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Theoretical and Experimental Study of the Functionalization Reaction of Allyl Glycidyl Ether with Sodium Hydrosulfide

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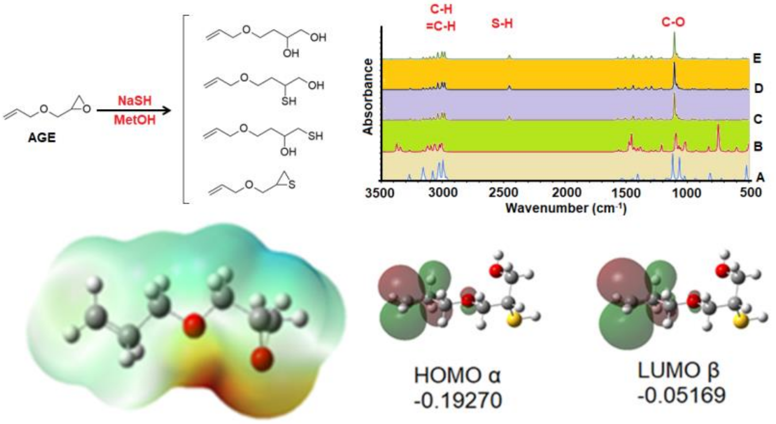
Graphical Abstract



Abstract. The spectral and theoretical analysis of functionalization reaction of 2-(prop-2-enoxymethyl) oxirane, also known as allyl glycidyl ether (AGE), with sodium hydrosulfide (NaSH), was carried out; employing the theory level DFT/B3LYP/6-31 + G (d,p) in Gaussian 09, the free software Multiwfn, and spectroscopic techniques (FTIR-ATR and Uv-Vis). Some of the potential products of this reaction are molecules of interest due to its potential application in the synthesis of polymers with relevant properties in storage and preservation systems, immobilization of thiolated molecules by disulfide bonds, and obtaining of nanostructured surfaces by coordination of noble metals. Theoretical results evidenced that the region of lower electron density of the allylic precursor corresponds to the carbons of the three-membered cycle in which nucleophilic addition occurs. Regarding the Uv-Vis analysis, this allowed determining that the theoretical results correlate with those obtained experimentally, with an energy absorption between 250 and 300 nm, and a band profile similar to that established theoretically for the episulfide derivative. On the other hand, the experimental infrared analysis of the product showed the presence of signals that are agree with the obtaining of 4-(allyloxy)-2-mercaptobutan-2-ol as the predominant reaction product of AGE and NaSH in methanol, this result being a consequence of the alkaline medium generated by the thiolating agent. In this way, is established that the functionalization conditions that favor the obtaining of 4-(allyloxy)-2-mercaptobutan-2-ol correspond to an AGE:NaSH 1:2 ratio in an alcoholic buffer system of a pH range of 7.0 – 8.0, which prevents the hydrolysis of the epoxide and the protonation of the thiolating agent.

Keywords: allyl monomer, epoxide, thiol compounds, α and β orbitals

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1. Introduction

In organic synthesis one of the most versatile intermediaries corresponds to the epoxy functional group. This organic compound contains a three-member cyclic ether that exhibits a high reactivity due, primarily, the angular tension present in the ring and the inductive effect generated by the presence of the oxygen atom; the molecules that present this functional group commonly undergo nucleophilic addition reactions, being able to obtain 1,2-disubstituted compounds with good yields by simple protocols [1-2]. This type of chemical reactions of the epoxy group is known as “epoxy click", characterized as a high-efficiency process influenced by steric factors and the pH; with the primordial advantage that can be developed at room temperature and, in the majority of cases, in the absence of catalysts, obtaining as a product of molecules with the presence of a primary or secondary alcohol, which exhibits the ability to undergo a second functionalization [3-8].

Some of the functionalizations carried out by the ring-opening reaction of the epoxy group include the synthesis of compounds such as acylomercaptans, hydroxy ethers, cyanohydrins, mercapto alcohols, among others [3-7]. Regarding the obtaining of sulfur compounds by opening epoxy groups have been developed protocols to synthesize, primarily, bis(hydroxyethyl thioethers), β-hydroxy thioethers, and β-mercapto alcohols [4-5, 9]. Concerning the first of these compounds, Azizi *et al* developed a high-performance organic synthesis method consistent with the principles of green chemistry, in which sodium sulfide is used as a sulfurizing agent for epoxides, obtaining the corresponding bis (hydroxyethylthioether) [9]. Likewise, Mesropyan *et al* reported the obtaining of bis(hydroxythioether) molecules by reaction with aromatic dithiols as sulfurizing agent [10]. On the other hand, the obtaining of β-hydroxythioethers is carried out by the reaction between the three-membered ring with molecules that have the thiol functional group, this chemical reaction is known as thiol-epoxy "click", characterized by presenting a high yield and constitute a regioselective process, and the resulting compound presents a reactive hydroxyl group; an example of this is the polymers obtained by Stuparu and Khan, who found that in the nucleophilic substitution reaction the thiol group is first transformed into thiolate ions and these are the ones that effect nucleophilic carbon attack of the epoxide ring [4]. Also, the obtaining of β-hydroxy thioethers using cyclic thiols has been reported and it has established that the synthesis of these compounds can be promoted by the addition of Lewis acids such as thionyl chloride ($COCl_2$) or boron trifluoride (BF_3), and by the addition of basic catalysts such as alumina or quaternary amines [5, 11].

Concerning the obtaining of β-mercapto alcohols or β-hydroxy mercaptans, several agents have been reported to obtain the thiol group, such as hydrogen sulfide, thiourea, or sulfur sodium borohydride. In the case of the research developed by Degl'Innocenti *et al* the synthesis of a sulfur compound derived from an organosilane was carried out to obtain the β-mercapto alcohols [5]; likewise, Wu *et al* developed the synthesis of a β-hydroxy mercaptan by functionalizing 1,2-epoxy-4-methyl pentane in carbon disulfide with the addition of sodium hydrogen sulfide in methanol, obtaining as a product 1-mercapto-4-methyl-2-pentanol [7]. In turn, Goodman *et al* used the protocol developed by Van Tamelen for the synthesis of trans-2-mercapto cyclo pentanol, using equimolar proportions of cyclopentene oxide and hydrogen sulfide ions, which were synthesized using an adaptation of the protocol used by Culvenor *et al*, in this, the saturation with hydrogen sulfide of a mixture of methanol and sodium hydroxide was carried out to obtain thiolating ions [12-14]. It is relevant to note that the thiolating agent, in this case, corresponds to sodium sulfhydrate (NaSH), a reducing agent derived from hydrogen sulfide, which acts as a thiolated of epoxides, sulfonate esters, halides, and aziridines [14]. The molecules obtained by this reaction present sulfur atoms in their structure, entities of particular interest for the scientific community since the organic compounds that have this element present a wide variety of applications, such as antioxidant agents, enzyme inhibitors, antagonists of calcium channels, antimicrobial agents, stabilizing agents, among others. In addition to this, the resulting compound has a reactive hydroxyl group, which can carry out different functionalization reactions, thereby exhibiting a potential application in surface modification on solids substrates; and can present a thiol group that permits generate disulfide bond formation, coordination of metal nanoparticles, experiment thiol click reactions, allow the immobilization of biomolecules, among others [14-23].

This wide variety of properties allows that the molecules with the presence of a thiol and hydroxyl group in their structure can be used in several applications, such as storage and conservation systems, due to the importance of polymers in this industry, it is of particular interest generate molecules with the presence of a carbon-carbon double bond, that can be polymerizable via free radicals, and a thiol functional group, or an epoxide functional group in which carry out a functionalization to obtain hydroxy mercaptans. An example of this molecules corresponds to an allylic monomer with the epoxide functional group, such as the present in the glycidyl ethers commonly used to obtain epoxy resins, being one of the monomers that meet these characteristics the commercial molecule allyl glycidyl ether [11-13]. Therefore, it is of interest in this investigation analyze the characteristics and properties of the epoxide three-member ring-opening reaction of the AGE using the thiolating agent NaSH, through theoretical and experimental tools, as well as the analysis of the potential products that can be formed according to pH, and the optimization of the reaction conditions.

2. Methodology

It was developed a spectral theoretical study of the precursor 2-(prop-2-enoxymethyl) oxirane and the potential products of its functionalization reaction with sodium hydrosulfide: 4-(allyloxy)-1-mercaptobutan-2-ol (ALLYLMERCAP-2-OL), 4-(allyloxy)-2-mercaptobutan-1-ol (ALLYLMERCAP-1-OL), 4-(allyloxy) butane-1,2-diol (ALLYLDIOL), 2-((allyloxy)methyl)thiirane (ALLYLTHI), using the density functional theory (DFT/B3LYP) with the set of bases 6-31+G (d,p) in Gaussian 09W/Gaussview 5.0.8 software package and Multiwfn software, obtaining the map of electrostatic potential, the infrared and the ultraviolet spectrum

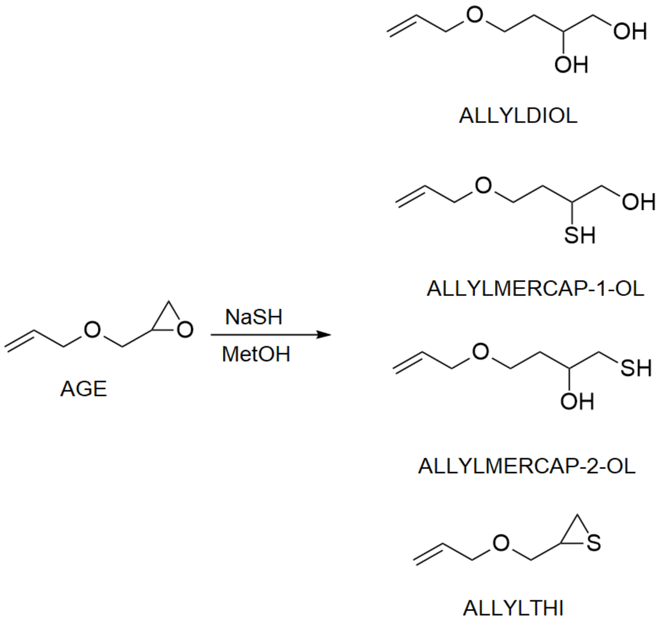

Figure 1. Possible products of the reaction between AGE and NaSH.

of the molecules. The level of theory employed for the study allows to solve the wave function using the Kohn-Sham orbitals and the Becke-3 hybrid base with the Lee-Yang-Parr (B3LYP) correlation, which permits analyze and generate optimal results in organic systems; also, the 6-31G (+) base considers the inclusion of polarization and diffuse functions.

In relation to the experimental procedure, the synthesis reaction was carried out using an AGE:NaSH 1:1 molar ratio, and AGE:methanol 1:2 volumetric ratio, in an ice bath, under constant stirring for four hours; then the product was taken to dryness in an oven heat flow at 50 °C. The product and the precursors were characterized by mid-infrared spectroscopy with Fourier transform in the technique of total attenuated reflectance (FTIR-ATR), using IRAffinity-1s spectrophotometric equipment of Shimadzu Co, with a SeZn crystal. In addition, the effect of the concentration on the chemical reaction was analyzed, varying the AGE: NaSH molar ratio by 1.0:0.5; 1.0:1.0; 1.0:1.5, and 1.0:2.0; and the products were characterized by FTIR-ATR and ultraviolet-visible (UV-vis) spectroscopy in a Shimadzu spectrophotometer UV-1700, PharmaSpec.

3. Results and discussion

3.1. Nucleophilic addition reaction between AGE and NaSH

The epoxy opening chemical reaction is a process of a regioselective nature, which depends on steric factors, electron density, the replacement pattern of the oxirane derivative, and the pH conditions of the reaction medium [24]. For this reaction it has been proposed that under alkaline or neutral conditions steric factors govern the course of the chemical reaction, which occurs through a bimolecular nucleophilic attack of the less substituted carbon nucleophile in an anti-Markovnikov type opening [24]. Concerning to acidic conditions, the process is governed by electronic factors, and it was postulated that the nucleophilic addition occurs through a unimolecular type mechanism, in which the first step is the protonation of the epoxide, then take place the opening of the ring before the addition, or through a bimolecular mechanism in which the attack occurs in concert and a positive charge develops on the more substituted carbon [24-25].

That is, under alkaline conditions the product obtained is that in the nucleophile is added to the less substituted carbon and under acidic conditions, to the more substituted carbon. For this reason, in the chemical opening reaction of the epoxide of the AGE with the thiolating agent NaSH, it can lead to the formation of different products according to the pH conditions, obtaining, in acid medium 4-(allyloxy)-2-mercapto-butan-1-ol, in neutral and basic medium 4-(allyloxy)-2-mercaptobutan-2-ol, and in strong basic medium, hydrolysis of the epoxide, obtaining 4-(allyloxy) butane-1,2-diol, and formation of the episulfide derivative 2-((allyloxy) methyl) thiirane (see Figure 1).

3.2. Map of the electrostatic potential of AGE and its sulfurized derivatives

The reactivity of the epoxide in the AGE molecule can be understood by the angular tension present in the ring and the inductive effect generated by the presence of the oxygen atom. Then, this segment of the molecule is a place with a high electron density in the oxygen atom and low electron density in the carbons bonded to it, which also experience a slight inductive effect of the linear ether found in the next carbon atom, which leads to the carbon atoms in the ring being an electrophile that easily undergo nucleophilic addition reactions [1-2]. This analysis can be evidenced in the electrostatic potential map of AGE (see Figure 2A), generated in the range of values from - 6.676 e^{-2} a.u. to 6.676 e^{-2} a.u., in which is observed that the region of major electronic density is around the oxygen, and the one with the lowest density is in the carbon of cyclic segment, and the carbon adjacent to them. In quantitative terms, the minimum value corresponds to -1.894102 a.u. and is located in the carbon atom adjacent to the three-member cycle, in terms of the maximum of the electrostatic potential, this corresponds to 0.855562 a.u. and is found in the oxygen atom of the epoxy ring.

As regards the hydrolysis product of the AGE in alkaline medium, ALLYLDIOL, in the map of the electrostatic potential of this (see Figure 2B), plotted in a range between - 7.588 e^{-2} a.u. and 7.588 e^{-2} a.u., is possible to identify that the electronic density is concentrated in the oxygen atoms, an event consistent with the electronegativity of these. In turn, as expected, the segments of lower electronic density are found in the carbons adjacent to the electronegative atoms. Presenting the segment with the lowest electronic density, a value of -2.312987 a.u. in the carbon linked to the terminal hydroxyl, this is consistent with the inductive effect of the adjacent alcohol in this germinal diol; as for the maximum electronic density, it has a value corresponding to 1.139621 a.u. and is located in the carbon adjacent to the vinylic bond.

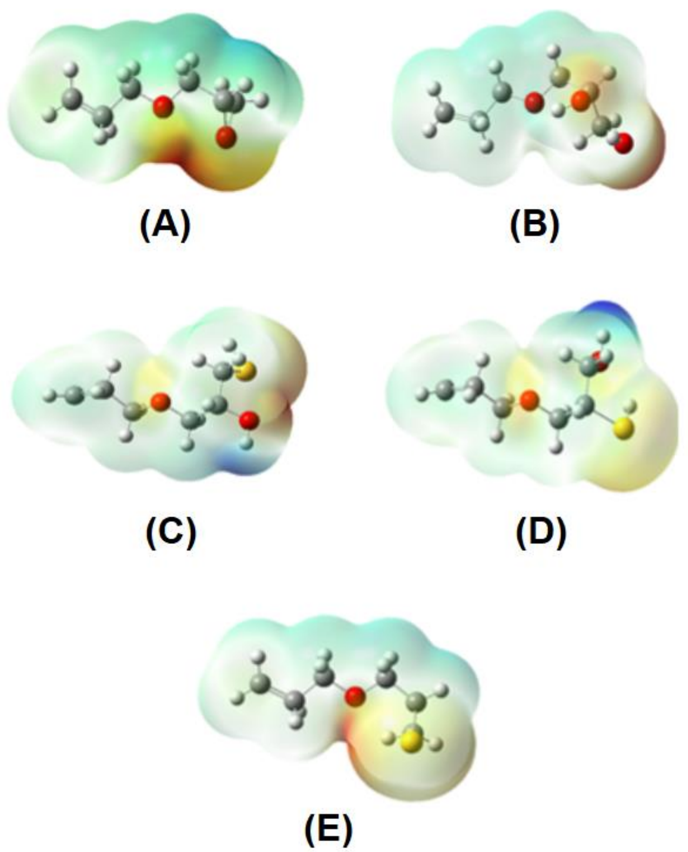

Figure 2. Map of the electrostatic potential of: (A) AGE, (B) ALLYLDIOL, (C) ALLYLMERCAP-2-OL, (D) ALLYLMERCAP-1-OL and (E) ALLYLTHI.

Table 1. Energy difference between type α and β frontier orbitals.

Molecule	ΔE α (Eh)	ΔE β (Eh)
AGE	0.27932	0.20929
ALLYLDIOL	0.29229	0.16841
ALLYLMERCAP-1-OL	0.01900	0.17914
ALLYLMERCAP-2-OL	0.17464	0.17574
ALLYLTHI	0.15796	0.16852

On the other hand, on surface of the electrostatic potential map of the product obtained in a moderated alkaline medium (- 6.473 e^{-2} a.u. – 6,473 e^{-2} a.u.) (see Figure 2C), ALLYLMERCAP-2-OL, a negative charge density is observed around to the oxygen and sulfur atoms, presenting a maximum around the oxygen of the alcohol, with a value of 2.067024 a.u., and a minimum of - 1.997198 a.u. in the segment between the oxygen of the alcohol and the sulfur of thiol. As for its structural isomer, ALLYLMERCAP-1-OL, obtained in an acid medium, the map of the electrostatic potential exhibits a similar behavior (see Figure 2D) (- 6.215 e^{-2} a.u – 6.215 e^{-2} a.u.), presenting a maximum around the oxygen of the alcohol, with a value of 2.215557 a.u., increase associated with the repulsion between the thiol and alcohol groups that adopt a geometry that generates a greater repulsion concerning the ALLYLMERCAP-2-OL; as regards the minimum, this is located in the carbon adjacent to the vinyl bond, with a value of -1.357101 a.u.. The discrepancy in the regions of minimum potential of the isomers is associated with the geometry of ALLYLMERCAP-2-OL, due to this configuration present a major repulsion between the thiol and alcohol groups.

Concerning the episulfide derivative, ALLYLTHI, it is observed that on the map of electrostatic potential (- 5.612 e^{-2} a.u - 5,612 e^{-2} a.u), the electronic density is concentrated around the oxygen atom of the ether bond and the sulfurized three-membered ring (see Figure 2E). Finding that maximum potential energy in the cyclic segment, with a value of 0.930641 a.u.; about the minimum, this is found in the carbon adjacent to the ring, with the value of - 1.855322 a.u., which is associated with the inductive effect exerted by oxygen and sulfur surrounding this atom of carbon.

3.3. Uv-Vis spectroscopy and frontier molecular orbitals

The analysis of the transition of electrons from the basal state to the excited one by promoting them from the HOMO orbital to the LUMO orbital and their evidence by the Uv-Vis spectroscopy was carried out employing the energy analysis of the molecules in DFT based on the theorem of Hohenberg-Kohn, which uses a functional hybrid of energy density, obtaining for the molecular orbitals HOMO and LUMO results of orbitals type α and β, this is associated with the fact that the molecules present a sum of electronic spins different to zero, due to this the substances are not in a state of singlet electronic spin, which generates that the α-type transition is associated with an electron with spin ½ and β to - ½, the border molecular orbitals being different for each transition and the most probable transitions are those with the lowest energy difference [26-27]. Figure 3 illustrates the molecular orbitals HOMO and LUMO of type α and β for each molecule with their respective energy value in Hartrees, from which the energy difference between the two frontier orbitals and the most probable transition is obtained, which are recorded in Table 1. On the other hand, AGE due to the presence of the epoxide group is an electrophile that experiences the nucleophilic attack at the site that has the largest HOMO coefficient, located in the three-member ring region [26].

Regarding the electronic transitions that electrons can present, these are predicted using the approximation of the inharmonic oscillator model, obtaining the force constants associated with the atoms in the bond, the maximum value for the AGE being 0.010, for the ALLYLDIOL 0.010, for ALLYLMERCAP-1-OL 0.010, ALLYLMERCAP-2-OL 0.018 and ALLYLTHI 0.012, values associated with the bonds and their chemical environment. Concerning the predicted Uv-Vis spectra, it shows that the maximum absorption occurs for all molecules between 250 and 300 nm, associated with the electronic transitions n-σ* of the bonds [28]. The episulfide derivate and diol molecules have a profile with two signals that show overlap, and the thiolated molecules and the precursor present a band profile like Gaussian behavior (Figure 3). When comparing the theoretical spectrum with those obtained experimentally for aqueous solutions of 2.5x10^{-5} M of the functionalization ratios AGE:NaSH (see Figure 4), it can be appreciated for each ratios absorption at a wavelength between 200 and 300 nm region in which the transitions of the n-σ* electrons are

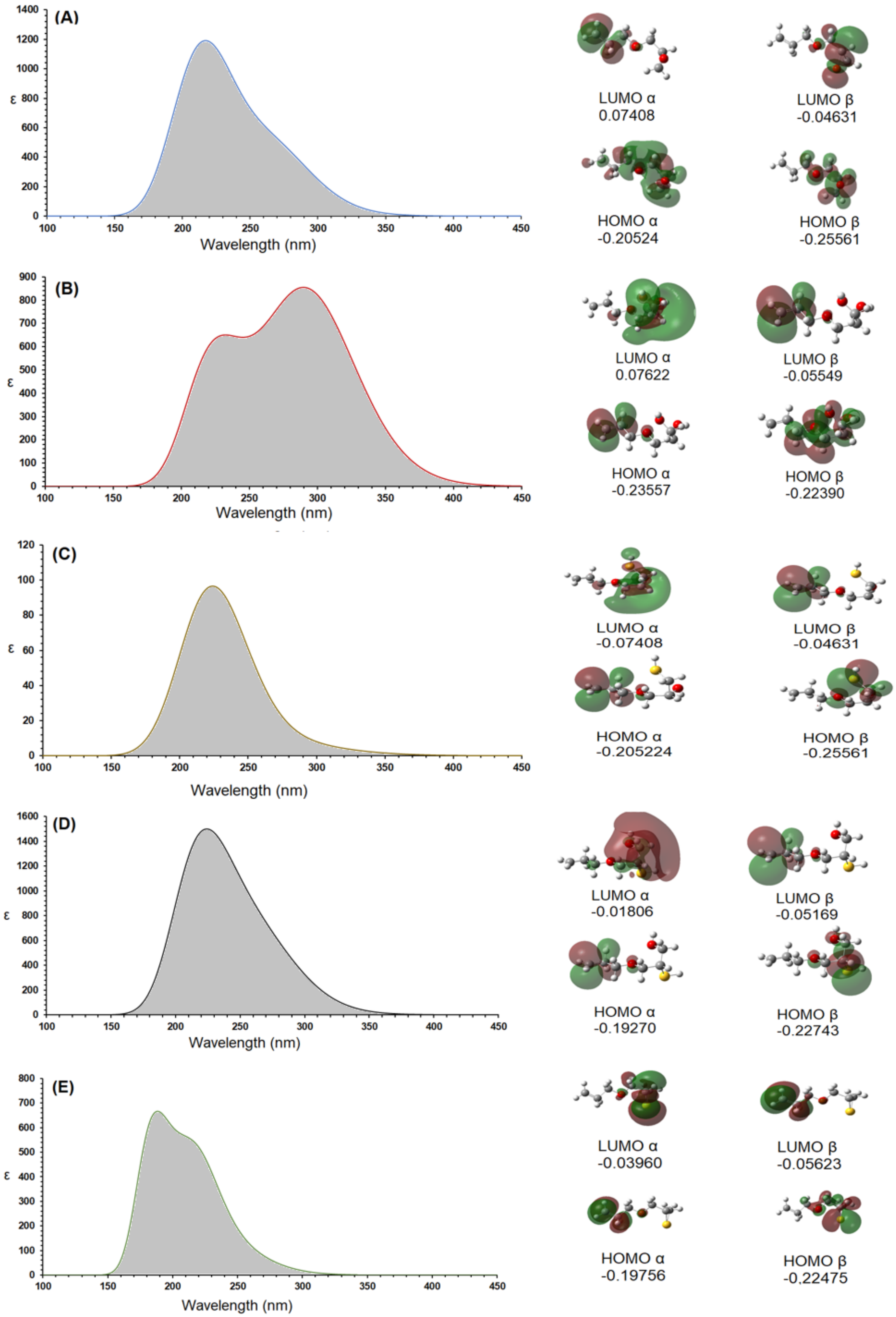

Figure 3. Theoretical Uv - Vis spectra and frontier molecular orbitals α and β of: (a) AGE, (b) ALLYLDIOL, (c) ALLYLMERCAP-2-OL, (d) ALLYLMERCAP-1-OL y (e) ALLYLTHI.

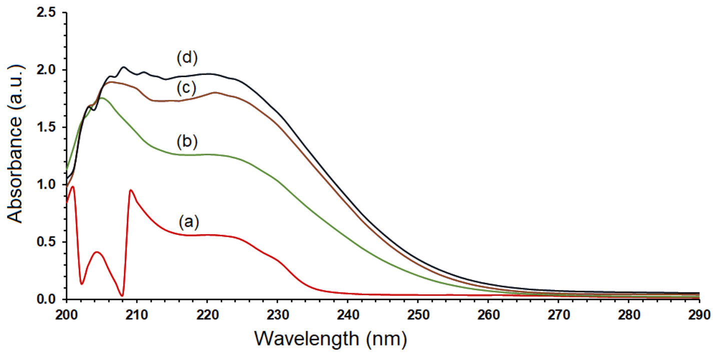

Figure 4. Experimental Uv-Vis spectrum of the AGE:NaSH systems: (a) 1.0:0.5; (b) 1.0:1.0; (c) 1.0:1.5, and (d) 1.0:2.0.

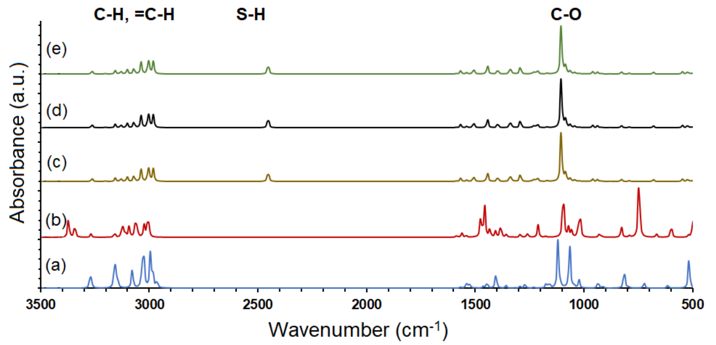

Figure 5. Theoretical mid-infrared spectra of: (a) AGE, (b) ALLYLDIOL, (c) ALLYLMERCAP-2-OL, (d) ALLYLMERCAP-1-OL y (e) ALLYLTHI.

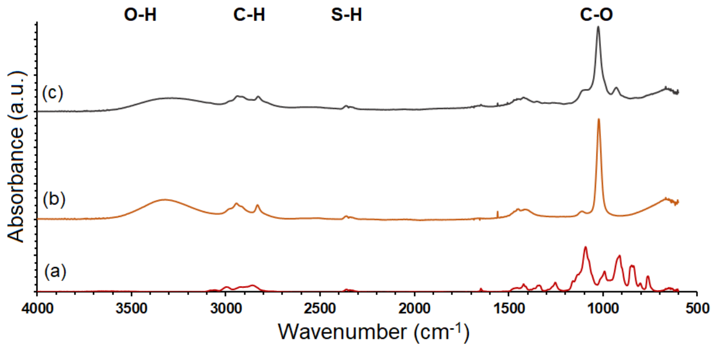

Figure 6. Experimental FTIR spectra of: a) AGE b) NaSH in methanol y c) product of the functionalization reaction of NaSH and AGE.

found, for the other hand, the increase in absorbance is associated with a higher concentration of the functionalized monomer.

It is observed that the experimental Uv-Vis profiles are associated with a behavior similar to the sum of the signals of ALLYLMERCAP-2-OL and ALLYLTHI compounds. In these spectra is evidenced that the contribution of the episulfide derivative is major for the ratios of higher concentration of NaSH, that is, for a reaction system under remarkably alkaline conditions, generated in the dissolution of NaSH in the methanol solvent. On the other hand, it is relevant to point out that the theoretical analysis was carried out considering the optimized geometry of a single molecule in the gaseous state, so that the predominant structure in the system under analysis varies concerning the behavior of the real system with the presence of a greater number of molecules and the interaction with the solvent.

3.4. Infrared spectroscopy

In the theoretical infrared spectrum, it is possible to observe common signals in each spectra (see Figure 5): the symmetric vibration of the C-H bond around 2960 and 2850 cm^{-1}, the asymmetric vibration of the C-H bond near to 2870 and 2930 cm^{-1}, the asymmetric flexion vibration of the C-H of 1470 cm^{-1}, the torsion and wagging vibrations of methylene at 1300 and 1350 cm^{-1}, the rocking of the C-H bond of methylene at 720 cm^{-1}, the signal associated with the tension vibration of =CH in 3100 and 300 cm^{-1}, the tension of C=C at 1680 - 1600 cm^{-1}, the flexion in the plane of =CH at 1400 cm^{-1}, and the signal associated with the tension vibration of the C-O bond of ethers at 1100 cm^{-1}. As for the most characteristic signals of each molecule, it is possible to observe in the AGE spectrum a signal around 900 cm^{-1} associated with the vibration of the C-O bond of cyclic ethers. Concerning the derivatives of the AGE with alcohol functions, the presence of signals associated with the vibrations of the O-H bonds is observed in the area close to 3000 - 3500 cm^{-1}. On the other hand, the sulfurized derivatives, present a characteristic signal related to the vibration of the S-H link at 2500 cm^{-1}, and a signal at 500 cm^{-1} associated with the C-S links [29].

On the other hand, the experimental results of the FTIR spectra (see Figure 6) of the product was compared with that of the corresponding precursors, observing that in the product spectrum there is a decrease in the signal associated with the deformation vibration of the epoxy group around 900 cm^{-1} compared to the AGE spectrum, which allows inferring the ring-opening associated with the functionalization of the monomer through the thiolating agent; besides, it is possible to observe around 2500 cm^{-1} a signal of weak intensity associated with the presence of S-H bond type. Notably, the characteristic signals theoretically predicted for the substances are observed in the experimental spectrum, decreasing their resolution due to molecular interactions and the capacity of the instrumental equipment; also, in the product spectrum, it is possible to evidence a signal associated with the S-H bond that is observed in the theoretical spectrum of thiolated compounds, which allows demonstrating the synthesis of molecules with the presence of these bonds, additionally, it is observed a signal of weak intensity close to 800 cm^{-1} that is evidenced in the spectrum of ALLILMERCAPTO-2-OL, the major product expected in reactions at moderately alkaline pH [29].

As for the analysis of NaSH concentration in the AGE functionalization, the vibration band of the O-H bond for the reaction mixtures is associated with the presence of methanol in them, additionally is observed in the AGE spectrum the vibration of asymmetric tension of the bonds of the epoxide group in the region between 800 and 900 cm^{-1}, likewise, by increasing the concentration of NaSH in the reaction is evidence the decrease of this band, associated at the opening of the 3-member cycle; as the increasing

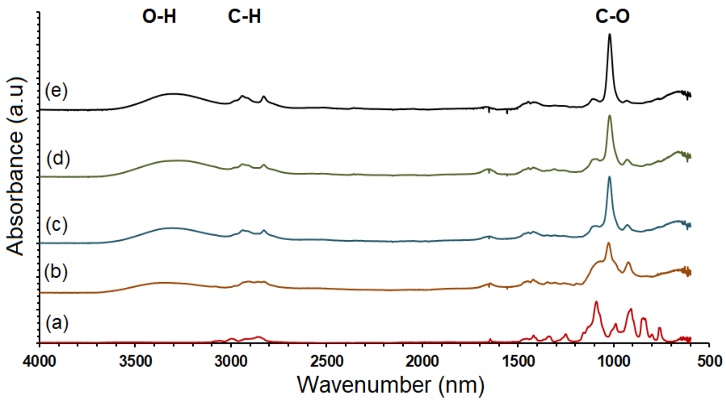

Figure 7. Experimental FTIR spectra of the AGE:NaSH molar relations a) 1.0:0.0; b) 1.0:0.5; c) 1.0:1.0; d) 1.0:1.5 y e) 1.0:2.0.

of NaSH in the reaction is evidence the decrease of this band, associated at the opening of the three-member cycle; as the increasing of the signal associated with the vibration of the C-O bond, the band close to 1200 cm^{-1}, and a displacement of this is observed in the reaction mixtures associated with the opening of the ring, that is, the absence of angular tension in the product, therefore, link vibrations occur in regions of lower energy. On the other hand, the signals of bond vibrations of the thiol group around 2500 cm^{-1} are not observed in the spectrum since these are bands of weak intensity. On the other hand, the isomers of β-hydroxy mercarptans are primarily differentiated by a signal close to 800 cm^{-1}, finding that the experimental spectra of the product are similar to the ALLYLMERCAPTAN-2-OL derivative, the expected compound of the reaction in moderated alkaline mediums.

The comparison between the theoretical and experimental results shows that the expected products in the reaction of functionalization of NaSH with AGE in methanol, can be associated primarily with ALLYLMERCAPTAN-2-OL and ALLYLTHI, molecules obtained in the reaction in an alkaline medium, a result of the dissolution of the NaSH compound in the solvent, in which are generated SH^- ions in the system, that reacts with the acidic protons of the alcohol, increases the pH of the medium to values close to 12, conditions in which the formation of the anti-Markovnikov product and the formation of episulfides is favored. Therefore, this approach to the study of the reaction allows to affirm that the appropriate reaction conditions for the opening of an epoxide functional group by the thiolating agent NaSH, must be carried out in a buffer medium with a pH in a range between 7.0 - 8.0, due to the fact that at a lower pH the SH^- ions undergo protonation generating SH_2, thus reducing the thiolating agent; in turn, at a higher pH, epoxide hydrolysis reactions and the formation of episulfides are favored.

4. Conclusions

The theoretical study, with DFT/B3LYP/ 6-31 G + (d, p), of the expected products in the functionalization reaction of the 2-(prop-2-enoxymethyl) oxirane with sodium hydrosulfide as a function of pH, was executed. The results allowed to evidence the charge density on the map of the electrostatic potential of the possible products is around the cyclic members and/or the oxygen and sulfur atoms. Also, it was analyzed the transitions of the HOMO - LUMO orbitals of type α and β associated with the promotion of electrons from the basal to the excited state in non-singlet electronic states, which for the studied molecules were evidenced in equivalent wavelengths (250 to 300 nm) to those found experimentally for the reaction in basic medium, with a band profile similar to that established theoretically for the episulfide derivative.

Concerning the infrared spectrum, the characteristic signals of each compound were obtained, evidencing that the isomers of β-hydroxymercarptans are primarily differentiated by a signal near to 800 cm^{-1}, finding that the experimental spectra of the product correspond mostly to the ALLYLMERCAPTAN-2-OL derivative. This compound can be favor in conditions of AGE: NaSH 1:2 ratio in an alcoholic buffer system with a pH range of 7.0 - 8.0, which prevents the hydrolysis of the epoxide and the protonation of the thiolating agent.

Conflict interest. Authors declare that there is no conflict of interest regarding the publication of this paper.

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