



Efficiency improvements of CO₂ utilization: the case of styrene carbonate synthesis in microdroplets conditions

Caterina ROVEGNO^{1,2}, Daniele URBANI^{1,2}, Eleonora POLO¹, Alessandro MASSI², and Paolo DAMBRUOSO^{1,*}

¹ Institute for the Organic Synthesis and Photoreactivity of the Italian National Research Council, Area della Ricerca di Bologna, Via P. Gobetti, 101 – 40129 – Bologna (Italy)

² Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari, 46 – 44121 Ferrara (Italy)

*Corresponding author: paolo.dambruoso@isof.cnr.it

Caterina Rovegno and Daniele Urbani equally contributed to this research

1. INTRODUCTION

Microdroplets (aerosol) reactions recently appeared in the literature as an innovative paradigm for organic transformations [1].

Reaction type	AF *
Claisen-Schmidt condensation	122
Oximation reaction	23
Two-phase reaction	6536
Eschenmoser coupling reaction	62

* AF = Acceleration factor

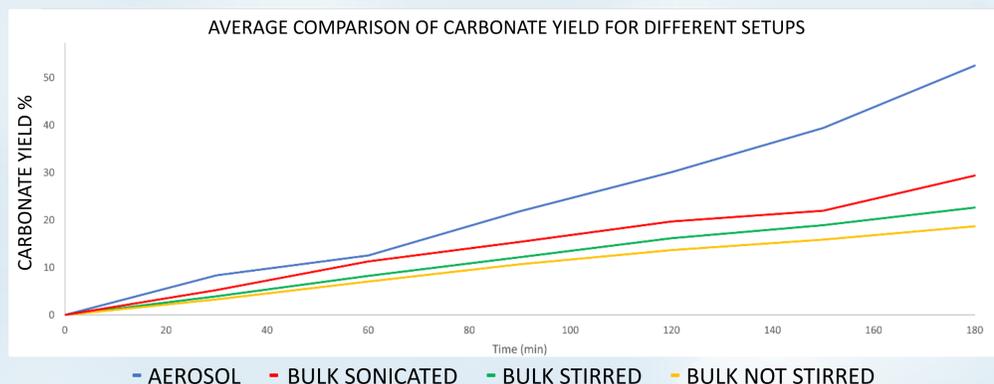
To date, only microdroplets reactions in inert gas atmosphere and photochemical oxidations in air, both in batch and continuous-flow conditions, have been reported, resulting in up to 4 orders of magnitude acceleration in respect of bulk counterparts.

2. THE OPPORTUNITY

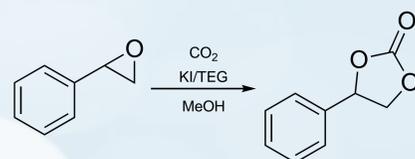
So far, only gas-liquid biphasic photochemical oxidations have been explored in microdroplets conditions [2]. We envisaged this new approach as an innovative tool in the realm of gas-liquid heterogeneous transformations. For this reason we expanded the scope of this method considering a CO₂ model reaction as a valuable target to explore this operative conditions.

6. THE PERFORMANCES AT ROOM TEMPERATURE

Reactions in bulk and microdroplets conditions were performed in triplicates obtaining the following results at RT.



3. THE MODEL REACTION



The styrene epoxide conversion to the corresponding carbonate was identified as the model reaction to explore this new paradigm. To this purpose, we targeted the KI/TEG* promoted reaction to study the effects of the microdroplets vs bulk reactions.

* TEG = triethylene glycol

4. THE METHODOLOGY

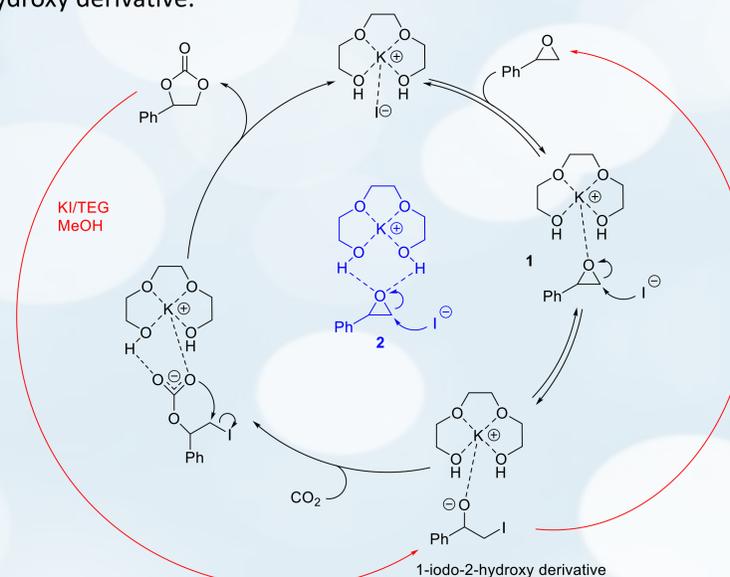
We compared the efficiency of the in-batch bulk reactions (both using magnetic stirring or sonication) vs in-batch aerosol conditions of the model reaction, in terms of:

- reaction rates
- products selectivities
- starting materials conversions.

The face-to-face comparison has been performed at various temperatures, in order to understand the effects of the microdroplets approach in the realm of gas-liquid biphasic reactions.

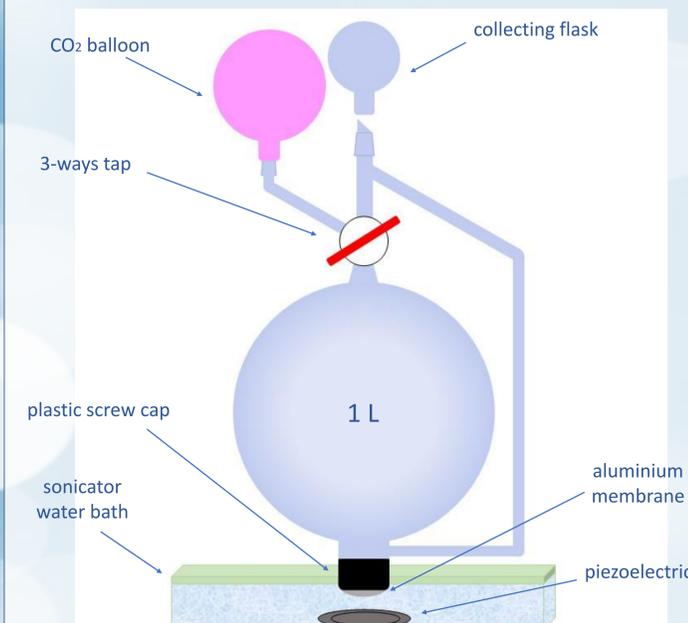
7. THE HIGH TEMPERATURE ISSUE

While bulk reactions performed at 50°C proceeded faster without any issue, aerosol reactions at the same temperature resulted in a carbonate side reaction with iodide anion, affording the 1-iodo-2-hydroxy derivative.



K⁺/TEG/oxygen epoxide complex **1**, depicted in the scheme, is based on Butera calculations [3], although TEG hydroxyls bonded to epoxide oxygen **2** has been earlier reported by Kaneko [4].

5. THE AEROSOL REACTOR



The apparatus used in our exploration consisted of a 1 L round bottom flask (RBF) with a 3-ways tap on top (the first one connected to a CO₂ balloon, the other one to a flask, in order to collect the condensed phase at the end of the reaction). A plastic screw cap with an aluminium membrane, on the bottom of the 1 L RBF, was the nebulization chamber, which had to be immersed in a sonication bath, in which the piezoelectric caused the reagents nebulization.

8. CONCLUSIONS

- In-batch microdroplets reactions at RT were three times accelerated in respect of the bulk counterparts
- higher temperatures affected the products distribution in aerosol conditions due to an unexpected side reaction
- microdroplets reaction procedures are being explored to improve the performances and avoid the side reaction.

References

- [1] C. Liu, J. Li, H. Chen, R. N. Zare, *Chemical Science* **2019**, 10, 9367–9373. [2] E. Kayahan, D. Urbani, P. Dambruoso, A. Massi, L. Braeken, T. Van Gerven, M. E. Leblebici, *Chemical Engineering Journal* **2021**, 408, 127357. [3] V. Butera, H. Detz, *ACS Omega*, **2020**, 5 (29), 18064-18072. [4] S. Kaneko, S. Shirakawa, *ACS Sustainable Chem. Eng.*, **2017**, 5, 2836-2840.