample via a 1 cm^3 gas-sampling loop onto a 30 m DB-5 megabore column, initially held at −25 °C and then temperature programmed to 250 °C at 8 °C min^{-1}. Replicate analyses of α-pinene and the alkenes showed that the analytical uncertainties were typically <3%.

The chemicals used (and their stated purities) were as follows: 2-methyl-1-pentene (99%), 2-methyl-1-hexene (96%), 2-methyl-1-heptene (99%), 2-methyl-1-nonene (97%), *trans*-2-hexene (97%), *trans*-2-heptene (99%), *trans*-2-octene (97%), and α-pinene (99.7%), Aldrich; 2-methyl-1-octene (98%), 2-methyl-1-undecene (95+%), 2-methyl-1-tridecene (99%), *trans*-2-nonene (98%), and *trans*-2-decene (97%), ChemSampCo; 2-methyl-1-decene (97%) and 2-methyl-1-dodecene (>97%), Rieke Metals; and NO (>99%), Matheson Gas Products. CH_3ONO was prepared and stored as described previously.[9] NO and the initial NO_2 concentrations were monitored using a Thermo Environmental Instruments Inc. Model 42 chemiluminescence $NO-NO_2-NO_x$ analyzer.

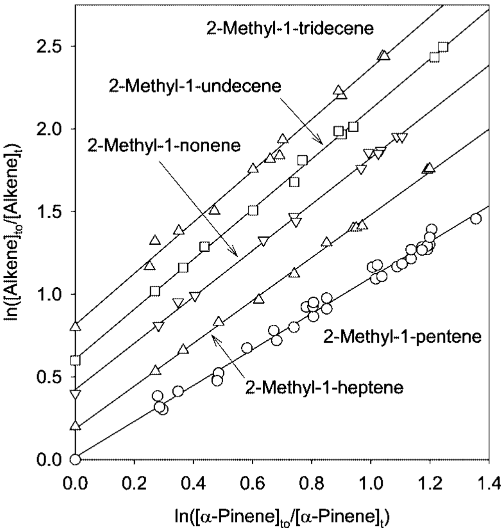

Figure 1. Plots of eq I for the reaction of OH radicals with 2-methyl-1-pentene, 2-methyl-1-heptene, 2-methyl-1-nonene, 2-methyl-1-undecene, and 2-methyl-1-tridecene at 299 ± 2 K, with α-pinene as the reference compound. Data for 2-methyl-1-heptene, 2-methyl-1-nonene, 2-methyl-1-undecene, and 2-methyl-1-tridecene have been displaced vertically by 0.20, 0.40, 0.60, and 0.80 units, respectively, for clarity.

Results

Irradiations of $CH_3ONO-NO-$alkene−α-pinene−air mixtures were carried out with one to two alkenes being present in the reactant mixtures in addition to α-pinene, these being as follows: 2-methyl-1-pentene + 2-methyl-1-heptene; 2-methyl-1-pentene + 2-methyl-1-octene; 2-methyl-1-pentene + 2-methyl-1-nonene; 2-methyl-1-pentene + 2-methyl-1-tridecene; 2-methyl-1-hexene + 2-methyl-1-nonene; 2-methyl-1-hexene + 2-methyl-1-decene; 2-methyl-1-hexene + 2-methyl-1-undecene; 2-methyl-1-heptene + 2-methyl-1-undecene; 2-methyl-1-heptene + 2-methyl-1-dodecene; 2-methyl-1-octene + 2-methyl-1-tridecene; 2-methyl-1-octene + 2-methyl-1-dodecene; 2-methyl-1-nonene + 2-methyl-1-tridecene; 2-methyl-1-undecene + 2-methyl-1-tridecene; 2-methyl-1-decene (two experiments); 2-methyl-1-tridecene; *trans*-2-heptene + *trans*-2-decene; *trans*-2-hexene + *trans*-2-nonene; *trans*-2-octene; *trans*-2-heptene + *trans*-2-nonene; *trans*-2-octene + *trans*-2-decene; *trans*-2-hexene + *trans*-2-decene (2 experiments); *trans*-2-hexene; and *trans*-2-heptene. In addition, three experiments with 2-methyl-1-octene + 2-methyl-1-dodecene (and no α-pinene) were carried out. Because of GC interferences with reaction products, the data for 2-methyl-1-tridecene in the α-pinene + 2-methyl-1-pentene + 2-methyl-1-tridecene and α-pinene + 2-methyl-1-nonene + 2-methyl-1-tridecene experiments, and for 2-methyl-1-dodecene in the α-pinene + 2-methyl-1-octene + 2-methyl-1-dodecene experiment were not used. Additionally, *trans*-2-decene was not resolved from one of its reaction products on the DB-5 column, and hence all data for *trans*-2-decene were obtained using the DB-1701 column.

The experimental data are plotted in accordance with eq I in Figures 1−4, and the rate constant ratios k_1/k_2 obtained from least-squares analyses of these data are given in Table 1. Rate constant ratios obtained for 2-methyl-1-pentene using two different GC columns and using different sample collection procedures for 2-methyl-1-pentene were in excellent agreement (within 4%), and rate constant ratios for *trans*-2-hexene, *trans*-2-heptene, *trans*-2-octene, and *trans*-2-nonene obtained using the two GC columns agreed to within

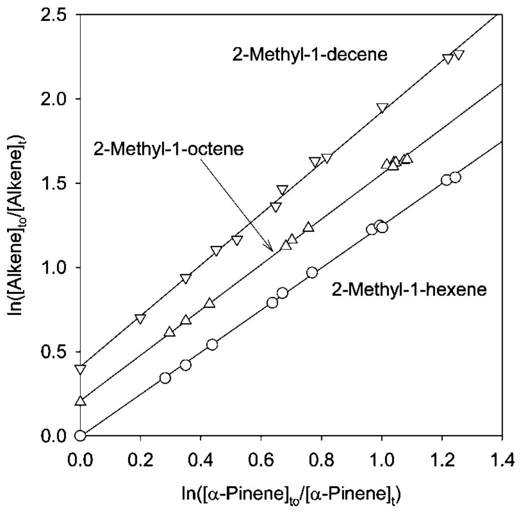

Figure 2. Plots of eq I for the reaction of OH radicals with 2-methyl-1-hexene, 2-methyl-1-octene, and 2-methyl-1-decene at 299 ± 2 K, with α-pinene as the reference compound. Data for 2-methyl-1-octene and 2-methyl-1-decene have been displaced vertically by 0.20 and 0.40 units, respectively, for clarity.

≤7% (see footnotes *d* and *f* of Table 1). The rate constant ratios k_1/k_2 given in Table 1 are placed on an absolute basis by use of a rate constant $k_2(\mathrm{OH}+\alpha\text{-pinene}) = 5.20 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 299 K,[6] and the resulting rate constants k_1 are also given in Table 1.

Rate constants have been measured previously for 2-methyl-1-pentene,[17] *trans*-2-heptene,[18] and 2-methyl-1-tridecene,[9] all using relative rate methods, and our values are compared to these literature rate constants in Table 2. Our rate constant for 2-methyl-1-pentene is 10% lower than that of Ohta,[17] while that for *trans*-2-heptene is in excellent agreement with the rate constants measured by O'Rji and Stone.[18] Our rate constant for 2-methyl-1-tridecene agrees to within 6% with that measured recently, using the same reference compound, by Aschmann and Atkinson,[9] after adjusting for the different temperatures employed in the two studies assuming that the rate constants for the reactions of OH radicals with 2-methyl-1-tridecene and α-pinene have similar temperature dependencies. The reason for the 10% difference between the rate constants measured here and by Ohta[17] for 2-methyl-1-pentene is not clear; we checked for incomplete collection of the volatile 2-methyl-1-pentene on the Tenax-TA solid adsorbent by also collecting samples into gastight syringes and transferring the samples onto the GC column using a gas sampling valve, with excellent agreement between the two sampling methods (see above and footnote *d* to Table 1).

Discussion

The rate constants measured here for the C_6−C_{14} 2-methyl-1-alkenes and the C_6−C_{10} *trans*-2-alkenes at 299 ± 2 K are plotted against carbon number in Figure 5. Clearly, the rate constants increase with increasing carbon number, with the increase in rate constant per additional CH_2 group being $(2.41 \pm 0.51) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the C_7−C_{14} 2-methyl-1-alkenes and $(3.44 \pm 0.66) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the C_7−C_{10} *trans*-2-alkenes, where the indicated errors are two least-squares standard deviations. These least-squares fits are shown as the solid lines in Figure 5. These increases per additional CH_2 group for the C_7−C_{14} 2-methyl-1-alkenes and the C_7−C_{10} *trans*-2-alkenes can be compared to the increase per additional CH_2 group in the C_4−C_{14} 1-alkenes of $(2.02 \pm 0.32) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 ± 1 K.[9] These increases per CH_2 group are derived from the differences in rate constants, each of which has an estimated overall uncertainty (in the rate constant ratios) of ∼±5%, and taking these overall uncertainties into account the increases in rate constant per additional CH_2 group become $(2.02 \pm 0.32) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the C_4−C_{14} 1-alkenes, $(2.41 \pm 0.76) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the C_7−C_{14} 2-methyl-1-alkenes, and $(3.44 \pm 1.76) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the C_7−C_{10} *trans*-2-alkenes. Within the estimated overall uncertainties, the increase per additional CH_2 group is reasonably consistent, with a weighted average of 2.1×10^{-12} cm^3 molecule^{-1} s^{-1} per additional CH_2 group in these three series of alkenes.

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Gas-Phase Reactions of OH Radicals with a Series of 2-Methyl-1-alkenes and *trans*-2-Alkenes at 299 ± 2 K

	k_1/k_2[a] with given reference compound		
alkene	2-methyl-1-octene	α-pinene	$10^{11}k_1$[b] (cm^3 molecule^{-1} s^{-1})
2-methyl-1-alkenes[c]			
2-methyl-1-pentene		1.09 ± 0.04 [d]	5.67 ± 0.21
2-methyl-1-hexene		1.25 ± 0.02	6.50 ± 0.11
2-methyl-1-heptene		1.29 ± 0.04	6.71 ± 0.21
2-methyl-1-octene		1.35 ± 0.03	7.02 ± 0.16
2-methyl-1-nonene		1.40 ± 0.04	7.28 ± 0.21
2-methyl-1-decene		1.51 ± 0.05	7.85 ± 0.26
2-methyl-1-undecene		1.51 ± 0.04	7.85 ± 0.21
2-methyl-1-dodecene	1.13 ± 0.02	1.53 ± 0.05 [e]	7.96 ± 0.26
2-methyl-1-tridecene		1.55 ± 0.07	8.06 ± 0.37
trans-2-alkenes[f]			
trans-2-hexene		1.17 ± 0.05	6.08 ± 0.26
trans-2-heptene		1.30 ± 0.06	6.76 ± 0.32
trans-2-octene		1.39 ± 0.04	7.23 ± 0.21
trans-2-nonene		1.45 ± 0.03	7.54 ± 0.16
trans-2-decene		1.50 ± 0.05	7.80 ± 0.26

[a] Indicated errors are two least-squares standard deviations. The estimated overall uncertainties in k_1/k_2 are ±5% or the two least-squares standard deviations, whichever are higher. [b] Placed on an absolute basis using a rate constant for the reaction of OH radicals with α-pinene of $k_2 = 5.20 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 299 K.[6] Indicated errors are two least-squares standard deviations and do not include the uncertainty associated with the rate constant k_2 for the reference compound α-pinene, which is expected to be ∼±10%.[15,16] [c] All with GC-FID analyses using collection onto Tenax and DB-5 column unless noted otherwise. [d] After collection of 2-methyl-1-pentene and α-pinene onto Tenax solid adsorbent and thermal desorption GC-FID, $k_1/k_2 = 1.08 \pm 0.03$ using a DB-5 column and $k_1/k_2 = 1.10 \pm 0.06$ using a DB-1701 column. After collection of 2-methyl-1-pentene in a syringe and transfer via a gas sampling valve onto a DB-5 column, and collection of α-pinene onto Tenax solid adsorbent and thermal desorption onto a DB-5 column (i.e., two separate GCs), $k_1/k_2 = 1.12 \pm 0.07$. In each case the indicated errors are two least-squares standard deviations. The cited rate constant ratio is from a least-squares analysis of the entire data set (Figure 1). [e] Obtained by combining k_1(2-methyl-1-dodecene)/k_2(2-methyl-1-octene) = 1.13 ± 0.02 with k_1(2-methyl-1-octene)/k_2(α-pinene) = 1.35 ± 0.03. [f] All with GC-FID analyses using collection onto Tenax and using both a DB-5 column and a DB-1701 column, apart from *trans*-2-decene, where only the DB-1701 column was used because of GC interferences on the DB-5 column (see text). Rate constant ratios k_1/k_2 obtained using DB-5 and DB-1701 columns were, respectively: *trans*-2-hexene, 1.16 ± 0.05 (3) and 1.19 ± 0.06 (3); *trans*-2-heptene, 1.27 ± 0.05 (3) and 1.36 ± 0.03 (2); *trans*-2-octene, 1.39 ± 0.05 (2) and 1.40 ± 0.04 (1); and *trans*-2-nonene, 1.45 ± 0.04 (2) and 1.46 ± 0.03 (1), where the errors are two least-squares standard deviations and the numbers in parentheses are the number of experiments using each GC column. The cited rate constant ratios are from least-squares analyses of the entire data set for each alkene (Figure 4).

TABLE 2: Comparison of Rate Constants Measured in this Work at 299 ± 2 K with Literature Values

alkene	$10^{11}k_1$ (cm^3 $molecule^{-1}$ s^{-1}) this work[a]	literature	ref
2-methyl-1-pentene	5.67 ± 0.21	6.26 ± 0.09 [b]	Ohta[17]
trans-2-heptene	6.76 ± 0.32	6.74 ± 0.24 [c]	O'Rji and Stone[18]
		6.91 ± 0.53 [d]	O'Rji and Stone[18]
2-methyl-1-tridecene	8.06 ± 0.37	8.69 ± 0.27 [e]	Aschmann and Atkinson[9]

[a] At 299 ± 2 K, relative to α-pinene. [b] At 298 ± 2 K, relative to k(OH+2-methyl-2-butene) = 8.69 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[6] [c] At 297 ± 2 K, relative to k(OH+propene) = 2.65 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[6] [d] At 297 ± 2 K, relative to k(OH+*trans*-2-butene) = 6.44 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[6] [e] At 295 ± 1 K, relative to k(OH+α-pinene) = 5.30 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.[6] The measured rate constant ratio was k_1(OH+2-methyl-1-tridecene)/k_2(OH+α-pinene) = 1.64 ± 0.05,[9] in excellent agreement with the value of 1.55 ± 0.07 measured here.

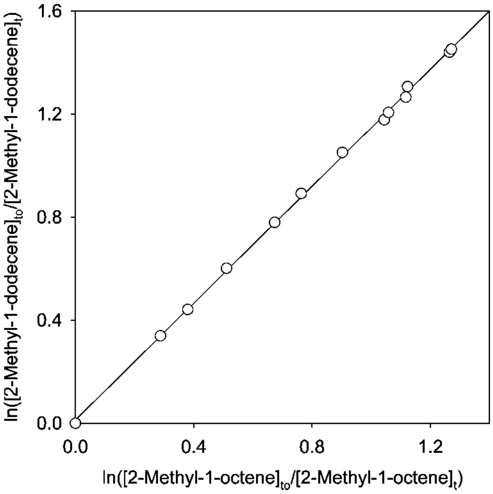

Figure 3. Plot of eq I for the reaction of OH radicals with 2-methyl-1-dodecene at 299 ± 2 K, with 2-methyl-1-octene as the reference compound.

The increase in OH radical reaction rate constant with increasing alkene carbon number can be interpreted as the increase being due (a) solely to H-atom abstraction from the C−H bonds of the alkyl substituent groups, with the rate constant increasing essentially linearly with carbon number (as done in Aschmann and Atkinson[9]), (b) solely to increasing activation of the C=C bond toward OH radical addition with increasing length of the alkyl substituent groups, R, in $CH_2=CHR$, $CH_2=C(CH_3)R$, and *trans*-$CH_3CH=CHR$, or (c) to a combination of the two. For the *n*-alkanes, the OH radical reaction proceeds only by H-atom abstraction and at 298 K the rate constant increases by (1.40 ± 0.05) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} per additional CH_2 group for the C_4-C_{14} *n*-alkanes.[6,9] The observed increase in the rate constant in the alkenes per additional CH_2 group of ≥2.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} suggests that not all of the increase is due to H-atom abstraction. It appears reasonable that for long-chain alkenes the addition of another CH_2 group located several carbon atoms from the C=C bond system should behave like a CH_2 group in an alkane. A first-approximation assumption is then to equate H-atom abstraction from alkyl substituent groups in alkenes to that in corresponding alkyl groups in alkanes. Rate constants for H-atom abstraction can be calculated using the estimation method of Kwok and Atkinson[14] (see also the Supporting Information to Aschmann and Atkinson[9]), and for the alkenes $CH_2=CHR$, $CH_2=C(CH_3)R$, and *trans*-$CH_3CH=CHR$, where R is $\geqslant CH_2CH_2CH_3$, the calculated rate constant per each additional CH_2 group is 1.41 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K.[14] After subtraction of the resulting partial rate constant for H-atom abstraction, the resulting room temperature rate constants for OH radical addition to the 1-alkenes,[9,13] 2-methyl-1-alkenes, and *trans*-2-alkenes are plotted against carbon number in Figure 6. The partial rate constants for OH radical addition to the 1-alkenes and 2-methyl-1-alkenes plateau at 3.7 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the 1-alkenes and 6.7 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the 2-methyl-1-alkenes, in both cases at a carbon number ≥ 10−11 (or correspondingly, for R in $CH_2=CHR$ and $CH_2=C(CH_3)R$ of $\geqslant C_8H_{17}$ in each case). This is analogous to recent measurements of rate constants for the reactions of NO_3 radicals with a series of 1-alkenes and 2-methyl-1-alkenes, where H-atom abstraction is expected to

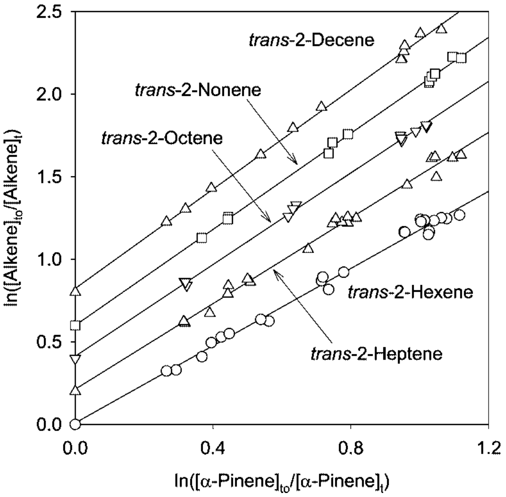

Figure 4. Plots of eq I for the reaction of OH radicals with *trans*-2-hexene, *trans*-2-heptene, *trans*-2-octene, *trans*-2-nonene, and *trans*-2-decene at 299 ± 2 K, with α-pinene as the reference compound. Data for *trans*-2-heptene, *trans*-2-octene, *trans*-2-nonene, and *trans*-2-decene have been displaced vertically by 0.20, 0.40, 0.60, and 0.80 units, respectively, for clarity.

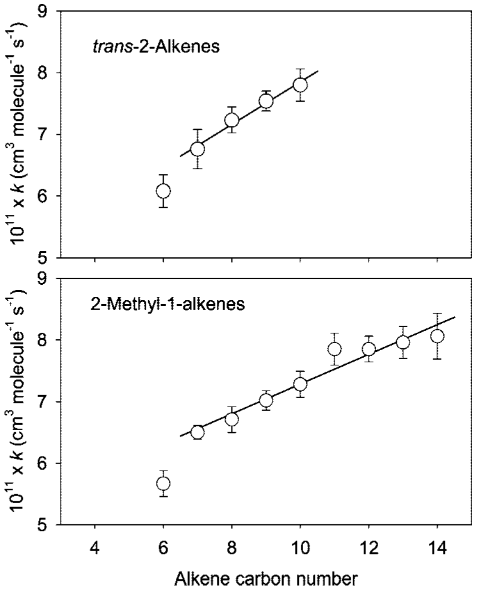

Figure 5. Plots of the rate constants measured here at 299 ± 2 K for the reactions of OH radicals with the C_6-C_{14} 2-methyl-1-alkenes (bottom) and C_6-C_{10} *trans*-2-alkenes (top). The solid lines are the least-squares fits to the rate constants for the C_7-C_{14} 2-methyl-1-alkenes (bottom) and C_7-C_{10} *trans*-2-alkenes (top).

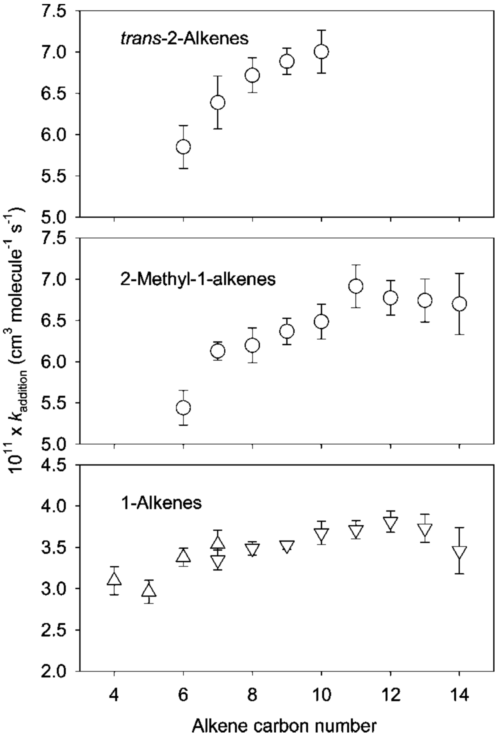

Figure 6. Plots of the rate constants, k(addition) = k(total) − k(abstraction), for the reactions of OH radicals with 1-alkenes (bottom), 2-methyl-1-alkenes (middle), and *trans*-2-alkenes (top). The values of k(abstraction) were calculated as described by Kwok and Atkinson,[14] and the rate constants k(total) were from the following sources: ○, this work; △, Atkinson and Aschmann at 295 ± 1 K;[13] ▽, Aschmann and Atkinson at 295 ± 1 K.[9]

TABLE 3: Parameters in Equations III and IV for OH Radical Addition to Alkenes at Room Temperature

	$10^{12}k$ (cm^3 molecule^{-1} s^{-1})		
alkene series	k_a	k_c	a
1-alkenes	28 [a]	9 [b]	0.35 [b]
2-methyl-1-alkenes	51 [a]	16 [b]	0.35 [b]
trans-2-alkenes	63 [a]	6 [b]	0.35 [b]

[a] Based on the high-pressure rate constants[6] for the reactions of OH radicals with propene (for the 1-alkenes), 2-methyl-1-propene (for the 2-methyl-1-alkenes), and *trans*-2-butene (for the *trans*-2-alkenes) at 295 K (1-alkenes[9,13]) or 299 K (2-methyl-1-alkene and *trans*-2-alkenes). [b] See text.

be of little or no importance,[6] yet the rate constants increase with increasing carbon number to a plateau at $\sim$C$_8$−C$_{10}$.[19] For the *trans*-2-alkenes, our OH radical rate data do not extend to a high enough carbon number to see a clear plateau in the addition rate constant after subtracting the calculated[14] rate constant for H-atom abstraction.

OH radical addition to C=C bond of alkenes has been shown to correlate with the alkene ionization potential[20] and with the energy of the highest occupied molecular orbital (HOMO).[21] For the 1-alkenes both the ionization potentials[22] and the calculated HOMO energies[21] reach a plateau at $\sim$C$_8$−C$_{10}$. This is consistent with our observation that, assuming H-atom abstraction from the C−H bonds of the alkyl substituent in alkenes occurs at the same rate as from C−H bonds in alkanes, the partial rate constants for OH radical addition also plateau at carbon numbers of ∼10−11 for the 1-alkenes and 2-methyl-1-alkenes (Figure 6).

We have empirically fitted the OH radical addition portion of the rate constant,

$$k(\text{total}) = k(\text{addition}) + k(\text{abstraction}) \qquad \text{(II)}$$

by

$$k(\text{addition}) = k_a + k_b \qquad \text{(III)}$$

where k_a is the rate constant for the simplest member of the series (propene, 2-methyl-1-propene, and *trans*-2-butene for the 1-alkenes, 2-methyl-1-alkenes, and *trans*-2-alkenes, respectively) and k_b is an “enhancement” rate constant. The enhancement rate constant k_b increases from zero to a plateau as the alkyl substituent group increases in length. We have empirically used eq IV, which has the necessary attributes, to estimate k_b,

$$k_b = k_c(1 - e^{-an}) \qquad \text{(IV)}$$

where k_c is the maximum enhancement rate constant for a given alkene series, n is the carbon number of the alkyl substituent group [n = (total carbon number − 3) for the 1-alkenes and n = (total carbon number − 4) for the 2-methyl-1-alkenes and *trans*-2-alkenes], and a is a constant. The observation that the maximum plateau value of k_b is attained at $n \sim 7$ suggests that $a \sim 0.4$. Using our present rate constants for the C$_6$−C$_{10}$ 2-methyl-1-alkenes and those of Atkinson and Aschmann[13] and

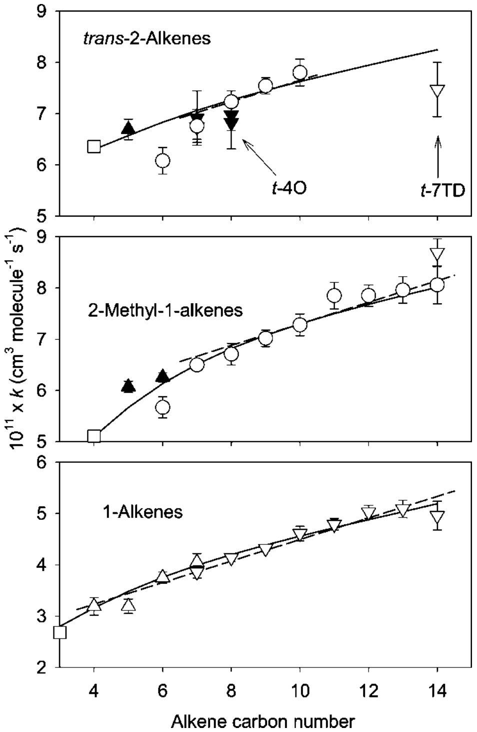

Figure 7. Plots of the rate constants, k(total) = k(addition) + k(abstraction), for the reactions of OH radicals with 1-alkenes (bottom), 2-methyl-1-alkenes (middle), and *trans*-2-alkenes (top). Measured rate constants: ○, this work; △, Atkinson and Aschmann at 295 ± 1 K;[13] ▽, Aschmann and Atkinson at 295 ± 1 K;[9] □, recommended rate constants for propene at 295 K and for 2-methyl-1-butene and *trans*-2-butene at 299 K;[6] ▲, Ohta at 298 ± 2 K;[17] ▼, O’Rji and Stone at 297 ± 2 K.[18] Rate constants are also shown in the top panel for the *trans*-internal alkenes *trans*-4-octene[18] (*t*-4O) and *trans*-7-tetradecene[9] (*t*-7TD). The solid lines are the fits to eqs II−IV, with the OH radical addition rate constants being calculated using the parameters from Table 3 and with the H-atom abstraction rate constants being calculated using the Kwok and Atkinson estimation method.[14] The dashed lines are fits over the carbon number ranges indicated assuming that H-atom abstraction increases with a rate constant of 2.1 × 10^{-12} cm^3 molecule^{-1} s^{-1} per additional CH$_2$ group (see text), and with the midpoint of the carbon number having the same rate constant as the least-squares fits shown in Figure 5 or, for the 1-alkenes, in Aschmann and Atkinson.[9]

Aschmann and Atkinson[9] for the C_4−C_9 1-alkenes, a least-squares regression of $\ln(k_c - k_b)/k_c$ against n leads to $a = 0.33 \pm 0.09$, where the error is two standard deviations. The values of the parameters used are listed in Table 3, with the values of k_a being the limiting high-pressure rate constants for the reactions of OH radicals with propene, 2-methyl-1-propene, and *trans*-2-butene,[6] and with a being set to 0.35, based on the plateau value of k_b being attained at $n \sim 7$ and the above least-squares analysis of the enhancement rate constants against n for $n \leq 6$. Interestingly, the maximum enhancement rate constants, k_c, for the 1-alkenes and 2-methyl-1-alkenes are in both cases 30% of the rate constant for the simplest member of the series, with a lesser fractional enhancement for the *trans*-2-alkenes.

The resulting fits to the present and literature rate data for the total rate constants, $k(\text{total}) = k(\text{addition}) + k(\text{abstraction})$, for the 1-alkenes, 2-methyl-1-alkenes, and *trans*-2-alkenes are shown as the solid lines in Figure 7, with generally very good agreement between measured and predicted rate constants for the 1-alkenes and 2-methyl-1-alkenes. Note that, even though the OH radical addition rate constant plateaus at $\geqslant C_{10}$−C_{11} (Figure 6), the total rate constant continues to increase for the $\geqslant C_{10}$−C_{11} 1-alkenes and 2-methyl-1-alkenes because of the contribution of H-atom abstraction which increases at a rate of 1.41×10^{-12} cm^3 molecule^{-1} s^{-1} per additional CH_2 group.[14] The dashed lines in Figure 7 are fits assuming that the increase in rate constant with carbon number are due solely to H-atom abstraction,[9] with a rate constant of 2.1×10^{-12} cm^3 molecule^{-1} s^{-1} per additional CH_2 group (see above).

For the internal alkenes, the available database is smaller and Figure 7 (top) shows all of the available data for the *trans*-alkenes, including *trans*-4-octene[18] and *trans*-7-tetradecene[9] in addition to the *trans*-2-alkenes. It should be noted that our present rate constant for *trans*-2-hexene is ∼10% lower than anticipated, as also is the case for 2-methyl-1-pentene. With the above interpretation of the rate constants for the reactions of OH radicals with alkenes, the percentage of H-atom abstraction at room temperature becomes ∼29% for 1-tetradecene and ∼16−17% for 2-methyl-1-tridecene and *trans*-2-tetradecene, with the percentage for 1-tetradecene being a factor of 1.4 lower than that previously estimated on the basis of the increase with carbon number being solely due to H-atom abstraction.[9]

Clearly, as noted previously,[9] product studies are needed to experimentally determine the fractions of the reactions of OH radicals with alkenes proceeding by OH radical addition and by H-atom abstraction. However, it should be noted that product studies will be complicated because of the formation of multifunctional products from both the OH radical addition and the H-atom abstraction pathways, which are likely to be difficult to identify and quantify.[6]

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References and Notes

(1) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys. Res.* **1995**, *100*, 8873.

(2) Hoekman, S. K. *Environ. Sci. Technol.* **1992**, *26*, 1206.

(3) Zielinska, B.; Sagebiel, J. C.; Harshfield, G.; Gertler, A. W.; Pierson, W. R. *Atmos. Environ.* **1996**, *30*, 2269.

(4) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press: New York, 2000.

(5) Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063.

(6) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.

(7) Atkinson, R. *J. Phys. Chem. Ref. Data,* **1989**, *Monogr. 1*, 1.

(8) Peeters, J.; Boullart, W.; Pultau, V.; Vandenberk, S.; Vereecken, L. *J. Phys. Chem. A* **2007**, *111*, 1618.

(9) Aschmann, S. M.; Atkinson, R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4159.

(10) Vakhtin, A. B.; Murphy, J. E.; Leone, S. R. *J. Phys. Chem. A* **2003**, *107*, 10055.

(11) Atkinson, R.; Tuazon, E. C.; Carter, W. P. L. *Int. J. Chem. Kinet.* **1985**, *17*, 725.

(12) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1998**, *30*, 577.

(13) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1984**, *16*, 1175.

(14) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.

(15) Kramp, F.; Paulson, S. E. *J. Phys. Chem. A* **1998**, *102*, 2685.

(16) Aschmann, S. M.; Tuazon, E. C.; Atkinson, R. *J. Phys. Chem. A* **2005**, *109*, 2282.

(17) Ohta, T. *Int. J. Chem. Kinet.* **1984**, *16*, 879.

(18) O'Rji, L. N.; Stone, D. A. *Int. J. Chem. Kinet.* **1992**, *24*, 703.

(19) Mason, S.; Arey, J.; Atkinson, R. *J. Phys. Chem. A*, to be submitted for publication.

(20) Grosjean, D.; Williams, E. L., II. *Atmos. Environ.* **1992**, *26A*, 1395.

(21) King, M. D.; Canosa-Mas, C. E.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2231.

(22) NIST. Structures and Properties, Version 2.0. *Standard Reference Database 25*; Stein, S. E., Ed.; Chemical Kinetics and Thermodynamics Division, National Insitute of Standards and Technology: Gaithersburg, MD, 1994 (Jan.).

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