Study on the Formation of Secondary Organic Aerosol by Ozonolysis of Citral in the Atmosphere

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ABSTRACT

A major research area in atmospheric chemistry focuses on the formation of secondary organic aerosol (SOA), which contains a large variety of low-volatility organic compounds when generated by the ozonolysis of monoterpenes. Thus, we apply quantum chemistry and kinetic calculations to investigate the ozonolysis of citral, which begins with the formation of primary ozonides (POZs) that decompose into Criegee intermediates (CIs). Although CIs have been previously implicated in tropospheric oxidation, the majority are simple compounds for their class, such as CH2OO· or CH3CHOO·. This study, however, reports on the generation and reaction kinetics of larger CIs, which have been shown to oxidize NO and SO2 into NO2 and SO3, respectively, leading to the production of nitric acid and sulfuric acid. Furthermore, the reactions between these CIs, and H2O and SO2 may serve as the dominant mechanism for removing the former from the troposphere, thereby determining the atmospheric CI concentrations. The low-volatility organic compounds potentially arising from the ozonolysis of citral, including aldehydes (–C(=O)H), ketones (–C(=O)–), alcohols (–OH), and hydroperoxides (–OOH), can form SOA through the nucleation, condensation, and/or partitioning of the condensed and gaseous phases.

Keywords: Secondary organic aerosol, Citral, Ozonolysis, Criegee intermediates

1 INTRODUCTION

Atmospheric aerosols significantly affect the earth’s radiation balance by absorbing and scattering solar radiation, leading to a decrease in atmospheric visibility and contributing to climate change. Moreover, due to the small particle size and large surface area of atmospheric aerosols, they provide a reaction bed for various atmospheric chemical processes and have a direct effect on human health (Oberdorster et al., 2005; Pope and Dockery, 2006). Atmospheric aerosols are mainly classified as either primary aerosols which are directly discharged into the atmosphere by an exhaust source, or secondary aerosols formed in the atmosphere from chemical reaction with gaseous components (Atkinson and Arey, 2003; Hallquist et al., 2009). Secondary organic aerosols (SOAs) are mainly formed from the oxidation processes of volatile organic compounds (VOCs) and account for a significant fraction of ambient tropospheric aerosols (Jimenez et al., 2009).

About 90% of the total global VOCs emissions that lead to SOAs formation come from biological sources, which including isoprene (C5H8), monoterpenes (C10H16), and sesquiterpenes (C15H24) (Guenther et al., 1995; Goldstein and Galbally, 2007; Friedman and Farmer, 2018; Stangl et al., 2019). Monoterpenes have been found to be the largest contributors to organic aerosol during the summer in the southeastern United States, with mean global emissions estimated to be approximately 107.5 TgC per year (Messina et al., 2016; Zhang et al., 2018; Nagori et al., 2019). As monoterpenes are unsaturated, they rapidly react with O3, OH and NO3 radicals, with estimated reaction rates for OH and NO3 radicals with most monoterpenes being larger than 10–11 cm3 molecules–1 s–1 and in the range of 10–18–10–14 cm3 molecules–1 s–1 for O3 with monoterpenes.
(Atkinson, 1997; Calogirou et al., 1999; Martínez et al., 1999; Orlando et al., 2000; Oliveira and Bauerfeldt, 2012). Using the 12-h daytime average OH radical concentration of 2 × 10^8 molecules cm^-3, 12-h nighttime average NO3 radical concentration of 2.5 × 10^7 molecules cm^-3 and 24-h average O3 concentration of 7 × 10^11 molecules cm^-3, the fast monoterpane ozonolysis reaction can compete with the OH reaction during the day and the NO3 reaction at night. Therefore, ozonolysis serves as an important monoterpane loss pathway (Orlando et al., 2000; Atkinson and Arey, 2003; Qin et al., 2018). In addition, a large variety of low-volatility organic compounds, including carbonyl compounds (aldehydes and ketones), hydroxyl compounds and organic acids, have been identified in SOAs generated from the ozonolysis of monoterpences, such as α-pinene, β-pinene, α-phellandrene, limonene, and sabinene (Jacksonet et al., 2016; Sato et al., 2016; Scorch et al., 2017). Therefore, SOAs formation by the oxidation of monoterpenes is mainly dominated by the ozonolysis reaction.

Monoterpenes generally contain 1–3 unsaturated >C=C< double bonds and are highly reactive. The proposed reaction mechanism for monoterpane ozonolysis starts with O3 addition to C=C double bonds, which lead to the formation of primary ozonide (POZ). The formed POZ will then rapidly decompose to form Criegee intermediates (CIs). Chemically activated CIs may undergo unimolecular decomposition or isomerization, or bimolecular reactions with H2O, NO and SO2 (Kleindienst et al., 2006; Jaoui et al., 2008; Lin et al., 2014; Jackson et al., 2017; Almatarneh et al., 2019), with many previous studies reporting the importance of bimolecular reactions for SOA formation.

Neeb et al. (1997) found that hydroxymethyl hydroperoxide (HMHP) was the sole product of the reaction between CH2OO and water H2O. HMHP can then be rapidly decomposed into low-volatility organic compounds such as methacrolein and methyl vinyl ketone (Sauer et al., 1999). Presto et al. (2005) reported SOA yields from the ozonolysis of α-pinene in the presence of NOx, suggesting that CIs can react with NOx, typically resulting in carbonyl and organic nitrate functionality. Mauldin et al. (2012) found that the oxidation of SO2 to H2SO4 by CIs leads to an increase in the production of sulfate aerosols in boreal forests. Sipilä et al. (2014) also reported that the reaction between SO2 and CIs formed from monoterpane ozonolysis is an important source of atmospheric sulfate and SOAs. In addition, Ye et al. (2018) studied α-pinene and limonene ozonolysis in the presence of SO2, finding that the reaction of SO2 with CIs was responsible for altering SOAs yields. Although these experimental studies indicated that bimolecular CIs reactions were related to SOAs formation, the chemical processes behind these interactions are not yet fully understood. Moreover, most theoretical studies have focused on small CIs, especially the simple carbonyl oxide CH2OO (Aplincourt and Ruiz-López, 2000; Vereecken et al., 2012; Nguyen et al., 2016). Therefore, it is necessary to study the specific mechanism of SOAs formation from large CIs formed from monoterpane ozonolysis.

As a natural acyclic monoterpane, citral is found in a wide variety of plants, such as Indian lemon grass species and Litsea cubeba, and can be used as a key ingredient for various chemical products (Rauber et al., 2005; Gil et al., 2007; Saddiq and Khayyat, 2010). Citral (3,7-dimethyl-2,6-octadienal) is a mixture of two isomeric acyclic monoterpane aldehydes, neral and geranial (Fig. 1), caused by cis-trans isomerism at the C=C bond near the aldehyde group. In this article, neral was used to theoretically explore the gas-phase ozonolysis of citral in the presence of H2O, NO and SO2, providing novel insights on the formation mechanisms of SOAs during monoterpenes ozonolysis and further deepening our understanding of the atmospheric SOAs.

2 COMPUTATIONAL METHODS

All geometric optimizations were performed using the Gaussian 09 program (Frisch et al., 2009). And in each elementary reaction, the geometric parameters of reactants, pre-reactive complex (PRC), intermediates (IMs), transition states (TSs) and products, were optimized using the M06-2X functional with the 6-31+G(d,p) basis set. Zheng et al. (2009) calculated the barrier heights of DBH24/08 database using 348 model chemistries, including heavy-atom transfer (HATBH6), nucleophilic substitution (NSBH6), unimolecular and association (UABH6), and hydrogen-transfer (HTBH6) reactions. The selected functional M06-2X/6-31+G(d,p) was proven to be reliable and appropriate for the configuration optimization and thermodynamic calculation of ozonolysis.
At the same level of theory, frequency calculations were performed to obtain zero-point energy corrections. The transition states were identified by only one imaginary frequency. More accurate single energies could be obtained using a larger basis set of 6-311++G(3df,3pd).

Using the KiSThelP program (Truhlar et al., 1996; Canneaux et al., 2014), rate constants were calculated using transition-state theory (TST) with Wigner tunneling correction at a pressure of 1.0 bar and 298 K. A scaling factor of 0.967 was applied to the frequency calculated at the M06-2X/6-31+G(d,p) level (Alecu et al., 2010).

When the reaction involved pre-reactive complexes, the reaction rate constants were calculated using the formula described in Eq. (1) (Shiroudi and Deleuze, 2014), as follows:

\[
K_{eq} \cdot k_1 \rightarrow \text{IM}
\]

where \( K_{eq} \) represents the equilibrium constant for the first reaction step, R1...R2 means the pre-reactive complexes. The thermodynamic expression of the equilibrium constant for gas-phase reactions is employed in KiSThelP, as described in Eq. (2) as follows:

\[
K_{eq} = e^{\frac{\Delta G_0^o(T)}{RT}}
\]

where \( \Delta G_0^o(T) \) is the associated standard reaction Gibbs energy at temperature \( T \) and \( R \) is the ideal gas constant. Furthermore, the unimolecular reaction rate constant \( (k_1) \) employed in KiSThelP is the thermodynamic equivalent of Eq. (3):

\[
k = \sigma \cdot k_0 \cdot T \cdot e^{\frac{\Delta G_0^o(T)}{k_bT}}
\]

where \( \sigma \) is the reaction path degeneracy; \( k_0 \) is Boltzmann’s constant; \( T \) is the temperature; \( h \) is Planck’s constant; \( R \) is the ideal gas constant and \( P_0 = 1 \) bar, with the \( RT/P_0 \) unit being the inverse of a concentration; \( \Delta n \) is 1 or 0 for gas-phase bimolecular or unimolecular reactions; and \( \Delta G_0^o(T) \) represents the standard Gibbs free energy of activation for the reaction.

The overall rate constant can be calculated according to Eq. (4) as follows:

\[
k_{overall} = K_{eq} \cdot k_1
\]

### 3 RESULTS AND DISCUSSIONS

#### 3.1 The Formation and Decomposition of Primary Ozonides

Atomic labels are marked in the structure of citral in Fig. 1. Fig. 2 depicts the detailed reaction...
Fig. 2. The mechanisms for the formation and decomposition of primary ozonides at the M06-2X/6-311++G(3df,3pd)/M06-2X/6-31+G(d,p) level of theory (kcal mol$^{-1}$).

Mechanism for the formation and decomposition of POZs, in which the potential barriers ($\Delta E_b$) and reaction heats ($\Delta E_r$) are also given. Evidently, the reaction of citral with O3 follows the Criegee mechanism, consisting of a three-step reaction: (1) formation of PRCs, (2) electrophilic addition forming 5-member-ring primary ozonides (POZs), and (3) decomposition of POZs.

The ozonolysis of citral initiates with the addition of two terminal O atoms of O3 to C2=C3 and C7=C8, obtaining two PRCs (PRC1 and PRC2), with the two reactions release 6.03 kcal mol$^{-1}$ and 4.91 kcal mol$^{-1}$ of heat, respectively. Then the POZs (IM1 and IM2) are formed through TS1 and TS2. The barrier heights of these two parallel processes are 4.20 kcal mol$^{-1}$ and 6.39 kcal mol$^{-1}$, and the exothermic heat is 65.86 kcal mol$^{-1}$ and 56.11 kcal mol$^{-1}$, respectively. Therefore, the reaction of O3 with citral occurs easily under conventional atmospheric conditions.

Energized POZs have a 5-membered ring, which decomposes promptly to form carbonyl compounds [IM3, (CH3)$_2$CO, IM5 and OHCCHO] and the corresponding CIs [IM4, (CH3)$_2$COO-, IM6 and OHCCHO-] through the cleavage of the C–C bond and one of the O–O bonds.

Table 1 lists the calculated rate coefficients $k$ of O3 with citral at 298 K. The predicted rate coefficient of O3 with citral at 298 K was $6.97 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, falling within the previously reported range of $10^{-19}$–$10^{-14}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. Additions to C2=C3 bond account for more than 99% of the branching ratio and thus, further analysis focuses on the fate after addition to C2=C3 bond only.
Table 1. Calculated rate constants for the ozonolysis of citral and Criegee intermediate reactions.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k_{298K}$ (cm$^3$ molecules$^{-1}$ s$^{-1}$ or s$^{-1}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citral + O$_3$ → PRC1 → IM1</td>
<td>$6.92 \times 10^{-17}$</td>
</tr>
<tr>
<td>Citral + O$_3$ → PRC2 → IM2</td>
<td>$4.57 \times 10^{-20}$</td>
</tr>
<tr>
<td>IM4 → DO</td>
<td>$1.59 \times 10^{-3}$</td>
</tr>
<tr>
<td>IM4 + H$_2$O → HAHP</td>
<td>$5.07 \times 10^{-16}$</td>
</tr>
<tr>
<td>IM4 + NO → IM3 + NO$_2$</td>
<td>$1.58 \times 10^{-22}$</td>
</tr>
<tr>
<td>IM4 + NO → IM1-NO(2)</td>
<td>$6.70 \times 10^{-21}$</td>
</tr>
<tr>
<td>IM4 + SO$_2$ → PRC-SO$_2$ → IM1-SO$_2$</td>
<td>$3.19 \times 10^{-10}$</td>
</tr>
<tr>
<td>IM3 + O$_3$ → PRC3 → IM8</td>
<td>$8.61 \times 10^{-19}$</td>
</tr>
</tbody>
</table>

* s$^{-1}$ for unimolecular reaction, cm$^3$ molecules$^{-1}$ s$^{-2}$ for bimolecular reactions.

3.2 Criegee Intermediate Reactions

The addition of O$_3$ to the C$_2$=C$_3$ bond will be decomposed into two CIs, (CH$_3$)$_2$COO$^-$ and IM4. The reactions of (CH$_3$)$_2$COO$^-$ have been widely investigated in recent studies (Vereecken et al., 2012; Chhantyal-Pun et al., 2017; Deng et al., 2018). In the atmosphere, the stabilized (CH$_3$)$_2$COO$^-$ can undergo unimolecular isomerization reaction to form CH$_2$=C(CH$_3$)OOH, and can also react with SO$_2$, NO$_2$, and H$_2$O (Deng et al., 2018). The present study focused on the fate of IM4, which may also undergo unimolecular reactions, or bimolecular reactions with water vapor and other trace gases, e.g., H$_2$O, SO$_2$ and NO$_2$. Fig. 3 shows the profile of the potential energy surface for the reaction of IM4. The single molecular degradation of large CIs includes the hydrogen-shift reaction, the bicyclic ring closure reactions and ring cyclization to form dioxirane (DO; Long et al., 2019). Instead of intramolecular hydrogen migration and the bicyclic ring closure reactions, IM4 can undergo ring cyclization to form DO via an exothermic process and with a reaction barrier of about 22.20 kcal mol$^{-1}$. The rate coefficients at 298 K were estimated as $1.59 \times 10^{-3}$ s$^{-1}$.

3.2.1 Reaction with H$_2$O

In atmospheric chemistry, one of the most important reactions is considered to be the reaction with H$_2$O because of its high abundance. Previous theoretical and experimental studies have shown that the reaction between CIs and H$_2$O occurs via three main reaction channels (Qi and Chao, 2007; Wang et al., 2019). The pathway to produce organic peroxides is likely to be thermodynamically and kinetically advantageous compared with the other two pathways. In this channel, the H-O bond in H$_2$O is broken to generate OH group and H atom. The obtained OH group is attached to the C atom, while the H atom is simultaneously combined with COO$^-$ to form hydroxyalkyl hydroperoxides (HAHP). This process crosses a small potential barrier of 3.31 kcal mol$^{-1}$ and is highly exothermic, generating 43.43 kcal mol$^{-1}$ of energy.

For reaction with water, the rate coefficient at 298 K was estimated as $5.07 \times 10^{-16}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ based on the TST, which is similar to the rate coefficient of $2.46 \times 10^{-16}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for CH$_3$CHO (Wang and Wang, 2017). Theoretical studies have also shown that the reaction between (CH$_3$)$_2$COO and water monomer is slow, and the rate coefficients at 298 K is $2.4 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ (Anglada and Sole, 2016).

When the relative humidity (RH) is 50%, the concentration of water vapor is about $3.8 \times 10^{17}$ molecules cm$^{-3}$. Then the effective bimolecular rate is $193$ s$^{-1}$, which is much higher than the unimolecular rate of $1.59 \times 10^{-3}$ s$^{-1}$.

3.2.2 Reaction with NO

In the presence of NO$_x$, CIs can react with NO radicals, resulting in the formation of carbonyl and organic nitrate functionality. Two reaction pathways were established for the reaction between CIs and NO. The first is the formation of a 5-membered ring adduct with a nitrogen-centered radical, with a reaction barrier calculated at 9.12 kcal mol$^{-1}$; then step by step the C-O bond and O-O bond will break, resulting in the formation of carbonyl compounds and NO$$_2$ The other pathway involves NO extraction of the terminal oxygen of CI, which directly generates carbonyl compounds and NO$$_2$ The reaction barrier for this pathway is slightly higher than that of cycloaddition, at 13.58 kcal mol$^{-1}$. 
Fig. 3. The profile of the potential energy surface for the reaction of Criegee intermediates at the M06-2X/6-311++G(3df,3pd)//M06-2X/6-31+G(d,p) level of theory (kcal mol$^{-1}$).

Overall, it may be concluded that the reaction between Cl and NO yields a carbonyl compound and NO$_2$, proceeding mostly through the formation of a cyclic intermediate. The NO reaction may act as a route for oxidizing NO to NO$_2$ in the atmosphere, affecting NO/NO$_2$ conversion rates. The associated NO-NO$_2$ cycling is particularly important for the production of tropospheric O$_3$ (Murray et al., 2013; Newsome and Evans, 2017; Ridley et al., 2017). O$_3$ is produced by the photolysis of NO$_2$ during the day, and reacts irreversibly with NO to form NO$_2$ at night. But the presence of Cls may compete with O$_3$ and reduce the reaction between NO and O$_3$ at night, leading to the accumulation of O$_3$.

The overall rate coefficient of IM4 with NO was estimated as $6.85 \times 10^{-21}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K, which is 2–3 orders of magnitude lower than the estimated rate coefficient (Vereecken et al., 2012). The concentrations of NO in forests, rural areas and cities are $3.3–4.8 \times 10^8$, $1.1 \times 10^{10}$ and $9 \times 10^{10}$ molecules cm$^{-3}$, respectively. Thus, the effective bimolecular rate of IM4 with NO is $2.26 \times 10^{-12}$–$6.17 \times 10^{-10}$ s$^{-1}$.

3.2.3 Reaction with SO$_2$

In the atmosphere, the Criegee intermediate IM4 can also undergo bimolecular reactions with SO$_2$, which begins with the formation of a pre-reactive complex (PRC-SO$_2$). This process releases 13.57 kcal mol$^{-1}$ of energy. Then the 5-membered ring adduct IM1-SO$_2$ is obtained via TS1-SO$_2$, with this process being constrained by a reaction barrier height of 1.02 kcal mol$^{-1}$ and being exothermic by 23.67 kcal mol$^{-1}$. Finally, the 5-membered ring intermediate breaks the O-O and C-O bonds to form a carbonyl compound (IM3) and SO$_3$. SO$_3$ condenses with water to form fine sulfate aerosol particles in the atmosphere, which not only affects global climate change, but also...
harms human health (Sarwar et al., 2013). This pathway can also account for non-OH sources in the atmosphere leading to increased sulfate aerosol production in coastal (Berresheim et al., 2014) and boreal forest environments (Mauldin et al., 2012).

The overall rate coefficient $k$ of SO$_2$ with IM4 is $3.19 \times 10^{-10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at ambient temperature and 760 Torr, which is close to the previously reported experimental values of $2.4 - 6.7 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for CH$_3$CHOO (Taatjes et al., 2013), $1.3 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for (CH$_3$)$_2$COO (Huang et al., 2015), and $(4.2 \pm 0.6) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for methyl vinyl ketone oxide (Caravan et al., 2020), as well as the theoretical values of $(3.68 \pm 0.02) \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for CH$_2$OO (Kuwata et al., 2015) and $5.27 - 6.54 \times 10^{-10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for MY-CIs (Deng et al., 2018). The concentration ranges of SO$_2$ is about $1.7 \times 10^{10}$ molecules cm$^{-3}$ in the boreal forest, $9 \times 10^{10}$ molecules cm$^{-3}$ in a megacity and $6.6 \times 10^9$ molecules cm$^{-3}$ in rural Europe (Vereecken et al., 2012); thus the effective bimolecular rate of IM4 with respect to the reaction with SO$_2$ is about 2.11–28.71 s$^{-1}$. If SO$_2$ is present in the atmosphere at a typical level of $5 \times 10^{11}$ molecules cm$^{-3}$ (~20 ppbv) (Deng et al., 2018), the effective bimolecular rate of IM4 with respect to the reaction with SO$_2$ is 159.5 s$^{-1}$.

### 3.3 Fate of IM3

As shown in Fig. 4, the carbonyl compound IM3 can further react with O$_3$ with ozone approaching the >C=C< bond forming a 5-member-ring IM8 compound via pre-reactant complexes (PRC3). This process contains a total excess energy of approximately 68.52 kcal mol$^{-1}$, which is sufficient to cause rapid ring breakage. The primary product channels were identified as IM9 (CH$_3$COCH$_2$CH$_2$CHOO·) + trans-glyoxal (OHCCHO) or levulinic aldehyde (CH$_3$COCH$_2$CH$_2$CHO) + Cls (OHCCCHO·), with potential barriers of 16.63 and 24.76 kcal mol$^{-1}$, respectively. The Cls OHCCCHO· and CH$_3$COCH$_2$CH$_2$CHOO· can further react with H$_2$O, SO$_2$ and NO to form the stabilized products glyoxal and levulinic aldehyde, respectively.

### 4 CONCLUSIONS

We applied quantum chemistry and kinetic calculations to identify the mechanism driving the ozonolysis of citral and gained the following insights:

1) POZs can be formed by the attachment of O$_3$ to C=C, after which carbonyl molecules and Cls can be formed by the simultaneous cleavage of the C-C bond of the forming 5-member-ring and one of the O-O bonds.

2) Cls can isomerize at a rate of $1.59 \times 10^{-3}$ s$^{-1}$. Additionally, they can bimolecularly react with H$_2$O and SO$_2$ at rates of 193 s$^{-1}$ and 159.5 s$^{-1}$, respectively, and, to a far lesser degree, with NO (at a rate of $2.26 \times 10^{-12}$ to $6.17 \times 10^{-10}$ s$^{-1}$). More importantly, Cls can oxidize SO$_2$ into SO$_3$, leading to the production of sulfuric acid.

![Fig. 4. The fate of IM3 with O$_3$.](https://example.com/figure4.png)

Fig. 4. The fate of IM3 with O$_3$ at the M06-2X/6-311++G(3df,3pd)/M06-2X/6-31+G(d,p) level of theory (kcal mol$^{-1}$).
The ozonolysis of citral potentially produces low-volatility species with increased water solubility, such as aldehydes [–C(=O)H], ketones [–C(=O)–], alcohols (–OH), and hydroperoxides (–OOH), which can form SOA through the nucleation, condensation, and/or partitioning of the condensed and gaseous phases.

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SUPPLEMENTARY MATERIAL

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REFERENCE


