Kinetics of the Methyl–Vinyl Radical + O₂ Reactions Associated with Propene Oxidation

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Supporting Information

ABSTRACT: The bimolecular rate coefficients of reactions CH₃CCH₂ + O₂ (1) and cis/trans-CH₂CHCH + O₂ (2a/3a) have been measured using a tubular laminar flow reactor coupled with a photoionization mass spectrometer (PIMS). These reactions are relevant in the combustion of propene. Pulsed excimer laser photolysis of a ketone or a bromide precursor molecule at 193 or 248 nm wavelength was used to produce radicals of interest homogeneously along the reactor. Time-resolved experiments were performed under pseudo-first-order conditions at low pressure (0.3–1.5 Torr) over the temperature range 220–660 K. The measured bimolecular rate coefficients were found to be independent of bath gas concentration. The bimolecular rate coefficients possess negative temperature dependence at low temperatures (T < 420 K) and appear to be independent of temperature at high temperatures (T > 420 K). Observed products of the reaction CH₃CCH₂ + O₂ were CH₄ and H₂CO, while for the reaction cis/trans-CH₂CHCH + O₂ observed products were CH₃CHO and HCO. Current results indicate that the reaction mechanism of both reactions is analogous to that of C₂H₅ + O₂. Methyl substitution of the vinyl radical changes its reactivity toward O₂ upward by ca. 50% if it involves the α-position and downward by ca. 30% if the methyl group takes either of the β-positions, respectively.

INTRODUCTION

Propene is the second simplest unsaturated hydrocarbon after ethene and serves as a key compound in the petrochemical industry. Propene is also an important intermediate species in the combustion of propane and larger hydrocarbons and has a significant impact on combustion processes. The presence of a double bond in the propene molecule gives it a relatively high thermal stability. Abstraction of the weakest H atom from propene molecule produces a resonance-stabilized allyl radical, which is highly stable against unimolecular decomposition. The allyl radical reacts very slowly with O₂ and can thus reach high concentrations under high temperature conditions. Consequently, the allyl radical is an important precursor in the formation of aromatic structures which may fuse together and finally lead to the soot formation. As shown in Scheme 1, four different radicals can be produced from propene via hydrogen abstraction reactions. Three of the four radicals (CH₃CH₂, cis-CH₂CHCH, and trans-CH₂CHCH) are vinyl-type and CH₃CHCH₂ is the resonance stabilized allyl radical.

Considering that the bond dissociation energy (BDE, D₀) of vinylic hydrogens is ~94 kJ/mol higher than that of the allylic hydrogens of propene, it is obvious that allyl radicals are produced in significantly higher abundance than methyl–vinyl radicals. Burke et al. performed a reaction flux analysis of the propene oxidation experiments conducted in a jet-stirred-reactor (JSR) and showed that in a mixture of 1.67% propene and 3.38% O₂ in helium (T = 970 K, equivalence ratio φ = 2.19), oxidation resulted in 54% formation of allylic radical and only 9% formation of the combined other three methyl–vinyl radicals. While they are formed with a relatively low abundance, methyl–vinyl radicals are highly reactive in comparison to the very unreactive allyl radical. If one considers specifically the kinetics of the methyl–vinyl + O₂ reactions, their impact on combustion chemistry turns out to be rather important and needs to be included in accurate combustion chemistry models. The Burke et al. reaction flux analysis of

Scheme 1. Production of Methyl–Vinyl and Allyl Radicals from Propene via Hydrogen Abstraction Reactions

![Scheme 1](Image 1)

"The C–H bond dissociation energies associated with the formation of allyl radical CH₂CHCH₂, methyl-vinyl radicals CH₃CH₂, trans-CH₂CHCH, and cis-CH₂CHCH are 360.7 kJ mol⁻¹, 443.9 kJ mol⁻¹, 461.1 kJ mol⁻¹, and 459.0 kJ mol⁻¹, respectively."

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propene oxidation also showed that 47% of the CH₂CHCH₂ radicals produced were consumed by the CH₂CHCH₂ + HO₂ reaction and only 14% were consumed by the CH₂CHCH₂ + O₂ reaction. Under the same conditions, however, almost all of the methyl–vinyl radicals produced were consumed via reaction with O₂.

Slagle et al. carried out an experimental kinetic study of the CH₂CHCH + O₂ reaction employing the laser photolysis–photoionization mass spectrometry (PIMS) method to produce and detect CH₂CHCH radicals. The bimolecular reaction rate coefficient was measured over the temperature range 296–600 K, and no dependence on temperature or bath gas concentration (pressure) was observed. However, a recent theoretical and computational study of trans-CH₂CHCH + O₂ reaction by Chen and Goldsmith show an explicit temperature dependence. Slagle et al. did not report whether they were investigating a single isomer or a mixture of both isomers (cis-CH₂CHCH or/and trans-CH₂CHCH).

The purpose of the present work is to perform direct kinetic experiments of reactions 1–3 individually:

\[ \text{CH}_2\text{CCH}_2 + \text{O}_2 \rightarrow \text{products} \]  
(1)

\[ \text{cis-CH}_3\text{CHCH} + \text{O}_2 \rightarrow \text{products} \]  
(2)

\[ \text{trans-CH}_2\text{CHCH} + \text{O}_2 \rightarrow \text{products} \]  
(3)

The aim is to better understand the temperature dependence of the bimolecular rate coefficients of these oxidation reactions and compare the experimental results with the computational results of Chen and Goldsmith, who combined high level ab initio calculations with master equation modeling to study the kinetics of reactions 1 and 3. To our knowledge, there are no previous measurements available on the CH₂CHCH₂ + O₂ reaction. The reaction of vinyl radical, CH₃CH + O₂, has importance in the modeling of combustion processes and has been studied extensively. The current study also aims to quantify the effect of an H atom substitution in vinyl radical by a methyl group on the oxidation kinetics.

**EXPERIMENTAL SECTION**

Pulsed excimer laser photolysis of a relevant precursor molecule was used to produce the radical of interest, and its decay was followed in real-time using a PIMS for which ionizing radiation was provided by a microwave-powered gas-discharge lamp. The experimental apparatus and procedures employed have already been described previously, hence only a brief description of experimental details specific to this work are presented in this section.

The reaction gas mixture flowing through the temperature controlled tubular reactor contained mostly the inert helium bath-gas (>99%) and molecular oxygen. The mixture contained a relatively small amount of precursor (<0.03%), which was introduced into the reactor by constantly bubbling helium through a temperature-controlled precursor cavity. The gas mixture containing the precursor was photolyzed using 193 nm (ArF) or 248 nm (KrF) radiation from an exciplex laser (ASX-750) along a reactor axis to achieve a homogeneous concentration of radicals along the reactor. All measurements were done under pseudo-first-order conditions, that is, [R]/[O₂] ≤ 0.05. For the production of methyl–vinyl radicals, the following precursors were used:

3-Methyl-3-butene-2-one precursor was used to produce CH₃CCH₂ radicals:

\[ \text{CH}_3\text{C(O)(CH}_3\text{)CH}_2 + \text{hν (193 nm)} \rightarrow \text{CH}_3\text{CCH}_2 + \text{CH}_3\text{CO} \]
\[ \rightarrow \text{CH}_3\text{CH}_2 + \text{CH}_3 + \text{CO} \]
\[ \rightarrow \text{other products} \]  
(P1a)

Since CH₃CO can further undergo chemically activated decomposition to give CO and CH₃, and methyl radical is one potential product of the reaction CH₃CCH₂ + O₂, another precursor, 2-bromopropene, was used in product detection measurements.

\[ \text{CH}_3\text{C(Br)(CH}_3\text{)CH}_2 + \text{hν (193 nm)} \rightarrow \text{CH}_3\text{CCH}_2 + \text{Br} \]
\[ \rightarrow \text{other products} \]  
(P1b)

For generating the CH₂CHCH radical, which has a cis- and a trans-isomer, the corresponding bromides were employed:

\[ \text{cis-CH}_2\text{CCHCHBr} + \text{hν (193/248nm)} \rightarrow \text{cis-trans-CH}_2\text{CCHCH} + \text{Br} \]
\[ \rightarrow \text{other products} \]  
(P2a)

\[ \text{trans-CH}_2\text{CCHCHBr} + \text{hν (193/248nm)} \rightarrow \text{trans-cis-CH}_2\text{CCHCH} + \text{Br} \]
\[ \rightarrow \text{other products} \]  
(P2b)

As shown in Figure 1, the isomerization barrier separating the cis-CH₂CHCH and trans-CH₂CHCH isomers is very small (<20 kJ/mol) and can be easily surpassed even if the newly formed methyl–vinyl radical loses some part of the excess energy (>140 kJ/mol) available after laser photolysis at 193 or 248 nm. Hence it is possible that although we have used cis-1-bromopropene and trans-1-bromopropene to produce cis-CH₂CHCH and trans-CH₂CHCH radicals, respectively, both these radicals may have isomerized to each other to some extent before being thermalized by collisions with the buffer gas molecules. Consequently, photolyzing isomERICALLY pure precursors at either wavelength may lead to an isomERIC mixture of cis-CH₂CHCH and trans-CH₂CHCH. The fact that we observed different decay rates depending on which precursor isomer was used indicates that equilibration of the two radical isomers was not achieved. Hereafter, the following notation is used to take this into account: reactions 2a and 3a represent the conditions in which radicals were produced using cis-1-bromopropene and trans-1-bromopropene precursors, respectively, and isomerization took place to an unknown extent.

\[ \text{cis(trans)-CH}_2\text{CCHCH} + \text{O}_2 \rightarrow \text{products} \]  
(2a)

\[ \text{trans(cis)-CH}_2\text{CCHCH} + \text{O}_2 \rightarrow \text{products} \]  
(3a)

The measurements were carried out under low pressure (0.3–1.5 Torr) conditions using a quartz or stainless steel reactor that had an inner diameter of 17 mm. The flow velocity in the reactor was maintained at about 5 m s⁻¹ in order to ensure that the gas-mixture was completely replaced between laser pulses with the employed repetition rate of 5 Hz. The reactor tube employed was either uncoated or coated with halocarbon wax or polydimethylsiloxane. The reaction mixture was continuously sampled via a 0.4 mm diameter hole on the reactor wall forming a beam expanding into high-vacuum. A conical skimmer selected the center portion of the beam, producing a collimated beam before it entered the ionization chamber.
pseudo-linear least-squares method was used to was accumulated from 3000
for the subsequent analysis. Typically the R decay signal pro
recorded using a multichannel scaler from 10 ms before and up
temporal ion signal (see insets in Figures 2 and 3) was
selected by the quadrupole mass-spectrometer followed by
energy of the 193 and 248 nm photon, assuming that the
lamp) with a CaF2 window and was used for the detection of
H2-lamp with a MgF2 window (10.2 eV) and an Ar-lamp with a
provided by a microwave-discharge of Cl2-helium mixture (Cl-
structure associated with accompanying Br-atom is formed in the ground state.

Initial radical concentrations were kept low, at, or below about 2 × 10^{11} \text{ cm}^{-3}, in order to suppress any radical–radical reactions. Under pseudo-first-order experimental conditions ([R] \ll [O_2]) with low initial radical concentrations, only two

Figure 1. Relative enthalpies at 298 K of the trans- and cis-methyl-vinyl isomers and allyl radical along with the isomerization saddle points in kJ/mol, calculated at the CCSD(T)/cc-pVTZ//CCSD/cc-
pVTZ level using the CCSD/cc-pVDZ//CCSD/cc-pVDZ vibrational frequencies. The details of electronic structure calculations are described in the Supporting Information, and Figure S1 shows calculated bond distances for the H atom shift in the transition structure associated with cis-CH_3CHCH ↔ CH_2CHCH_2 isomerization. The colored horizontal lines represent the maximum energy available for the isomerization of the nascent cis-CH_3CHCH and trans-CH_3CHCH radicals produced by the photolysis of cis-1-bromopropene and trans-1-bromopropene at 193 and 248 nm, respectively, and were calculated by subtracting the bond dissociation energy (BDE) of C−Br bond (BDE(cis-1-bromopropene) = 337.6 kJ mol\(^{-1}\) and BDE(trans-1-bromopropene) = 334.7 kJ mol\(^{-1}\)) from the energy of the 193 and 248 nm photon, assuming that the accompanying Br-atom is formed in the ground state.

Figure 2. A bimolecular plot for the CH_3CCH_2 + O_2 reaction measured at T = 363 K and p = 0.73 Torr. The shown uncertainties are 1σ. On the top left corner is a typical CH_3CCH_2 radical decay profile with \(k_{\text{decay}}\) (CH_3CCH_2) = 87 ± 5.9 s\(^{-1}\). On the bottom right corner are shown the observed ion signal profiles of CH_3 (blue) and H_2CO (red), the expected reaction products. The colored horizontal lines represent the maximum energy available for the isomerization of the nascent cis-CH_3CHCH and trans-CH_3CHCH radicals produced by the photolysis of cis-1-bromopropene and trans-1-bromopropene at 193 and 248 nm, respectively, and were calculated by subtracting the bond dissociation energy (BDE) of C−Br bond (BDE(cis-1-bromopropene) = 337.6 kJ mol\(^{-1}\) and BDE(trans-1-bromopropene) = 334.7 kJ mol\(^{-1}\)) from the energy of the 193 and 248 nm photon, assuming that the accompanying Br-atom is formed in the ground state.

containing the PIMS. Ionization radiation (8.9–9.1 eV) was provided by a microwave-discharge of Cl\(_2\)-helium mixture (Cl\(_2\)-lamp) with a CaF\(_2\) window and was used for the detection of all three vinyl-type radicals, which have an \(m/z\) value of 41 (C\(_2\)H\(_3\)). The observed reaction products were ionized with a H\(_2\)-lamp with a MgF\(_2\) window (10.2 eV) and an Ar-lamp with a LiF window (11.6–11.8 eV). The ions produced were mass-selected by the quadrupole mass-spectrometer followed by their detection using an off-axis electron multiplier. The temporal ion signal (see insets in Figures 2 and 3) was recorded using a multichannel scaler from 10 ms before and up to 70 ms after each laser pulse and transferred to a computer for the subsequent analysis. Typically the R decay signal profile was accumulated from 3000–8000 repetitions before the nonlinear least-squares method was used to fit an exponential function, \([R]_t = A + [R]_0 \times \exp(-k't)\), to the data. Here \([R]_0\) is proportional to the radical concentration at time \(t\), \(k'\) is the pseudo-first-order decay rate coefficient, and \(A\) is the background signal.

Initial radical concentrations were kept low, at, or below about 2 × 10^{11} \text{ cm}^{-3}, in order to suppress any radical–radical reactions. Under pseudo-first-order experimental conditions ([R] \ll [O_2]) with low initial radical concentrations, only two

significant reactions, A and B, contribute to the loss rate of radical R:

\[
R + O_2 \rightarrow \text{products} \\
R \xrightarrow{\text{wall}} \text{heterogeneous loss} \quad \text{(B)}
\]

Reaction A is the bimolecular gas-phase reaction between R and the reactant (O\(_2\)) and is the primary interest in the current work. Reaction B is denoted as \(k_{\text{wall}}\) and involves radical losses on the reactor wall as well as other slow first-order reactions (e.g., with radical precursor, with impurities in buffer gas, etc.) without added reactant. The first-order decay rate without added reactant, \(k_{\text{wall}}\), was determined in the beginning and end of each bimolecular rate coefficient measurement. The first-order decay rate coefficient \(k'\) was then measured as a function of [O\(_2\)], where the fastest \(k'\) obtained was typically at least 5 × \(k_{\text{wall}}\). Since the only significant reactions consuming R during the experiments were reactions A and B, the bimolecular reaction rate coefficient \(k(R + O_2)\) could be obtained from the slope of the \(k'\) versus [O\(_2\)] plot according to the equation \(k' = k(R + O_2) \times [O_2] + k_{\text{wall}}\). Typical bimolecular plots to obtain \(k(R + O_2)\) are shown in Figures 2 and 3.

The precursors 2-bromopropene (Sigma-Aldrich, > 99%), cis-1-bromopropene (Sigma-Aldrich, > 97%), trans-1-bromopropene (Sigma-Aldrich, > 99%), and 3-methyl-3-buten-2-one (TCI, > 95%) were degassed by several freeze–thaw cycles before use. Helium (Messer-Griesheim, purity of 99.9996%) and O\(_2\) (Aga, purity of 99.998%) were used as supplied. The gas pressures were monitored by capacitance pressure gauges. Estimated temperature uniformity of the reactor was ±2 K.
The measured bimolecular rate coefficients of reactions 1 CH₃CCH₂ + O₂, (2a) cis(trans)-CH₃CHCH + O₂, and (3a) trans(cis)-CH₃CHCH + O₂ are presented in Table 1 along with the corresponding experimental conditions. The estimated uncertainty of the bimolecular rate coefficients is ±20%. This originates from uncertainties in fitting processes, in flow rate measurements, and slight temperature fluctuations (±2 K) during measurements.

The radical decay signals along with the corresponding product formation signals are shown in Figures 2 and 3. Formaldehyde (H₂CO, Ar/LiF) and methyl radical (CH₃, H₂/MgF₂) were observed as products of reaction 1. For reactions 2a and 3a, the observed products were formyl radical (HCO, H₂/MgF₂) and acetaldehyde (CH₃CHO, H₂/MgF₂). Assuming an analogy with the reaction C₂H₃ + O₂ → CHO + H₂CO, the expected products are H₂CO and acetyl radical (CH₃CO) for reaction 1 and HCO and CH₃CHO for reactions 2a and 3a. The calculations of Chen and Goldsmith¹⁄₄ for reactions 1 and 3 at low pressures and temperatures support our expectations. We did not directly observe any signal for the formation of CH₃CHO at m/z = 43 for reaction 1; we believe that the formed CH₃CHO underwent chemically activated decomposition to produce CH₃ and CO, of which CH₃ was observed at m/z = 15. This is likely since the products of the CH₃CCH₂ + O₂ → H₂CO + CH₃CO reaction channel are formed with ∼90 kcal/mol (377 kJ/mol) of excess energy¹⁴ and the threshold energy for decomposition CH₃CHO → CH₃ + CO is only about 15.6 kcal/mol (65.3 kJ/mol).²⁴ None of the product signals were detected in the absence of O₂. Hence, we conclude that under the experimental conditions of our measurements, the major product channels are the formation of H₂CO and CH₃CO for reaction 1 and the formation of HCO and CH₃CHO for reactions 2a and 3a. The nature of the products formed for reactions 1, 2a, and 3a indicate that the reaction mechanism involves the formation of a cyclic intermediate containing an O−O bond, decomposition of which is a highly exothermic process.

The nonlinear least-squares method was used to fit the equation $I(P^*) = B + I_0(P^*)(1 - \exp(-k't))$ to the formation signals of the closed-shell products CH₃CHO and H₂CO. Here parameters $B$, $I_0(P^*)$, and $k'$ are the non-time-resolved background signal, the signal value at $t = \infty$, corresponding to channel yield × [React]₀, and the pseudo-first-order decay rate coefficient. Since the other two products, CH₃ and HCO, are open-shell species and react with O₂, although the CH₃ + O₂ reaction is very slow ($k' ≤ 0.03 \text{ s}^{-1}$) under our experimental conditions, the following expression was fitted to the signal profiles:

$$I(P^*) = B + I_0(P^*)\left(\frac{k'}{k' - k_P}\left(\exp(-k'_t) - \exp(-k't)\right)\right)$$

where $k'_P$ is a pseudo-first-order rate coefficient of the reaction of the open-shell species with O₂ and is treated as an individual fitting parameter.

Experiments were performed at different temperatures and pressures to determine the bath gas concentration dependence and temperature dependence of the measured bimolecular rate coefficients. No bath gas concentration dependence (pressure dependence) was observed for the rate coefficients of reactions 1−3, an observation that is in agreement with the computational results of Chen and Goldsmith¹⁸ under low-pressure conditions of the current work. Similarly, no pressure dependence has been observed for the C₂H₃ + O₂ reaction.¹⁵−²² Arrhenius plots of the bimolecular rate dependencies have been observed for the C₂H₃ + O₂ reaction.

**RESULTS AND DISCUSSION**

The nonlinear least-squares method was used to fit the equation $I(P^*) = B + I_0(P^*)(1 - \exp(-k't))$ to the formation signals of the closed-shell products CH₃CHO and H₂CO. Here parameters $B$, $I_0(P^*)$, and $k'$ are the non-time-resolved background signal, the signal value at $t = \infty$, corresponding to channel yield × [React]₀, and the pseudo-first-order decay rate coefficient. Since the other two products, CH₃ and HCO, are open-shell species and react with O₂, although the CH₃ + O₂ reaction is very slow ($k' ≤ 0.03 \text{ s}^{-1}$) under our experimental conditions, the following expression was fitted to the signal profiles:

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coefficients of CH₃CCH₂ + O₂, cis(trans)-CH₃CHCH + O₂, and trans(cis)-CH₃CHCH + O₂ reactions measured in this work are shown in Figure 4. Also shown are the results of previous measurements of the CH₃CHCH + O₂ and CH₂CH + O₂ reactions as well as the results of recent calculations of Chen and Goldsmith for the CH₂CH + O₂ and trans(cis)-CH₃CHCH + O₂ reactions. As can be seen from Figure 4, the measured bimolecular rate coefficient of reaction 1 has negative temperature dependence up to about 414 K and becomes temperature independent at higher temperatures. Likewise, the bimolecular rate coefficients of reactions 2a and 3a measured in this work behave similarly to reaction 1 and have negative temperature dependence up to about 363 K and become temperature independent at higher temperatures. The thermal stability of the employed precursors limited the upper bound of our experimental temperature range. The Arrhenius expression \[ k = A \times \exp \left( -\frac{E_a}{RT} \right) \] where \( k \) is the bimolecular rate coefficient, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, and \( R \) is the gas constant, was fitted to the measured bimolecular reaction rate coefficients of reactions 1, 2a, and 3a over the above-mentioned negative temperature dependence range. The following expressions were obtained: \( k_1 = (6.51 \pm 0.4) \times 10^{-12} \exp(1.69 \pm 0.14 \text{ kJ mol}^{-1}/\text{RT}) \text{ cm}^3 \text{ s}^{-1} (T = 3a) \) measured in this work behave similarly to reaction 1 and have negative temperature dependence up to about 414 K and become temperature independent at higher temperatures. Likewise, the bimolecular rate coefficients of reactions 2a and 3a measured in this work behave similarly to reaction 1 and have negative temperature dependence up to about 363 K and become temperature independent at higher temperatures. The thermal stability of the employed precursors limited the upper bound of our experimental temperature range. The Arrhenius expression \[ k = A \times \exp \left( -\frac{E_a}{RT} \right) \] where \( k \) is the bimolecular rate coefficient, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, and \( R \) is the gas constant, was fitted to the measured bimolecular reaction rate coefficients of reactions 1, 2a, and 3a over the above-mentioned negative temperature dependence range. The following expressions were obtained: \( k_1 = (6.51 \pm 0.4) \times 10^{-12} \exp(1.69 \pm 0.14 \text{ kJ mol}^{-1}/\text{RT}) \text{ cm}^3 \text{ s}^{-1} (T =
Agreement can be obtained over the investigated temperature range. The Chen and Goldsmith results, which are compared by multiplying the computational results with constant factors, show in Figure 1. However, we observed that the bimolecular processes possess similar temperature dependence. In addition, the negative activation energies obtained for reactions 1, 2a, and 3a are close to each other and close to the $E_a = -1.41 \pm 0.18$ kJ mol$^{-1}$ (T = 200–363 K) value Eskola and Timonen obtained for the CH$_3$CH + O$_2$ reaction.

In Figure 4, our experimental results are compared with the computational results of Chen and Goldsmith. By comparing the temperature dependencies of the CH$_3$CH + O$_2$ and trans-CH$_2$CH + O$_2$ reactions measured in this work together with previous measurements of the CH$_3$CH + O$_2$ and CH$_2$CH + O$_2$ reactions, as well as with the results of the recent calculations of Chen and Goldsmith for the CH$_3$CH + O$_2$ and trans-CH$_2$CH + O$_2$ reactions. Also shown (dashed lines) are fits of the Arrhenius expression to the negative temperature dependence portions of the current measurements.

218–414 K), $k_{\text{max}} = (2.99 \pm 0.2) \times 10^{-12} \exp(1.40 \pm 0.18 \text{kJ mol}^{-1}/RT) \text{cm}^3 \text{s}^{-1}$ (T = 220–363 K), and $k_a = (2.86 \pm 0.2) \times 10^{-12} \exp(1.80 \pm 0.18 \text{kJ mol}^{-1}/RT) \text{cm}^3 \text{s}^{-1}$ (T = 220–363 K). The negative activation energies obtained for reactions 1, 2a, and 3a are close to each other and close to the $E_a = -1.41 \pm 0.18$ kJ mol$^{-1}$ (T = 200–363 K) value Eskola and Timonen obtained for the CH$_3$CH + O$_2$ reaction.

As discussed in the Experimental Section, CH$_3$CH radical can undergo cis $\leftrightarrow$ trans isomerization with the surplus energy it gains in the photolysis process of the precursor molecule using 193 or 248 nm radiation. In addition, photolysis at 193 nm provides sufficient energy for further isomerization to the allyl radical, see Figure 1. The relative enthalpies of the isomers and their isomerization barriers are shown in Figure 1. However, we observed that the bimolecular rate coefficients of reactions 2a and 3a were independent of photolysis wavelength. This observation shows that any (small) amount of allyl radical possibly produced in measurements using 193 nm photolysis had a negligible effect on kinetic results, because no allyl can be formed in 248 nm photolysis, see Figure 1. Dibble et al. carried out an RRKM/Master Equation analysis of the trans $\leftrightarrow$ cis isomerization of chemically activated 1-methylallyl (CH$_3$CHCHCH$_3$) radical produced in the OH + trans-CH$_3$CHCHCH$_3$ reaction. The analysis was performed at different levels of initial excitation as a function of total pressure and temperature. Their results suggest that an initial excitation of 5 kcal/mol (21 kJ/mol) or more above the trans $\leftrightarrow$ cis isomerization barrier results in constant cis/trans population ratio under low-pressure conditions. The calculated cis/trans population ratio, however, depended on the employed density functional theory method. The results of Dibble et al. may explain why the bimolecular rate coefficients of reactions 2a and 3a measured in this work do not depend on photolysis wavelength employed (193 or 248 nm), although the initial excitation of CH$_3$CH radicals was significantly above the cis $\leftrightarrow$ trans isomerization barrier.

However, we also observed that when the trans-CH$_3$CHCHBr precursor was used to produce the CH$_3$CH radicals, we obtained a slightly but systematically larger rate coefficient for the CH$_3$CH + O$_2$ reaction compared with the rate coefficient obtained when the cis-CH$_3$CHCHBr precursor was used. Because it is very likely that isomerization did take place to some, but unknown extent, the trans(cis)-CH$_3$CHCH + O$_2$ and cis(trans)-CH$_3$CHCH + O$_2$ notation was employed, as described in the Experimental Section. The current observation that the trans(cis)-CH$_3$CHCH + O$_2$ reaction is slightly faster than the cis(trans)-CH$_3$CHCH + O$_2$ reaction is in line with the Chen and Goldsmith calculations which show that the potential energy surface (PES) of the trans-CH$_3$CHCH + O$_2$ reaction is slightly more attractive than the PES of the cis-CH$_3$CHCH + O$_2$ reaction. We conclude that the photolysis of the trans-CH$_3$CHCHBr or cis-CH$_3$CHCHBr precursor at 193 or 248 nm results in a mixture of CH$_3$CH radicals for which the initial (nascent) isomer is still in excess after thermalization.

Current results may also be used to interpret the OH + CH$_3$CHCH$_2$ $\rightarrow$ cis(trans)-CH$_3$CHCH + H$_2$O ($\Delta H_{f}^{298.15 \text{K}} \approx -35 \text{kJ/mol}$) and the subsequent cis(trans)-CH$_3$CHCH + O$_2$ reaction system. Since the cis(trans)-isomerization barrier is about 18 kJ/mol (see Figure 1) at room temperature, the excitation energy of nascent cis(trans)-CH$_3$CHCH radical may exceed the barrier by as much as 17 kJ/mol, close to the above-discussed 5 kcal/mol (21 kJ/mol), which in the case of 1-methylallyl, was enough to lead significant isomerization before thermalization. However, in this case the H$_2$O molecule takes a portion of the 35 kJ/mol energy released in the radical-forming reaction, so that the chemical excitation of the cis(trans)-CH$_3$CHCH radical is lower than the possible maximum, but might still be more than enough to lead to significant isomerization.

To the best of our knowledge, the kinetic measurements carried out by Slagle et al. employing PIMS is the only study available in the literature regarding the cis(trans)-CH$_3$CHCH + O$_2$ reaction, and their results are presented in Figure 4. The experimental technique used by Slagle et al. is similar to ours and in the temperature range 296 K–600 K, they observed that the rate coefficient of the cis(trans)-CH$_3$CHCH + O$_2$ reaction is independent of temperature and bath gas concentration.
Clearly, this observation is in disparity with our results. We observe explicit negative temperature dependence for the cis/ trans-CH₃CHCH + O₂ reactions and the temperature dependence is in good agreement with the computational results of Chen and Goldsmith.¹⁴ Additionally, the bimolecular reaction rate coefficient Slagle et al.¹³ measured is on average about 40% faster than those measured in the present work for the cis/trans-CH₃CHCH + O₂ reactions. Such an offset associated with these two apparatuses has already been observed previously.²²,²⁶

Finally, comparing the bimolecular rate coefficients of reactions 1, 2a, 3a, and k(CH₂CH + O₂)²² shown in Figure 4 manifest that substituting the α-H-atom in vinyl radical with a methyl group increases the rate of the reaction by almost 50%, whereas substituting either β-H-atom of the vinyl radical with a methyl group decreases the rate of reaction by around 30%. The increase of reactivity upon substituting an α-H-atom of a radical with a methyl group has been observed many times before²⁶ but the reduction of reactivity upon substituting a β-H-atom with a methyl group is a new observation.²⁷

**CONCLUSION**

In this study, we have measured the bimolecular rate coefficients of the CH₃CCH₂ + O₂ and cis-trans-CH₃CHCH + O₂ reactions over wide temperature ranges at low pressures. The bimolecular rate coefficients of all the three reactions were found to have a negative temperature dependence at temperatures below about 380 K and appear to become independent of temperature at somewhat higher temperatures, in good agreement with the recent computational study of Chen and Goldsmith.¹⁴ On the other hand, current results show that the CH₃CCH₂ + O₂ reaction is faster and trans-CH₃CHCH + O₂ reaction slower than those measured in the present work for the CH₃CCH₂ + O₂ reaction at somewhat higher temperatures, independent of temperature at somewhat higher temperatures, in good agreement with the recent computational study of Chen and Goldsmith.¹⁴

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