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ABSTRACT

Unsaturated alcohols are volatile organic compounds (VOCs) characterizing the emissions of plants. Changes in climate together with related increases of biotic and abiotic stresses are expected to strengthen these emissions in the future. Ozonolysis of unsaturated alcohols is one of the oxidation pathways that control their fate in the atmosphere. The rate coefficients of gas-phase O_3 reaction with seven C_5 to C_8 unsaturated alcohols have been determined at 296 K using both absolute and relative kinetic methods. The following rate coefficients have been obtained (in cm^3 $molecule^{-1}$ s^{-1}) from the absolute method: $(1.1\pm0.2)\times10^{-16}$ for *cis*-2-penten-1-ol, $(1.2\pm0.2)\times10^{-16}$ for *trans*-2-hexen-1-ol, $(6.4\pm1.0)\times10^{-17}$ for *trans*-3-hexen-1-ol, $(5.8\pm0.9)\times10^{-17}$ for *cis*-3-hexen-1-ol, $(2.0\pm0.3)\times10^{-17}$ for 1-octen-3-ol and $(8.4\pm1.3)\times10^{-17}$ for *trans*-2-octen-1-ol and from the relative method: $(1.27\pm0.11)\times10^{-16}$ for *trans*-2-hexen-1-ol, $(5.01\pm0.30)\times10^{-17}$ for *trans*-3-hexen-1-ol, $(4.13\pm0.34)\times10^{-17}$ for *cis*-3-hexen-1-ol, $(1.40\pm0.12)\times10^{-16}$ for *trans*-4-hexen-1-ol. Alkenols display high reactivity with ozone with lifetimes in the hour range. Rate coefficients show a strong and complex dependence on the structure of the alkenol, particularly the relative position of the OH group towards the C=C double bond. The results are discussed and compared to the available literature data and four Structure Activity Relationship (SAR) methods.

KEYWORDS: unsaturated alcohols, Green Leaf Volatile (GLV), ozonolysis, absolute kinetic method, relative kinetic method, Structure Activity Relationship (SAR) approaches

Introduction

It is widely accepted that ozone plays a key role in controlling both atmospheric chemistry and climate change. This is due to its oxidative and light-absorbing properties which present a threat for all the ecosystem elements[1,2] and to its role in producing hydroxyl (OH) radical which initiates the majority of oxidation processes in the atmosphere[3]. Therefore, ozone reactivity has been a subject of intensive studies and continues to be of significant concern worldwide. Background ozone concentrations in remote areas are generally within a few µg m^{-3}, yet, in many locations, they have been shown to increase steadily in the past decades partly due to increased global emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs)[4–7].

Unsaturated alcohols or alkenols are VOCs emitted by numerous plants due to biological activity (photosynthesis, transpiration…) and cell decomposition[8]. More specifically, C_6 and C_9 compounds have been shown to be ubiquitous species characterizing the emissions of plants, with stronger releases under biotic and abiotic stresses with transient emission rates up to 2 orders of magnitude larger than monoterpenes[9]. Once in the atmosphere, the double bond present in the carbon skeleton makes such alcohols quite reactive towards the atmospheric oxidants, thus contributing to the oxidative capacity of the atmosphere. While reactions of unsaturated alcohols with OH radical are relatively well known[10], reactions with ozone have been less investigated and uncertainties remain on their reactivity and atmospheric impact. These latter reactions make unsaturated alcohols relatively short-lived (atmospheric lifetimes around minutes to hours)[11] and usually associated with the formation of organic acids[12], organic hydroperoxydes[13], and secondary organic aerosols[14] (SOA) which often appear as a haze over forests[15].

Regarding O_3 + alkenols literature kinetics data, only ambient temperature rate coefficients have been reported. The kinetics of *cis*-2-penten-1-ol was first investigated by Grosjean and Grosjean[16], but the obtained value for the rate coefficient $(1.69\pm0.25)\times10^{-16}$ cm^3 molecule^{-1} s^{-1} is inconsistent with two more recent studies[14,17] which reported $(1.15\pm0.07)\times10^{-16}$ cm^3 molecule^{-1} s^{-1} and $(1.05\pm0.20)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}, respectively. The O_3 kinetics of *trans*-2-hexen-1-ol was recently studied by Gibilisco et al.[18] and Lin et al.[19]. The obtained rate coefficients differ by almost a factor of 3, with values of $(0.60\pm0.07)\times10^{-16}$ cm^3 molecule^{-1} s^{-1} and $(1.66\pm0.22)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}, respectively. The rate coefficients for the reaction of O_3 with *trans*-3-hexen-1-ol measured by Gibilisco et al.[18], Lin et al.[19] and Kalalian et al.[17] are $(5.83\pm0.86)\times10^{-17}$, $(6.19\pm0.72)\times10^{-17}$ and $(6.24\pm1.37)\times10^{-17}$ cm^3 molecule^{-1} s^{-1}, respectively. For *cis*-3-hexen-1-ol, the study of Grosjean et al.[20] is about twice higher than those of Atkinson et al.[21], Gibilisco et al.[18], Lin et al.[19], and Chen et al.[22], raising the concern about the kinetic rate coefficients obtained for *cis*-2-penten-1-ol by Grosjean and Grosjean[16]. The rate coefficient for the reaction of O_3 with *trans*-4-hexen-1-ol was measured only by Lin et al.[19], who reported $(1.05\pm0.21)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}. For 1-octen-3-ol ozonolysis, to the best of our knowledge, only Li et al.[23] investigated the kinetics. Table S1 summarizes the above available literature data.

The objective of this work was thus to investigate the ozone kinetics of a series of seven unsaturated alcohols from C_5 to C_8:

$$cis-2-\text{penten}-1-\text{ol} + O_3 \rightarrow \text{Products} \quad (1)$$

$$trans-2-\text{hexen}-1-\text{ol} + O_3 \rightarrow \text{Products} \quad (2)$$

$$trans-3-\text{hexen}-1-\text{ol} + O_3 \rightarrow \text{Products} \quad (3)$$

$$cis-3-\text{hexen}-1-\text{ol} + O_3 \rightarrow \text{Products} \quad (4)$$

$$trans-4-\text{hexen}-1-\text{ol}+O_3 \rightarrow \text{Products} \quad (5)$$

$$1-\text{octen}-3-\text{ol}+O_3 \rightarrow \text{Products} \quad (6)$$

$$trans-2-\text{octen}-1-\text{ol}+O_3 \rightarrow \text{Products} \quad (7)$$

Two complementary experimental setups were implemented using absolute and relative kinetics methods.

The results will help resolving the inconsistencies noted above on the rate coefficients and better understand the atmospheric impacts of such compounds in the context of increasing O_3 background concentrations and climate change. Note that this work represents the first investigation of *trans*-2-octen-1-ol + O_3 kinetics. Further, developing structure-activity relationships (SAR) for atmospheric chemistry models needs consistent and extended kinetic databases to which the present work aims to contribute, especially the effect of the position of the double bond with respect to the –OH functional group. Four different SAR approaches proposed in the literature[24,25,26,27] were tested against alkenols ozonolysis kinetics, including the present results.

Experimental part

Pseudo first order kinetic set-up (Douai Teflon chamber)

A series of kinetic experiments for *cis*-2-penten-1-ol, *trans*-2-hexen-1-ol, *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, 1-octen-3-ol and *trans*-2-octen-1-ol were performed in a Teflon chamber of about 300 L at a temperature of 296±2 K and atmospheric pressure of purified air[28,29]. This chamber is equipped with inlet and outlet ports used for introducing reactants and taking samples from the reaction mixture. All the connections between the reaction chamber and the instruments were operated via Teflon tubes. Liquid aliquots of alcohols were first vaporized in the chamber under a stream of pure air and the mixture was left to stabilize for ~1h. Preliminary tests were

dedicated to the study of alcohol stability in the reactor. Wall losses of alcohols appeared to be negligible in the present conditions (loss rate < 3% per hour for all alcohols). Ozone was produced separately by an O_3 generator (C-Lasky C-010-DTI) based on electrical discharge on pure zero air flow. After stabilization of the alcohol inside the chamber (1σ of three measurements by Fourier Transform Infrared (FTIR) spectroscopy below 3%), a few tens of mL of O_3 were sampled with a gas syringe and added to the reaction mixture under a high flow of air (about 20 L min^{-1}), thus enhancing the prompt mixing of the reactants and starting the reaction.

Pseudo-first order conditions were set up with alcohol initial concentrations $[alc]_{t_0}$ ((0.34-3.6)×10^{14} molecules cm^{-3}) in excess (at least 10 times higher) over that of ozone $[O_3]_{t_0}$ ((1.4-17)×10^{12} molecules cm^{-3}). The alcohol concentration can thus be assumed to be constant during the experiment. Eq. 1 describes the ozone concentration decay taking into account the ozone wall loss rate (k_w in s^{-1}).

$$-\frac{d[O_3]_t}{dt} = k \times [alc]_{t_0} \times [O_3]_t + k_w \times [O_3]_t \qquad \text{(Eq. 1)}$$

with k the rate coefficient for the reaction between the studied alcohol and O_3 and $[O_3]_t$ is the concentration of ozone at time t. Eq. 1 can be simplified into:

$$-\frac{d[O_3]_t}{dt} = k_{obs} \times [O_3]_t \qquad \text{(Eq. 2)}$$

where $k_{obs} = k \times [alc]_{t_0} + k_w$ is the pseudo-first-order rate constant. Integrating Eq. 2 yields:

$$ln\left(\frac{[O_3]_{t_0}}{[O_3]_t}\right) = k_{obs} \times t \qquad \text{(Eq. 3)}$$

Plotting $ln\left(\frac{[O_3]_{t_0}}{[O_3]_t}\right)$ vs t leads to a straight line with zero intercept and a regression coefficient $k_{obs} = k \times [alc]_{t_0} + k_w$. Plotting k_{obs} vs $[alc]_{t_0}$ finally gives the rate coefficient k as the regression coefficient and k_w as the intercept.

The ozone decay was monitored by a UV-absorption O_3 analyzer (Environment SA 42M) with a resolution time of 10 s. Preliminary tests showed that the investigated alcohols were not absorbing at the wavelength of the ozone instrument (253.7 nm). Alcohol calibration curves (Figures S1-S6) were carefully determined through FTIR spectroscopy using a 10 m optical length White cell[30].

Formation of OH radical through the ozonolysis of hexenols was reported by Atkinson et al.[21] (OH yield of about 26%). No OH scavenger was used in the Douai Teflon chamber, except for 1-octen-3-ol where two experiments were performed with excess of cyclohexane (200 and 1000 ppm). In these two experiments, about 90% of the OH were scavenged by cyclohexane. It should be stressed, however, that any OH radical formed will react with the alcohol but would not affect the ozone decay in a significant manner at the high initial alcohol/ozone concentration ratios employed. The two experiments noted above were carried out to confirm the absence of effect on the O_3 decay.

Primary products from reactions of unsaturated compounds with O_3 are mainly carbonyls[31]. Potential interferences from these carbonyls in the O_3 analyzer are expected to be negligible since the absorption cross section ratios between ozone and carbonyls at 253.7 nm (detection wavelength of the O_3 analyzer) are in the range of 400 to 4000[32]. Hence, carbonyl absorption will be negligible compared to that of ozone. Consistently, Peters et al.[33] found no interferences for commercial ozone monitor for a series of VOCs including alcohols and carbonyls.

Concentrations of *cis*-2-penten-1-ol, *trans*-2-hexen-1-ol, *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, 1-octen-3-ol and *trans*-2-octen-1-ol were measured in the following IR ranges, respectively: 960-1081 cm^{-1}, 956-1032 cm^{-1}, 934-1000 cm^{-1}, 997-1096 cm^{-1}, 913-940 cm^{-1}, and 900-1050 cm^{-1}.

Relative rate kinetic set-up (Iasi ESC-Q-UAIC reaction chamber)

A series of kinetic experiments for *trans*-2-hexene-1-ol, *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, and *trans*-4-hexene-1-ol were performed at 298 K and 1 atm of air pressure, using the facilities of the Environmental Simulation Chamber made out of Quartz from "Alexandru Ioan Cuza" University of Iasi (ESC-Q-UAIC), Romania. The reactor consists of three quartz tubes with a total length of 4.1 m and a total volume of 760 L. The homogeneous mixture of compounds inside the reactor is achieved by two Teflon fans. The reactor can be evacuated down to 10^{-2} mbar. Both ends are closed with anodized aluminum flanges and are provided with multiple inlet and outlet ports. A Bruker Vertex 80 FT-IR spectrometer was used for collecting IR spectra over a White type mirror system with an optical path length of 492 m at a resolution of 1 cm^{-1}. A more detailed description of the reactor can be found in literature[34]. The relative kinetics method was employed for rate coefficient measurements using *trans*-2-butene and cyclohexene as reference compounds with k(*trans*-2-butene+O_3) = $(2.00\pm0.50)\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} [35] and k(cyclohexene+O_3) = $(7.44\pm1.86)\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} [36]. 1,3,5-Trimethylbenzene was used as OH scavenger in concentrations such that more than 90% of any OH radicals produced was suppressed during the ozonolysis of unsaturated compounds. For *trans*-3-hexene-1-ol only, two other additional scavengers were employed: cyclohexane and di-butyl ether. The reason was to check whether or not the nature of the scavengers plays any role in this study. Preliminary tests to measure wall depositions of *trans*-2-hexene-1-ol, *trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, and *trans*-4-hexene-1-ol revealed the following wall loss rates (k_{WL}): $(4.93\pm0.45)\times10^{-5}$ s^{-1}, $(4.35\pm0.50)\times10^{-5}$ s^{-1}, $(5.08\pm0.51)\times10^{-5}$ s^{-1} and $(6.04\pm0.53)\times10^{-5}$ s^{-1}, respectively. No wall deposition was observed for the reference compounds. In the gas-phase system, besides the reaction of alkenols with ozone, reference compounds would also react with ozone (reactions (8) and (9)):

$$trans-2-\text{butene} + O_3 \rightarrow \text{Products} \qquad (8)$$

$$\text{cyclohexene} + O_3 \rightarrow \text{Products} \qquad (9)$$

For the unsaturated alcohols and reference compounds the following kinetic equations are valid in the relative method approach:

$$-\frac{\mathrm{d}[alc]_t}{\mathrm{d}t} = k \times [alc]_t \times [O_3]_t + k_{WL} \times [alc]_t \qquad \text{(Eq. 4)}$$

$$-\frac{\mathrm{d}[reference]_t}{\mathrm{d}t} = k_{ref} \times [reference]_t \times [O_3]_t \qquad \text{(Eq. 5)}$$

where $[alc]_t$ and $[reference]_t$ are the concentrations of the alcohols and reference compounds at time t. Integrating and combining these two equations yields the following relation between the alcohols and reference concentrations and the O_3 reaction rate coefficients:

$$\ln\frac{[alc]_{t_0}}{[alc]_t} - k_{WL} \times (t - t_0) = \frac{k}{k_{ref}} \ln\frac{[reference]_{t_0}}{[reference]_t} \qquad \text{(Eq. 6)}$$

where $[alc]_{t_0}$ and $[reference]_{t_0}$ are the initial concentrations of unsaturated alcohols and reference compounds, k and k_{ref} are the rate coefficients of the reaction of alcohols and reference compounds with ozone.

The initial concentrations were estimated based on the weighted amounts injected into the reaction chamber, as the difference of the syringe weights with the liquid compound and without liquid compound measured right after the injection, leading to the following average values (in molecules cm^{-3}, where the uncertainties are two standard deviations): $(7.37\pm0.39)\times10^{13}$ for alcohols, $(8.12\pm1.62)\times10^{13}$ for *trans*-2-butene, $(4.69\pm0.78)\times10^{13}$ for cyclohexene. Regarding OH scavengers, their concentrations (in molecules cm^{-3}) were calculated based on the volume injected: 2.30×10^{15} for 1,3,5-trimethylbenzene, 3.00×10^{16} for cyclohexane and 5.60×10^{15} for di-butyl ether. The OH scavenger concentration was estimated to suppress up to 90% of OH radicals considering

185 the initial concentrations of the alcohols and reference compounds and their reactivity toward OH
186 radicals[37].

187 The target alcohols, references and OH scavengers were obtained commercially with the
188 following purities: *cis*-2-penten-1-ol (Aldrich, > 96%), *trans*-2-hexen-1-ol (Aldrich, ≥ 95%),
189 *trans*-3-hexen-1-ol (Aldrich, 97%), *cis*-3-hexen-1-ol (Fluka, > 98%), 1-octen-3-ol (Aldrich, ≥
190 98%), *trans*-2-octen-1-ol (Aldrich, 97%), *trans*-4-hexen-1-ol (Aldrich, 97%), *trans*-2-butene
191 (Aldrich, 99%), cyclohexene (Aldrich, 99%), 1,3,5-trimethylbenzene (Aldrich, 98%), cyclohexane
192 (Carl-Roth, > 99.5%), di-butyl ether (Aldrich, 99.3%). They were used as received without further
193 purification. At Iasi ESC-Q-UAIC, synthetic air (Messer-Griesheim, 99.999%) and oxygen
194 (Messer-Griesheim, 99.999%) were used while ozone was produced photochemically by passing
195 a flow of O_2 over a VUV-Hg lamp mounted inside a tube and connected to the reactor. Extra pure
196 zero air was produced in Douai with pure air generator (Claind AZ 2020) with relative humidity
197 RH < 2 ppm, CO and CO_2 < 80 ppb.

198 **Results and discussion**

199 *Rate coefficients*

200 An example of pseudo-first order kinetic plots representing k_{obs} as a function of $[alc]_{t_0}$ is
201 displayed in Figure 1 for *trans*-2-octen-1-ol. The kinetic plots for the other 5 alkenols are provided
202 in Supporting Information (Figures S7-S11). All plots show very good linearity with close to zero
203 intercepts. The ozone rate coefficients obtained from the slope of these plots are (in 10^{-17} cm^3
204 $molecule^{-1}$ s^{-1}): 11.0±2.0 for *cis*-2-penten-1-ol, 12.0±2.0 for *trans*-2-hexen-1-ol, 6.4±1.0 for *trans*-
205 3-hexen-1-ol, 5.8±0.9 for *cis*-3-hexen-1-ol, 2.0±0.3 for 1-octen-3-ol and 8.4±1.3 for *trans*-2-octen-
206 1-ol. Quoted uncertainties are two standard deviations and represent the statistical error on the
207 ozone decays (about 5%) combined with the uncertainty coming from alcohol concentrations (of

about 15%, both statistical and systematic errors). The final uncertainty on k, $\Delta(k)$, was calculated using the error propagation method through Eq. 7 and is about 16% for each rate coefficient.

$$\frac{\Delta(k)}{k} = \sqrt{\left(\frac{\Delta k_{obs}}{k_{obs}}\right)^2 + \left(\frac{\Delta[alc]_{t_0}}{[alc]_{t_0}}\right)^2} \qquad \text{(Eq. 7)}$$

Studies performed in Iasi by using the relative kinetic method measured simultaneously the reference decay and the degradation of hexenols during the ozonolysis. The total measured decay of hexenols during the experiments was counted from 20% to 35% (about 48% for O_3) from which (91.0±3.3)% of *trans*-2-hexen-1-ol, (91.5±7.8)% of *trans*-3-hexen-1-ol, (83.4±4.6)% of *cis*-3-hexen-1-ol and (91.4±1.8)% of *trans*-4-hexen-1-ol reacted with ozone. Fairly linear distributions of the data points on the kinetic slopes can be observed in Figure 2 (*trans*-2-hexen-1-ol) and Figures S12-S14 (*trans*-3-hexen-1-ol, *cis*-3-hexen-1-ol, and *trans*-4-hexen-1-ol) in Supplementary Information. Table 1 reports the experimental results obtained from the relative kinetic investigations. The ratios between rate coefficients of hexenols and reference compounds (k/k_{ref}) and the attributed uncertainties (2σ) were retrieved from linear regression analysis. Uncertainties for k values were obtained by propagating 10% error from the k_{ref} values and 2σ from the slope of our experimental data. The value of k(average) and its associated uncertainty is derived from the weighted average for k values. The control test experiment (relative kinetics between *trans*-2-butene and cyclohexene) presented in Supplementary Information (Figure S15) shows a maximum of 5% difference between the measured and literature rate coefficients ratios ($k_{cyclohexene+O3}/k_{trans\text{-}2\text{-}butene+O3}$), this slight difference being covered by the proposed uncertainties. One could notice the very good agreement between the O_3 rate coefficients obtained for *trans*-3-hexen-1-ol when three different OH radical scavengers were used. These results proved that the effect of OH radical could be suppressed by using any of the scavengers.

Table 2 compares the rate coefficients obtained in the present work (absolute and relative methods) with literature data, where available. The rate coefficient obtained for *cis*-2-penten-1-ol ($(1.1\pm0.2)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}) is in excellent agreement with the determinations of O`Dwyer et al.[14] and Kalalian et al.[17] who found $(1.15\pm0.07)\times10^{-16}$ cm^3 molecule^{-1} s^{-1} and $(1.05\pm0.20)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}, respectively, while about 33% lower than the study from Grosjean and Grosjean[16] of $(1.69\pm0.25)\times10^{-16}$ cm^3 molecule^{-1} s^{-1}. All previous literature studies used the absolute kinetics method except Kalalian et al.[17], who used the relative method. Grosjean and Grosjean[16] carried out only three experiments under 55% relative humidity using cyclohexane as scavenger with no variation of the initial alkenol concentration, leading to probably less reliable results. A higher rate coefficient value may also point to unknown secondary losses such as impurities in *cis*-2-penten-1-ol. Yet, with a stated purity of 99%,[16] the 1% impurity should have reacted with O_3 at a fairly high rate coefficient of about 5×10^{-15} cm^3 molecule^{-1} s^{-1} in order to yield the 30% higher *cis*-2-penten-1-ol + O_3 rate coefficient measured by Grosjean and Grosjean[16]. Reactions of Criegee Intermediates (CI) with alkenols may also be evoked as potential additional loss of alkenols. In the absence of kinetics data, an alkenol + CI rate coefficient of about 1×10^{-13} cm^3 molecule^{-1} s^{-1} can be estimated based on the reactivity of CI with alkenes[38] and alcohols[39]. The comparison of the rate of alkenol + O_3 ($r_{O3} = k\times[O_3]\times[alc]$, with $k = 1.1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} in the case of *cis*-2-penten-1-ol and $[O_3] = 1\times10^{12}$ molecules cm^{-3}) with the estimated rate of alkenol + CI ($r_{CI} = k_{CI}\times[CI]\times[alc]$ with $k_{CI} = 1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} and [CI] estimated at 1×10^6 molecules cm^{-3}) leads to a ratio of about 1000. This value indicates that alkenol reactions with CI are probably not significant in the present chamber experiments. Hence, the possible discrepancies in the rate constants between the present work and literature values cannot be explained by CI reactions with alkenols.

For *trans*-2-hexen-1-ol, a rate coefficient of $(1.2\pm0.2)\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} was obtained by the absolute kinetic method and $(1.27\pm0.11)\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} by the relative rate kinetic approach. Both investigations are virtually similar and are in good agreement with the last study by Lin et al.[19] ($(1.66\pm0.22)\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}) while significantly larger (about a factor of two) than Gibilisco et al.[18] who found $(5.98\pm0.73)\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. However, in this latter study, it was mentioned that OH radicals were not sufficiently scavenged and the results should be considered with caution. Gibilisco et al.[18] corrected the obtained rate coefficients by inclusion of self-canceling terms of $-k_{hexenol}\int[OH]dt$ and $-k_{reference}\int[OH]dt$ based on the assumption that references have identical rate coefficients against ozone and similar OH radical yields of 26% as reported for isoprene and *trans*-3-hexen-1-ol.

For *trans*-3-hexen-1-ol and *cis*-3-hexen-1-ol where the double bond is further from the –OH group compared to *trans*-2-hexen-1-ol, lower rate coefficients are obtained in the present work, $(6.4\pm1.0)\times10^{-17}$ and $(5.8\pm0.9)\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, when employing the pseudo-first order kinetic method and $(5.01\pm0.30)\times10^{-17}$ and $(4.13\pm0.34)\times10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} when using relative rate kinetics. Experimental evidence for other unsaturated alcohols[14,40] as well as quantum chemistry calculations[19] supports a higher rate coefficient when the double bond is in α position with respect to the -OH functional group, as is the case with *trans*-2-hexen-1-ol. It should be noted that both 3-hexen-1-ol isomers (*cis*- and *trans*-) display a relatively similar reactivity towards O_3, while literature reviews on alkene + O_3 kinetics indicate that *trans*- isomers are generally more reactive than *cis*- due to a higher pre-exponential factor[41,42]. Consistently, a slightly higher rate coefficient value can be observed for the *trans*- isomer in comparison with the *cis*-isomer, though this conclusion could be encompassed if the uncertainties level is considered. It is important to mention that rate coefficient values obtained for 3-hexen-1-ol isomers agree within

30% with the literature values obtained by using different methods and simulation chambers as those used in present investigations (see Table 2). However, most of the difference could be explained considering the assumed errors of about 20% of the reference rate coefficients used in the relative rate method. As for *cis*-2-penten-1-ol, only three experiments were performed by Grosjean et al.[20] for *cis*-3-hexen-1-ol with no variation of the initial alkenol concentration. This may explain the discrepancies observed for $k_{cis\text{-3-hexen-1-ol+O3}}$ between Grosjean et al.[20], on the one hand, and the other studies (including the present work), on the other hand.

The kinetic values for *trans*-4-hexen-1-ol (in cm^3 $molecule^{-1}$ s^{-1}) are in good agreement for both reference compounds ($(14.1\pm1.7)\times10^{-17}$ with *trans*-2-butene and $(13.9\pm1.8)\times10^{-17}$ with cyclohexene) and with Lin et al.[19] ($(10.5\pm1.4)\times10^{-17}$) considering the uncertainties. In an attempt to compare the rate coefficient of *trans*-2-hexen-1-ol, *trans*-3-hexen-1-ol and *trans*-4-hexen-1-ol, a virtually similar reactivity for *trans*-2-hexen-1-ol and *trans*-4-hexen-1-ol is observed while the rate coefficient for *trans*-3-hexen-1-ol is about three times lower.

For 1-octen-3-ol, our value is in excellent agreement with the only literature data from Li et al.[23]. Finally, the present work reports the first O_3 rate coefficient for *trans*-2-octen-1-ol.

As observed in many studies on alkenes + O_3 reaction kinetics[43,44], a higher degree of alkyl substitution of the double bond generally leads to a higher rate coefficient. Considering all rate coefficients known for alkenols + O_3 (Table S1) suggests that it is also the case for alkenols. Note that the highest k value is for 3-methyl-2-buten-1-ol ($> 4.39\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}) which is a tri-substituted compound. This phenomenon has been explained by an inductive effect produced via the enhancement of the π-orbital electron density for higher substituted compounds, leading to a lowering of the activation energy.

In the case of unsaturated compounds, the hydroxyl function group is expected to induce an electron-donating effect on the adjacent bonds, thus enhancing the electronic density of the double bond and increasing the reactivity of the unsaturated compound. Comparing the O_3 reactivity of alkenols with that of the corresponding alkenes as a function of the distance between –OH and C=C displays a puzzling picture, as shown in Figure 3. While for 1-alken-3-ols, the rate coefficient ratio k(O_3+alkenol)/k(O_3+alkene) is higher than 1, as expected, the reverse is observed for all other alkenols. The highest ratio of about 2 is calculated for 1-octen-3-ol/1-octene and 1-nonen-3-ol/1-nonene. Mason et al. showed that C_3 to C_{10} 1-alkenes all react with O_3 with rate coefficients around 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} without any effect of the carbon chain length[45]. Interestingly, the present results indicate that the substitution by OH at the α-position to the C=C bond in 1-alkenes increases the rate coefficient up to a factor two. In addition to the electron-donating effect of the –OH group, this may be due to the formation of a strong pre-reactive complex through hydrogen bond interaction between O_3 and -OH[19]. Noteworthy, 2-alken-1-ols like 2-penten-1-ol (which are α-alkenols) do not show such reactivity increase between alkenes and alkenols, probably due to steric effects. Further experimental and theoretical investigations of reaction mechanisms of α-alkenols + O_3 may help understanding their reactivity.

Structure-Activity Relationships (SAR)

Rate coefficients can be estimated using different methods involving structure reactivity relationships. Atkinson and Carter[24] applied a methodology used by the US Environmental Protection Agency under the AOPWIN (Atmospheric Oxidation Program for Windows) to estimate ozone rate coefficients. Calvert et al.[25] developed SAR methods using the group-additivity approach and factors contributions. Pfrang et al.[26] used correlations and rate coefficients for basic structures multiplied by group reactivity factors for corresponding substituents. More

recently, a new SAR method was developed implying the contribution of inductive effect of heteroatoms and total steric effects based on the earlier work of McGillen et al.[46] on alkenes and extended by McGillen et al.[27] to heteroatomic unsaturated VOCs.

The different SAR approaches cited above were applied to evaluate their suitability as alternative tools for rate coefficient estimation for the reactions of unsaturated alcohols with ozone. Where applicable, the experimental values were calculated by averaging rate coefficients obtained in the present work by the pseudo-first order approach and the relative rate kinetic method. In Table 3, the experimental k values (k_{exp}) can be compared with the calculated values obtained using the different SAR approaches (k_{SAR}) on the investigated compounds. The earliest methodologies proposed in the literature on SAR estimations of rate coefficients show large discrepancies with the experimental results. Poor agreement was also noticed when using the SAR approach from Pfrang et al.[26] (except for 3-hexen-1-ol isomers) despite the more complex methodology involved. Using McGillen et al.[27] methodology (details are provided in the Supplementary Information), a very satisfactory estimate is obtained for *cis*-2-penten-1-ol, *trans*-2-hexen-1-ol and *trans*-2-octen-1-ol, with agreement with our results between 2% and 20%. For the others alkenols, the ratios k_{SAR}/k_{exp} vary between 0.29 and 0.59. The strongest disagreement is obtained for *trans*-4-hexen-1-ol (k_{SAR}/k_{exp} = 0.29) for which the experimental finding is three times larger than the calculated rate coefficient. Because of the distance between –OH and C=C in *trans*-4-hexen-1-ol (–OH is in δ position towards C=C), no inductive effect is considered in the SAR calculation. Consistently, the experimental rate coefficient of the corresponding alkene (*trans*-2-hexene) with O_3 (1.53×10^{-16} cm^3 $molecule^{-1}$ s^{-1})[37]is close to that obtained in the present work for *trans*-4-hexen-1-ol (1.40×10^{-16} cm^3 $molecule^{-1}$ s^{-1}). Therefore, the low k_{SAR}/k_{exp} ratio reflects a weakness in the SAR method, probably regarding a change in the reaction mechanisms as suggested by McGillen et al.[27]. Based

on the overall agreement, it is suggested that the SAR method from McGillen et al.[27] estimates the rate coefficients from ozonolysis of unsaturated alcohols much closer to the experimental data than the other above-mentioned approaches.

Ozonolysis rate coefficients were also computed for a range of other alkenols using the SAR method from McGillen et al.[27]. Values are reported in Figure 4 as a function of experimental ones (see Table S1). Besides the compounds already included in McGillen et al.[27] analysis (with updated values from Kalalian et al.[17] and the present work), fourteen new compounds were added (see Table S1, compounds in italic). It can be seen that calculated rate coefficients are within a factor of 2 of the experimental rate coefficients. A linear regression (forced through zero) on the data yields a slope coefficient of 0.64±0.11 (2σ uncertainty), indicating that SAR calculated rate coefficients are mostly lower than experimental ones. As stressed above, this may suggest unknown changes in reaction mechanisms of alkenol ozonolysis. Additional experiments are clearly needed to better characterize these mechanisms and improve structure activity relationships.

Atmospheric implications

The rate coefficients determined in the present work allow calculating the lifetime τ of alkenols in the atmosphere when reacting with O_3, using $\tau = 1/(k\times[O_3])$. Assuming an average ozone concentration of 1.6×10^{12} molecules cm^{-3} (about 65 ppb at 295 K and 1 atm)[47] leads to lifetimes of a few hours (Table 4). The corresponding lifetimes when reacting with OH, NO_3 and Cl can be similarly calculated and are reported also in Table 4. Comparing with OH, NO_3 and Cl reactions indicates that ozonolysis is a competitive oxidation process, especially during the night and at low NO_x environments where OH and NO_3 concentrations are low, respectively. In addition, in the

perspective of increasing ozone concentrations in the future[48], an increasing impact of ozonolysis may be expected in the degradation of alkenols.

Conclusions

The rate coefficients of a series of seven unsaturated alcohols with ozone have been determined using two complementary setups, allowing both absolute and relative kinetics methods to be employed. Good agreement has been obtained between the two methods. Alkenols appear to have high reactivity with ozone with lifetime in the hour range. Rate coefficients show a strong and complex dependence on the structure of the alkenol, particularly the relative position of the OH group towards the C=C double bond. Four SAR approaches were tested against the investigated compounds, the most recent from McGillen et al.[27] displaying the best results. Yet, efforts are still needed to better understand the reaction mechanisms and unravel the links between the structure and the reactivity of alkenols with O_3.

Supporting Information

Details for evaluating SAR rate coefficients using McGillen et al.[27] methodology, ambient temperature ozonolysis rate coefficients of alkenols (Table S1), IR calibration curves for unsaturated alcohols with the corresponding integrated band intensities (IBI, Figures S1-S6), kinetic plots from the absolute and relative rate methods (Figures S7-S14), relative kinetic plot of ozone reaction with *trans*-2-butene *vs* cyclohexene, (data obtained from control experiments in ESC-Q-UAIC chamber; 1,3,5-trimethylbenzene was used as OH scavenger) (Figure S15).

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Table 1: Experimental results from the relative kinetic measurements employed in the present study for the ozonolysis of a series of alkenols.

Alcohol	OH scavenger	Reference	k/k_{ref}	$k \times 10^{17}$ (cm^3 $molecule^{-1}$ s^{-1})	k (average) $\times 10^{17}$ (cm^3 $molecule^{-1}$ s^{-1})
trans-2-hexen-1-ol	1,3,5-TMB	*trans*-2-butene	0.66±0.04	13.1±1.5	12.7±1.1
		cyclohexene	1.65±0.12	12.3±1.5	
trans-3-hexen-1-ol	1,3,5-TMB	*trans*-2-butene	0.24±0.02	4.84±0.62	5.01±0.30
		cyclohexene	0.74±0.04	5.49±0.62	
	cyclohexane	*trans*-2-butene	0.24±0.03	4.77±0.70	
		cyclohexene	0.65±0.08	4.86±0.74	
	di-butyl ether	cyclohexene	0.67±0.08	4.98±0.75	
cis-3-hexen-1-ol	1,3,5-TMB	*trans*-2-butene	0.20±0.01	4.07±0.47	4.13±0.34
		cyclohexene	0.57±0.04	4.21±0.50	
trans-4-hexen-1-ol	1,3,5-TMB	*trans*-2-butene	0.71±0.05	14.1±1.7	14.0±1.2
		cyclohexene	1.87±0.16	13.9±1.8	

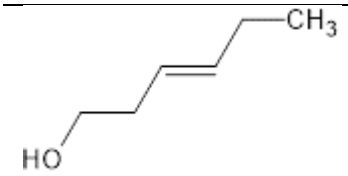
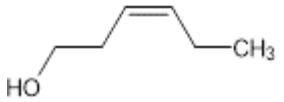
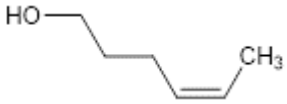
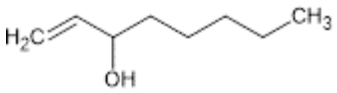
Table 2: Rate coefficients obtained in the present work using the absolute rate (pseudo first order) method (AR) and relative rate method (RR) compared with literature data.

Alcohol	$k \times 10^{17}$ (cm^3 $molecule^{-1}$ s^{-1})[a]	Reference
cis-2-penten-1-ol	**11.0±2.0 (AR)**	**This work**
	16.9±2.5 (AR)	Grosjean and Grosjean[16]
	11.5±0.7 (AR)	O`Dwyer et al.[14]
	10.5±2.0 (RR)	Kalalian et al.[17]
trans-2-hexen-1-ol	**12.0±2.0 (AR)** **12.7±1.1 (RR)**	**This work**
	6.0±0.7 (RR)	Gibilisco et al.[18]
	16.6±2.2 (AR)	Lin et al.[19]
trans-3-hexen-1-ol	**6.4±1.0 (AR)** **5.01±0.30 (RR)**	**This work**
	5.8±0.9 (RR)	Gibilisco et al.[18]
	6.2±0.7 (AR)	Lin et al.[19]
	6.2±1.4 (RR)	Kalalian et al.[17]
cis-3-hexen-1-ol	**5.8±0.9 (AR)** **4.13±0.34 (RR)**	**This work**
	10.5±0.7 (AR)	Grosjean et al.[20]
	6.4±1.7 (RR)	Atkinson et al.[21]
	6.0±0.9 (RR)	Gibilisco et al.[18]
	5.5±0.7 (AR)	Lin et al.[19]
	6.05±0.38 (RR) 5.78±0.65 (AR)	Chen et al.[22]
trans-4-hexen-1-ol	**14.0±1.2 (RR)**	**This work**
	10.5±1.4 (AR)	Lin et al.[19]
1-octen-3-ol	**2.0±0.3 (AR)**	**This work**
	1.9±0.2 (AR)	Li et al.[23]

trans-2-octen-1-ol	**8.4±1.3 (AR)**	**This work**

a: quoted uncertainties from the present work correspond to 2σ

Table 3: The comparison of different SAR methods and the ratio of k_{exp}/k_{SAR}. k_{exp} are the average of the absolute and relative rate coefficients obtained in the present work, where applicable.

Alcohol	k_{exp} (this work) (cm^3 $molecule^{-1}$ s^{-1})	k_{SAR} (cm^3 $molecule^{-1}$ s^{-1})	k_{SAR}/k_{exp}
 *cis*-2-penten-1-ol	1.10×10^{-16}	1.30×10^{-16} [a]	1.18
		1.20×10^{-16} [b]	1.09
		1.38×10^{-17} [c]	0.13
		1.08×10^{-16} [d]	**0.98**
 *trans*-2-hexen-1-ol	1.23×10^{-16}	2.00×10^{-16} [a]	1.61
		1.90×10^{-16} [b]	1.54
		1.38×10^{-17} [c]	0.11
		0.99×10^{-16} [d]	**0.80**
 *trans*-3-hexen-1-ol	5.71×10^{-17}	2.00×10^{-16} [a]	3.57
		1.90×10^{-16} [b]	3.33
		3.65×10^{-17} [c]	0.64
		2.80×10^{-17} [d]	**0.49**
 *cis*-3-hexen-1-ol	4.97×10^{-17}	1.30×10^{-16} [a]	2.63
		1.20×10^{-16} [b]	2.44
		3.68×10^{-17} [c]	0.74
		2.80×10^{-17} [d]	**0.56**
 *trans*-4-hexen-1-ol	1.40×10^{-16}	2.00×10^{-16} [a]	1.43
		1.90×10^{-16} [b]	1.35
		5.66×10^{-17} [e]	0.40
		4.11×10^{-17} [d]	**0.29**
 1-octen-3-ol	2.00×10^{-17}	1.20×10^{-17} [a]	0.60
		1.00×10^{-17} [b]	0.50
		3.72×10^{-18} [c]	0.19
		1.18×10^{-17} [d]	**0.59**
 *trans*-2-octen-1-ol	8.40×10^{-17}	2.00×10^{-16} [a]	2.38
		1.90×10^{-16} [b]	2.27

	1.38×10^{-17} [c]	0.16
	0.99×10^{-16} [d]	**1.18**

[a] Atkinson and Carter[24], [b] Calvert et al.[25], [c] Pfrang et al.[26], [d] McGillen et al.[27], [e] Pfrang et al.[49] (for *trans*-4-hexen-1-ol, the OH group being far from the C=C double bond, the SAR from Pfrang et al.[26] for alkenols was not used but that developed for alkenes by Pfrang et al.[49]).

Table 4: Comparison of atmospheric lifetimes of unsaturated alcohols with respect to removal by O_3, OH radicals, NO_3 radicals and Cl atoms. Average concentrations used: $[O_3] = 1.6\times10^{12}$ molecules cm^{-3} [47], $[OH] = 2\times10^{6}$ radicals cm^{-3} [50], $[NO_3] = 5\times10^{8}$ radicals cm^{-3} [51], $[Cl] = 10^{4}$ atoms cm^{-3} [52]. Values in italic correspond to SAR calculations.

Alcohol	k_{O3} (cm^3 molecule^{-1} s^{-1}) [a]	τ_{O3} (h)	k_{OH} (10^{-10} cm^3 molecule^{-1} s^{-1})	τ_{OH} (h)	k_{NO3} (10^{-13} cm^3 molecule^{-1} s^{-1})	τ_{NO3} (h)	k_{Cl} (10^{-10} cm^3 molecule^{-1} s^{-1})	τ_{Cl} (h)
cis-2-penten-1-ol	11.0	1.5	1.17 [b]	1.2	2.34 [c]	2.4	3.00 [d]	93
trans-2-hexen-1-ol	12.3	1.4	0.81 [e]	1.7	1.56 [f]	3.6	3.45 [g]	81
trans-3-hexen-1-ol	5.71	3.0	1.05 [h]	1.3	2.67 [f]	2.1	3.24 [g]	86
cis-3-hexen-1-ol	4.97	3.4	1.12 [i]	1.2	3.58 [j]	1.6	3.04 [g]	91
trans-4-hexen-1-ol	14.0	1.2	*0.534* [m]	*2.6*	2.93 [f]	1.9	-	-
1-octen-3-ol	2.00	8.6	*0.16* [n]	*8.7*	*0.0099* [n]	*560*	4.03 [k]	69
trans-2-octen-1-ol	8.40	2.0	*0.28* [n]	*5.0*	*0.20* [n]	*28*	-	-

[a] this work (average of absolute and relative determinations); [b] Orlando et al.[53]; [c] Average of Pfrang et al.[54] and Zhao et al.[55]; [d] Average of Grira et al. [56] and Rodriguez et al.[57]; [e] Average of Gibilisco et al.[58] and Davis and Burkholder[59]; [f] Pfrang et al.[26]; [g] Average of Grira et al. [56] and Gibilisco et al.[60]; [h] Average of Gibilisco et al.[61]; Peirone et al.[62] and Gibilisco et al.[58]; [i] Average of Gibilisco et al.[58], Jimenez et al. [63], Atkinson et al.[21] and Davis and Burkholder[59]; [j] Average of Pfrang et al.[26] and Atkinson et al.[21]; [k] Grira et al.[56]; [m] Pfrang et al. [49]; [n] Pfrang et al.[26]; -: no data

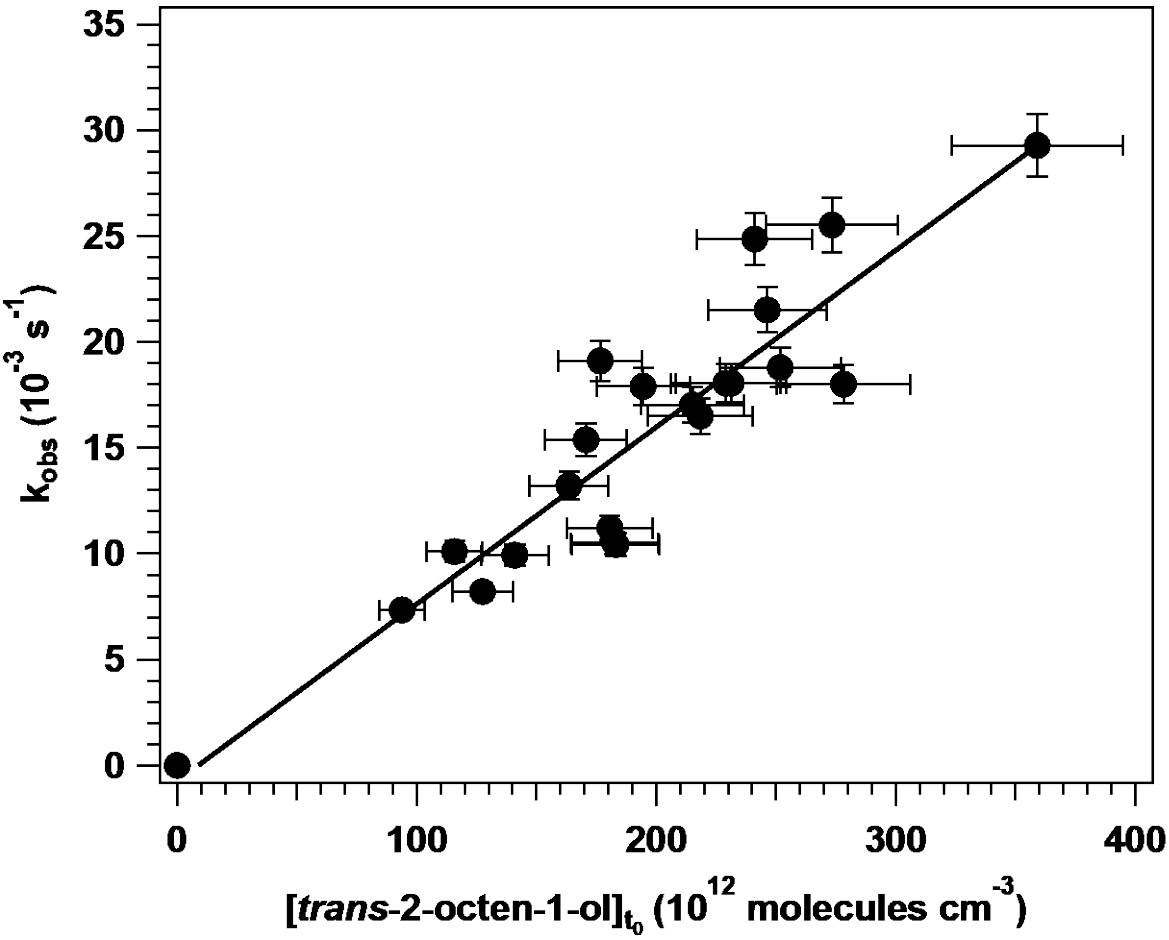
Figures

Figure 1: Kinetic plot of *trans*-2-octen-1-ol ozonolysis.

Figure 2: Relative kinetic plot of ozone reaction with *trans*-2-hexen-1-ol versus (●) cyclohexene and (○) *trans*-2-butene, using 1,3,5-trimethylbenzene as OH scavenger.

Figure 3: Relationship between O_3 rate coefficient ratio and number of carbon atoms between -OH and C=C. For example, cis-2-penten-1-ol ($OHCH_2$-CH=CH-CH_2-CH_3) has one carbon atom between -OH and C=C. Stars (∗) represent data for 1-alken-3-ols (7 compounds) while circles (●) represent other alkenols (14 compounds). Rate coefficients for alkenes are from Calvert et al.[25] while those for alkenols are reported in Table S1.

Figure 4: Ozonolysis of alkenols: rate coefficients calculated by SAR (see McGillen et al.[27] and Supplementary Information) vs those determined experimentally at 298 K (see **Table S1**). The solid line is a linear regression over all the data (26 data) going through zero. The uncertainty on the slope corresponds to 2 standard deviations (2σ). One compound, 3-methyl-2-buten-1-ol, was excluded from the linear regression (see main text).



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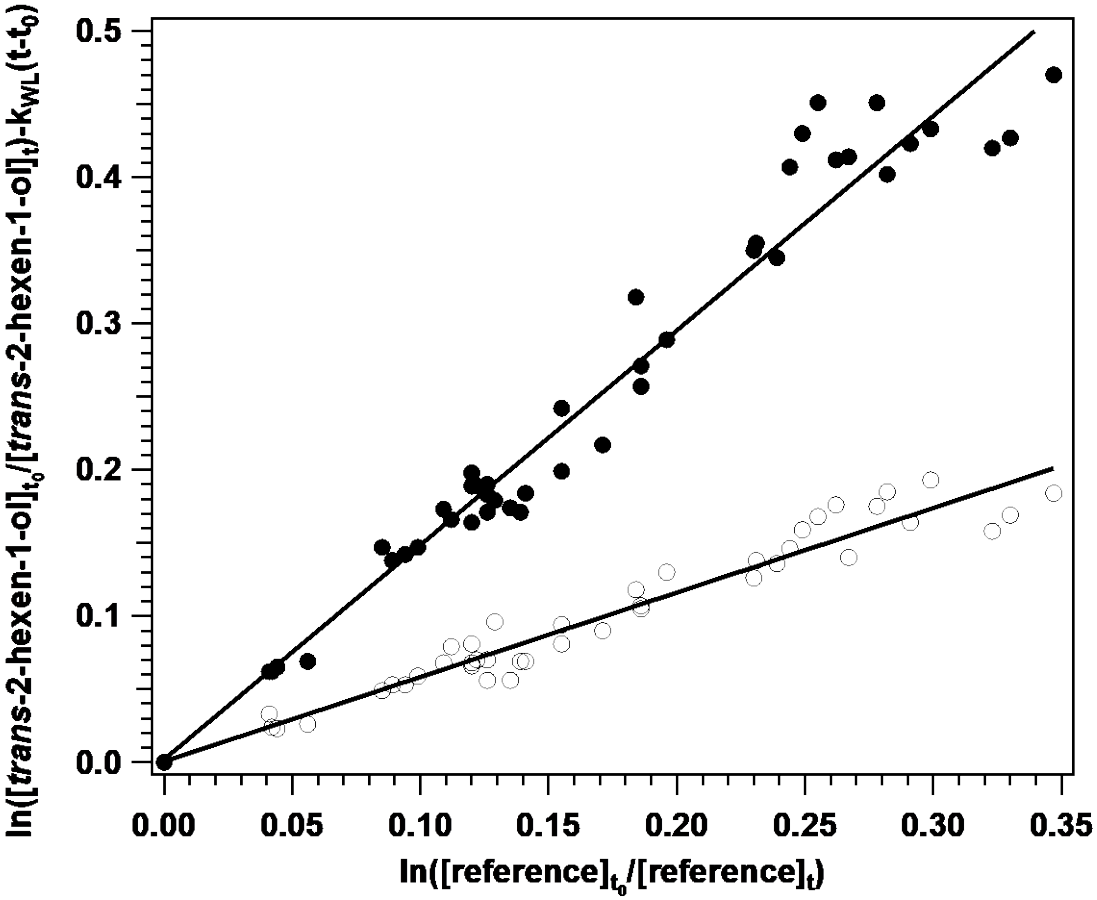

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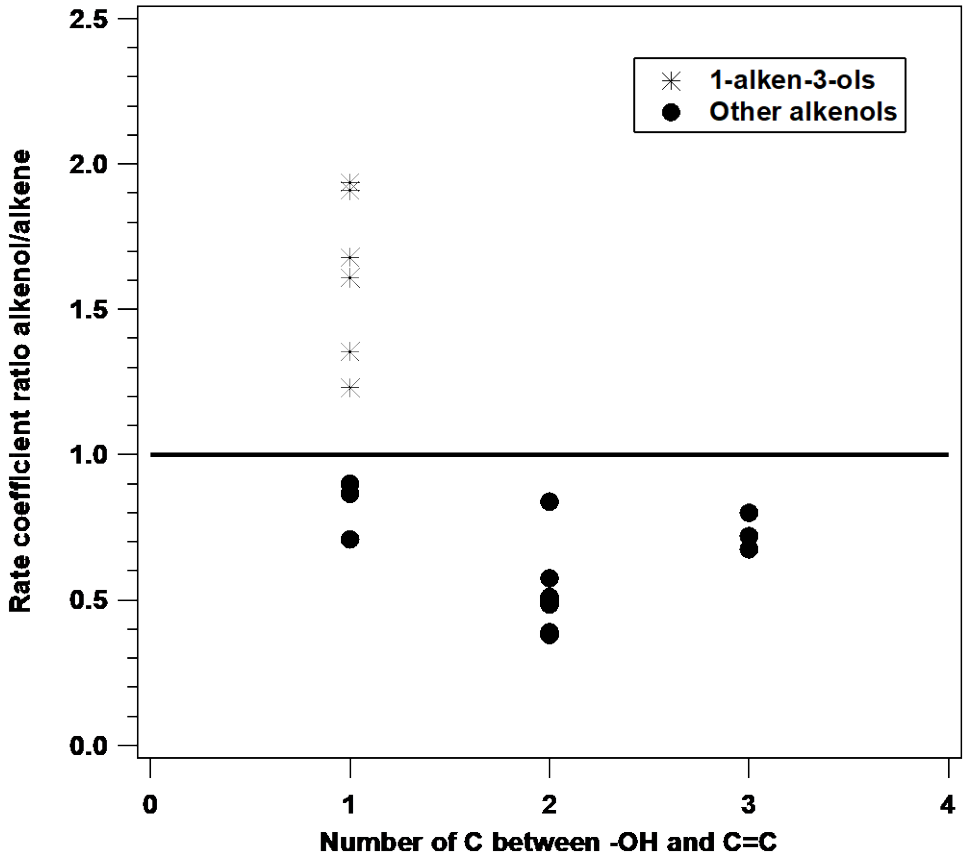

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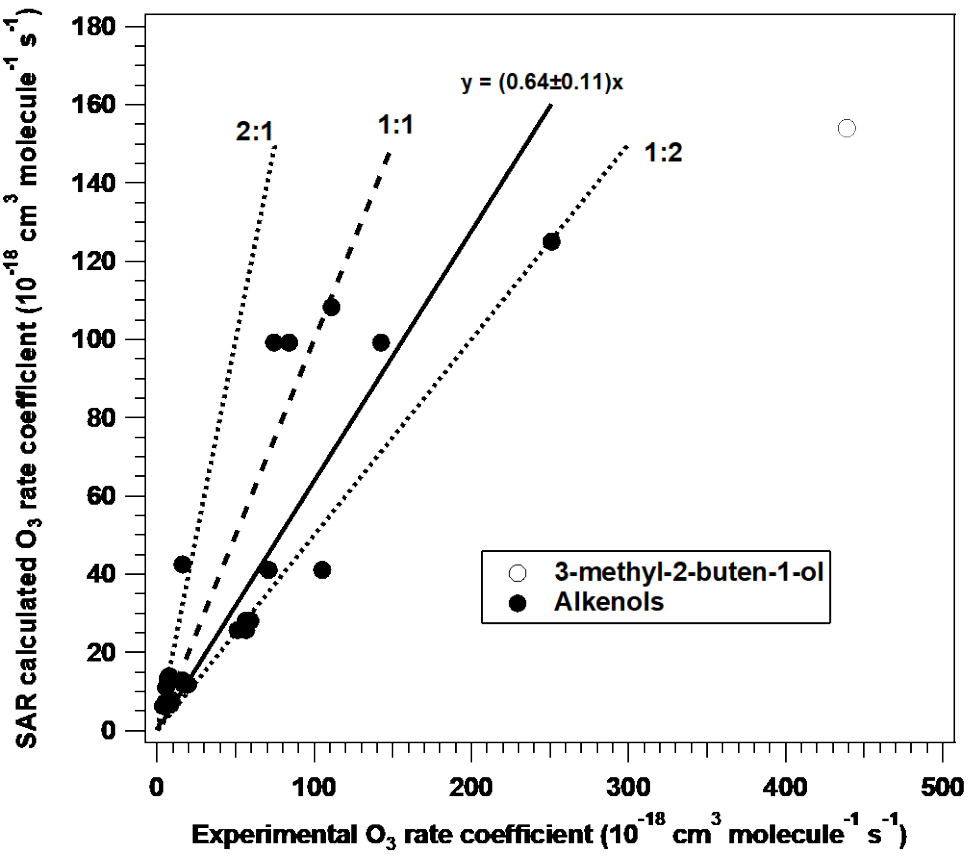

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TOC Graphic