

Plasma-driven Organic Synthesis: Waste-free Epoxidation

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Abstract: Plasma-liquid interactions have received growing attention in recent years for their relevance in many emerging applications such as plasma medicine, agriculture, water treatment and nanoparticle synthesis. Here we explore the use of non-thermal atmospheric pressure plasmas for organic synthesis and demonstrate the potential of plasmas for an epoxidation process that eliminates the oxidant waste stream of current chemical methods.

Keywords: plasma-liquid interaction, plasma synthesis, epoxidation.

1. Introduction

Non-thermal plasmas operating at atmospheric pressure open the possibility of novel processing of liquids that were not possible in conventional vacuum systems due to vapour pressure limitations.¹ As a result, the interest in plasmas interacting with liquids has grown exponentially in recent years (See Fig. 1), with applications ranging from medicine² and agriculture³ to nanoparticle synthesis⁴ and water treatment⁵.

In addition to these applications, non-thermal atmospheric pressure plasmas interacting with organic liquids have also the potential to be used for novel chemical synthesis processes. Particularly exciting are plasma-driven processes in which one has the potential of eliminating waste streams.

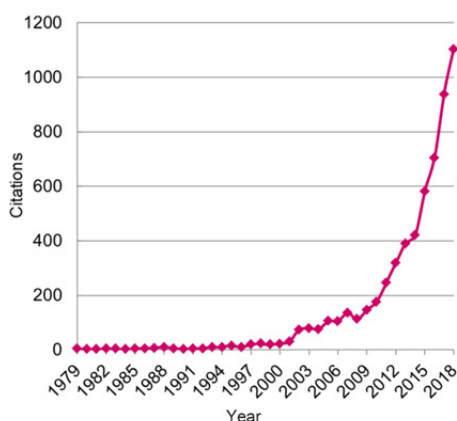


Fig. 1- Citations per year ("plasma and liquids" OR "plasma liquid"). Source: Web of Science.

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.⁶ Besides the obvious logistic and economic implications, these waste streams have a detrimental environmental impact that will compromise

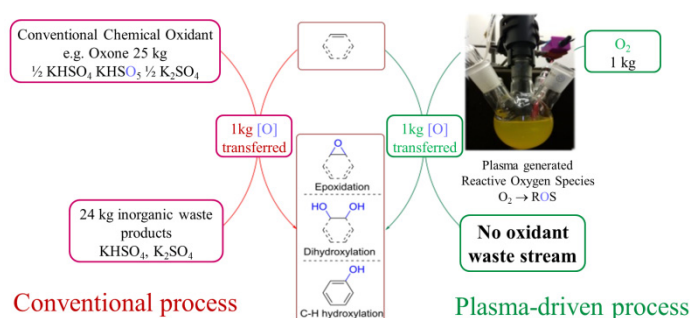


Fig. 2- Comparison of traditional chemical oxidation (left) and a plasma-driven oxidation process (right).

the ability of future generations to meet their own manufacturing needs. This is the case of many existing oxidation processes. For example, the widely used oxidant oxone produces ~25 kg of waste per kg of oxygen transferred, whilst plasma-driven oxidation has the potential to completely eliminate this waste stream (see Fig. 2).

In this study, we focus on plasma-driven epoxidation, i.e. the formation of epoxides from alkenes. Epoxides are key building blocks in the chemical industry and are important intermediates in the preparation of many products (drugs, paints, adhesives, sealants, plastics, etc).⁷ The demand for epoxides is difficult to estimate because much of the production never reaches the open market, but is used in-house to produce derivatised products. 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 2026.⁸

Conventionally, epoxides are prepared by reacting alkenes with sacrificial oxygen donors and various oxygen donors have been investigated over the years. The ultimate oxygen donor for these epoxidation reactions is molecular oxygen (O_2), as this is readily available in air and once incorporated into the target molecule it leaves no waste. 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.

Other small molecules that could potentially act as oxygen donors and produce small waste streams have 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). 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.

Owing to the lack of reactivity of small molecular oxygen donors and alkenes, peracids are often used to drive epoxidation reactions. 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 10kg of waste stream per kg of oxygen transferred.

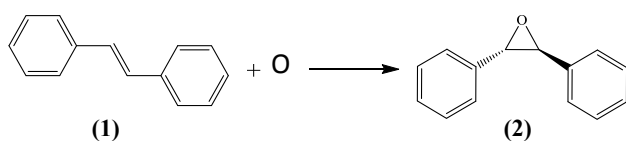
Notwithstanding recent advances in the field of catalytic epoxidation,⁹ the ultimate scheme for synthesising epoxides is the direct reaction of alkenes with atomic oxygen, as this would require no sacrificial material, no catalyst and produce no waste stream.

2. Results and discussion

It is well-documented that oxygen containing plasmas can produce significant amounts of atomic oxygen^{10,11} and therefore exposure of an alkene to such plasmas has the potential to lead to epoxide formation.

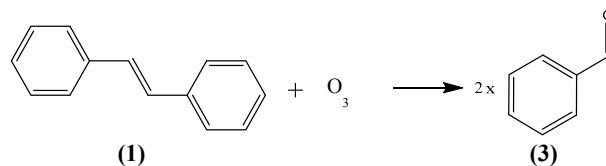
In this study, atomic oxygen is generated using an RF COST jet¹² operated in mixtures of He/O_2 and delivered to a solution containing the alkene trans-stilbene (**1**). The experimental setup is similar to that reported in [13], where it was shown that atomic oxygen generated in the gas plasma readily dissolves into aqueous solutions where it can react with organic substrates.

Experimental results demonstrate that atomic oxygen readily dissolves in the solution and reacts with the alkene to form epoxide (**2**) (Scheme 1):



Scheme 1- Epoxidation of trans-Stilbene.

In addition, gas chromatography mass spectrometry (GCMS) analysis of the treated liquid reveals also the presence of benzaldehyde (**3**). The formation of benzaldehyde is primarily attributed to the ozonolysis reaction of trans-Stilbene (**1**) with ozone generated in the system (Scheme 2):



Scheme 2- Ozonolysis of trans-Stilbene.

The distance between the plasma jet nozzle and the liquid surface as well as the oxygen content in the feed gas and the input power are critical elements that affect the ratio of epoxide to aldehyde formed in the system.

3. Conclusions

Although further work is required to increase the yield and selectivity of the process, the results obtained so far show the potential for a waste-free plasma-driven epoxidation process in which atomic oxygen generated in atmospheric pressure non thermal plasma reacts with an alkene to yield epoxide.

In addition to its synthetic value, selective epoxidation of alkenes could also provide a new means for the quantification of atomic oxygen in atmospheric pressure plasma systems.

4. Acknowledgement

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5. References

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