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***trans*-Stilbene epoxidation by He+O₂ atmospheric pressure plasma: epoxidation without oxidant waste-stream**

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Abstract

Plasmas interacting with organic liquids can lead to novel synthetic processes that are not feasible with conventional vacuum systems due to vapor pressure limitations. Of particular interest are processes that eliminate the generation of waste-streams. Here we show that He+O₂ plasma can drive the epoxidation of alkenes in solution, in a process that generates epoxides without oxidant waste-streams, runs at room temperature and atmospheric pressure, and requires no catalyst. The reactions between different reactive oxygen species generated in the plasma and the target alkene, *trans*-stilbene in this study, have been identified and optimization of the plasma conditions within the constraints of the current experimental set-up have led to yields of ~70%, which are of preparative interest.

Keywords: epoxidation; plasma synthesis; COST jet; atomic O; plasma-liquid interaction

1. Introduction

Advancements in non-thermal plasmas operating at atmospheric pressure have made possible novel processing of liquids that were not conceivable in conventional vacuum systems due to vapor pressure limitations.^[1] In addition to their rapidly growing use in medicine,^[2] agriculture and food industries,^[3,4] catalysis,^[5-7] nanoparticle synthesis^[8] and water treatment,^[9] the interaction of plasmas with organic liquids opens up two additional avenues of research: the development of novel organic compounds for

the characterization of plasmas and the use of gas plasma in novel chemical synthesis processes.^[10-13]

Despite the limited success of early studies of plasma-driven organic synthesis in low-pressure systems in the 70's, direct treatment of liquids at atmospheric pressure provides a new paradigm for the interaction of plasma species with organic molecules. In particular, these reactions often create excited intermediates and when generated in the liquid phase, these intermediates undergo many collisions, which lead to the rapid removal of excess energy and favor chemical pathways different from those observed in low pressure gaseous systems. As a result of the new possibilities of atmospheric pressure plasma-liquid systems, plasma-driven organic synthesis is receiving renewed attention and recent studies have demonstrated, for example, plasma-initiated radical chemistry, oxidation of fullerenes and environmentally friendly production of peroxyxynitrite.^[14-16]

Of particular interest, are novel synthetic processes that eliminate waste streams. This is the case because conventional manufacturing of chemical compounds typically generates large amounts of waste. Actual numbers depend on the sector, but it has been reported that bulk and fine chemical industries generate 1 to 50 times more waste than desired product and this can go up to 100 times in the pharmaceutical sector.^[17] Besides the obvious logistic and economic implications, these waste streams have a detrimental environmental impact that will compromise the ability of future generations to meet their own manufacturing needs.

In this study of we focus on the synthesis epoxides, key building blocks in the chemical industry that are used as intermediates in the preparation of many products (drugs, paints, adhesives, sealants, plastics, etc). The demand for epoxides is difficult to estimate because much of the production is used in-house to produce derivatized products and never reaches the open market. Some, however, reach the open market and for example, the global Epoxidized Soybean Oil (ESBO) market is projected to reach \$691.7 Million by 2026, at a compound annual growth rate (CAGR) of 11.04% from 2016 to 2026.^[18]

Epoxides are typically synthesized by oxidizing alkenes (See **Scheme 1**). Various oxygen donors have been investigated in the past with the ultimate oxygen donor being molecular oxygen (O₂) because

it is readily available and once incorporated into the target molecule it generates no oxidant waste stream. However, the only industrial epoxidation reaction in which this has been achieved is the production of ethylene oxide; and even in this case an expensive silver catalyst is needed.^[19] Other small molecules that could potentially act as oxygen donors and produce small waste streams have also been investigated. For example, hydrogen peroxide (H_2O_2) has received a lot of attention as upon donation of oxygen, the generated ‘waste’ stream is simply water (H_2O).^[20] Unfortunately, hydrogen peroxide is not active enough on its own and requires the use of catalysts and even then, it has limited applicability. Furthermore, due to its hazardous reactivity, hydrogen peroxide requires specialized transport and storage, and industrial scale production of hydrogen peroxide via the anthraquinone oxidation process is not environmentally friendly.

Scheme 1. Epoxidation of an alkene

Owing to the lack of reactivity of small molecular oxygen donors with alkenes, catalysts and peracids (i.e. organic compounds with an $\text{O}=\text{C}-\text{O}-\text{OH}$ functional group that can readily donate an oxygen atom) are often used to drive epoxidation reactions.^[21] A widely used peracid is m-chloroperbenzoic acid (mCPBA), which although effective, is also corrosive and explosive, leads to chlorinated waste products and even under optimum epoxidation conditions, it produces more than 10 kg of waste stream per kg of oxygen transferred.

As an alternative, here we explore the use of reactive oxygen species generated in an oxygen-containing atmospheric-pressure plasma to drive the epoxidation process. The plasma increases the reactivity of the precursor O_2 while providing an oxidant waste-stream free process. Early studies of plasma-driven epoxidation have shown that the yields (i.e. moles of epoxide divided by moles of

consumed alkene) were too low to be of preparative interest (<50%) and the required experimental conditions were often too complex.^[22-24] To better understand the process and improve the yield of epoxide, we identify the chemical reactions triggered by different reactive oxygen species generated in the plasma and optimize the discharge conditions to maximize the production of epoxide.

2. Experimental setup and methods

Figure 1(a) shows the COST plasma jet used in this study. The COST jet is an RF capacitively coupled plasma jet that consists of two stainless-steel electrodes (length 30 mm, thickness 1 mm) with a gap in between them of 1 mm sandwiched between two quartz plates. One electrode is powered by a 13.56 MHz sinusoidal voltage and the other one is grounded. The device can be operated at atmospheric pressure in helium and generates homogeneous plasma over a wide range of voltages, typically 150–320 Vrms. In this study, helium (1.4 slm) is used as background gas and a small admixture of oxygen (O₂) is introduced to generate reactive oxygen species. The oxygen flow is varied from 0 sccm to 10 sccm. Further details, characteristics and recent applications of the COST plasma jet can be found in references [25, 26].

When operated in the homogeneous α -mode in He+O₂, the COST jet can generate atomic O in concentrations on the order of 10^{15} cm^{-3} at a few Watts of input power.^[27] The jet can also generate singlet oxygen O₂(a¹A_g) in similar concentrations at low O₂ admixtures and tens of watts of applied RF power.^[28] Operation at higher powers are likely to produce higher O and O₂(a¹A_g) concentrations but modifications to the original COST jet, e.g. introduction of dielectric layers over the electrodes or operation at higher frequencies, would be required to delay/prevent the transition to a constricted γ -mode.^[29]

Figure 1. (a) A photograph of the micro-plasma jet operating in He+O₂ taken with a digital camera (Nikon D7000) and an exposure time of 1 s. (b) Schematic of the experimental system for the plasma-driven epoxidation of *trans*-stilbene.

As in previous studies and to maintain a high flux of atomic O to the liquid without significantly perturbing the liquid surface, the gap between the jet nozzle and the liquid surface is kept at 4 mm (see **Figure 1(b)**).^[13] The substrate being treated is kept in a solution in a flask that has a cooling jacket to keep the temperature of the solution constant during the experiment. Water is used in the cooling circuit and a dry ice condenser is used in the exhaust to minimize the loss of liquid through evaporation. During operation, the liquid surface is slightly depressed on the jet axis due to the directed helium flux and the momentum transferred from the gas flow to the liquid causes the formation of vortices that drive the mixing of the liquid. Faster reaction times are expected when using more vigorous mixing mechanisms, such as magnetic stirrers.

The alkene used in this study was *trans*-stilbene (98%, Alfa Aesar), which was dissolved in

acetonitrile (anhydrous, $\geq 99.8\%$, VWR Chemicals) to create an alkene solution. *trans*-Stilbene was chosen for its non-volatility as well as product stability for a reliable determination of conversion, yield and selectivity using gas chromatography. The initial concentration and volume of the treated solutions were 10 mM and 10 mL, respectively. Samples were treated for periods ranging from 20 min to 120 min.

Products of the reaction of plasma species with *trans*-stilbene were identified by gas chromatography mass spectrometry (GCMS-QP2010 Ultra/SE, Shimadzu). The GCMS was equipped with a Rtx-5MS capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). A Shimadzu 40 Headspace Sampler was used to introduce the liquid samples automatically in the GCMS and this was configured to use split injection and an injection volume of 1 μL . The carrier gas was He and the flow rate 65 mL/min (constant flow rate).

The column was kept at 50°C for 1 min after injection, and the temperature was then increased to 180 °C at 20 °C/min, held at 180°C for 5 min and increased to 250 °C at 20 °C/min. The temperature was held at 250°C for 2 min before cooling, giving a total run time of 18 min per sample. Compounds labeled in the chromatograms have been identified not only by their mass spectra but also by comparing their retention time with purified commercially available samples. Prior to the plasma experiments, calibration curves matching the concentration of each compound to the area observed in the chromatograms were obtained using the purified commercial compounds. Naphthalene ($\geq 99\%$, Sigma Aldrich) was added to all samples to serve as a reference for the quantitative analysis.

For the experiment in which singlet oxygen is photosynthesized, 5 mg of Rose Bengal was added to a *trans*-stilbene solution (10 mM, 25 mL) and then illuminated with a neon lamp with a power surface density of 60 mW/cm². The solution was stirred during the process and water cooling and a dry ice condenser were used to minimize heating of the solution and solvent loss through evaporation. Oxygen was passed through a drying tube containing anhydrous CaCl₂ (96%, Sigma Aldrich) and molecular sieves and then bubbled through the solution. The solution was exposed to photosynthesized singlet oxygen for 4 h, with GCMS analysis performed every hour.

A Static 300 ozone generator (Ambiox Ltd, Gwent, UK) operated in oxygen and with the exhaust flowing through a long (>2 m) tube was used to generate ozone with negligible amounts of atomic oxygen and singlet oxygen. This ozone was then bubbled through the *trans*-stilbene solution. The initial concentration and volume of the solution were 10 mM and 25 mL respectively, and samples were also analyzed by GCMS every hour.

3. Results and discussions

3.1 Reactions between the main three reactive oxygen species ($O_2(a^1A_g)$, O_3 , O) and *trans*-stilbene

It is anticipated that atomic oxygen plays a key role in the formation of epoxide as only one single oxygen atom needs to be incorporated into the alkene (See **Scheme 1**). However, $He+O_2$ plasmas lead to a number of additional reactive oxygen species that can, in principle, react with either the alkene (*trans*-stilbene) or the epoxide, thereby affecting the yield of the process. The three main reactive oxygen species generated in dry $He+O_2$ plasmas are singlet oxygen $O_2(a^1A_g)$, ozone O_3 and atomic oxygen O .^[30]

In this section we study the reactivity of each of these species and identify the main products of their reaction with *trans*-stilbene.

3.1.1 Singlet oxygen ($O_2(a^1A_g)$)

Due to the low energy required to excite O_2 into singlet oxygen (<1eV), it is possible to photo-synthesize singlet oxygen without producing atomic oxygen or ozone (O_2 dissociation threshold >5eV). In this study we use Rose Bengal (95%, Sigma Aldrich) as a photosensitizer. Rose Bengal absorbs light at 450–580 nm, with a maximum absorbance at 540 nm. Once excited, it can transfer excess energy to ground state oxygen to generate $O_2(a^1A_g)$.^[31]

It is known, that the relative ratio of the photooxidation products has a strong dependence on the conditions in which singlet oxygen is produced. For example, at room temperature with CCl_4 as a solvent and Tetraphenylporphine (TPP) as photosensitizer, the yield of *trans*-stilbene diendoperoxide

is 16% and that of benzaldehyde 80%. However, at -78 °C with acetone as a solvent, *trans*-stilbene diendoperoxide is produced with a yield of 76%. **Figure 2(b)** shows the reaction mechanism leading to the formation of epoxide and benzaldehyde based on existing literature.^[32-34]

Figure 2. (a) GCMS chromatogram of the *trans*-stilbene solution after 4 h photo-oxidation experiment. (b) Reactions leading to the formation of benzaldehyde and epoxide during the reaction of O₂(a¹A_g) and *trans*-stilbene solution. []⁺ denotes an intermediate product that is rapidly deactivated. Ar stands for aryl, phenyl in this study.

As shown in **Figure 2(a)**, for our experimental conditions, O₂(a¹A_g) leads primarily to the production of benzaldehyde, *cis*-stilbene and two unidentified products. Benzaldehyde, *cis*-stilbene, and unidentified product ① can be detected after 1 h of treatment while unidentified product ② becomes detectable only after 2 h. The unidentified products ① and ② could be undesirable endoperoxides,^[35,36] but these are not readily identifiable solely from the GCMS data and further analysis have not been performed because these compounds are not observed in samples treated with He+O₂ plasma.

Quantitative analysis of the chromatogram reveals that after 4 h the *trans*-stilbene consumption is

3.6 mM and the production of epoxide and benzaldehyde is 0.05 mM and 0.34 mM, respectively. This indicates that only ~1% of the *trans*-stilbene is converted into the desired epoxide and that benzaldehyde and epoxide account for about 5% of the products of the reaction between singlet oxygen and *trans*-stilbene. Conversion to *cis*-stilbene accounts for 26% with unidentified compounds ① and ② being the main byproducts.

Control experiments to verify that Rose Bengal and radiation on their own did not degrade the solution show that indeed there is no change in the *trans*-stilbene concentration if the solution is exposed to the dye or the light separately. In addition, when the 10 mM *trans*-stilbene solution is replaced with another one with the same concentration of *trans*-stilbene epoxide (98%, Sigma Aldrich), no epoxide is consumed, and no additional products are detected in the GCMS chromatograms.

These results indicate that the contribution of singlet oxygen to the formation of epoxide is negligible and that although it can lead to the undesired consumption of *trans*-stilbene, its presence does not lead to a significant destruction of epoxide.

3.1.2 Ozone (O₃)

The GCMS chromatograms of samples exposed to ozone generated by the ozone generator indicate that benzaldehyde is the only product in the first 4 h of treatment and that a very small amount of benzoic acid starts to be detected after 5 h (**Figure 3(a)**). Benzaldehyde is an expected product of the ozonolysis of *trans*-stilbene (**Figure 3(b)**) and the presence of the acid can be explained as a further oxidation of the aldehyde.^[37] Quantitatively, the concentrations of benzaldehyde and *trans*-stilbene after 5 h are 12.8 mM and 3.5 mM, respectively. Taking into account that one molecule of *trans*-stilbene leads to the formation of two benzaldehyde molecules, the yield of benzaldehyde due to the ozonolysis of *trans*-stilbene is >98%. Additional control experiments indicate that benzaldehyde and *trans*-stilbene epoxide are fairly stable in the presence of ozone for the typical duration of the plasma experiments (<2 h).

Figure 3. (a) GCMS chromatogram of the *trans*-stilbene solution after 5 h exposure to O_3 . (b) Main reaction process leading to the formation of benzaldehyde. $[]^+$ denotes an intermediate product that is rapidly deactivated.

Therefore, it can be concluded that ozone does not contribute to the formation of epoxide and instead it readily leads to the generation of benzaldehyde. Although ozone leads to the undesired consumption of *trans*-stilbene, its presence does not lead to a significant destruction of the epoxide.

3.1.3 Atomic oxygen (O)

Since no means to produce atomic O without significant traces of singlet oxygen and/or ozone were available, the reactivity of atomic oxygen with *trans*-stilbene was studied by analyzing the products generated after the exposure of a *trans*-stilbene solution to a $He+O_2$ plasma and eliminating the known contributions of singlet oxygen and ozone.

Figure 4. (a) GCMS chromatogram of the *trans*-stilbene solution after exposure to the He+O₂ plasma jet for 20 min at 240 Vrms and an O₂ flow rate of 4 sccm. (b) Atomic O reactions leading to the formation of epoxide (k_1) and carbonyl compound (k_2). $[\]^+$ denotes an intermediate product that is rapidly deactivated.

The chromatogram of a *trans*-stilbene solution exposed to a He+O₂ plasma for 20 min is shown in **Figure 4(a)**. The chromatogram reveals the presence of benzaldehyde, epoxide, and two additional carbonyl compounds which are isomers of the desired epoxide. This result indicates that atomic O attacks the carbon double bond, forming an intermediate adduct that rearranges to either the desired epoxide or carbonyl compounds (**Figure 4(b)**). Previous studies suggest that in the liquid phase the reaction rate k_1 for generating epoxide is about four times larger than the reaction rate k_2 for isomerizing carbonyl compounds.^[38]

The lack of *cis*-stilbene and unidentified products ① and ② after exposure to plasma suggests that the amount of singlet oxygen delivered from the plasma to the liquid is negligible for the experimental conditions of this study. The presence of benzaldehyde, on the other hand, suggests that significant amounts of ozone dissolve in the liquid.

Quantitative analysis of the chromatogram reveals that the concentration of *trans*-stilbene consumed after 20 min is 4.5 mM, and that the concentration of produced benzaldehyde and epoxide are 1.8 mM

and 2.8 mM, respectively.

These results indicate that epoxide is produced primarily by atomic O and that additional carbonyl compounds are inevitably generated. Due to the undesired presence of ozone, benzaldehyde is the main by-product of after the plasma treatment and therefore in order to increase the yield of epoxide, conditions that favor the production of atomic oxygen over ozone should be explored.

3.2 Optimization of the plasma treatment conditions

It is known that in the plasma the ratio of the concentration of atomic O to that of ozone depend on the O₂ content in the background gas and the discharge voltage.^[30,39] Therefore, plasma conditions can be tuned to favor the formation of epoxide.

Figure 5 shows the concentrations of *trans*-stilbene, epoxide and benzaldehyde as a function of the O₂ concentration in the background gas after a 20 min plasma treatment. As shown in the figure, the concentration of *trans*-stilbene decreases with increasing O₂ concentration due to the larger production of reactive oxygen species at high oxygen concentrations. The concentration of epoxide first increases with increasing O₂ concentration, peaks at about 4 sccm and then decreases. In contrast to the epoxide, the concentration of benzaldehyde increases monotonically with increasing O₂ concentration.

Figure 5. Concentration of *trans*-stilbene, epoxide and benzaldehyde as a function of the admixture of O₂ in the background gas. Voltage 240 Vrms and a helium flow rate 1.4 slm.

These trends of epoxide and benzaldehyde are similar to that of the densities of atomic O and O₃ measured in a He+O₂ COST jet by Ellerweg *et al.*^[27] These trends are well-understood based on the generation mechanisms of atomic O and ozone in these discharges:^[30]

At low oxygen concentrations, any increase makes more oxygen available for dissociation (R1) and leads to an increase of atomic oxygen. However, further increases in the O₂ concentration lead to the quenching of O and the formation of ozone (R2).

To increase the yield of *trans*-stilbene epoxide, operation at low oxygen concentration is recommended. However, due to the lower density of reactive species, the time required for the reaction to reach completion increases.

Figure 6. Concentration of *trans*-stilbene, epoxide and benzaldehyde as a function of the applied voltage. Helium and oxygen flow rate 1.4 slm and 2 sccm, respectively.

Figure 6 shows the concentration of *trans*-stilbene, epoxide and benzaldehyde as a function of the discharge voltage after 20 min plasma treatment. In the current experimental set up, operation at voltages higher than 320 Vrms results in the discharge transitioning into constricted γ -mode. The consumption of *trans*-stilbene increases at higher powers as a more intense discharge is generated.

Interestingly, the concentration of the desired epoxide increases with the discharge voltage but that of benzaldehyde remains fairly constant. This result agrees with other studies that have shown that higher voltages promote the formation of atomic O and the destruction of ozone.^[40]

According to the above two experiments, it is concluded that the conditions for maximum yield of epoxide are ~ 2 sccm O_2 admixture and as high voltage as possible. To avoid transition into the constrained γ -mode, the voltage is set to 300 Vrms in subsequent experiments.

Figure 7. Time evolution of the concentration of *trans*-stilbene, epoxide and benzaldehyde during exposure to He+ O_2 plasma (300 Vrms, 1.4 slm He and 2 sccm O_2).

Figure 7 shows the time evolution of the concentrations of epoxide, benzaldehyde and *trans*-stilbene when the *trans*-stilbene solution is treated with a 1.4 slm He plasma with a 2 sccm O_2 admixture at 300 Vrms. Under these experimental conditions, the concentration of epoxide is significantly higher than that of benzaldehyde. After 80 min, $\sim 90\%$ of the initial *trans*-stilbene (10 mM) has reacted and the concentration of epoxide and benzaldehyde are 6.2 mM and 3.5 mM, respectively. This corresponds to an epoxide yield of $\sim 70\%$, which is of practical relevance, particularly taking into account that this is achieved without catalyst.

Figure 8. The results of GCMS of the *trans*-stilbene epoxide solution treated by the He+O₂ micro-plasma jet for 60 min.

As shown in **Figure 7**, overexposure of the solution to the plasma leads to the destruction of epoxide, whose concentration drops from 6.2 mM to 5.7 mM in 40 min. Previous experimental results suggest that singlet oxygen and ozone do not destroy epoxide readily and therefore it is argued that atomic oxygen is the main species reacting with the epoxide. A chromatogram of an epoxide solution exposed to the He+O₂ plasma is shown in **Figure 8**. Benzaldehyde is observed after 20 min plasma exposure and benzeneacetaldehyde and the unidentified product ① are detected after 40 min.

Quantitative analysis show that the degradation of epoxide is slower than the epoxidation of *trans*-stilbene as after 1 h of plasma treatment, the epoxide concentration decreases only by 18%, whereas in the same amount of time more than 80% of the *trans*-stilbene is converted to epoxide. The lack of benzeneacetaldehyde and unidentified product ① in samples that still contain *trans*-stilbene suggests that kinetically epoxidation is favored over epoxide degradation. Therefore, it is possible to avoid epoxide degradation by conducting experiments in excess of alkene.

4. Conclusion

In conclusion, it is shown that epoxidation of *trans*-stilbene by He+O₂ plasma provides an epoxidation method that does not require catalysts and eliminates the oxidant waste-stream of conventional epoxidation processes.

The epoxidation reaction is shown to be mainly driven by atomic oxygen generated in the plasma, whereas singlet oxygen and ozone trigger undesirable reactions that limit the final yield of the process.

As a result, the yield of *trans*-stilbene epoxide is shown to increase at low oxygen concentrations and high input power as these conditions favor the formation of O over ozone. Yields of up to ~70% can be achieved at room temperature and without catalysts.

Over exposure to plasma can lead to the slow degradation of the generated epoxide but since this reaction is kinetically slower than the epoxidation reaction, epoxide degradation can be prevented by operating in an excess of *trans*-stilbene.

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References

- [1] P. J. Bruggeman, M. J. Kushner, B. R. Locke, J. G. E. Gardeniers, W. G. Graham et al. *Plasma Sources Sci. Technol.* **2016**, 25, 053002.
- [2] X. Lu, G. V. Naidis, M. Laroussi, S. Reuter, D. B. Graves, K. Ostrikov, *Phys. Rep.* **2016**, 630, 1.
- [3] D. P. Park, K. Davis, S. Gilani, C. Alonzo, D. Dobrynin, G. Friedman, A. Fridman, A. Rabinovich, G. Fridman, *Curr. Appl. Phys.* **2013**, 13, S19.
- [4] A. Shaw, G. Shama, F. Iza, *Biointerphases*. **2015**, 10, 029402.
- [5] S. Xu, S. Chansai, C. Stere, B. Inceesungvorn, A. Goguet, K. Wangkawong, S. F. R. Taylor, N. Al-Janabi, C. Hardacre, P. A. Martin, X. Fan, *Nature Catalysis*. **2019**, 2, 142.
- [6] A. Tou, H. Kim, H. Einaga, Y. Teramoto, A. Ogata, *Chem. Eng. J.* **2019**, 355, 380.
- [7] Z. Jia, M. B. Amar, D. Yang, O. Brinza, A. Kanaev, X. Duten, A. Vega-González, *Chem. Eng. J.* **2018**, 347, 913.
- [8] D. Mariotti, R. M. Sankaran, *J. Phys. D: Appl. Phys.* **2010**, 43, 323001.
- [9] J. E. Foster, B. S. Sommers, S. N. Gucker, I. M. Blankson, G. Adamovsky, *IEEE Trans. Plasma Sci.* **2012**, 40, 1311.
- [10] C. C. Beltrán, E. A. Palmer, B. R. Buckley, F. Iza, *Chem. Commun.* **2015**, 51, 1579.
- [11] A. Wright, J. Fuster, A. Shaw, H. Bandulasena, B. R. Buckley, F. Iza, *Plasma Chem. Plasma Process.* **2018**, 38, 1169.
- [12] H. Suhr, *Angew. Chem. Int. Edit.* **1972**, 11, 781.
- [13] J. Benedikt, M. Mokhtar Hefny, A. Shaw, B. R. Buckley, F. Iza, S. Schäkermann, J. E. Bandow, *Phys. Chem. Chem. Phys.* **2018**, 20, 12037.
- [14] Y. Gorbanev, D. Leifert, A. Studer, D. O'Connell, V. Chechik, *Chem. Commun.* **2017**, 53, 3685.
- [15] S. P. Jiang, S. X. Duan, K. Q. Liu, X. Y. Yang, C. Cheng, J. X. Li, G. W. Wang, *R. Soc. Open sci.* **2017**, 4, 170658.
- [16] R. Zhou, R. Zhou, K. Prasad, Z. Fang, R. Speight, K. Bazaka, K. Ostrikov, *Green Chem.* **2018**, 20, 5276.

- [17] R. A. Sheldon, *Green Chem.* **2017**, *19*, 18.
- [18] L. Wood, “*Epoxidized Soybean Oil Market by Raw Material, Application, End-use Application - Global Forecast to 2026*”, **2017** Research and Markets
- [19] Y. Lei, F. Mehmood, S. Lee¹, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss, S. Vajda¹, *Science*. **2010**, *328*, 224.
- [20] J. Rudolph, K. L. Reddy, J. P. Chiang, K. B. Sharpless, *J. Am. Chem. Soc.* **1997**, *119*, 6189.
- [21] M. G. Clerici, P. Ingallina, *Catal. Today*. **1998**, *41*, 351.
- [22] Y. Suga, H. Sekiguchi, *Thin solid films*. **2006**, *506*, 427.
- [23] G. Gambus, P. Patino, B. Mendez, A. Sifontes, J. Navea, P. Martin, Taylor P, *Energy Fuels*. **2001**, *15*, 881.
- [24] P. Patino, N. Sanchez, H. Suhr, N. Hernandez, *Plasma Chem. Plasma Process.* **1999**, *19*, 241.
- [25] J. Golda, J. Held, B. Redeker, M. Konkowski, P. Beijer, A. Sobota, G. Kroesen, B. S. J. Braithwaite, S. Reuter, M. M. Turner, *J. Phys. D: Appl. Phys.* **2016**, *49*, 84003.
- [26] Y. Gorbanev, J. Golda, V. Schulz-von der Gathen, A. Bogaerts, *Plasma*. **2019**, *2*, 316.
- [27] D. Ellerweg, J. Benedikt, A. von Keudell, N. Knake, V. Schulz-von der Gathen, *New J. Phys.* **2010**, *12*, 013021.
- [28] J. S. Sousa, K. Niemi, L. J. Cox, Q. Th. Algwari, T. Gans, D. O’Connell, *J. Appl. Phys.* **2011**, *109*, 123302.
- [29] D. W. Liu, F. Iza, M. G. Kong, *Plasma Process. Polym.* **2009**, *6*, 446.
- [30] K. McKay, D. X. Liu, M. Z. Rong, F. Iza, M. G. Kong, *J. Phys. D: Appl. Phys.* **2012**, *45*, 172001.
- [31] G. Smith, W. G. McGimpsey, M. C. Lynch, I. E. Kochevar, R. W. Redmond, *Photochem. Photobiol.* **1994**, *59*, 135.
- [32] M. Matsumoto, S. Dobashi, K. Kondo, *Tetrahedron Lett.* **1977**, *18*, 2329.
- [33] P. D. Bartlett, M. E. Landis, *J. Am. Chem. Soc.* **1977**, *99*, 3033.
- [34] M. Matsumoto, S. Dobashi, K. Kondo, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 185.
- [35] B. M. Kwon, C. S. Foote, S. I. Khan, *J. Org. Chem.* **1989**, *54*, 3378.
- [36] H. R. Li, L. Z. Wu, C. H. Tung, *J. Am. Chem. Soc.* **2000**, *122*, 2446.
- [37] O. Horie, G. K. Moortgat, *Atmospheric Environment Part A, General Topics*. **1991**, *25*, 1881.
- [38] H. Suhr, *Plasma Chem. Plasma Process.* **1989**, *9*, 7S.
- [39] N. Knake, V. Schulz-von der Gathen, *Eur. Phys. J. D.* **2010**, *60*, 645.
- [40] N. Knake, S. Reuter, K. Niemi, V. Schulz-Von Der Gathen, J. Winter, *J. Phys. D: Appl. Phys.* **2008**, *41*, 194006.

Graphical abstract / Table of content

He+O₂ atmospheric pressure plasmas can drive the epoxidation of alkenes in solution, in a process that generates epoxides with yields of up to ~70% at room temperature and atmospheric pressure, without the need for catalyst and without generating oxidant waste-streams.