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

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Highlights

- The rate coefficient of H\textsubscript{2}O and SO\textsubscript{2} with CIs are close to the previously reported experimental and theoretical value.

- CIs can react with SO\textsubscript{2} forming a five-membered ring adduct through a low barrier, and then break the O-O and C-O bonds to form carbonyl compound and SO\textsubscript{3}.

- Ozonolysis of Citral can produce low volatile organic compounds, which can form SOA.
ABSTRACT

Understanding secondary organic aerosol (SOA) formation mechanisms is a major focus of atmospheric chemistry research. A large variety of low volatile organic compounds have been detected in SOA generated from the ozonolysis of monoterpenes. In this article, quantum chemistry and kinetic calculations are used to study the mechanism of Citral ozonolysis. The reaction starts from the formation of primary ozonides (POZs), which can decompose to Criegee intermediates (CIs). CIs have previously been implicated in tropospheric oxidation, but most of them are the simplest compounds in the class, such as CH$_2$OO· or CH$_3$CHOO·. In the present study, the production of larger CIs and their reaction kinetics with H$_2$O, NO and SO$_2$ are reported. CIs have been shown to oxidize NO and SO$_2$, leading to the production of nitric acid and sulfuric acid via NO$_2$ and SO$_3$ formation. Reaction with H$_2$O and SO$_2$ may be the dominant pathway for tropospheric removal of CIs and determine their atmospheric concentration. The ozonolysis of Citral can produce low volatile organic compounds, including aldehydes (−C(=O)H), ketones (−C(=O)−), alcohols (−OH), and hydroperoxides (−OOH), which can form SOA by nucleation, condensation, and/or partitioning between the condensed and gaseous phases.

Keywords: Secondary organic aerosol; Citral; Ozonolysis; Criegee intermediates
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 (C_5H_8), monoterpenes (C_{10}H_{16}), and sesquiterpenes (C_{15}H_{24}) (Friedman and Farmer, 2018; Goldstein and Galbally, 2007; Guenther et al., 1995; 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; Nagori et al., 2019; Zhang et al., 2018). As monoterpenes are unsaturated, they rapidly react with O_3, OH and NO_3 radicals, with estimated reaction rates for OH and NO_3 radicals with most monoterpenes being
larger than $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and in the range of $10^{-19}$-$10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for O$_3$ with monoterpenes (Martínez et al., 1999; Atkinson, 1997; Calogirou et al., 1999; Orlando et al., 2000; Oliveira and Bauerfeldt, 2012). Using the 12-h daytime average OH radical concentration of $2 \times 10^6$ molecule cm$^{-3}$, 12-h nighttime average NO$_3$ radical concentration of $2.5 \times 10^8$ molecule cm$^{-3}$ and 24-h average O$_3$ concentration of $7 \times 10^{11}$ molecule cm$^{-3}$, the fast monoterpene ozonolysis reaction can compete with the OH reaction during the day and the NO$_3$ reaction at night. Therefore, ozonolysis serves as an important monoterpene loss pathway (Atkinson and Arey, 2003; Orlando et al., 2000; Qin, et al., 2018). In addition, a large variety of low volatile organic compounds, including carbonyl compounds (aldehydes and ketones), hydroxyl compounds and organic acids, have been identified in SOAs generated from the ozonolysis of monoterpenes, such as α-pinene, β-pinene, α-phellandrene, limonene, and sabinene (Jackson 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 to 3 unsaturated >C=C< double bonds and are highly reactive. The proposed reaction mechanism for monoterpene ozonolysis starts with O$_3$ 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 H$_2$O, NO and SO$_2$ (Almatarneh et al., 2019; Jackson et al., 2017; Jaoui et al., 2008; Kleindienst et al.,...
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 CH$_2$OO and water H$_2$O. HMHP can then be rapidly decomposed into low volatile 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 NO$_x$, suggesting that CIs can react with NO, typically resulting in carbonyl and organic nitrate functionality. Mauldin et al. (2012) found that the oxidation of SO$_2$ to H$_2$SO$_4$ by CIs, leads to an increase in the production of sulphate aerosols in boreal forests. Sipilä et al. (2014) also reported that the reaction between SO$_2$ and CIs formed from monoterpene 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 SO$_2$, finding that the reaction of SO$_2$ 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 CH$_2$OO (Aplincourt and Ruiz-López, 2000; Nguyen et al., 2016; Vereecken et al., 2012). Therefore, it is necessary to study the specific mechanism of SOAs formation from large CIs formed from monoterpene ozonolysis.
As a natural acyclic monoterpene, 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 (Gil et al., 2007; Rauber et al., 2005; Saddiq and Khayyat, 2010). Citral (3,7-dimethyl-2,6-octadienal) is a mixture of two isomeric acyclic monoterpene 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 H$_2$O, NO and SO$_2$, providing novel insights on the formation mechanisms of SOAs during monoterpenes ozonolysis and further deepening our understanding of the atmospheric SOAs.

**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 (IM), transition states (TS) 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 (Sun et al., 2018; Wang et al., 2019). At the same level of theory, frequency calculations were performed to obtain zero-point energy corrections. The transition states was 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:

\[
R_1 + R_2 \overset{k_n}{\rightarrow} R_1 \cdots R_2 \overset{k_i}{\rightarrow} \text{IM} \quad (1)
\]

where, \(K_{eq}\) represents the equilibrium constant for the first reaction step, \(R_1\ldots R_2\) 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:

\[
K_{eq} = e^{\frac{\Delta G^0(T)}{RT}} \quad (2)
\]

where, \(\Delta G^0(T)\) 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):

\[
k = \sigma \frac{k_b T}{h} \left( \frac{RT}{P^0} \right)^{\Delta n} e^{-\frac{\Delta G_0(T)}{kT}} \quad \text{(3)}
\]

where, \( \sigma \) is the reaction path degeneracy; \( k_b \) 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 \( \Delta G_0(T) \) represents the standard Gibbs free energy of activation for the reaction.

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

\[
k_{overall} = K_{eq} k_1 \quad \text{(4)}
\]

**RESULTS AND DISCUSSIONS**

*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 mechanism for the formation and decomposition of POZs, in which the potential barriers (\( \Delta E_b \)) and reaction heats (\( \Delta E_i \)) are also given. Evidently, the reaction of Citral with \( O_3 \) follows the Criegee mechanism, consisting of a three-step reaction: (1) Formation of PRCs; (2) Electrophilic addition forming five-member-ring primary ozonides (POZs); (3) Decomposition of POZs.
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)

The ozonolysis of Citral initiates with the addition of two terminal O atoms of O$_3$ to C$_2$=C$_3$ and C$_7$=C$_8$, obtaining two PRCs (PRC1 and PRC2), with the two reactions release 6.03 and 4.91 kcal/mol 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 and 6.39 kcal/mol, and the exothermic heat is 65.86 kcal/mol and 56.11 kcal/mol, respectively. Therefore, the reaction of O$_3$ with Citral occurs easily under conventional atmospheric conditions.

Energized POZs have a five-membered ring, which decomposes promptly to form carbonyl compounds (IM3, (CH$_3$)$_2$CO, IM5 and OHCCCHO) and the
corresponding CIs (IM4, (CH₃)₂COO⁻, IM6 and OHCCCHOO⁻) through the cleavage of the C–C bond and one of the O–O bonds.

**Table 1.** Calculated Rate Constants for the ozonolysis of Citral and Criegee intermediate reactions

<table>
<thead>
<tr>
<th>Reactions</th>
<th>k₂₉₈K ( (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) ) or ( \text{s}^{-1})¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citral+O₃→PRC1→IM1</td>
<td>6.92×10⁻¹⁷</td>
</tr>
<tr>
<td>Citral+O₃→PRC2→IM2</td>
<td>4.57×10⁻²⁰</td>
</tr>
<tr>
<td>IM₄→DO</td>
<td>1.59×10⁻³</td>
</tr>
<tr>
<td>IM₄+H₂O→HAHP</td>
<td>5.07×10⁻¹⁶</td>
</tr>
<tr>
<td>IM₄+NO→IM₃+NO₂</td>
<td>1.58×10⁻²²</td>
</tr>
<tr>
<td>IM₄+NO→IM₁-NO(2)</td>
<td>6.70×10⁻²¹</td>
</tr>
<tr>
<td>IM₄+SO₂→PRC-SO₂→IM₁-SO₂</td>
<td>3.19×10⁻¹⁰</td>
</tr>
<tr>
<td>IM₃+O₃→PRC₃→IM₈</td>
<td>8.61×10⁻¹⁹</td>
</tr>
</tbody>
</table>

¹ \( \text{s}^{-1}\) for unimolecular reaction, \( \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for bimolecular reactions

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 6.97×10⁻¹⁷ \( \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), falling within the previously reported range of \( 10^{-19} \text{-} 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). 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 $C_2=C_3$ bond only.

**Criegee intermediate reactions**

The addition of $O_3$ to the $C_2=C_3$ bond will be decomposed into two CIs, $(CH_3)_2COO$· and IM4. The reactions of $(CH_3)_2COO$· have been widely investigated in recent studies (Chhantyal-Pun et al., 2017; Deng et al., 2018; Vereecken et al., 2012).

In the atmosphere, the stabilized $(CH_3)_2COO$· can undergo unimolecular isomerization reaction to form $CH_2=C(CH_3)OOH$, and can also react with $SO_2$, $NO_2$, and $H_2O$ (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., $H_2O$, $SO_2$ 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 (Long et al., 2019). Instead of intramolecular hydrogen migration and the bicyclic ring closure reactions, IM4 can undergo ring cyclization to form dioxirane (DO), via an exothermic process and with a reaction barrier of about 22.20 kcal/mol. The rate coefficients at 298 K were estimated as $1.59 \times 10^{-3}$ s$^{-1}$. 
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 Cl$_2$Is and H$_2$O occurs via three main reaction channels (Qi and Chao, 2007; Wang et al., 2019). The pathway to produce organic peroxides 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 energy barrier.
barrier of 3.31 kcal/mol and is highly exothermic, generating 43.43 kcal/mol of energy.

For reaction with water, the rate coefficient at 298 K was estimated as $5.07 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ based on the TST, which is similar to the rate coefficient of $2.46 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for CH$_3$CHOH (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$^3$ molecule$^{-1}$ 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$^{-1}$.

**Reaction with NO**

In the presence of NOx, 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, 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.
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$^3$ molecule$^{-1}$ 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 $9 \times 10^{10}$ molecule cm$^{-3}$, respectively. Thus, the effective bimolecular rate of IM4 with NO is $2.26 \times 10^{12}-6.17 \times 10^{10}$ s$^{-1}$.

**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 of energy. Then the five-membered ring adduct IM$_1$-SO$_2$ is obtained via TS$_1$-SO$_2$, with this process being constrained by a reaction barrier height of 1.02 kcal/mol and being exothermic by 23.67 kcal/mol. Finally, the five-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$^3$ molecule$^{-1}$s$^{-1}$ at ambient temperature and 760 Torr, which is close to the previously reported experimental values of $2.4 \sim 6.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$ for CH$_3$CHOO (Taatjes et al., 2013), $1.3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$ for (CH$_3$)$_2$COO (Huang et al., 2015), and (4.2 ± 0.6)$\times$ $10^{-11}$ cm$^3$ molecule$^{-1}$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$^3$ molecule$^{-1}$s$^{-1}$ for CH$_2$OO (Kuwata et al., 2015) and $5.27 \sim 6.54 \times 10^{-10}$ cm$^3$ molecule$^{-1}$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 Mega city 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 $2.11 \sim 28.71$ 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$^{-1}$.

**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 five-member-ring IM8 compound via
pre-reactant complexes (PRC3). This process contains a total excess energy of approximately 68.52 kcal/mol, which is sufficient to cause rapid ring breakage. The primary product channels were identified as IM9 

$\text{(CH}_3\text{COCH}_2\text{CH}_2\text{CHOO}^-) + \text{trans-glyoxal (OHCHCO)}$ or levulinic aldehyde $\text{(CH}_3\text{COCH}_2\text{CH}_2\text{CHO}) + \text{Cl (OHCHCOO}^-)$, with potential barriers of 16.63 and 24.76 kcal/mol, respectively. The CIs OHCHCOO$^-$ 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.

![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)](attachment:image)

CONCLUSIONS

In this study, quantum chemistry and kinetic calculations were used to reveal the mechanism of Citral ozonolysis, allowing some valuable conclusions to be drawn: (1) O$_3$ can add to the C=C double bonds forming POZs, and then the C–C bond and one of the O–O bonds can be cleaved at the same time to form carbonyl molecules and
Criegee intermediates (CIs). (2) CIs can undergo isomerization at a rate of $1.59 \times 10^{-3}$ s$^{-1}$, and react bimolecularly with H$_2$O, NO, and SO$_2$ at the rate of 193, 2.26$\times$10$^{-12}$–6.17$\times$10$^{-10}$ and 159.5 s$^{-1}$. CIs will mainly react with H$_2$O and SO$_2$. More importantly, CIs can oxidize SO$_2$ to SO$_3$, leading to the production of sulfuric acid. (3) The ozonolysis of Citral can produce low volatile and more water soluble species, such as aldehydes (−C(=O)H), ketones (−C(=O)−), alcohols (−OH), and hydroperoxides (−OOH), which can form SOAs by nucleation, condensation, and/or partitioning between the condensed and gaseous phases.

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