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Unsaturated Alcohols and Products Obtained During Their Chemical Transformation

Abstract

Unsaturated alcohols are essential organic compounds, with allyl alcohol being the first representative of this class. It is an industrially significant olefinic alcohol that can serve as a raw material or precursor for the synthesis of various chemical compounds. Numerous important substances are obtained through the chemical transformations of unsaturated alcohols, particularly allyl alcohol. Consequently, the study of their chemical reactions is of great interest. This study focuses on the chemical transformations of unsaturated alcohols, with particular emphasis on oxidation and hydrogenation reactions, as well as their corresponding transformation products.

Keywords: *unsaturated alcohols, oxidation, hydrogenation, saturated, allyl.*

Introduction

Alcohols are classified into saturated, unsaturated, and aromatic alcohols based on the nature of the hydrocarbon radical. Unsaturated alcohols are obtained by replacing the hydrogen in ethylene- or acetylene-type compounds with a hydroxyl group (Babayev, et al., 2024). Unsaturated alcohols are important volatile organic compounds (VOCs) in the atmosphere, and emitted through anthropogenic and biogenic sources. Anthropogenic sources VOCs (AVOCs) are heavily influenced by industrial production and manufacturing. For example, methyl allyl alcohol is an important unsaturated alcohol, mainly comes from chemical process, transport and industry, and the annual output is about 6000 tons in China product (Kunling, et al., 2021). Unsaturated alcohols are

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considered acid-sensitive substances (Li, et al., 2016). Allyl alcohol is the first representative of the class of unsaturated alcohols and an oxygen-containing organic compound. It is a colorless liquid with a pungent, mustard-like odor. Allyl alcohol is soluble in water as well as in many organic solvents, and its chemical structure is CH_2=CH−CH_2OH. It is an industrially significant olefinic alcohol that serves as a raw material and precursor for various chemical compounds. Simple and complex ethers can be easily synthesized from allyl alcohol. Its conversion to acrolein occurs through the mediation of alcohol dehydrogenase. Additionally, allyl alcohol is used in optical resins, protective glass, paints and coatings, polymer cross-linking agents, as well as in the production of pharmaceuticals, organic chemicals, plastics, herbicides, and pesticides (Shashkova, et al., 2024; Mehrnaz, et al., 2024).

Chemical transformation reactions of unsaturated alcohols

Unsaturated alcohols play a crucial role in various industrial applications, particularly in fine chemistry, fragrance production, and pharmaceutical synthesis (Ghomaria, et al., 2014). Unsaturated alcohols from essential oils have been effectively oxidized to their corresponding unsaturated aldehydes using potassium permanganate supported on copper(II) sulfate pentahydrate. Valuable compounds such as geranial and cinnamaldehyde, which are widely used in the food, cosmetic, perfumery, and pharmaceutical industries, were obtained in high yields (>60%) through two activation methods: microwave irradiation and conventional heating (Luu Thi, 2018). Unsaturated alcohols are released into the atmosphere from both anthropogenic and biological sources. While NO_3 radical-initiated reactions of unsaturated alcohols play a significant role in secondary organic aerosol (SOA) formation, they have been less extensively studied. In this research, the rate constants for the reactions between NO_3 radicals and 2-methyl-2-propen-1-ol ($2M_2P_1O$), (E)-4-hexen-1-ol (t-$4H_1O$), and 4-penten-2-ol ($4P_2O$) were determined at 298 ± 2 K using relative rate methods. The obtained rate constants were 3.41 ± 0.51 ($2M_2P_1O$), 6.45 ± 0.66 (t-$4H_1O$), and 0.56 ± 0.15 ($4P_2O$), expressed in units of 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (Lin Hu,et al.,2024).

Research

Allylic alcohols are highly versatile compounds utilized across various industrial processes. The transfer hydrogenation of α,β-unsaturated carbonyl compounds presents an attractive method for synthesizing allylic alcohols. This approach eliminates the need for stoichiometric and hazardous reagents like $NaBH_4$ or $LiAlH_4$. Additionally, unlike conventional catalytic hydrogenations, these reactions do not require specialized equipment such as autoclaves or high-pressure reactors. As a result, transfer hydrogenation protocols are both more cost-effective and safer (Farrar-Tobar, et al., 2018). Pd nanoparticles synthesized from S-dodecylthiosulfate can serve as catalysts for both the isomerization and hydrogenation of allyl alcohol, depending on the solvent used in the reaction. The reaction mechanism involves a Pd-alkyl intermediate, with regioselectivity determined by either the Markovnikov or anti-Markovnikov addition pathways. Generally, nonpolar solvents favor the isomerization of allyl alcohol to propanal, whereas polar protic solvents facilitate its hydrogenation to 1-propanol. Pd nanoparticles capped with shorter alkylthiolate ligands exhibit lower regioselectivity in the isomerization reaction due to the increased surface ligand density of hexanethiolate-capped Pd nanoparticles compared to their dodecanethiolate-capped counterparts synthesized under identical conditions. These findings highlight that manipulating the structure and conformation of alkanethiolate ligands on Pd nanoparticles can lead to the development of highly selective and efficient catalytic materials. Additionally, the exceptional stability of these soluble nanocatalysts is demonstrated by the successful recycling of dodecanethiolate-capped Pd nanoparticles for the isomerization reaction up to 14 times (Elham, et al., 2012). Acrylic acid, the selective oxidation product of allyl alcohol, is one of the most important monomers in the industry. Acrylic acid and its esters are widely used in the production of acrylic fibers, lacquer coatings,

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adhesives, paints, textile auxiliaries, as well as in the paper and leather industries (Babayev, et al, 2024; Ruinan, et al., 2022; Minsu, 2017). The oxidation and pyrolysis of two unsaturated alcohols, prenol and isoprenol, were investigated over a temperature range of 500–1100 K. The study revealed distinct reactivity patterns for each compound, which were successfully captured by a newly developed kinetic model. Isoprenol primarily undergoes a single unimolecular reaction, yielding formaldehyde and isobutene through a six-membered transition state. This reaction mechanism is likely relevant for all unsaturated alcohols with a C=C double bond located at the γ-position relative to the hydroxyl group. Additional oxidation and pyrolysis products in the reactor effluent originate from the secondary reactions of isobutene and formaldehyde. In contrast, the reactivity of prenol is significantly influenced by the different positioning of its double bond, shifting the reaction mechanism from unimolecular decomposition to radical-driven processes. Prenol undergoes typical reaction pathways, such as hydrogen abstraction and radical addition to the C=C double bond, yet the presence of the hydroxyl functional group alters its thermochemical behavior. This leads to limited low-temperature chemistry, resulting in the formation of aldehydes and ketones. Notably, such low-temperature chemistry is absent in the oxidation of 2-methyl-2-butene, despite its structural similarity to prenol (Ruben, et al., 2016).

Conclusion

Unsaturated alcohols are industrially significant compounds, as their chemical transformations yield valuable products. The hydrogenation of unsaturated alcohols results in the formation of saturated alcohols. One such example is the hydrogenation of allyl alcohol, which produces 1-propanol, a widely used solvent and chemical intermediate in various industrial sectors. Additionally, acrylic acid is a selective oxidation product of allyl alcohol. Acrylic acid and its esters are essential for the production of acrylic fibers, lacquer coatings, adhesives, paints, textile auxiliaries, as well as applications in the paper and leather industries.

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