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Rate Constants for the Gas-Phase Reactions of NO_3 Radicals and O_3 with C_6-C_{14} 1-Alkenes and 2-Methyl-1-alkenes at 296 ± 2 K

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Rate constants for the gas-phase reactions of NO_3 radicals and O_3 with a series of C_6-C_{14} 1-alkenes and 2-methyl-1-alkenes have been measured at 296 ± 2 K and atmospheric pressure of air using relative rate methods. For the NO_3 radical reactions, the rate constants obtained (in units of 10^{-14} cm^3 $molecule^{-1}$ s^{-1}) were: 1-hexene, 2.00 ± 0.16; 1-octene, 2.35 ± 0.15; 1-decene, 2.55 ± 0.16; 1-dodecene, 2.79 ± 0.36; 1-tetradecene, 2.87 ± 0.21; 2-methyl-1-pentene, 43.8 ± 2.3; 2-methyl-1-hexene, 52.4 ± 2.5; 2-methyl-1-octene, 57.8 ± 2.6; 2-methyl-1-nonene, 60.8 ± 2.9; 2-methyl-1-undecene, 60.8 ± 3.3; 2-methyl-1-tridecene, 60.3 ± 3.4; and cycloheptene, 49.4 ± 2.0. For the O_3 reactions, the rate constants obtained (in units of 10^{-17} cm^3 $molecule^{-1}$ s^{-1}) were: 1-hexene, 0.898 ± 0.054; 1-heptene, 1.05 ± 0.07; 1-octene, 1.01 ± 0.04; 1-decene, 1.11 ± 0.05; 1-dodecene, 1.38 ± 0.14; 1-tridecene, 1.92 ± 0.12; 1-tetradecene, 2.44 ± 0.24; 2-methyl-1-pentene, 1.26 ± 0.13; 2-methyl-1-heptene, 1.35 ± 0.05; 2-methyl-1-octene, 1.38 ± 0.06; 2-methyl-1-decene, 1.48 ± 0.07; 2-methyl-1-undecene, 1.46 ± 0.11; and 2-methyl-1-tridecene, 2.85 ± 0.42. The rate constants for the NO_3 radical reactions significantly increase with increasing carbon number, attaining a plateau at $\geq C_{14}$ for the 1-alkenes and at $C_{10}-C_{14}$ for the 2-methyl-1-alkenes. In contrast, the rate constants for O_3 reactions increase only slightly with increasing carbon number up to $\sim C_{10}$ for the 1-alkenes and $\sim C_{12}$ for the 2-methyl-1-alkenes, with the significant increase in the measured rate constants for the $>C_{10}$ 1-alkenes and $>C_{12}$ 2-methyl-1-alkenes possibly being due to heterogeneous reactions. Reasons for the observed trends in NO_3 radical and O_3 reaction rate constants with alkene carbon number are discussed.

Introduction

Alkenes are ubiquitous components of ambient air owing to their emissions from both biogenic and anthropogenic sources.[1−4] Within urban atmospheres they typically comprise ~10% of nonmethane volatile organic compounds,[5] making understanding their atmospheric degradation pathways important. In the troposphere, alkenes react with hydroxyl (OH) and nitrate (NO_3) radicals and ozone (O_3), with the dominant reaction depending on the time of day and the specific alkene.[5,6] These reactions proceed via initial addition to the C=C bond(s) and, in the case of the OH and NO_3 radical reactions, by abstraction of a hydrogen atom from the C−H bonds of substituent alkyl groups, with the addition process dominating.[5−8]

While most kinetic studies of alkene reactions have focused on the OH radical reactions,[5,6] few systematic studies of the effect of carbon number on the reaction rate constants have been conducted. Recently, two studies[9,10] showed that for $\leq C_{14}$ 1-alkenes, 2-methyl-1-alkenes, and *trans*-2-alkenes, the OH radical reaction rate constants increase with carbon number. It was proposed[10] that this increase was partially due to an increase in the rate constant for OH radical addition to the C=C bond, which attains a plateau value at $\sim C_{10}$, and with H-atom abstraction being of minor importance. As a part of our kinetic investigation of the reactions of alkenes with OH radicals,[9,10] NO_3 radicals, and O_3 as a function of carbon number, in this work we have measured rate constants for the gas-phase reactions of NO_3 radicals and O_3 with a series of C_6-C_{14} 1-alkenes and 2-methyl-1-alkenes at 296 ± 2 K and atmospheric pressure.

Experimental Methods

The experimental methods used were generally similar to those previously described.[11] All experiments were carried out in the dark in a ~7000 L all-Teflon chamber equipped with a Teflon-coated fan to ensure rapid mixing of reactants, in the presence of ~735 Torr total pressure of purified dry air at 296 ± 2 K. Rate constants for the NO_3 radical and O_3 reactions were measured using a relative rate technique in which the disappearance rate of an alkene was determined relative to that of a reference compound, whose rate constant is reliably known, thereby allowing the absolute rate constant of the alkene to be determined.[11]

Provided that the alkene and the reference compound were removed only by reaction with NO_3 radicals or O_3 according to reactions 1 and 2

$$\left.\begin{matrix}NO_3\\ O_3\end{matrix}\right\} + \text{alkene} \rightarrow \text{products} \tag{1}$$

$$\left.\begin{matrix}NO_3\\ O_3\end{matrix}\right\} + \text{reference compound} \rightarrow \text{products} \tag{2}$$

then

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$$\ln\left\{\frac{[\text{alkene}]_{t_0}}{[\text{alkene}]_t}\right\} - D_t = \frac{k_1}{k_2}\left[\ln\left\{\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right\} - D_t\right] \tag{I}$$

where $[\text{alkene}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the alkene and the reference compound, respectively, at time t_0, $[\text{alkene}]_t$ and $[\text{reference compound}]_t$ are the concentrations of the alkene and the reference compound, respectively, at time t, D_t is a term to take into account any dilution caused by additions to the chamber during an experiment (see below), and k_1 and k_2 are the respective rate constants for reactions 1 and 2. A plot of $\{\ln([\text{alkene}]_{t_0}/[\text{alkene}]_t) - D_t\}$ against $\{\ln([\text{reference compound}]_{t_0}/[\text{reference compound}]_t) - D_t\}$ should then be a straight line of slope k_1/k_2 and zero intercept.

Typically, two alkenes plus the reference compound were present in each experiment. For the NO_3 radical reactions, NO_2 was also added to the reactant mixtures to lengthen the reaction times and to minimize secondary reactions.[8,11] Initial reactant concentrations (molecule cm^{-3}) within the chamber were: alkenes and reference compound, $\sim 2.4 \times 10^{13}$ each; and NO_2, $(2.4–9.6) \times 10^{13}$. NO_3 radicals were generated from the thermal decomposition of dinitrogen pentoxide (N_2O_5)[11]

$$N_2O_5 \xrightarrow{M} NO_2 + NO_3 \tag{3}$$

with three to four additions of N_2O_5 to the chamber being made during an experiment. Each N_2O_5 addition corresponded to an initial concentration of N_2O_5 in the chamber of $(0.5–2.6) \times 10^{13}$ molecule cm^{-3}, and the parameter D_t was 0.0015 per N_2O_5 addition to the chamber. Thiophene was used as the reference compound in the 1-alkene experiments, whereas cycloheptene was used for experiments with the 2-methyl-1-alkenes. The rate constant for cycloheptene was also determined relative to that for *trans*-2-butene using the same experimental conditions as those noted above.

For the O_3 reactions, in addition to the alkenes and reference compound, an excess of cyclohexane was included in the reactant mixtures to scavenge >97% of the OH radicals formed from the alkene + O_3 reactions.[5,6,11] Initial reactant concentrations (molecule cm^{-3}) within the chamber were: alkenes and reference compound, $\sim 2.4 \times 10^{13}$ each; and cyclohexane, $(0.7–1.0) \times 10^{16}$. During each experiment, four to seven additions of 50 cm^3 of O_3 in O_2 diluent were made to the chamber, with each O_3/O_2 addition corresponding to an initial concentration of O_3 in the chamber of $\sim 5 \times 10^{12}$ molecule cm^{-3}. The parameter D_t was 0.0007 per O_3 addition to the chamber. 1-Octene was used as the reference compound for the 1-alkenes, whereas 2-methyl-1-heptene was used as the reference compound for the 2-methyl-1-alkenes. Rate constants for 1-octene and 2-methyl-1-heptene were also measured relative to that for 1-butene using the same experimental conditions as those noted above.

The concentrations of the alkenes and reference compounds were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). For the analyses of *trans*-2-butene and 1-butene, gas samples were collected from the chamber in a 100 cm^3 all-glass, gastight syringe and were transferred via a 1 cm^3 stainless steel loop and gas sampling valve onto a 30 m DB-5 megabore column initially held at −25 °C for 2 min and then temperature programmed to 200 °C at 8 °C min^{-1}. For the analyses of the other alkenes and thiophene, 100 cm^3 volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 or 30 m DB-5 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_8−C_{10}, and C_{10}-C_{14} alkenes, respectively) and then temperature programmed to 250 °C at 8 °C min^{-1}. Replicate analyses of the alkenes within the chamber prior to reaction always agreed to within 5% and generally to within 1 to 2%, indicating the absence of any significant wall decays.

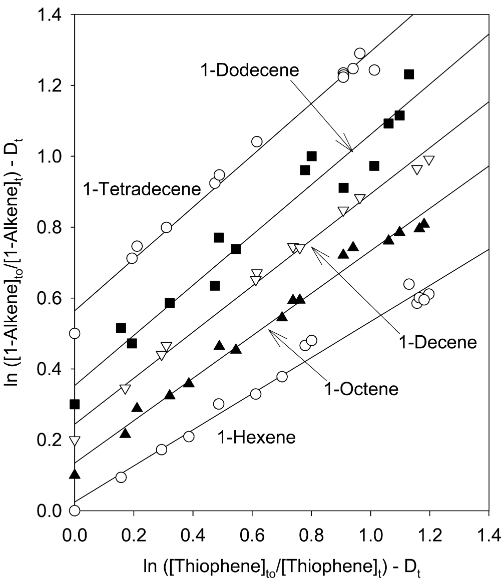

Figure 1. Plots of eq I for the gas-phase reactions of the NO_3 radical with 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-tetradecene using thiophene as the reference compound. The data shown for each alkene are from multiple experiments, as detailed in Table S1 of the Supporting Information. Data for 1-octene, 1-decene, 1-dodecene, and 1-tetradecene are displaced vertically by 0.10, 0.20, 0.30, and 0.50 units, respectively, for clarity.

The chemicals used, their stated purities, and their sources were: 1-hexene (99%), 1-heptene (99+%), 1-decene (94%), 1-dodecene (95%), 1-tetradecene (92%), 2-methyl-1-pentene (99+%), 2-methyl-1-hexene (96%), 2-methyl-1-heptene (99%), 2-methyl-1-nonene (97%), cyclohexane (99.9%; HPLC grade), cycloheptene (97%), and thiophene (99+%), Aldrich; 1-octene (99.9%), 2-methyl-1-octene (98%), 2-methyl-1-undecene (95+%), and 2-methyl-1-tridecene (99%), ChemSampCo; 2-methyl-1-decene (97%), Rieke Metals; and 1-butene (≥99%), *trans*-2-butene (≥95%), and NO (>99%), Matheson Gas Products. N_2O_5 was prepared as previously described[12] and stored under vacuum at 77 K. NO_2 was prepared immediately prior to use by reacting NO with an excess of O_2, and O_3 was prepared as needed by a Welsbach T-408 ozone generator.

Results

NO_3 Radical Reactions. Experiments were conducted with one or two alkenes plus the reference compound being present in the reactant mixtures, as listed in Table S1 in the Supporting Information. No effect of varying the initial NO_2 concentration by a factor of two on the measured rate constant ratios was observed. Because of GC interferences with reaction products, the 2-methyl-1-tridecene data from the 2-methyl-1-hexene + 2-methyl-1-tridecene + cycloheptene experiment were not used.

The experimental data for the NO_3 radical reactions are plotted in accordance with eq I in Figures 1−3, and the rate constant ratios, k_1/k_2, obtained from least-squares analyses of these data are given in Tables 1 (1-alkenes) and 2 (2-methyl-1-alkenes). For the 1-alkenes, the measured rate constant ratios

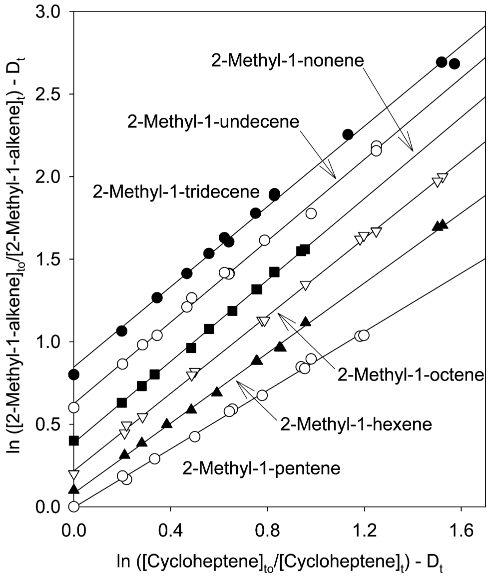

Figure 2. Plots of eq I for the gas-phase reactions of the NO_3 radical with 2-methyl-1-pentene, 2-methyl-1-hexene, 2-methyl-1-octene, 2-methyl-1-nonene, 2-methyl-1-undecene, and 2-methyl-1-tridecene using cycloheptene as the reference compound. The data shown for each alkene are from multiple experiments, as detailed in Table S1 of the Supporting Information. Data for 2-methyl-1-hexene, 2-methyl-1-octene, 2-methyl-1-nonene, 2-methyl-1-undecene, and 2-methyl-1-tridecene are displaced vertically by 0.10, 0.20, 0.40, 0.60, and 0.80 units, respectively, for clarity.

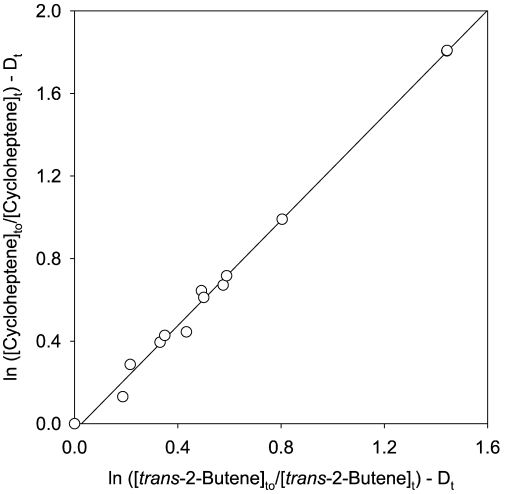

Figure 3. Plot of eq I for the gas-phase reaction of the NO_3 radical with cycloheptene using *trans*-2-butene as the reference compound. The data shown are from three experiments with initial NO_2 concentrations of (4.8–9.6) × 10^{13} molecule cm^{-3}.

are placed on an absolute basis by use of a rate constant of $k_2(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K,[8] and the resulting rate constants, k_1, are also given in Table 1. For the 2-methyl-1-alkenes, the measured rate constant ratios, k_1/k_2, are placed on an absolute basis by using the rate constant measured here for the reaction of NO_3 radicals with cycloheptene, $k_2(NO_3 + \text{cycloheptene}) = (4.94 \pm 0.20) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, and are given in Table 2. Our rate constant for cycloheptene, measured relative to that for *trans*-2-butene of $k_2(NO_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1},[6] is in excellent agreement with the literature relative rate constants of Atkinson et al.[16] and Kind et al.[17] and is in agreement within the experimental error with the absolute rate constant of Martinez et al.[18] (Table 2).

O_3 Reactions. Again, one or two alkenes plus the reference compound were present during each of the O_3 experiments (Table S2 in the Supporting Information), and sufficient cyclohexane was included to scavenge >97% of OH radicals generated during the reactions. For the majority of experiments, the GC-FID analyses were carried out using a DB-1701 column. However, in experiments involving 1-decene, a chromatographic interference between 1-decene and a product of the 1-octene (the reference compound) reaction occurred, and hence a DB-5 column was used for the GC-FID analyses during these experiments. It was also observed that 2-methyl-1-nonene coeluted with cyclohexanol, a product of the OH + cyclohexane reaction, [11] and hence a rate constant for the reaction of O_3 with 2-methyl-1-nonene could not be obtained, and 2-methyl-1-octene and 2-methyl-1-decene were therefore included for study.

The experimental data for the O_3 reactions are plotted in accordance with eq I in Figures 4−6, and the rate constant ratios, k_1/k_2, obtained from least-squares analyses of these data are given in Tables 3 (1-alkenes) and 4 (2-methyl-1-alkenes). The rate constant ratios, k_1/k_2, measured for the 1-alkenes are placed on an absolute basis using the rate constant k_2 measured here for the reaction of O_3 with 1-octene relative to that for 1-butene, of $k_2(O_3 + \text{1-octene}) = (1.01 \pm 0.04) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, and are listed in Table 3. Similarly, the rate constant ratios, k_1/k_2, measured for the 2-methyl-1-alkenes are placed on an absolute basis using the rate constant k_2 measured here for the reaction of O_3 with 2-methyl-1-heptene relative to that for 1-butene, of $k_2(O_3 + \text{2-methyl-1-heptene}) = (1.35 \pm 0.05) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, and are listed in Table 4. Our rate constant for the reaction of O_3 with 1-octene at 296 ± 2 K is 20% lower than the absolute measurement of Grosjean and Grosjean at 293 ± 1 K.[21] No literature rate data are available for the reaction of O_3 with 2-methyl-1-heptene.

Discussion

Comparison with Literature Values. Selected literature room-temperature rate constants for the alkenes studied here, together with literature recommendations at 296 K for propene, 1-butene, and 2-methylpropene, are also included in Tables 1−4 for comparison. For the NO_3 radical reactions, the relative rate constant of Canosa-Mas et al.[14] for 1-hexene is in excellent agreement with our value, and those of Canosa-Mas et al.[14] for 1-pentene and 1-heptene are consistent with our data with respect to the trend in NO_3 radical reaction rate constant with carbon number (Figure 7). In contrast, the absolute rate constant of Martinez et al.[15] for 1-hexene is a factor of 4.6 higher than our rate constant, and their rate constant for 1-pentene[15] is significantly higher than that of Canosa-Mas et al.[14] and is also inconsistent with our data. For the remaining 1-alkenes and all of the 2-methyl-1-alkenes studied here, no literature data are available for comparison.

Substantially more literature data are available for the O_3 reactions, and Tables 3 and 4 contain selected recent literature values. For the 1-alkenes, our present rate constants are in good agreement (to within ∼±25%) with the literature values of Japar et al.,[19] Treacy et al.,[20] Grosjean and Grosjean,[21] and Avzianova and Ariya.[22] However, the absolute rate constants of Atkinson et al.[24] for 1-hexene and 1-heptene are higher than the present values by factors of 1.3–1.6 for unknown reasons. For the 2-methyl-1-alkenes studied here, only 2-methyl-1-pentene has been previously studied, and our present rate constant is in excellent agreement with those of Avzianova and Ariya[22] and

TABLE 1: Rate Constant Ratios, k_1/k_2, and Rate Constants, k_1, for the Reactions of NO_3 Radicals with a Series of 1-Alkenes at 296 ± 2 K, Together with Selected Literature Data

		$10^{14} \times k_1$ (cm^3 molecule^{-1} s^{-1})	
	k_1/k_2[a]	this work[b]	literature
propene			0.924[c]
1-butene			1.32;[c] 1.24 ± 0.08[d]
1-pentene			1.48 ± 0.08;[e] 6.19 ± 0.38[f]
1-hexene	0.509 ± 0.040	2.00 ± 0.16	1.81 ± 0.11;[e] 9.32 ± 0.71[f]
1-heptene			2.01 ± 0.15[e]
1-octene	0.599 ± 0.038	2.35 ± 0.15	
1-decene	0.650 ± 0.039	2.55 ± 0.16	
1-dodecene	0.709 ± 0.091	2.79 ± 0.36	
1-tetradecene	0.731 ± 0.052	2.87 ± 0.21	

[a] At 296 ± 2 K, relative to thiophene. Indicated errors are two least-squares standard deviations. [b] At 296 ± 2 K. The measured rate constant ratios, k_1/k_2, are placed on an absolute basis using $k_2(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[8] Indicated errors are two least-squares standard deviations and do not include the uncertainty in the rate constant, k_2. [c] Recommended value at 296 K.[6] [d] From Aschmann et al.[13] At 296 ± 2 K, relative to thiophene. The measured rate constant ratio $k_1/k_2 = 0.316 \pm 0.020$ (erroneously cited in ref 13 as 0.0316 ± 0.020) is placed on an absolute basis using $k_2(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[8] [e] From Canosa-Mas et al.[14] At 296 ± 1 K, relative to 1-butene. The measured rate constant ratios are placed on an absolute basis using $k_2(NO_3 + \text{1-butene}) = 1.32 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[6] [f] From Martinez et al.[15] Absolute rate measurement at 298 K.

TABLE 2: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for the Reactions of NO_3 Radicals with a Series of 2-Methyl-1-alkenes and with Cycloheptene at 296 ± 2 K, Together with Selected Literature Data

	k_1/k_2 relative to[a]		$10^{14} \times k_1$ (cm^3 molecule^{-1} s^{-1})	
	trans-2-butene	cycloheptene	this work[b]	literature
2-methylpropene				34.4[c]
2-methyl-1-pentene		0.887 ± 0.026	43.8 ± 2.3	
2-methyl-1-hexene		1.06 ± 0.02	52.4 ± 2.5	
2-methyl-1-octene		1.17 ± 0.02	57.8 ± 2.6	
2-methyl-1-nonene		1.23 ± 0.03	60.8 ± 2.9	
2-methyl-1-undecene		1.23 ± 0.04	60.8 ± 3.3	
2-methyl-1-tridecene		1.22 ± 0.05	60.3 ± 3.4	
cycloheptene	1.27 ± 0.05		49.4 ± 2.0[d]	48.4 ± 1.6;[e] 54.2 ± 2.4;[f] 57.0 ± 10.0[g]

[a] At 296 ± 2 K. Indicated errors are two least-squares standard deviations. [b] At 296 ± 2 K. The measured rate constant ratios, k_1/k_2, for the 2-methyl-1-alkenes are placed on an absolute basis using $k_2(NO_3 + \text{cycloheptene}) = (4.94 \pm 0.20) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Indicated errors are two least-squares standard deviations. [c] Recommended value at room temperature.[6] [d] Measured rate constant ratio, k_1/k_2, is placed on an absolute basis using $k_2(NO_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K.[6] Indicated errors are two least-squares standard deviations and do not include the uncertainty in the rate constant for the reaction of NO_3 radicals with *trans*-2-butene. [e] From Atkinson et al.[16] At 298 ± 2 K, relative to *trans*-2-butene. The measured rate constant ratio $k_1/k_2 = 1.24 \pm 0.04$ is placed on an absolute basis using $k_2(NO_3 + \textit{trans}\text{-2-butene}) = 3.90 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6] [f] From Kind et al.[17] At 298 ± 2 K, relative to *trans*-2-butene. The measured rate constant ratio $k_1/k_2 = 1.39 \pm 0.06$ is placed on an absolute basis using $k_2(NO_3 + \textit{trans}\text{-2-butene}) = 3.90 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[6] [g] From Martinez et al.[18] Absolute rate measurement at 298 K.

Grosjean and Grosjean,[25] although the latter[25] was measured at 287 ± 1 K and would be expected to be ~20% higher at 296 K.[6]

Effect of Carbon Number on the NO_3 Radical Reaction Rate Constants. Our present rate constants for the NO_3 radical reactions with 1-alkenes and 2-methyl-1-alkenes are plotted as a function of alkene carbon number in Figure 7, together with the 296 K relative rate constants of Canosa-Mas et al.[14] for 1-pentene, 1-hexene, and 1-heptene and of Aschmann et al.[13] for 1-butene. For both the 1-alkenes and the 2-methyl-1-alkenes, the rate constants increase rapidly with carbon number and then attain (2-methyl-1-alkenes) or approach (1-alkenes) a plateau value that is a factor of about two to three higher than the rate constants for the simplest member of each alkene series (Figure 7). This increase in rate constant with carbon number could be due to an increase in H-atom abstraction from the C−H bonds of the alkyl substituent groups, an increase in the partial rate constant for NO_3 radical addition to the C=C bond, or both. The room-temperature rate constants for the reactions of NO_3 radicals with the C_6−C_{10} *n*-alkanes, which proceed only by H-atom abstraction from the C−H bonds of the CH_2 and CH_3 groups, are in the range of $(1.1–2.8) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.[6] These H-atom abstraction rate constants are two and three orders of magnitude lower than the rate constants measured here for the 1-alkenes and 2-methyl-1-alkenes, respectively, suggesting that H-atom abstraction from the alkenes is of negligible importance and cannot account for the observed effect of carbon number on the reaction rate constants. Furthermore, a recent study using in situ Fourier transform infrared spectroscopy of HNO_3 formation from the reactions of NO_3 radicals with *trans*-2-butene and 1-octene shows that for both reactions, H-atom abstraction accounts for ≤6% of the overall NO_3 radical reaction at room temperature (Tuazon and Atkinson, unpublished data, 2008; Supporting Information). These product data indicate that the partial rate constant for H-atom abstraction from the reaction of NO_3 radicals with 1-octene is $< 1.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at room temperature. Therefore, H-atom abstraction from the CH_2 and CH_3 groups in the 1-alkenes and, especially, the 2-methyl-1-alkenes studied here is of negligible importance.

Therefore, the increase in reaction rate with increasing carbon number for the 1-alkenes and 2-methyl-1-alkenes (Figure 7) must be due to an increase in the rate of NO_3 radical addition to the alkene C=C bond. The plateau in the rate constant beyond ~C_{12} can be attributed to the increasing distance between the C=C bond and additional CH_2 groups, leading to no additional donation of electron density to the C=C bond once they are

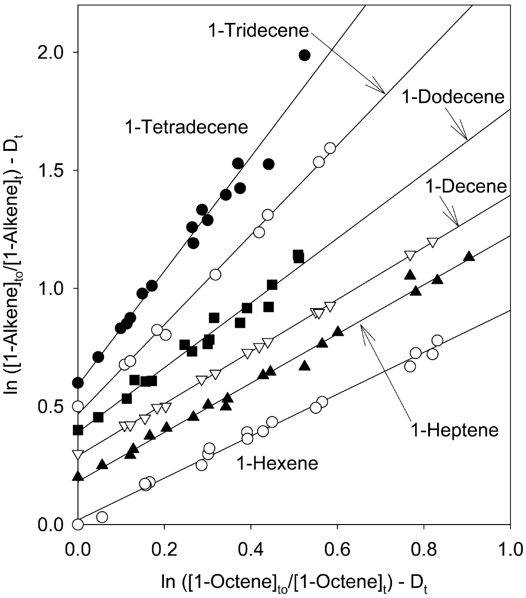

Figure 4. Plots of eq I for the gas-phase reactions of O_3 with 1-hexene, 1-heptene, 1-decene, 1-dodecene, 1-tridecene, and 1-tetradecene using 1-octene as the reference compound. The data shown for each alkene are from multiple experiments, as detailed in Table S2 in the Supporting Information. Data for 1-heptene, 1-decene, 1-dodecene, 1-tridecene, and 1-tetradecene are displaced vertically by 0.20, 0.30, 0.40, 0.50, and 0.60 units, respectively, for clarity.

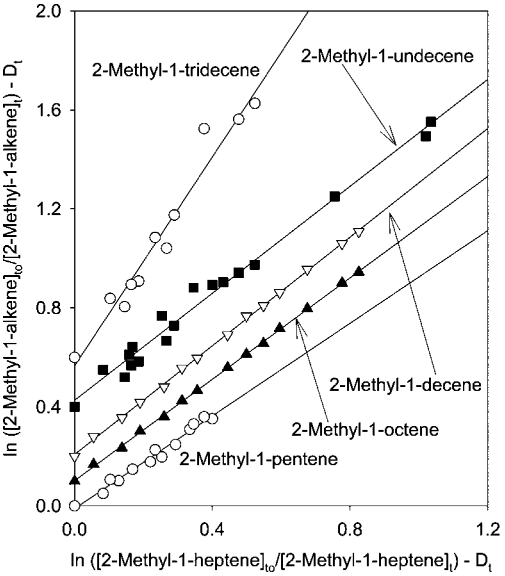

Figure 5. Plots of eq I for the gas-phase reactions of O_3 with 2-methyl-1-pentene, 2-methyl-1-octene, 2-methyl-1-decene, 2-methyl-1-undecene, and 2-methyl-1-tridecene using 2-methyl-1-heptene as the reference compound. The data shown for each alkene are from multiple experiments, as detailed in Table S2 in the Supporting Information. Data for 2-methyl-1-octene, 2-methyl-1-decene, 2-methyl-1-undecene, and 2-methyl-1-tridecene are displaced vertically by 0.10, 0.20, 0.40, and 0.60 units, respectively, for clarity.

sufficiently distanced.[26-28] NO_3 and OH radical addition to the C=C bond of alkenes has previously been shown to correlate with the alkene ionization potential[26] and with the energy of the highest occupied molecular orbital (HOMO).[27,28] For the 1-alkenes, both the ionization potentials[29] and the calculated HOMO energies[28] reach a plateau at $\sim C_8 - C_{10}$. This is consistent with our observation that the partial rate constants for NO_3 radical addition also plateau at carbon numbers $\geq C_{10}$ for the 1-alkenes and 2-methyl-1-alkenes (Figure 7).

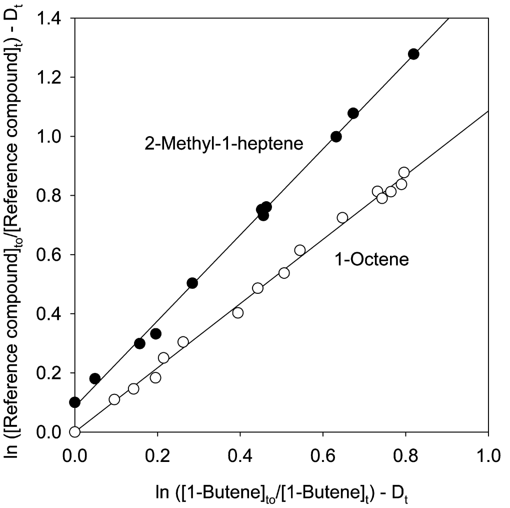

Figure 6. Plots of eq I for the gas-phase reactions of O_3 with 1-octene and 2-methyl-1-heptene using 1-butene as the reference compound. The data shown are from three experiments for each compound. Data for 2-methyl-1-heptene are displaced vertically by 0.10 units for clarity.

As was done previously for the addition pathway of the OH radical reaction,[10] we assume that the NO_3 radical addition rate constant can be expressed as

$$k_{\text{total}} = k_{\text{addition}} = k_a + k_{\text{enhancement}} \tag{II}$$

where k_a is the rate constant for the simplest member of the series (propene and 2-methylpropene for the 1-alkenes and the 2-methyl-1-alkenes, respectively) and $k_{\text{enhancement}}$ is a term to represent the enhancement of this rate constant due to the presence of an alkyl substituent group. The enhancement term increases from zero to a plateau value as the alkyl substituent group increases in length, and we have used eq III[10] to empirically fit our data

$$k_{\text{enhancement}} = k_b(1 - e^{-an}) \tag{III}$$

where k_b is the maximum enhancement rate constant for a given alkene series (i.e., the plateau rate constant equals $k_a + k_b$), 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 a is a constant. Therefore

$$k_{\text{total}} = k_a + k_b(1 - e^{-an}) \tag{IV}$$

The resulting nonlinear least-squares fits are shown as the solid lines in Figure 7, with $k_a = 0.924 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, $k_b = (2.35 \pm 0.32) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, and $a = (0.17 \pm 0.04)$ for the 1-alkenes and $k_a = 3.44 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, $k_b = (2.94 \pm 0.54) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, and $a = (0.29 \pm 0.14)$ for the 2-methyl-1-alkenes, where the indicated errors are two standard errors.

Effect of Carbon Number on the O_3 Reaction Rate Constants. Because both the O_3 and NO_3 radical reactions proceed via electrophilic addition and increasing the length of the alkyl chain increases the electron density surrounding the C=C bond (see above), it would seem logical that alkene reactivity toward O_3 would show a similar trend to that observed for NO_3 radicals. However, the rate constants for the O_3 reactions increase only slowly with increasing carbon number up to 1-decene for the 1-alkenes and 2-methyl-1-undecene for the 2-methyl-1-alkenes, with the 296 K rate constants for 1-decene and 2-methyl-1-undecene being ~15% and ~30%,

TABLE 3: Rate Constant Ratios, k_1/k_2, and Rate Constants, k_1, for the Reactions of O_3 with a Series of 1-Alkenes at 296 ± 2 K, Together with Selected Literature Data

	k_1/k_2 relative to[a]		$10^{17} \times k_1$ (cm^3 $molecule^{-1}$ s^{-1})	
	1-butene	1-octene	this work[b]	literature
propene				0.968[c]
1-butene				0.928[c]
1-pentene				1.07 ± 0.04;[d] 0.92 ± 0.05;[e] 0.96 ± 0.16;[f] 0.87 ± 0.02[g]
1-hexene		0.889 ± 0.040	0.898 ± 0.054	1.11 ± 0.03;[d] 1.08;[h] 1.21 ± 0.28;[i] 1.02 ± 0.06;[e] 0.97 ± 0.14;[f] 0.96 ± 0.02[g]
1-heptene		1.04 ± 0.05	1.05 ± 0.07	1.73 ± 0.19;[i] 0.94 ± 0.04;[f] 0.92 ± 0.03[g]
1-octene	1.09 ± 0.04		1.01 ± 0.04[j]	1.25 ± 0.04[f]
1-decene		1.10 ± 0.02	1.11 ± 0.05	0.80 ± 0.14[f]
1-dodecene		1.37 ± 0.12	1.38 ± 0.14	
1-tridecene		1.90 ± 0.08	1.92 ± 0.12	
1-tetradecene		2.42 ± 0.21	2.44 ± 0.24	

[a] At 296 ± 2 K. Indicated errors are two least-squares standard deviations. [b] At 296 ± 2 K. Unless otherwise noted, the measured rate constant ratios k_1/k_2 for the 1-alkenes are placed on an absolute basis using $k_2(O_3 + \text{1-octene}) = (1.01 \pm 0.04) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. Indicated errors are two least-squares standard deviations. [c] Recommended value at 296 K.[5,6] (Note that the value of *B* cited in Table 2 of ref 6 should be 1744 K rather than 1774 K). [d] From Japar et al.[19] Absolute rate measurement at 299 ± 2 K. [e] From Treacy et al.[20] Absolute rate measurements at 298 K. [f] From Grosjean and Grosjean.[21] Absolute rate measurements at 286−293 K. [g] From Avzianova and Ariya.[22] At room temperature (not specified), relative to propene. The measured rate constant ratios are placed on an absolute basis using $k_2(O_3 + \text{propene}) = 9.9 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.[22] [h] From Adeniji et al.[23] Absolute rate measurement at 294 ± 2 K. [i] From Atkinson et al.[24] Absolute rate measurement at 296 ± 2 K. [j] The measured rate constant ratio, k_1/k_2, is placed on an absolute basis using $k_2(O_3 + \text{1-butene}) = 9.28 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K.[5,6] Indicated errors are two least-squares standard deviations and do not include the uncertainty in the rate constant k_2

TABLE 4: Rate Constant Ratios, k_1/k_2, and Rate Constants, k_1, for the Reactions of O_3 with a Series of 2-Methyl-1-alkenes at 296 ± 2 K, Together with Selected Literature Data

	k_1/k_2 relative to[a]		$10^{17} \times k_1$ (cm^3 $molecule^{-1}$ s^{-1})	
	1-butene	2-methyl-1-heptene	this work[b]	literature
2-methyl-propene				1.13[c]
2-methyl-1-butene				1.33 ± 0.14;[d] 1.43 ± 0.02[e]
2-methyl-1-pentene		0.936 ± 0.083	1.26 ± 0.13	1.25 ± 0.11;[d] 1.31 ± 0.18[f]
2-methyl-1-heptene	1.45 ± 0.05		1.35 ± 0.05[g]	
2-methyl-1-octene		1.02 ± 0.02	1.38 ± 0.06	
2-methyl-1-decene		1.10 ± 0.02	1.48 ± 0.07	
2-methyl-1-undecene		1.08 ± 0.07	1.46 ± 0.11	
2-methyl-1-tridecene		2.11 ± 0.30	2.85 ± 0.42	

[a] At 296 ± 2 K. Indicated errors are two least-squares standard deviations. [b] At 296 ± 2 K. Unless otherwise noted, the measured rate constant ratios, k_1/k_2, for the 2-methyl-1-alkenes are placed on an absolute basis using $k_2(O_3 + \text{2-methyl-1-heptene}) = (1.35 \pm 0.05) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. Indicated errors are two least-squares standard deviations. [c] Recommended value at 296 K.[5,6] [d] From Grosjean and Grosjean.[21] Absolute rate measurement at 288 ± 1 K (2-methyl-1-butene) or 287 ± 1 K (2-methyl-1-pentene). [e] From Avzianova and Ariya.[22] Relative to propene at room temperature (not specified). Placed on an absolute basis using $k_2(O_3 + \text{propene}) = 9.9 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.[22] [f] Grosjean and Grosjean.[25] Absolute rate measurement at 289 ± 4 K. [g] Measured rate constant ratio, k_1/k_2, is placed on an absolute basis using $k_2(O_3 + \text{1-butene}) = 9.28 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K.[5,6] Indicated errors are two least-squares standard deviations and do not include the uncertainty in the rate constant k_2.

respectively, higher than those for the simplest member of each series. Although wall losses of the alkenes were observed to be of negligible importance (Experimental Methods), the significant increase in reaction rate constants for the larger and less volatile alkenes ($>C_{10}$ for the 1-alkenes and $>C_{12}$ for the 2-methyl-1-alkenes) could possibly be due to heterogeneous reactions involving the chamber walls and/or aerosol particles formed in the reactions. Linear least-squares fits to the rate data for the $<C_{10}$ 1-alkenes and for the $\leq C_{12}$ 2-methyl-1-alkenes are shown as the solid lines in Figure 8. The slopes of these lines indicate that the reaction rate increases by only 1–3% per additional CH_2 group.

The difference in the response of the reaction rates as a function of alkyl chain length between the NO_3 radicals and O_3 may be attributed to differences in the reaction mechanism. Although both reactions proceed via an electrophilic addition, the NO_3 radical adds to one of the carbons of the C=C bond, whereas O_3 adds across the double bond via a cycloaddition pathway.[5] Because of this difference in the addition mechanism, the effects of steric hindrance appear to be more pronounced in the O_3 reactions than in the corresponding NO_3 radical reactions. An impact of substituent steric effects on the O_3 + alkene reactions has been previously noted,[20−22,30,31] initially by Treacy et al.[20] who proposed on the basis of empirically determined Arrhenius factors that the electron-donating abilities of alkyl substituents were directly compensated for by an increase in substituent steric hindrance resulting in essentially identical reaction rate constants for all 1-alkenes at room temperature.[20,21] This offset of electron-donating abilities and steric hindrance has been supported by more recent work.[30,31] In particular, McGillen et al.[31] have developed a structure−reactivity relationship for the estimation of rate constants for the reactions of O_3 with acyclic alkenes and dienes on the basis of the interplay of inductive and steric effects. Interestingly, whereas there is no obvious effect of ring-strain energy upon addition rate constants for the reactions of NO_3 and OH radicals with cycloalkenes,[16,32] there is a significant effect of ring strain on the O_3 reactions.[33,34] This influence of ring strain upon rate constants further supports the idea that the effects of steric hindrance in the O_3 reactions are much more pronounced than those in the corresponding NO_3 or OH radical reactions.

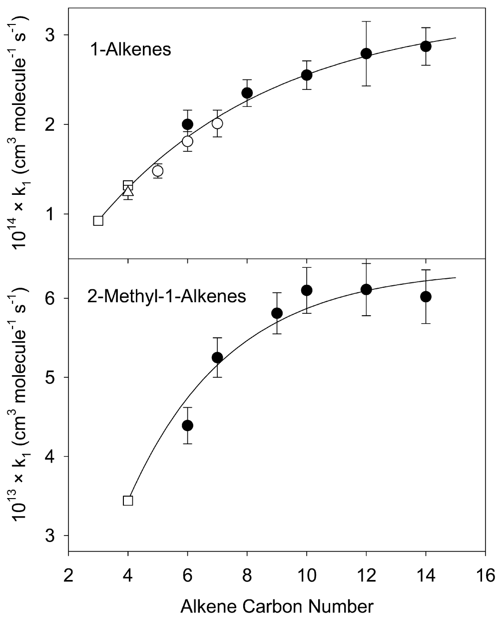

Figure 7. Plots of the measured rate constants for the reactions of 1-alkenes (top) and 2-methyl-1-alkenes (bottom) with the NO_3 radical as a function of alkene carbon number: □, recommended rate constants for propene, 1-butene, and 2-methylpropene;[5,6] ●, this work; ○, rate constants of Canosa-Mas et al.[14] for 1-pentene, 1-heptene, and 1-octene; △, rate constant of Aschmann et al.[13] for 1-butene. Solid lines are unweighted nonlinear least-squares fits to eq IV, with: 1-alkenes, $k_{\text{total}} = [0.924 + 2.35(1 - e^{-0.17(x-3)})] \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}; 2-methyl-1-alkenes, $k_{\text{total}} = [3.44 + 2.94(1 - e^{-0.29(x-4)})] \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, where x is the alkene carbon number. (Also see the text.)

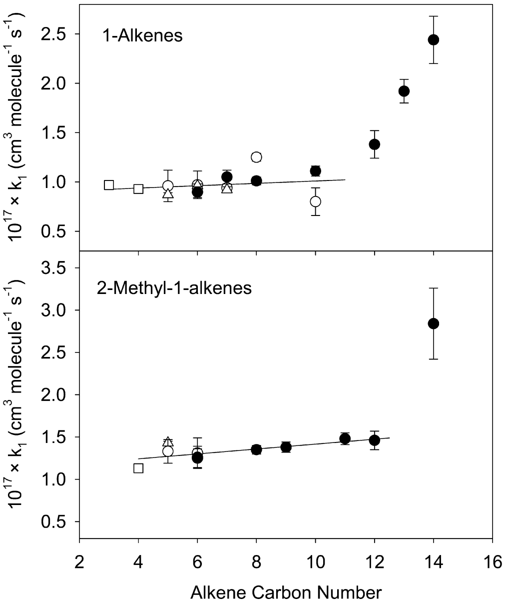

Figure 8. Plots of the measured rate constants for the reactions of 1-alkenes (top) and 2-methyl-1-alkenes (bottom) with O_3 as a function of alkene carbon number: □, recommended rate constants for propene, 1-butene, and 2-methylpropene;[5,6] ●, this work; ○, rate constants of Grosjean and Grosjean[21,25] at 286−293 K; △, room temperature rate constants of Avzianova and Ariya.[22] The significant increase in reaction rate constants for the larger and less volatile alkenes $\geq C_{12}$ is likely due to heterogeneous reactions involving chamber walls and/or aerosol particles. Solid lines are unweighted linear least-squares fits to all of the data shown for the $\leq C_{10}$ 1-alkenes ($k_{\text{total}} = [(0.889 \pm 0.104) + (0.012 \pm 0.015)x] \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}) and $\leq C_{12}$ 2-methyl-1-alkenes ($k_{\text{total}} = [(1.13 \pm 0.07) + (0.029 \pm 0.009)x] \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}), where x is the alkene carbon number.

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Supporting Information Available: Summaries of NO_3 and O_3 radical experiments and "HNO_3 Formation from the Gas-Phase Reactions of NO_3 Radicals with 1-Octene and *trans*-2-Butene" by E. C. Tuazon and R. Atkinson, unpublished data, December 2008. This material is available free of charge via the Internet at http://pubs.acs.org.

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