Indian Journal of Chemistry
Vol. 65, June 2026, pp. 624-628
DOI: 10.56042/ijc.v65i6.21916

Note

DFT study of the oxonium addition reaction on the double bonds of limonene

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Received 23 July 2025; accepted (revised) 10 June 2026

This research aims to theoretically explore the reaction between limonene and hydrochloric acid (HCl) using the density functional theory (DFT) method with the RB3LYP/6-311G model. From a thermodynamic perspective, it justifies the possibility of the reaction and predicts the resulting product. Fukui indices are used to identify the preferred sites for the nucleophilic attack of limonene on the oxonium ion H_3O^+. The transition states of the reactions are calculated and discussed. Finally, global reactivity indices are examined to support the stability of the formed compounds, particularly α-terpinol and β-terpinol.

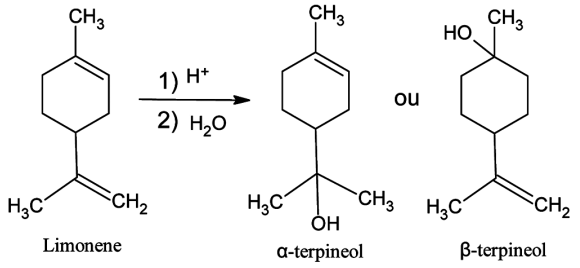
Keywords: DFT, FUKUI indexes, Global reactivity indices, Limonene, Nucleophilic

Monoterpenes are compounds naturally emitted by wood-based materials, as well as paints, varnishes, and cleaning products[1,2]. Thus, monoterpenes could directly and indirectly influence indoor air quality. Some articles have demonstrated the involvement of high concentrations of monoterpenes in triggering skin irritations, eye discomfort, and mucous membrane irritation in humans. They can even cause allergies[3,4]. Monoterpenes with unsaturated carbon-carbon bonds can react with various oxidizing agents such as O_3 and the radicals OH° and NO_3°, which have been found in indoor environments[5-8]. As secondary plant metabolites, monoterpenes exhibit a highly diverse chemical nature. They enable plants to defend against biotic and abiotic stress factors, serve as chemical signals through which the plant communicates with its environment (including other plants and organisms), lack a universal function, and are differently represented in various plant families, genera, and species. This diversity makes them useful as chemotaxonomic markers[9,10].

Limonene, a monoterpene belonging to the terpene family, is a molecule with a dual nature. Through the lens of a mirror, one side reveals the fragrance of lemon, while the other emanates the scent of orange, containing D-limonene (or R (+) -limonene). It is obtained through the distillation of essential oil extracted by steam distillation from the orange peel, with the fruit pulp being utilized for its juice. Limonene, the most extensively studied terpene, is recognized as a skin sensitizer, along with its oxidation products (carvone, limonene oxide, limonene-2-hydroperoxide)[11,12]. Limonene is also listed among the contact allergens identified by the Scientific Committee on Cosmetic and Non-Food Products (SCCNFP)[12-14].

In this article, we conducted a theoretical study on the reaction between limonene and hydrochloric acid (HCl) in an aqueous environment. The resulting compound obtained is α-terpineol and β-terpineol. This reaction is expressed as shown in Scheme 1.

The density functional theory (DFT) calculation method was employed in this study utilizing the B3LYP function along with the 6-311G basis set[15-19]. We investigated the thermodynamic aspects of the possibility and stereoselectivity of the reaction between limonene and hydrochloric acid (HCl). The properties of the products were determined using the Fukui indices approach for the limonene reactant. The chemical reactivity of these products was interpreted through the analysis of global reactivity indices, which included HOMO-LUMO energy gaps, ionization potential (I), electron affinity (A), electrophilicity index (ω), chemical potential (μ), hardness (η), softness (S), and overall electrophile index (ω).



Scheme 1 — Oxonium addition reaction on the double bonds of limonene.

Materials and Methods

Theoretical calculations are based on the Density Functional Theory using the hybrid functional B3LYP with a 6-311G basis set through Gaussian 09 software[15-19]. The electronic structures of the stationary points were determined using Becke's three-parameter hybrid exchange functional associated with the gradient-corrected correlation functional of Lee, Yang, and Parr B3LYP methods and have been analyzed by the natural bond orbital method (NBO[20-22]. In addition to optimizing the geometry of α-terpineol and β-terpineol, Initially, we calculated the thermodynamic parameters ΔE_r , ΔH_r and ΔG_r we delved into their chemical reactivity through a comprehensive analysis of various global reactivity indices including ionization potential(I)[23], electron affinity (A),[24] electronegativity (χ),[25] hardness η,,[26] softness (S)[27], overall electrophile index ω[28]. Which are based on the energy of the HOMO and the LUMO. Aiming to generate a stable structured product within these two structures.

- The ionization energy or ionization potential (I), defined as the minimum energy required to extract an electron from an atom or molecule, has been calculated by the following relationship:

$$I = -E_{HOMO} \quad \ldots \text{Eq. (1)}$$

- The electron affinity (A) denoting the released energy due to the capture of an electron has been estimated *via* the following relation:

$$A = -E_{LUMO}. \quad \ldots \text{Eq (2)}$$

$$\mu = \frac{-(I+A)}{2} \quad \text{Eq. (3)}$$

$$\eta = \frac{I-A}{2} \quad \ldots \text{Eq. (4)}$$

$$S = \frac{1}{\eta} \quad \ldots \text{Eq. (5)}$$

$$\omega = \frac{\mu^2}{2\eta} \quad \ldots \text{Eq. (6)}$$

Result and Discussion

Thermodynamic study

We have studied from a thermodynamic perspective the possibility of the reaction of limonene with hydrochloric acid in an aqueous medium, In order to predict the possibility of the formation of α-terpineol and β-terpineol and to compare the reactivity of these molecules, we determined under standard conditions of temperature and pressure (T = 298.15 K; P = 1 atm (1 atm = 101.325 kPa)), the variations in reaction energy ΔE_r, variations in reaction enthalpy ΔH_r, variations in reaction free enthalpy ΔG_r, and the Zero Point Energy (ZPE) corresponding to reactions I. As shown in Table 1, the variations in reaction free enthalpy ΔG_r are all negative; therefore, these reactions are thermodynamically possible and favored. Furthermore, we have observed that the value of the reaction free enthalpy changes ΔG_r, corresponding to reaction II, is higher in absolute value than the value of the reaction free enthalpy changes corresponding to reaction I. This led us to conclude that reaction II is thermodynamically more stable than reaction I. Therefore, the C15=C20 double bonds in the limonene molecule are more reactive than the C4=C5 double bond belonging to the same molecule (Fig. 1).

In the same way, we found that the value of the change in energy ΔE_rcorresponding to reaction II is higher in absolute value than the value of the change in energyΔE_rcorresponding to reaction I. This confirms once again that the C15=C20 bond in the limonene molecule is more reactive than the C4=C5 double bond in the same molecule. Therefore, the reaction II is thermodynamically more stable than reaction I.

Prediction of local reactivity of reactants using FUKUI indexes for limonene

Local Fukui functions (FFs) are tools that are useful for assessing the reactivity of various sites in the reactant molecules for nucleophilic (f_K^+) and electrophilic (f_K^-) attacks[29].

The FFs can be calculated with the two Equations, respectively:

$f_K^+ = [q_K(N+1) - q_K(N)]$, for a nucleophilic attack

$f_K^- = [q_K(N) - q_K(N-1)]$, for an electrophilic attack

Or $q_K(N)$, $q_K(N+1)$ and $q_K(N-1)$ corresponding to the electronic population of the K atom in the neutral, anionic, and cationic molecule, respectively. it can be inferred that the most active centers in the second-degree Fukui indices f_k^2 have values greater than zero[30].

One can observe from Table 2 that among the carbon numbers 4 and 15 in limonene, higher f_K^+ values are

Table 1 — Calculated values (kcal.mol^{-1}) of reaction energy variations ΔEr, reaction free enthalpy variations ΔGr, reaction enthalpy variations ΔHr, and the zero-point energy (ZPE)

	The products	ΔE_r	ΔE_r + ZPE	ΔH_r	ΔG_r
		B3LYP / 6-311G			
Reaction..I	α-terpineol	–466,827380	–933,667076	–466,826436	–466,877291
Reaction. II	β-terpineol	–466,829023	–933,669747	–466,828078	–466,877305

exhibited. This suggests that these sites are more likely to be attacked by the nucleophile OH^-Alternatively, carbon 15 has a lower value of the second-degree Fukui indices f_k^2. Besides, the attack reaction on carbon 15 is more favorable than that on carbon 4, which helps to justify that the attack on carbon 15 ultimately leads to the formation of a more stable β-terpineol compound than α-terpineol.

Study of Transition States

We optimized the transition states of the acidification reaction in aqueous solution of limonene. The action was performed on the double bond, whether inside or outside the reacted molecule's cycle. We obtained two conformations of the transition states.

Theoretical calculations indicate that the formation of the β-Terpineol compound is favored compared to that of the α-Terpineol compound. Using DFT/B3LYP calculation methods with the standard 6–311G basis set, we observed a significantly higher Hartree-Fock energy for the formation of the β-Terpineol compound ($|E_{HF}| = 467{,}1046\ a.u$)), in comparison to the α-Terpineol compound ($|E_{HF}| = 467{,}1027\ a.u$), as illustrated in Fig. 2. This difference accounts for the increased stability of the β-Terpineol compound.

Study of global reactivity

The HOMO-LUMO gap is the energy difference between the occupied electronic orbitals and the lowest unoccupied ones. Its significance lies in the electronic and optical properties of products, and their chemical reactivity prediction[31,32]. The HOMO represents the highest orbital containing electrons, while the LUMO corresponds to the empty orbital just above the HOMO. When the gap is relatively small, electrons can easily move from the HOMO to the LUMO. The calculated reactivity indices are summarized in Table 3. The chemical hardness ($\eta = (E_{LUMO}-E_{HOMO})/2$) measures the resistance of a molecule system to electron transfer and evaluates the ability of a compound to accept or donate electrons during a chemical reaction. The higher the charge of molecules, the greater their chemical hardness. Table 3 shows that α-terpineol represents a lower hardness compared to β-terpineol (η=3,5465eV), implying that this molecular retains fewer electrons in its environment. The chemical potential ($\mu = (E_{LUMO}+E_{HOMO})/2$) is a thermodynamic quantity that measures the potential energy of a system to undergo a chemical reaction. This parameter plays a crucial role in the study of chemical reactions and allows the prediction

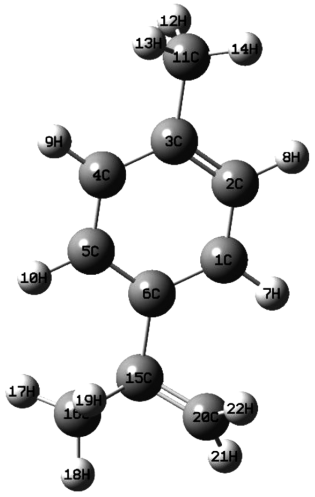


Fig. 1 — Optimized geometry for the limonene compound

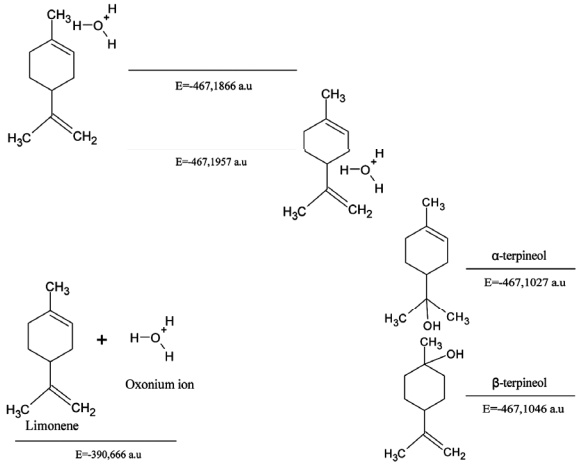


Fig. 2 — Energy profile of reactions leading to α-Terpineol and β-Terpineol compounds.

Table 2 — FUKUI indexes for Limonene

Limonene atoms	f_K^+	f_K^-	$f_k^2 = f_K^+ - f_K^-$
C_4	–0,106	–0,193	0,087
C_5	–0,140	–0,193	0,053
C_{15}	–0,049	–0,069	0,020
C_{20}	–0,122	–0,144	0,022

Table 3 — HOMO and LUMO energies, energy difference ΔE, chemical potential, softness, chemical hardness, electrophile index, and dipole moment of the α-terpineol and β-terpineol

Products		E_{LUMO} (eV) ±0,0002	ΔE(eV) ±0,0002	η (eV) ±0,0002	S (eV^{-1}) ±0,00002	μ (eV) ±0,0002	ω (eV) ±0,002
α-terpineol	–6,1559	0,6392	6,7951	3,3975	0,2943	–2,7584	1,1198
β-terpineol	–6,7279	0,3652	7,0931	3,5465	0,2820	–3,1814	1,4269

of the direction in which a chemical reaction is likely to proceed toward equilibrium. The higher chemical potential of α-terpineol (μ = -2,7584 eV) should also be noted. Additionally, the softness values (S) demonstrate a minimum value (indicative of high reactivity) corresponding to α-terpineol. This observation is consistent with the results obtained from the gap (ΔE) study.

The global electrophilicity index (ω) has also been calculated to assess the reactivity of α-terpineol and β-terpineol with respect to electrophilic reactions. It is based on the fact that the electrophilic reactions involve the attack of an electrophilic compound on a nucleophilic site. According to Table 3, the β-terpineol exhibits a higher electrophilic index (ω = 1,4269 eV), suggesting that this product is more electrophilic.

These results have allowed us to conclude that Reaction II is more favored than Reaction I, thereby confirming the findings previously obtained through thermodynamic analysis. It can be inferred that β-terpinene is more stable than α-terpinene.

Conclusions

In this word, we conducted a theoretical examination of the reaction between limonene and oxonium ion, with a specific focus on the two double bonds C4=C5 and C15=C20 within the same molecule of the reactant. Theoretical calculations were performed using the DFT/B3LYP method and the standard 6-311G basis set. The obtained results are as follows:

- Thermodynamic analysis supports the feasibility of this reaction.
- The prediction of the local reactivity of reactants, utilizing FUKUI indices for limonene, identified the sites susceptible to attack.
- Investigation of the transition state was carried out. A global reactivity study was conducted to justify the molecular stability.

Finally, we concluded that β-terpineol is more stable than the α-terpineol compound.

Acknowledgements

We extend our sincerest gratitude to all individuals who contributed to the completion of this article, including our colleagues for their valuable insights and feedback, the reviewers for their meticulous assessment, and the editorial team for their guidance throughout the publication process.

Authors' contributions

Abdelahad. El Addali: Visualization, Writing - review & editing. Ismail. Hassab: Conceptualization, Methodology, Software, Formal analysis, Writing - review & editing. Zakaryae. El-Kiri: Conceptualization, Methodology, Software, Formal analysis, Writing - review & editing, Supervision. Abdellah EL Boukili, Lahcen boudad, Bouchra. Maroufi and Chakir. El Mahjoub: Resources.

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