Nigerian Research Journal of Chemical Sciences **(ISSN: 2682-6054)**
Volume 12, Issue 1, 2024

CONTINUOUS GAS PHASE PHOTOCATALYTIC OXIDATION OF 1-HEXENE OVER TiO_2

E. A. Kamba, *E. C. Ajiduku and R. Odoh
Department of Chemical Sciences,
Federal University Wukari, Wukari, Nigeria.
*Corresponding Author: emmanuelcajiduku@gmail.com

Accepted: June 12, 2024. Published Online: June 21, 2024

ABSTRACT

The majority of chemical reactions in industry need high temperatures and pressures, while photocatalytic reactions can occur at ambient temperature and standard atmospheric pressure. To study the latter, this work focuses on employing Type-A ultraviolet (UVA)-activated TiO_2 to drive organic processes. Through a novel coating technique, TiO_2 power was immobilized on glass beads which was then used to fill the entire volume of the reactor. The gas-phase photooxidation of 1-hexene using the designed reactor resulted in the production of butyloxirane and 2-hexenal as the major products, identified through GC-MS analysis. Further tandem reaction of the products with diisopropylamine in toluene solvent, yielded other products including two novel unidentified products. More complex analysis such as Nuclear Magnetic Resonance (NMR) is required to identify these products. Nevertheless, the study allowed to establish the possible nature of some of the reactive species created during the partial photooxidation of 1-hexene. Hence, these experiments helped to demonstrate the versatility of the TiO_2 based photoreactors.

Keywords: Gas phase phototocatalysis, photooxidation, Catalyst immobilisation, UVA-activated TiO_2, Spin adhesive coating, 1-hexene.

INTRODUCTION

In many areas of society, the development of more energy-efficient technologies has increased recently due to worries about climate change and energy security. In 2011, it was estimated that the global energy demand of the chemical industry was 40 EJ (1 EJ =1×1018 J), which is approximately 7% of energy production worldwide. More worrisome is that this amount has been predicted to double by 2050 [1]. Therefore, developing more efficient chemical syntheses is a critical first step toward lowering our CO_2 emissions.

Many important chemical processes require high temperatures and pressures, even in the presence of a catalyst [2]. On the other hand, photocatalytic processes require much

milder energy sources and can happen at ordinary temperature and pressure [3]. This offers inexpensive, low-energy alternatives for common synthetic reactions.

The optimization of TiO_2 mediated photocatalytic in flow reaction systems has received a significant attention of academia for decades [4]. Particularly, studies have been performed aimed at producing of propylene oxide directly from propylene over TiO_2 catalyst [5-8].

Two main strategies were adopted in order to improve the photoepoxidation of propylene: first is the physical modification to the system, which focused on changing reaction conditions such as the reaction temperature, UV irradiation and concentration of reagent [9]. The second strategy is the modification of the nature and structure of the catalyst. Murcia-López *et al.* [10] successfully increase the production of propylene oxide in their reactor by 10% when they varied both the temperature and the ratio of propylene to oxygen in the gas stream. Similarly, Nguyen, Chan and Wu were also able to improve the selectivity of their photoepoxidation processes by 54% when they shifted from pure TiO_2 to Au-doped titanium silicates [11]. Despite the relative stability of photogenerated epoxides, the high reactivity of the different partial oxidation products is an indication that many potentially useful compounds are almost impossible to collect directly from TiO_2 gas flow photoreactors.

Therefore, the present work aims to demonstrate the viability of the created reactor for the production of epoxides, which would be achieved through establishing a tandem reaction system in order to take advantage of these highly reactive products. The tandem system consists of a one-pot reaction mixture connected to the gas stream, effectively allowing for the immediate use of the partial photooxidation products in synthetic reactions.

MATERIALS AND METHODS

Catalyst Immobilisation

Spin Adhesive Coating (SAC)

The glass beads were cleaned with acetone and ethanol before being refluxed in 5 M NaOH for 30 minutes to enhance the surface OH group density and promote catalyst adhesion [4, 5]. The glass beads were rinsed with deionized water until the washings are neutral, washed again with acetone, compressed air dried, and precisely weighed (± 0.5 mg). They were placed overnight in a rotating drum with suitable quantities of commercial TiO_2 (Degussa P25) to yield loadings of 1, 3, 5, and 7 mg/g, followed by a second weighing to confirm the catalyst loading. A small sample of base-treated and untreated beads will be coated with P25 (0.3 mg/g) using this procedure to assess the significance of the base treatment [5].

Flow Reactor Design

A gas-phase flow reactor was used. The reactor was designed separately, although it was subsequently discovered to be comparable to that of Verbruggen *et al* [6].

The reactor (Figure 1) was made out of a quartz tube (400 mm length, 24/28 mm internal/external diameter) The reactor's tube volume was filled with immobilized catalyst, and each end was sealed with a rubber bung. Steel tubing (6 mm external diameter) was inserted into the rubber bungs to allow gas inlet and outlet of the reactor. Type-A ultraviolet lamp was used as the source of light. To contain the radiation, the reactor was encased with aluminium foil. 1-hexene was introduced at regulated flow rates through the headspace vapour of a Dreschel container.

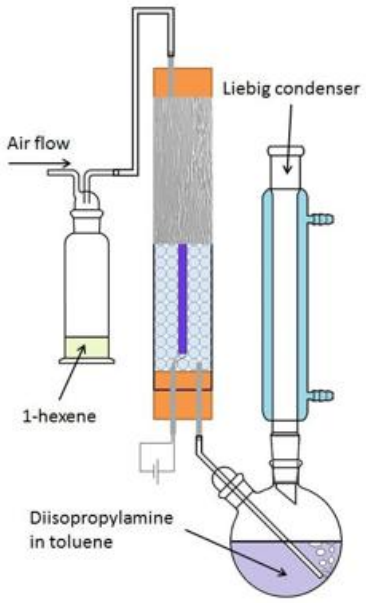


Figure 1: Flow reactor assembly with nucleophile/solvent trap.

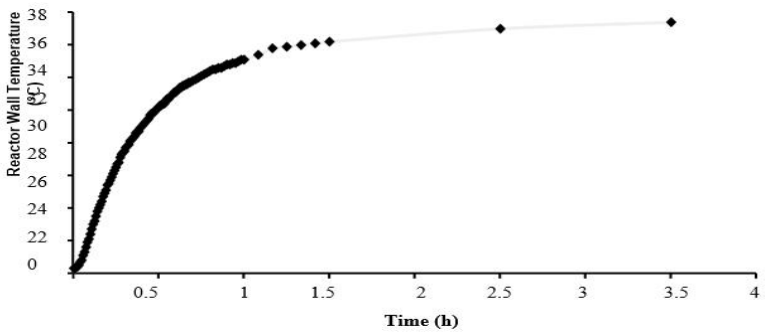


Figure 2: Flow reactor temperature profile.

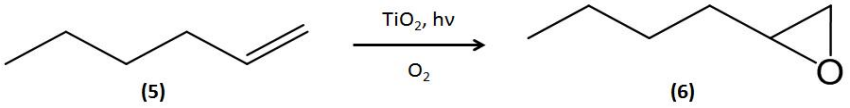
1-Hexene Oxidation

Flow Reactions

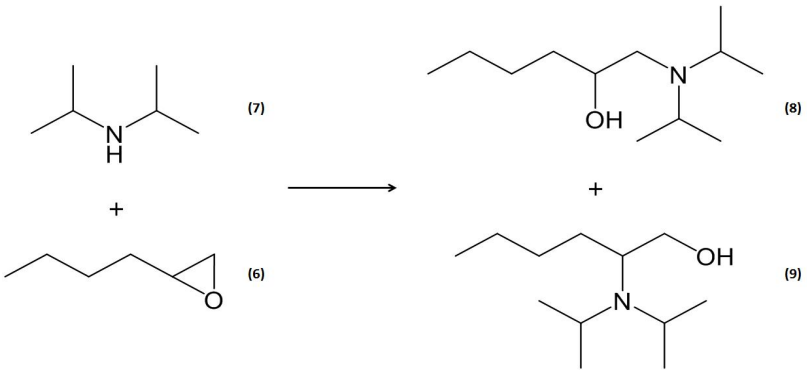
In this study, a two-stage reaction technique was developed. First, 1-hexene was partially oxidized within the reactor in the presence of photocatalyst. The sSecond stage is the chemical trapping of the products of the first stage, the reactor's exhaust. Instead of collecting the products, the reaction exhaust was bubbled through a magnetically agitated diisopropylamine solution with 1-hexene as the substrate. To minimize solvent/product loss, a Liebig condenser was attached to the exhaust flask along with the use of both toluene and deionized water as solvents. The reactor exhaust was run into clean toluene as a control experiment to detect photooxidation products [12].

RESULTS AND DISCUSSION

1-Hexene was selected as the substrate due to its well-known propensity for photocatalytic epoxidation to produce electrophilic epoxide species that could react with an amine or other nucleophile [13-15].



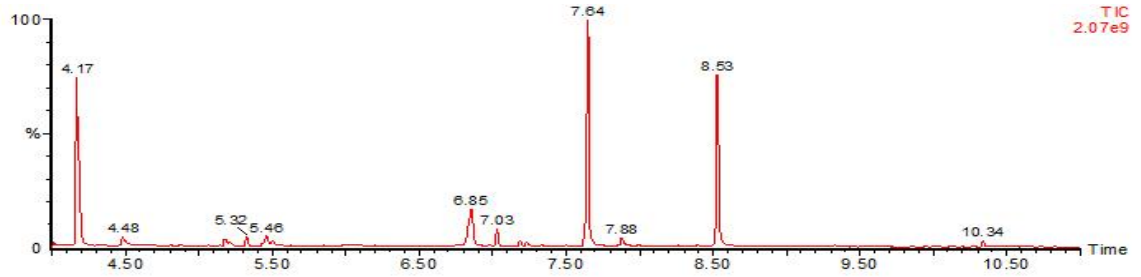
Scheme 1: Photocatalytic epoxidation of 1-hexene



Scheme 2**:** Nucleophilic addition of diisopropylamine to butyloxirane

Organic (Toluene) Trapping Solution: GC-MS Analysis

The chromatogram in Figure 3 revealed a variety of signals after several hours of reaction. The origin of each peak was discovered through separate analysis of each reaction component; a summary is provided in Table 1.



Retention times displayed in minutes

Figure 3: Typical chromatogram of the organic reaction mixture.

Table 1. Overview of the main GC-MS signals and their origins.
Compounds with uncertain identity are shown in brackets.

Retention Time (min.)	Source	Identity
4.17	Oxidation	Butyloxirane
4.48	Diisopropylamine	(Diisopropylethylamine)
5.18	Oxidation	(2-hexanal)
5.32	Toluene	Ethylbenzene/xylene
5.46	Toluene	Ethylbenzene/xylene
6.85	Reaction	Unknown
7.03	Oxidation	Unknown
7.64	Reaction	Unknown **(Product A)**
7.88	Reaction	Diisopropylformamide
8.53	Reaction	Unknown **(Product B)**
10.34	Reaction	Unknown

The peak at 4.17 minutes was only present in the reactor exhaust/toluene and final reaction mixtures. Its mass spectrum (Figure 4) also agreed well with that of butyloxirane in the National Institute of Standards and Technology (NIST) database [16].

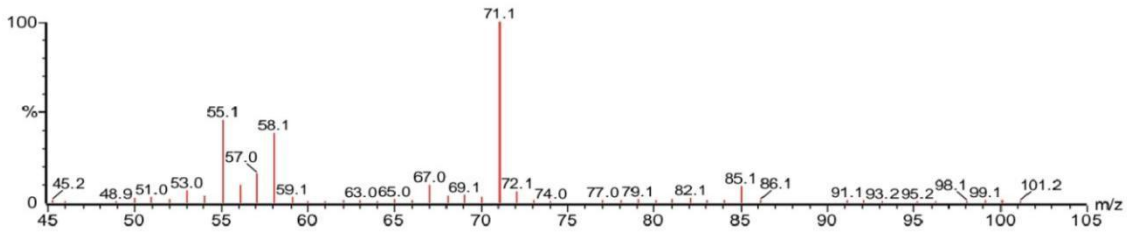


Figure 4: Mass spectrum of the species with 4.17 minutes retention time, most likely butyloxirane.

The peak at 4.48 min was only present in the diisopropylamine/toluene and final reaction mixtures. Its mass spectrum suggested diisopropylethylamine (Hünig's base), merely an impurity in the diisopropylamine. The peak at 5.18 minutes (not labelled) was only present in the reactor exhaust/toluene and final reaction mixtures and is likely to be 2-hexenal (Figures 5 and 6) suggesting double bond migration, as reported by Pillai and Sahle–Demessie [17].

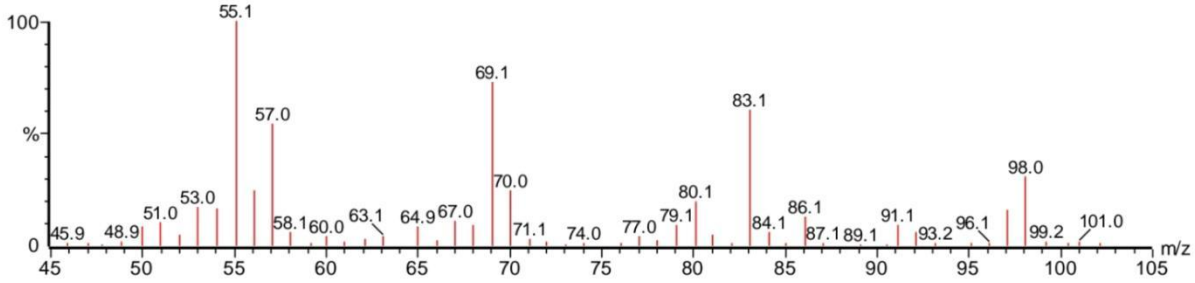


Figure 5: Mass spectrum of the species with 5.18 minutes retention time, most likely 2-hexenal.

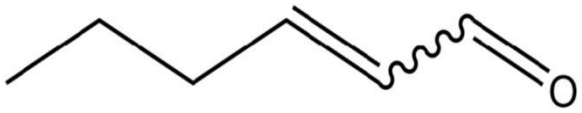


Figure 6: Structure of 2-hexenal.

Ethylbenzene and an isomer of xylene are shown by the peaks at 5.32 and 5.46 minutes, respectively. The presence of these peaks in every solution under test suggests that they originated from toluene. Due to its exclusive presence in the final reaction mixture, the peak at 6.85 minutes can only have originated from the tandem reaction. The NIST database did not identify this mass spectrum (Figure 7), however the most similar matches did have a diisopropylamino moiety. The presence of a nitrogen atom is at least suggested by the even-numbered major pieces and the odd-numbered molecular ion peak (141.2 amu). An unidentified byproduct of the oxidation event was the 7.03 minutes signal.

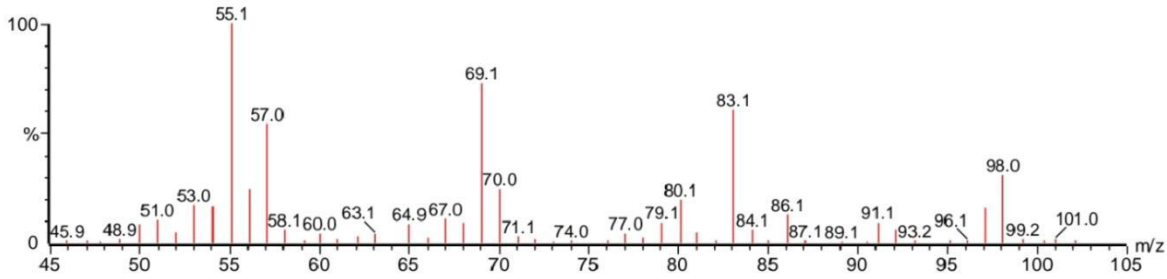


Figure 7: Mass spectrum of the unknown species with 6.85 minutes retention time.

The large signal at 7.64 minutes was only present in the final reaction mixture and therefore a product (product A) of the tandem reaction. Its mass spectrum (Figure 8), while not recognised by the NIST library, 113 is indicative of a nitrogen atom-containing molecule with some sort of alkyl chain; the nitrogen is evidenced as before, and the alkyl chain by the 14 amu difference between most of the fragments.

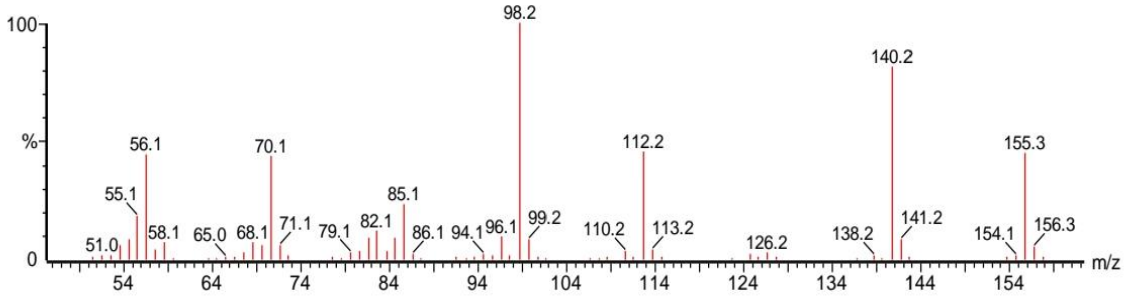


Figure 8: Mass spectrum of product A (retention time 7.64 minutes)

The small peak at 7.88 minutes was also only present in the final reaction mixture and was identified (with 92.1% probability) as diisopropylformamide. The second large peak at 8.53 minutes was another product (product B) of the tandem reaction, and the mass spectrum (Figure 9) suggests the same structure as Product A with an extra CH_2 group, evidenced by an m/z peak larger by 14 amu.

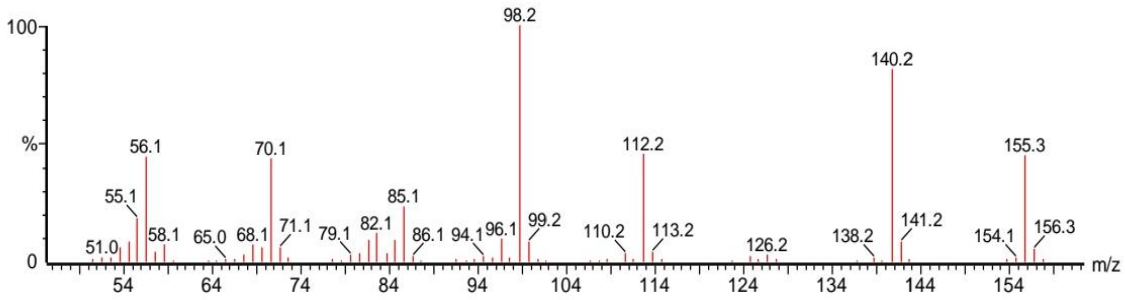


Figure 9: Mass spectrum of product B (retention time 8.53 minutes)

The final, small peak (10.34 minutes) was also only present in the final reaction mixture. The mass spectrum also indicates the presence of nitrogen.

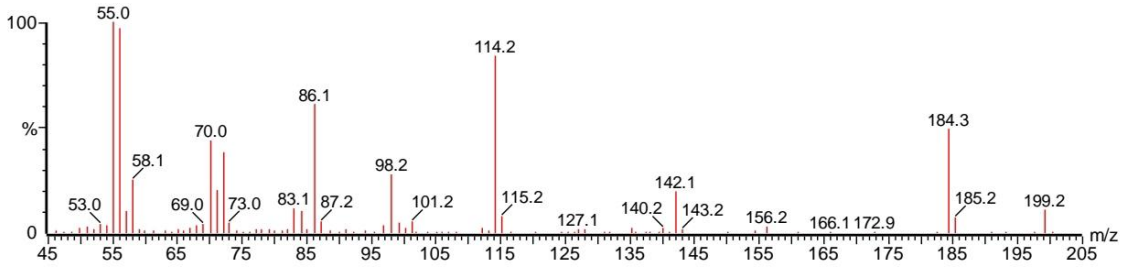


Figure 10: Mass spectrum of the unknown product with 10.34 minutes retention time.

Unfortunately, none of the tandem reaction products exhibited the molecular ion peak of (8) or (9). In fact, when commercial butyloxirane and diisopropylamine were later combined at room temperature, the products were not actually formed (Figure 11). A different oxidation product must therefore be responsible for the reaction.

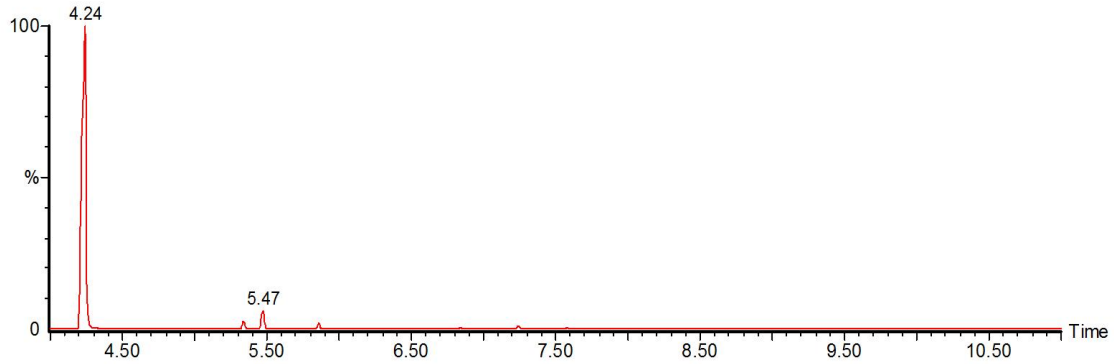
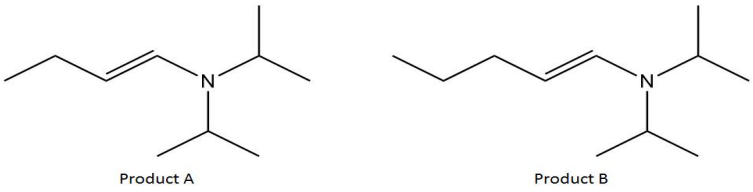
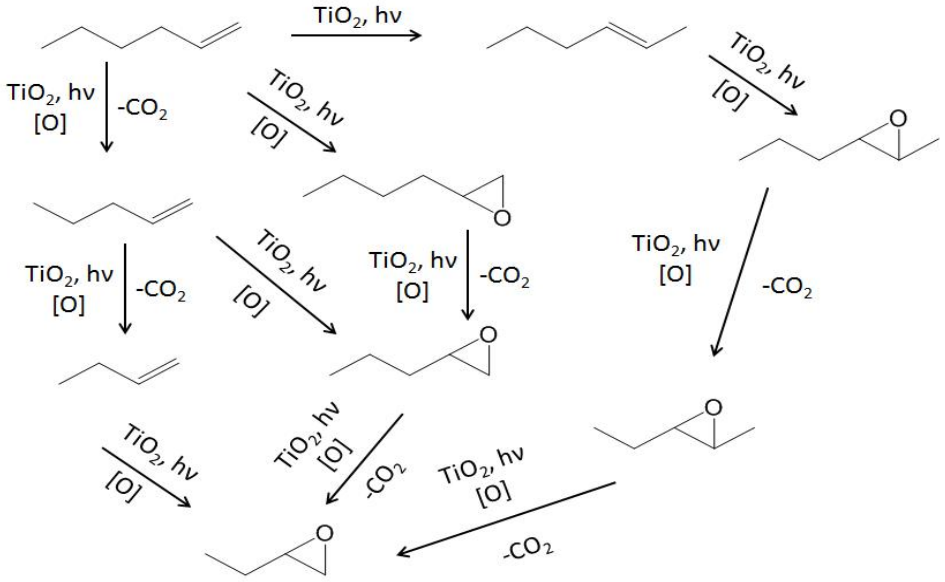


Figure 11: Chromatogram of the epoxide/amine mixture. The epoxide signal can be seen at 4.24 minutes and the toluene impurities around 5.47. No reaction products were observed.

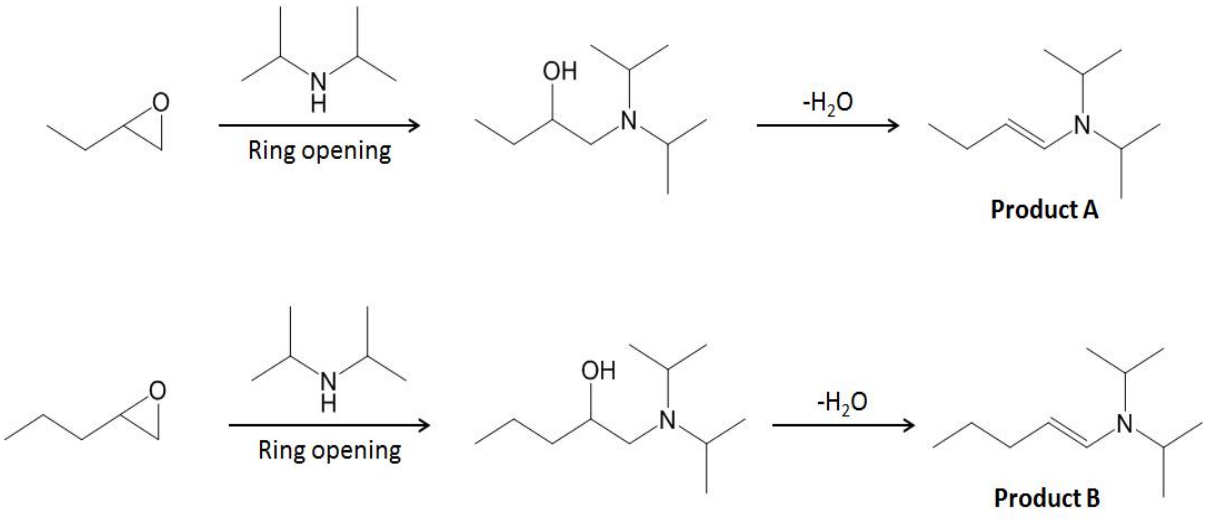
Based on the fragmentation patterns and possible reaction mechanisms, products A and B may be the following compounds:



The compounds may have been formed via a number of routes (Schemes 3 and 4)



Scheme 3: Some of the many potential mechanistic photooxidation routes of 1-hexene. Photocatalytic double bond migration has been reported in the literature [18-20].



Scheme 4: Nucleophilic addition of diisopropylamine to two possible oxidation products, followed by subsequent dehydration to yield candidates for products A and B

It is necessary to identify the oxidation products that are currently unknown yet are accountable for the reaction. Although photooxidation of 1-hexene can produce aldehydes and other species [16]. The toluene-trapped exhaust contained only traces of compounds other than butyloxirane (Figure 12).

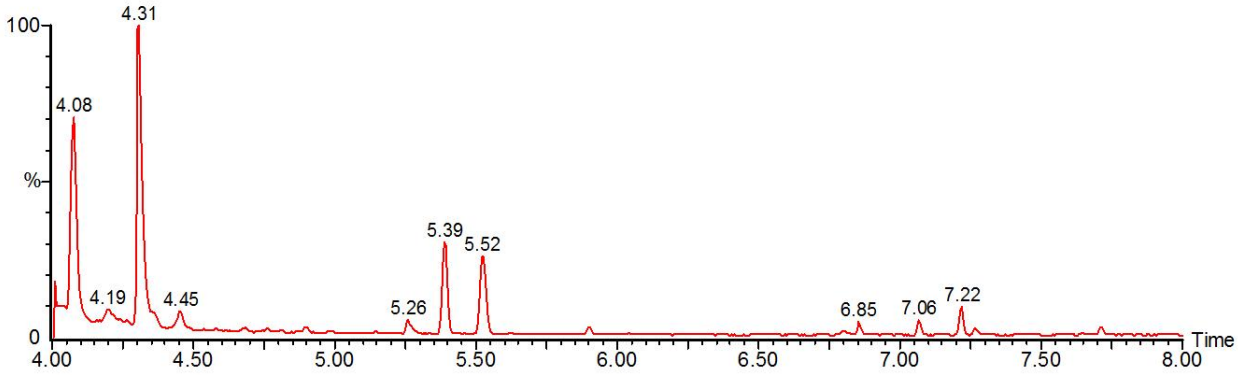


Figure 12: Chromatogram of 1-hexene photooxidation products in toluene.

Oxidation products eluted at 4.31, 5.26, 7.06, 7.22 and 7.26 min. All other signals arise from toluene impurities.

Short-lived, radical species may thus be to blame for the reaction. If this is the case, adding a radical scavenger like (2,2,6,6-Tetramethyl-piperidin-1-yl) to the reaction would affect the rate of reaction product appearance. While the alkene functionality of 1-hexene is most susceptible to oxidation due to its increased electron density [21] the high-energy, reactive intermediates of interest may result from oxidation of other centres

CONCLUSION

This work successfully designed and executed a gas-phase, flow-type photoreactor. Utilizing a readily available, commercially available photocatalyst (Degussa P25) with high activity, the immobilization process was easy to carry out. The primary benefit in this instance is that the only energy source was UVA radiation from a cold cathode fluorescent light that operated at low power. Then, utilizing only molecular oxygen and UVA radiation, the simple epoxidation of 1-hexene was achieved. Although butyloxirane and diisopropylamine did not undergo the anticipated nucleophilic ring-opening reaction, previously undiscovered high-energy oxidation intermediates were effectively captured in a subsequent reaction. The GC-MS analysis of the tandem reaction mixture revealed two different product signals, which served as evidence for this reaction. By analysing the GC-MS data for the two species it was possible to propose their molecular structure as well as a potential synthetic pathway for each

molecule. The synthesised molecules are particularly important as their presence is only poorly recorded in literature and routes to their synthesis are complicated and expensive. The tandem reaction technique used in this study might be commercially feasible. It might even result in chemical syntheses that were previously impossible. It also offers a simple, affordable, and energy-saving substitute for intricate multi-step reactions.

REFERENCES

[1]. Elzinga, D., Baritaud, M., Bennett, S., Burnard, K., Pales, A. F., Philibert, C. & West, K. (2014). Energy technology perspectives 2014: harnessing electricity's potential. International Energy Agency (IEA), Paris, France.

[2]. Kamba, E. A. & Yerima, E. A. (2023) .Gas-phase Photocatalytic Oxidation of 1-Hexene Using Heterogeneous Semiconductor Materials. *Afri. Sci. Rep*. 2 (2023) 64

[3]. Kamba, E. A., Ugwuja, D. I., Yerima, E. A. & Egah, G. O. (2022). An efficient photoreactor design and its application in photo-oxidation of acetone *Chem. of the total env.* 3(1), 1-7

[4]. Christopher, G., Kulandainathan, M. A. & Harichandran, G. (2015). Comparative study of effect of corrosion on mild steel with waterborne polyurethane dispersion containing graphene oxide versus carbon black nanocomposites. *Prog. in Org. Coatings*, 89, 199-211.

[5]. Clayden J., Greeves N., Warren S. & Wothers, P. (2001). Organic Chemistry, Oxford University Press, New York, 2001.

[6]. Verbruggen, S. W., Ribbens, S., Tytgat, T., Hauchecorne, B., Smits, M., Meynen, V. & Lenaerts, S. (2011). The benefit of glass bead supports for efficient gas phase photocatalysis: case study of a commercial and a synthesised photocatalyst. *Chem. Eng. J*, *174*(1), 318-325.

[7]. Nair, V., Muñoz-Batista, M. J., Fernández-García, M., Luque, R. & Colmenares, J. C. (2019). Thermo-photocatalysis: environmental and energy applications. *ChemSusChem*, 12(10), 2098-2116.

[8]. Nguyen, T. T. M., Wissing, L. & Skjøth-Rasmussen, M. S. (2013). High temperature methanation: Catalyst considerations. *Cat. today*, 215, 233-238.

[9]. Montjoy, D.G., Wilson, E.A.K., Hou, H., Graves, J.D. & Kotov, N.A. (2023). Photocatalytic cyclohexane oxidation and epoxidation using hedgehog particles. *Nat Commun*. 15;14(1):857

[10]. Murcia-López, S., Hidalgo, M.C. & Navío, J.A. (2011). Synthesis, characterization and photocatalytic activity of Bi-doped TiO_2 photocatalysts under simulated solar irradiation *App. Cat. A: General* 404(1-2), 59-67.

[11]. Nguyen, V., Chan, H. & Wu, J. C. S. (2013) Synthesis, characterization and photo-epoxidation performance of Au-loaded photocatalysts *J. Chem. Sci*. 125(4), 859–867.

[12]. Khomane, R. B., Kulkarni, B. D., Paraskar, A. & Sainkar, S. R. (2002). Synthesis, characterization and catalytic performance of titanium silicalite-1 prepared in micellar media, *Mater. Chem. Phys.*, 76, 99–103.

[13] Du, H., Fang, M., Chen, J. & Pang, W. (1996). Synthesis and characterization of a novel layered titanium silicate JDF-L1, *J. Mater. Chem.*, 6, 1827.

[14]. Zhao, Q., Li, P., Li, D., Zhou, X., Yuan, W. & Hu, X. (2008). Synthesis and characterization of titanium silicate-1 supported on carbon nanofiber, *Mic. Mes. Mater.*, 108, 311–317.

[15]. Pędziwiatr, P., Mikołajczyk, F., Zawadzki, D., Mikołajczyk, K. & Bedka, A. (2018). Decomposition of hydrogen peroxide - kinetics and review of chosen catalysts, *Acta Innov.*, 26, 45–52.

[16]. Standard Reference Data Program National Institute of Standards and Technology 100 Bureau Dr., Stop 6410 Gaithersburg, MD 20899-6410 NIST Standard Reference Database 100 | NIST

[17]. Pillai, U. R. & Sahle-Demessie, E. (2002). A highly efficient oxidation of cyclohexaneover VPO catalysts using hydrogen peroxide. C*hem. Comm.* (18), 2142-2143

[18]. Nguyen, V.-H., Lin, S. D., Chi, J. Sheng Wu & Bai, H. (2014). Artificial sunlight and ultraviolet light induced photo-epoxidation of propylene over V-Ti/MCM-41 photocatalyst, *Beilstein J. Nanotechnol*, 5, 566–576.

[19] Lousada, C. M., Johansson, A. J., Brinck, T. & Jonsson, (M0. (2012). Mechanism of H_2O_2 Decomposition on Transition Metal Oxide Surfaces, *J. Phys. Chem. C*, 116, 9533–9543.

[20]. Perez Ferrandez, D.M., de Croon, M. H. J. M.,Schouten, J. C. & Nijhuis, T. A. (2013). Gas-Phase Epoxidation of Propene with Hydrogen Peroxide Vapor, *Ind. Eng. Chem. Res.*, 52, 10126–10132.

[21]. Li, H., Xu, B., Deng, B., Yan, X. & Zheng, Y. (2014). Epoxidation of 1-hexene with hydrogen peroxide over nitrogen-incorporated TS-1 zeolite, *CATCOM*, 46, 224–227.