



# Efficiency improvements of CO<sub>2</sub> utilization: the case of styrene carbonate synthesis in microdroplets conditions

Caterina ROVEGNO<sup>1,2</sup>, Daniele URBANI<sup>1,2</sup>, Eleonora POLO<sup>1</sup>, Alessandro MASSI<sup>2</sup>, and Paolo DAMBRUOSO<sup>1,\*</sup>

<sup>1</sup> 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)

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

\*Corresponding author: [paolo.dambruoso@isof.cnr.it](mailto: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

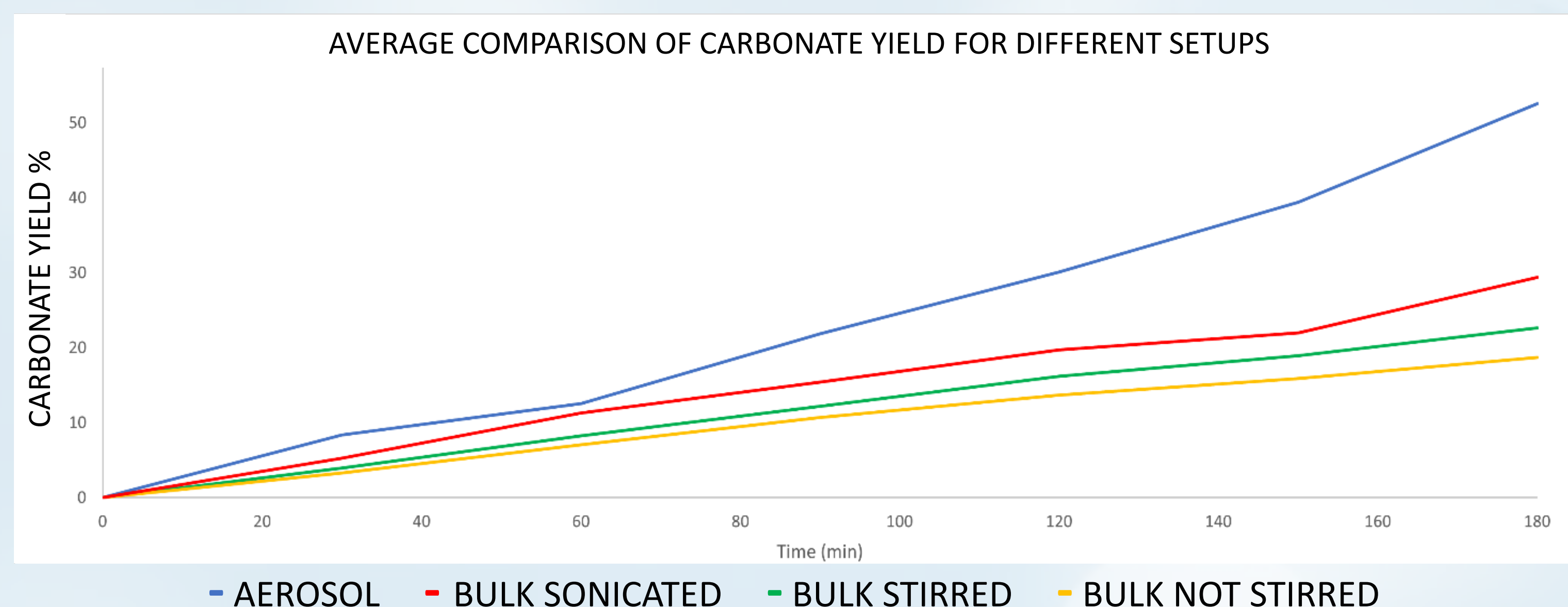
To date, only microdroplets reactions in inert gas atmosphere and photochemical oxidations in air, both in batch and continuous-flow conditions, have been reported, resulting in up to 4 orders of magnitude acceleration in respect of bulk counterparts.

## 2. THE OPPORTUNITY

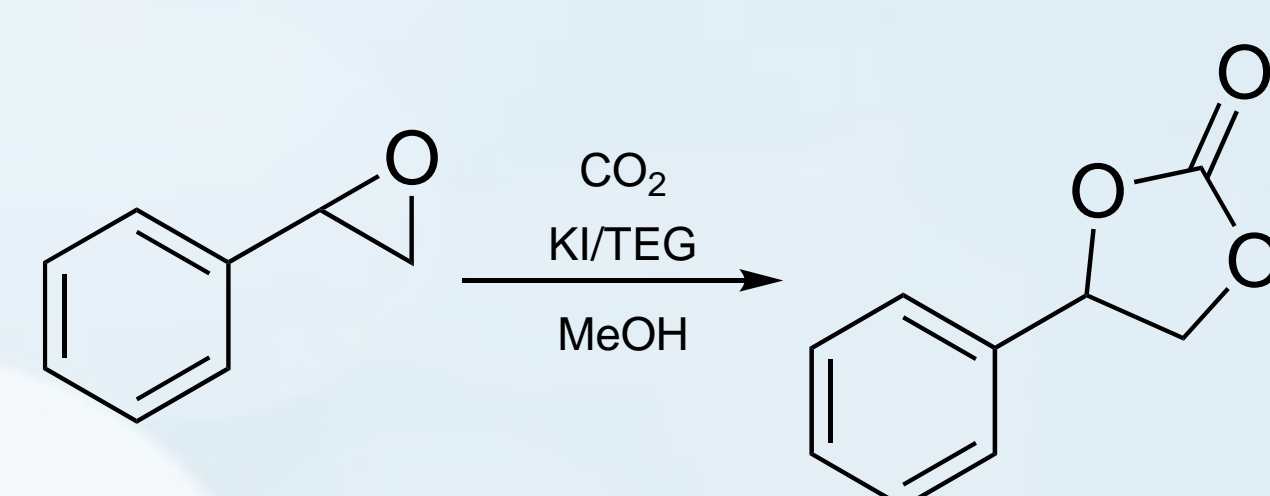
So far, only gas-liquid biphasic photochemical oxidations have been explored in microdroplets conditions [2]. We envisaged this new approach as an innovative tool in the realm of gas-liquid heterogeneous transformations. For this reason we expanded the scope of this method considering a CO<sub>2</sub> 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

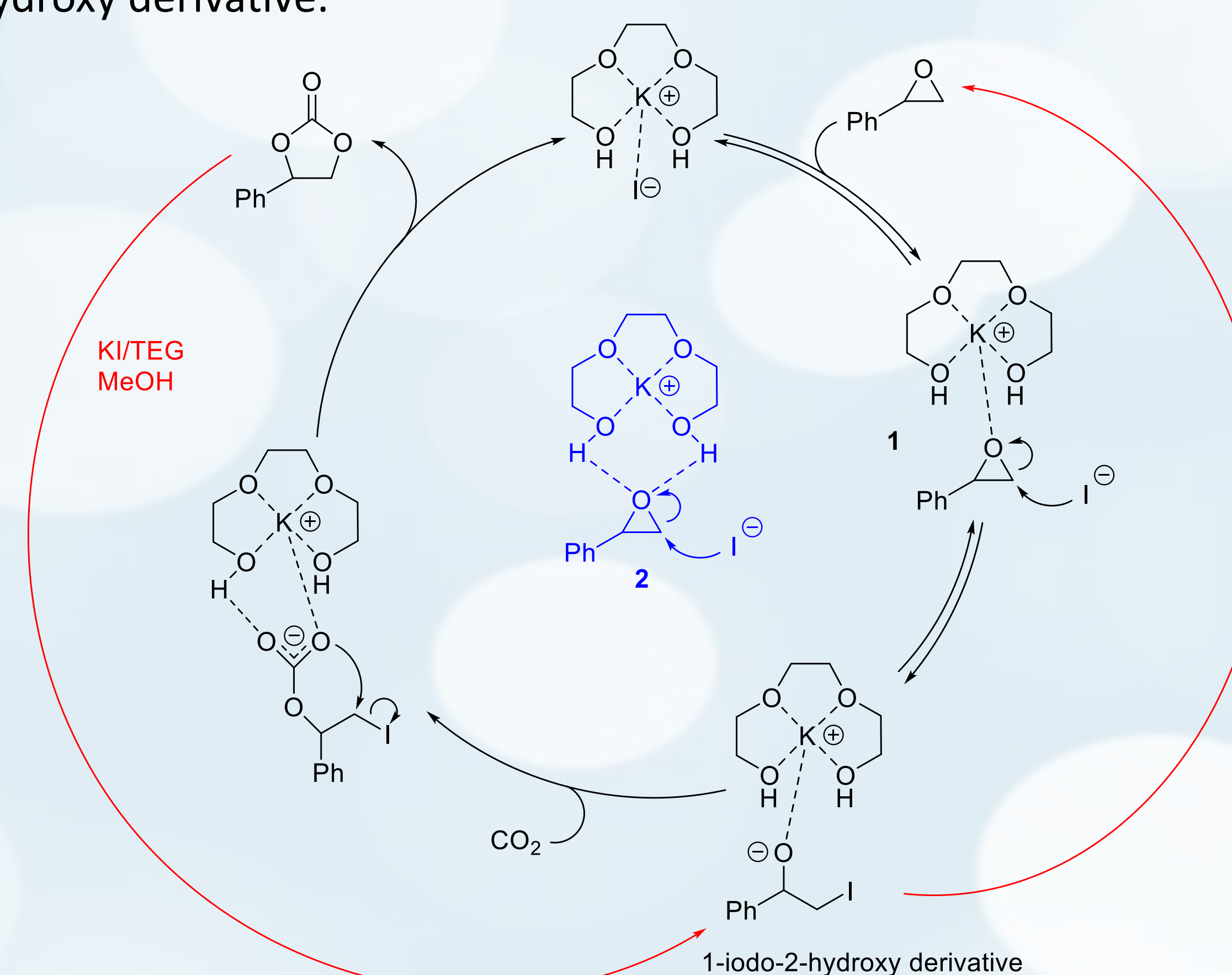
We compared the efficiency of the in-batch bulk reactions (both using magnetic stirring or sonication) vs in-batch aerosol conditions of the model reaction, in terms of:

- 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.

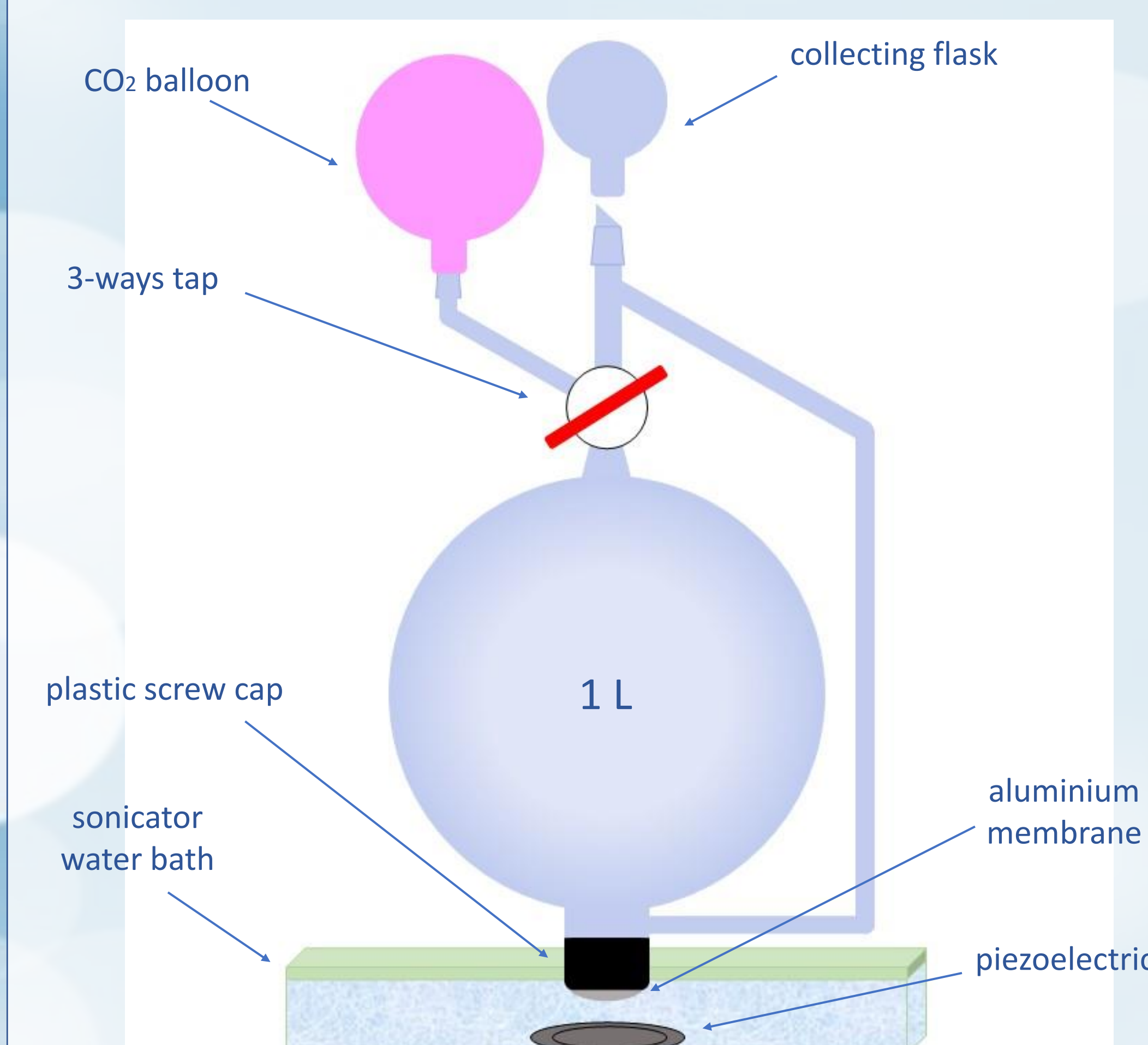
## 7. THE HIGH TEMPERATURE ISSUE

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<sup>+</sup>/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 CO<sub>2</sub> 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.