Probing the Reactivity of Singlet Oxygen with Cyclic Monoterpenes

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ABSTRACT: Monoterpenes represent a class of hydrocarbons consisting of two isoprene units. Like many other terpenes, monoterpenes emerge mainly from vegetation, indicating their significance in both atmospheric chemistry and pharmaceutical and food industries. The atmospheric recycling of monoterpenes constitutes a major source of secondary organic aerosols. Therefore, this contribution focuses on the mechanism and kinetics of atmospheric oxidation of five dominant monoterpenes (i.e., limonene, α-pinene, β-pinene, sabinene, and camphene) by singlet oxygen. The reactions are initiated via the ene-type addition of singlet oxygen (O₂Δg) to the electron-rich double bond, progressing favorably through the concerted reaction mechanisms. The physical analyses of the frontier molecular orbitals agree well with the thermodynamic properties of the selected reagents, and the computed reaction rate parameters. The reactivity of monoterpenes with O₂Δg follows the order of α-pinene > sabinene > limonene > β-pinene > camphene, i.e., α-pinene and camphene retain the highest and lowest reactivity toward singlet oxygen, with rate expressions of k(T) (M⁻¹ s⁻¹) = 1.13 × 10⁸ exp (−48(kJ)/RT(K)) and 6.93 × 10⁸ exp (−139(kJ)/RT(K)), respectively. The effect of solvent on the primary reaction pathways triggers a slight reduction in energy, ranging between 12 and 34 kJ/mol.

1. INTRODUCTION

Plants emit nearly 98% of the total non-methane volatile organic compounds into the atmosphere, 20% of which comprises monoterpenes. Monoterpenes represent a class of C₁₀ members of terpene hydrocarbons, the biogenic (naturally occurring) volatile organic compounds (BVOC) with high chemical reactivity and annual global emission rate of between 128 and 450 Tg per year. Figure 1 summarizes the chemical structure of monoterpenes features two isoprene units, constituting the major component of essential oils in various plant matters and can be isolated from trees for anti-inflammatory and antimicrobial drug synthesis. An alternative source of monolterpene emission includes woody household products.

Limonene and pinene are among the most abundant monoterpenes operating in the global tropospheric chemistry, being produced in relatively noticeable quantities by vegetation such as aromatic plants, flowers, and leaves. Limonene arises mainly from young plant leaves, and its formation rate reduces rapidly based on the age and extent of oxidation of the leaves. Moreover, this monocyclic monoterpene is significantly utilized in medicinal chemistry and disease treatment, due to its antitumor and antibacterial activity, and dietary formulations. Over 80% of the total monoterpene emission from a Monterey pine (Pinus radiata) comprises α- and β-pinene, and it has also been evidenced that about 50% of the emitted monoterpene from forests and tree species in the United States consists of α-pinene. Other examples of bicyclic monoterpenes are camphene and sabinene, which are minor constituents of many essential oils from plants such as turpentine, rosemary, ginger, and valerian.

Figure 1. Oxidation products of limonene, α-pinene, and β-pinene by O₂Δg.
Tropospheric hydrocarbons such as monoterpenes have relatively high molecular weights, thus their atmospheric oxidation gives rise to semivolatile organic compounds and secondary organic aerosol (SOA). SOAs originate primarily from the oxidation of BVOCs including monoterpenes. Subsequently, SOA plays a significant part in climate change and global radiation imbalance due to their involvement in the absorption and scattering of solar radiation. For instance, SOA are significant constituents of atmospheric fine particulate matters (PM2.5) as well as various haze pollution episodes.17

Monoterpenes find further applications in aromatization of cleaning products, paintings, air fresheners, and flavoring agents due to their pleasant fragrance. Therefore, the risk of accumulation of atmospheric oxidation products (i.e., SOA) could be substantial in enclosed, poorly ventilated spaces.

The maximum rate of singlet O₂ formation by energy-transfer mechanism in a polluted atmosphere is approximated to be 4 × 10⁻¹² mol L⁻¹ s⁻¹, which corroborates the significant role of such reactive oxygen species as atmospheric oxidants.18

Reactions of singlet oxygen with electron-rich acceptors such as olefins, dienes, and aromatic compounds are grouped into [4 + 2]-cycloadditions, [2 + 2]-cycloadditions, and so-called ene reactions. Ene reaction is based on the interaction of O₂ with an unsaturated compound containing an allylic hydrogen, during which the allylic hydrogen is abstracted in association with a reorganization of the bonding to give allylhydroperoxides.19 Oxidation of substrates with conjugated double bonds by singlet oxygen is feasible through [4 + 2]-cycloaddition, resulting in the synthesis of endoperoxides. Furthermore, the [2 + 2]-cycloaddition of the singlet oxygen to one double bond results in 1,2-dioxetane, and apparently olefins with unreachable allylic hydrogen atoms tend to give [2 + 2]-adducts.20 However, it should be noted that all of the reactions can compete for the same substance if the molecular structure allows it.21

Previous research efforts have investigated the oxidation of monoterpenes to SOA by OH radical,22,23 ozone,24–26 hydrogen peroxide,27–29 and nitrogen oxides,30–32 reporting the yield of the corresponding carbonyl compounds as the predominant products as a result of the oxidative cleavage of the C=C bonds.33 However, the role of a highly reactive singlet molecular oxygen in the photo-oxidation of monoterpenes has not been properly addressed in the literature. Some experimental studies elucidating the product distribution of dye-sensitized oxidation of terpenoid biogenic hydrocarbons (i.e., limonene, α- and β-pinene) in different media demonstrated the formation of organic aerosols.3,4,34,35 The aim of this contribution is to report modes of reactions between singlet oxygen and monoterpenes with a prime focus on deriving kinetic parameters.

2. RESULTS AND DISCUSSION

2.1. Mechanism and Kinetics of Singlet Oxidation of Monoterpenes. Due to the extreme electrophilic nature of singlet oxygen, the introduction of oxygen atoms into monoterpenes during photo-oxidation will occur at the molecular site where the Fukui function for an electrophilic attack (f⁻¹) displays its maximum value. This parameter indicates the most reactive site of chemical systems for electrophilic substitution reactions. According to Figure 2, the f⁻¹ indices are the largest at >C=C< sites associated with the higher photo-oxidation reactivity of nucleophile substrates therein.

The interaction between the nucleophile’s HOMO and the electrophile’s LUMO plays a vital role in elucidating the reaction dynamics, as though the larger LUMO—HOMO energy gaps lead to the decelerated chemical reactivity. E₇(HOMO) for selected monoterpenes and E₇(LUMO) for singlet oxygen are shown in Figure 3. Apparently, α-pinene appears to be most reactive toward singlet oxygen, whereas camphene exhibits the least reactivity among all. Based on the electron cloud distribution in Figure 3, the valence orbital electrons highly engulf the π-bond, justifying the Fukui indices results (Figure 2) to designate >C=C< as the most favorable molecular site for electrophilic attacks.

Table 1 lists the global hardness (η), softness (S), electronegativity (χ), chemical potential (μ), and electrophilicity index (ω) of the species derived from the computed HOMO and LUMO energy levels, enabling the predictions of the respective chemical characteristics of the species. Camphene remains the hardest reagent with the highest electronegativity and the lowest chemical potential. Apparently, the higher electronegativity signifies the lower chemical activity, all of which connotes a higher oxidation resistance.36

Thus, the following trend of chemical reactivity of the species is predicted herein: α-pinene > sabinene > limonene > β-pinene > camphene. The stated reactivity sequence accords well with the arrangement of the energy gap between LUMO and HOMO.
of O₂ ¹Δ₈ and HOMO of monoterpene species in Figure 3, i.e., the smaller the energy gap, the higher the reactivity.

The following sections present the mechanisms of reaction of each of the aforementioned monoterpenes with singlet oxygen, discussing in detail the energy potentials and kinetics features of the reactions.

2.1.1. Limonene. Figure 4 displays the optimized structure of limonene. According to the acquired reactivity indices in Figure 2, the most vulnerable site for electrophilic attack rests on the trisubstituted double bond (C₁= C₂). Therefore, the plausible reaction mechanisms for singlet oxidation of limonene should involve the ene reaction and [2 + 2]-cycloaddition. The latter failed to locate a genuine transition state despite our best efforts. Thus, the overall reaction merely involves ene-type reaction of O₂ ¹Δ₈ with limonene’s unconjugated double bond to form allylic hydroperoxides. Yet, our computational model failed to optimize related diradicals as potential intermediates in the ene reactions of limonene photo-oxidation, prompting to suggest a concerted mechanism for the ene-type addition of singlet oxygen to the limonene structure.

As illustrated in the proposed reaction mechanism in Figure 5, singlet oxygen clings to the limonene’s cyclohexene ring at the C₂ atom, bearing analogous barrier enthalpies of TS₂ and TS₁ around 40 kJ/mol. Hydrogen abstraction from the methylene group (in P₃) appears relatively energetically more favorable as compared to that from the methyl group (in P₂). The C₂ atom represents an alternative reactive spot for the addition of singlet oxygen enduring a relatively higher enthalpy barrier of TS₁ (50 kJ/mol). In accordance to the computed Fukui indices in Figure 2, this enthalpic behavior is justifiable as the C₂ position is the most favorable site for an electrophilic attack.

Although the electrophilic Fukui functions demonstrate that the likelihood of the C₈=C₉ site to be attacked by electrophiles is negligible, the corresponding transition state values (TS₁ and TS₆) compare well with the transition states for the attack on the C₁=C₂ in-ring double bond. As previously illustrated in Figure 1, the literature suggests that the product distribution from the photo-oxidation of limonene consists of terpene alcohols that are being reduced from P₁, P₂, and P₃ hydroperoxides, whose RO–OH bond efficiently undergoes a cleavage. Table 2 lists the reaction rate coefficient for the bimolecular reactions involved in the interaction of limonene with the singlet oxygen, fitted to the Arrhenius equation of \( k(T) = A \exp(-E_a/RT) \) at a high pressure limit for the temperature range of 300 and 600 K.

Table 2

| reaction                  | \( A \) (s⁻¹ or cm³ molecule⁻¹ s⁻¹) | \( E_a \) (kJ/mol) |
|--------------------------|------------------------------------|-------------------|
| limonene + O₂ ¹Δ₈ → P₁    | \( 1.53 \times 10^{-13} \)         | 57                |
| limonene + O₂ ¹Δ₈ → P₂    | \( 1.87 \times 10^{-13} \)         | 48                |
| limonene + O₂ ¹Δ₈ → P₃    | \( 9.71 \times 10^{-13} \)         | 49                |
| limonene + O₂ ¹Δ₈ → P₄    | \( 3.43 \times 10^{-13} \)         | 54                |
| limonene + O₂ ¹Δ₈ → P₅    | \( 2.25 \times 10^{-13} \)         | 49                |

Figure 5. Reaction mechanism of the singlet oxidation of limonene. The enthalpies are obtained at the 6-311+g(d,p) level of theory and are reported in kJ/mol.

The branching ratios for the bimolecular reaction channels are evaluated based on the Arrhenius parameters for \( k_i(T) \) given in Table 2. Figure 6 plots the \( k_i/ \sum k_i \) verifying channel TS₃ as the dominant reaction pathway and P₃ as the major primary product according to the reaction network. In a qualitative agreement with the experimental results by Chalchat et al.,⁵⁷ P₃ constituted ~40% of the initial product yield from the photochemical hydroperoxidation of limonene.
in the presence of oxygen. In general, photo-oxidation of the products of limonene features −OOH/−OH/−O substitution at para position.7,37 This is consistent with our prediction of P3 as the likely dominant initial intermediate.

A subsequent H-transfer step into the outer OH group in the P3 intermediate liberates a water molecule and forms the experimentally detected product of carvone (P4) via an accessible energy barrier of only 30 kJ/mol.

In addition to carvone, terpene alcohols constitute the major experimentally detected products from the photo-oxidation of limonene. As illustrated above, these molecules most likely arise from a radical-induced mechanism that begins with the fission of the O−OH bonds in the P1−P6 intermediates. For instance, the four para-substituted terpene alcohols account for 60% of the total product yields from the photo-oxidation of limonene.37 Clearly, these compounds may originate from the scission of the O−OH bond in the predicted dominant P3 intermediate followed by H abstraction by the phenoxy-type O atom and structural arrangements. Products feature ipso substitution, most likely directly stemming from the P1 moiety or via an intramolecular transfer of the OOH group along the reaction P3 → P1. Such a step proceeds without encountering a reaction as an intrinsic barrier in a thermodynamically neutral reaction.

2.1.2. Pinene. Figures 7, 8, and 9 depict the optimized structures of α- and β-pinene. The f−1 indices (Figure 2) reveal

![Figure 6. Plot of branching ratios of different reaction pathways as a function of temperature (K).](image)

![Figure 7. Structures of para-substituted terpene alcohols.](image)

![Figure 8. Structures of ipso-substituted terpene alcohols.](image)

![Figure 9. Optimized structures of α-pinene (left) and β-pinene (right) computed at B3LYP/6-311+g(d,p) level of theory.](image)

C2 in α-pinene and C1 in β-pinene structures as the most preferred sites of interaction with electrophilic species. We were unable to locate the transition structures for the [2 + 2]-cycloaddition of singlet oxygen to pinene, certifying that the formation of hydroperoxides as the sole light-induced oxidation product of α- and β-pinene stems from ene-type reaction.

The reaction mechanisms of the singlet oxidation of α- and β-pinene are displayed in Figures 10 and 11, respectively. The figures reveal that the ene reaction proceeds with the addition of singlet oxygen to the in-ring C2 atom of α-pinene and the abstraction of allylic hydrogen from the methyl group via concerted or stepwise mechanisms. The stepwise TS2 barrier overshoots the concerted TS1 by 20 kJ/mol, leaving the concerted mechanism as the dominating reaction pathway for the formation of P1 hydroperoxide. The product P1 is also

![Figure 10. Reaction mechanism of the singlet oxidation of α-pinene. The enthalpies are obtained at the 6-311+g(d,p) level of theory and are in kJ/mol.](image)

![Figure 11. Reaction mechanism of the singlet oxidation of β-pinene. The enthalpies are obtained at the 6-311+g(d,p) level of theory and are in kJ/mol.](image)
attainable through a stepwise channel via a facile transformation of the diradical (P₂) to hydroperoxide (P₁).40 Jefford et al.4 recorded similar observation, identifying P₁ as the utmost product from the ¹O₂-initiated atmospheric oxidation of α-pinene.

Moreover, as shown in Figure 11, the ene-type addition of the singlet oxygen to C₁ atom within a β-pinene structure (the one with the highest Fukui function value) occurs similarly in both stepwise and concerted fashions through TS₁ (57 kJ/mol) and TS₄ (49 kJ/mol) steps. Apparently, the concerted mechanism (TS₄) is the governing reaction channel triggering the formation of P₂ hydroperoxide as the major product of the singlet oxidation of β-pinene. The stepwise TS₁ channel, on the other hand, gives rise to the production of a diradical P₀, which further branches into two exit routes, resulting in two types of hydroperoxide adducts, P₂ and P₃. The product P₂ resides in a significant well-depth in reference to the entrance channel, affirming its greater stability as compared to P₃ hydroperoxide. Besides, TS₂ signifies a trivial transition barrier leading to the formation of the main product P₂.

Table 3 presents the fitted Arrhenius parameters. According to the computed reaction rate coefficients, the α-pinene + O₂

| reaction | A (s⁻¹ or cm³ molecule⁻¹ s⁻¹) | Eₐ (kJ/mol) |
|----------|-------------------------------|------------|
| α-pinene + O₂ ¹Δₓ → P₁ | 2.51 × 10⁻¹³ | 57 |
| α-pinene + O₂ ¹Δₓ → P₂ | 3.50 × 10⁻¹³ | 63 |
| P₁ → P₁ | 3.19 × 10⁻¹² | 12 |
| β-pinene + O₂ ¹Δₓ → P₁ | 1.18 × 10⁻¹³ | 64 |
| P₁ → P₂ | 2.93 × 10⁻¹² | 25 |
| P₁ → P₃ | 1.16 × 10⁻¹² | 45 |
| β-pinene + O₂ ¹Δₓ → P₁ | 2.99 × 10⁻¹² | 56 |

¹Δₓ reaction proceeds predominantly by the ene addition of the singlet delta oxygen to C₂ atom to form P₁ hydroperoxide in a concerted mechanism. Oxidation of β-pinene by ¹O₂ similarly proceeds through a concerted channel, giving rise to the formation of P₁ hydroperoxide via an enthalpy barrier of 49 kJ/mol.

Data in Table 3 afforded the estimation of the branching ratios of the bimolecular reaction channels for α- and β-pinene as shown in Figure 12. In view of this finding, the concerted TS₁ channel remains the dominant reaction pathway for the singlet oxidation of α-pinene, and there exists a moderate decline in the branching ratio value as the temperature increases, reflecting the reverse effect of temperature on the reaction rate constant of the concerted mechanism of the singlet oxygen addition to α-pinene.

In a similar fashion, the concerted TS₄ step leads to the reaction pathways for the singlet oxidation of β-pinene and the calculated branching ratios show that the contribution of the concerted mechanism (k₄) noticeably diminishes as the temperature increases. Nonetheless, at atmospheric relevant temperatures (i.e., 300 K), reaction of β-pinene with singlet oxygen largely ensues via the concerted mechanism.

2.1.3. Camphene and Sabinene. There exists a resemblance between the structure of camphene (Figure 13) and β-pinene owing to the presence of an exocyclic double bond. Therefore, the addition of a singlet oxygen to camphene in an ene reaction mode occurs at the C₁ position via a stepwise mechanism.

According to the mechanism of the singlet-oxygen-initiated atmospheric oxidation of camphene shown in Figure 14, the initial reaction between camphene and singlet oxygen
comprises O₂ \( \Delta g \) addition to the terminal carbon atom of C₁ via sizable thermal enthalpy (TS₂) amounting to 132 kJ/mol. The resulting highly unstable diradical (P₂) is then transformed to the P₃ hydroperoxide adduct through a readily accessible transition state TS₃ through an enthalpic barrier of 30 kJ/mol.

Table 4 assembles the fitted high-pressure limiting Arrhenius parameters. The relatively high activation barrier of camphene

| reaction | \( A \) (s⁻¹ or cm³ molecule⁻¹ s⁻¹) | \( E_a \) (kJ/mol) |
|----------|-------------------------------|-----------------|
| camphene + O₂ \( \Delta g \) \( \rightarrow \) P₁ | 1.15 \( \times \) 10⁻¹² | 139 |
| P₁ \( \rightarrow \) P₂ | 3.58 \( \times \) 10⁻¹² | 33 |

Table 5. Arrhenius Parameters for Sabinene Oxidation by Singlet Oxygen

| reaction | \( A \) (s⁻¹ or cm³ molecule⁻¹ s⁻¹) | \( E_a \) (kJ/mol) |
|----------|-------------------------------|-----------------|
| sabinene + O₂ \( \Delta g \) \( \rightarrow \) P₁ | 5.12 \( \times \) 10⁻¹⁵ | 62 |

According to Figures 17 and 18, the effect of solvent is revealed through a systematic energy reduction in the barrier enthalpies of the transition states, intermediates, and final products along the major channels of the singlet oxygen interaction with each monoterpene substrate. The reduced enthalpies (involving solvent effect) with reference to the gas-phase system range from 12 kJ/mol (P₁ value in \( \alpha \)-pinene) to 34 kJ/mol (P₇ value in limonene). Although the reaction barrier enthalpies are influenced by solvent effects, the product distribution and reaction channels remain intact.

3. CONCLUSIONS

Introduction of singlet oxygen to the cyclic monoterpenes exclusively follows the ene reaction pathway to yield the corresponding allylic hydroperoxides. Limonene and sabinea photo-oxidation transpire through concerted mechanisms, whereas singlet oxidation of \( \beta \)-pinene and camphene proceed via stepwise mechanism, resulting in the formation of diradical intermediates. In the case of \( \alpha \)-pinene, the concerted channel ensues the most energetically favorable pathway. In terms of reactivity, \( \alpha \)-pinene and sabinea exhibit the highest reactivity, while camphene is kinetically evidenced to be the lowest reactive species incurring relatively high activation energy of 139 kJ/mol.

4. METHODOLOGY

Gaussian 09 program⁴⁴ deployed the unrestricted density functional theory in acquiring optimized energies and geometries of the reacting species due to its accuracy in computing singlet biradical properties.⁴⁵,⁴⁶ For that reason, we utilize the B3LYP functional with the extended 6-311+g(d,p)⁴⁷ basis set.
A simple approximate spin-projection (AP) scheme\textsuperscript{48,49} served to correct the final energies of species displaying biradical characters. For this, the approximate spin-projected energy \( E^{\text{AP}} \) has been derived from the energies of the broken-symmetry \( E^{\text{BS}} \) and pure high-spin \( E^{\text{HS}} \) states according to eq 1.

\[
E^{\text{AP}} = f^{\text{AP}} E^{\text{BS}} - (f - 1) E^{\text{HS}}
\]

where \( f^{\text{AP}} \) denotes the spin-projection factor

\[
f^{\text{AP}} = \frac{\langle S_z^{2}\rangle^{\text{HS}} - s(s + 1)}{\langle S_z^{2}\rangle^{\text{HS}} - \langle S_z^{2}\rangle^{\text{BS}}}
\]

and \( \langle S_z^{2}\rangle^{\text{HS}} \) and \( \langle S_z^{2}\rangle^{\text{BS}} \) signify the expectation values of the spin contamination pertinent to the pure high-spin and broken-symmetry states, respectively. We verified the transition structures via intrinsic reaction coordinate calculations. ChemRate software\textsuperscript{50} facilitated the calculation of the reaction rate constants, within the temperature range of 300 – 600 K based on the Arrhenius equation. The electrophilic Fukui indices, serving as indicators for molecular site’s reactivity toward electrophilic addition reactions, are quantified by Dmol\textsuperscript{3} code\textsuperscript{51} in Material Studio package at the B3LYP functional while applying a double numerical plus d-functions atomic basis set.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This study has been supported by grants of computing time from the National Computational Infrastructure (NCI) in Canberra and the Pawsey Supercomputing Centre (iVEC) in Perth. N.Z. acknowledges the Iraqi government for awarding PhD scholarships.

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