



# Efficiency in CO<sub>2</sub>-utilization strategies: The case of styrene carbonate synthesis in microdroplets conditions

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## ABSTRACT

The styrene oxide to styrene carbonate conversion performed in CO<sub>2</sub> atmosphere, herein selected as a case study, was implemented in microdroplets (aerosol) reactions at the preparative scale (3.5 mmol of the starting material) and mild conditions (1 atm CO<sub>2</sub> pressure), within a custom-made ultrasonic nebulization reactor. Upon optimization of the promoter stoichiometry (1 eq of 4.3 TEG/KI ratio) and methanol (MeOH) dilution (7.5 mL of 2.5 v/v MeOH/TEG), performances under mass transfer-limited conditions of this novel methodological paradigm have been compared at 25 °C and 50 °C with those implemented as: a) no-stirred, b) stirred, and c) sonicated bulk reactions. Complete selectivity and an apparent acceleration factor (AAF) of 1.9 was registered at both temperature for microdroplets reactions in respect with the sonicated counterparts, these latter performing better than the other bulk reactions. These significative efficiency improvements, candidate aerosol reactions as a preferred process intensification approach in the realm of effective CO<sub>2</sub>-utilization strategies and, in general, in the development and exploitation of gas-liquid two-phase reactions.

## 1. Introduction

The emission of CO<sub>2</sub> in the atmosphere has dramatically increased over the last two decades, causing global warming and consequent environmental damages. [1] In this scenario, net-zero CO<sub>2</sub> emissions are actively pursued through the balance between anthropogenic emissions and removals from the atmosphere ('sinks'). [2] Accordingly, carbon capture and storage (CCS) strategies are being developed using different types of solid and liquid adsorbents. [3] An attractive complementary approach to the storage of CO<sub>2</sub> is its re-use, that means the valorization of CO<sub>2</sub> as renewable C1-building block to produce added-value chemicals and fuels, thus compensating the energy consumption and costs associated with its capture and transport ('carbon dioxide refinery' concept). [4] Indeed, carbon capture and utilization (CCU) methodologies are currently attracting a lot of interest from academia and process industry, [5] with some important challenges to be faced due to the high chemical stability of CO<sub>2</sub> and the need to develop innovative processes competitive with those already established by the petrochemical

industry. Hence, in order to overcome energetic-environmental-economic issues, [6] utilization of CO<sub>2</sub> as a chemical feedstock should be designed under mild conditions (ambient or moderate temperature and pressure) using low-cost sustainable catalysts (non-noble metals, [7] organocatalysts [8]), eventually with the support of enabling technologies such as flow chemistry [9] to improve the chemical efficiency of the whole process.

In recent years, microdroplet-based technologies have also emerged as valuable synthetic tools at the preparative scale in virtue of the remarkable acceleration of reactions in microdroplets compared to the conventional bulk-phase counterparts. [10] Microdroplets generated in microfluidic channels, [11] microemulsions, [12] and aerosols [13] behave, in fact, as confined and high-surface-area units (microreactors) with unique features at the droplet interface (pH alteration, accumulation of reagents, effective diffusion, concentration effect by fast solvent evaporation, etc.). [10] In particular, various homogeneous liquid phase and liquid-liquid two-phase reactions have been reported to occur on the millisecond timescale in aerosols, representing successful milestones in

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this field. [13] Although much less explored, gas-liquid two-phase reactions have been also demonstrated to be accelerated by applying different nebulization technologies. [14–16] Case studies, including work of our groups, [15a] have been focused on aerobic oxidations, [14] singlet oxygen photooxidations [15] and, very recently, on the formation of carbamic acids from amines using CO<sub>2</sub> as nebulization gas. [16] Notably, although this latter study was conducted at the analytical scale with an electrosonic spray ionization (ESSI) source, it allowed to elucidate the mechanism of CO<sub>2</sub> activation at the gas-liquid interface and the origin of the much faster kinetics in aerosol than in the bulk, thus paving the way for the development of innovative and highly effective CCS strategies. In general, microdroplets chemistry appears particularly promising in the realm of biphasic gas-liquid transformations, since the mass transfer across the interface, which is often the rate-controlling step in this type of reactions, is inherently favored by the increased surface-area-to-volume (SA/V) ratio in microdroplets. [10].

The synthesis of cyclic carbonates from epoxides and CO<sub>2</sub> is a fundamental pillar of the carbon dioxide refinery as it has been estimated that, together with the dry reforming of methane, it could consume up to 25% of waste CO<sub>2</sub> produced annually. [8a] A previous work performed in conventional stirred batch reactors suggested that the synthesis of cyclic carbonates with CO<sub>2</sub> is a mass-transfer limited reaction. [17] This literature data encouraged us to conduct a comparative study of the reaction of styrene oxide (SO) with CO<sub>2</sub> promoted by a practical and sustainable catalytic system at ambient pressure under bulk and microdroplet conditions, with the final aim to detect any eventual appreciable enhancement in the production rate of the styrene carbonate (SC) product (Fig. 1).

In this proof-of-concept study, ultrasonic nebulization (UN), which produces micrometer-sized droplets from an acoustically excited membrane, [18] was chosen for aerosol generation due to the preparative value of this technique, as already reported for the synthesis of a diverse range of materials [19] and discrete molecules. [20] Additionally, in the present design, UN offered the opportunity to build a closed reacting system to avoid the consumption of large amounts of CO<sub>2</sub> as it would happen, instead, with pneumatic nebulization using CO<sub>2</sub> as sheath gas. The effect of temperature variation on product selectivity in bulk and aerosol experiments has been also considered in this study, along with the resulting mechanistic implications to ultimately evaluate opportunities and limitations of the presented CO<sub>2</sub>-utilization methodology.

## 2. Experimental section

### 2.1. Materials

Styrene oxide (>98%) was purchased from TCI Europe N.V.; Methanol (HPLC grade, ≥99.9%), Triethylene glycol (≥99.0%) and Potassium Iodide (≥99.0%) were purchased from Merck; CDCl<sub>3</sub> (99.8%) was purchased from CortecNet. All chemicals were used without any further purification.

### 2.2. Optimized reaction mixtures preparation and reaction procedures

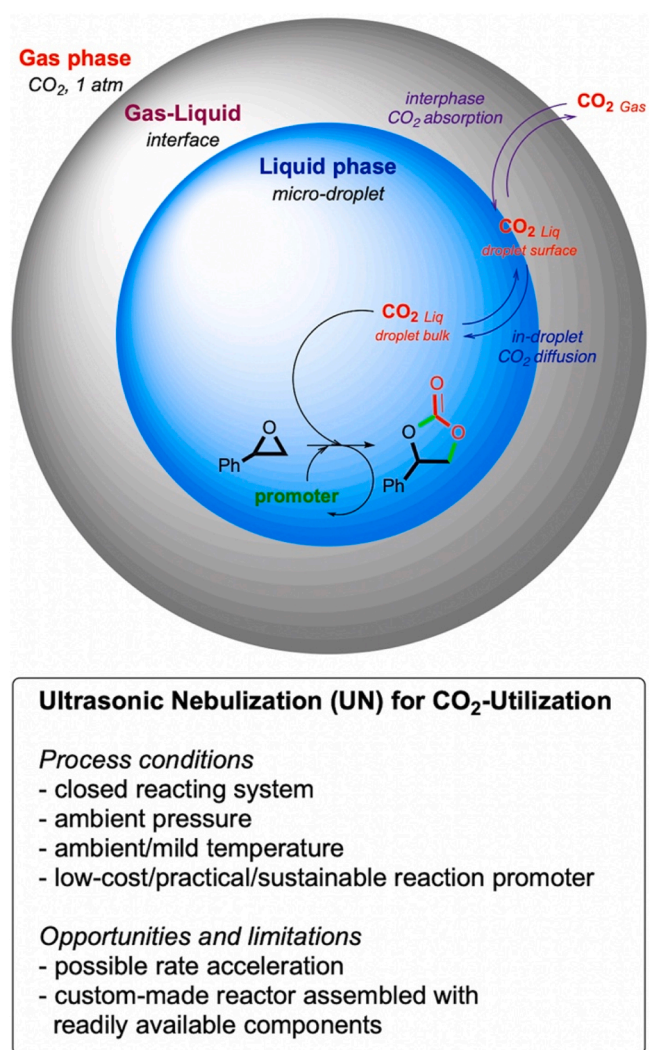
Only optimized procedures thoroughly assessed by careful experimentation are reported herein.

#### 2.2.1. Reaction mixtures preparation

In a 10 mL vial, the homogeneous reaction mixtures were prepared by stirring at RT (90 min, 950 rpm) a mixture of styrene oxide (SO, 0.4 mL, 3.5 mmol, 1 eq), potassium iodide (KI, 0.581 mg, 3.5 mmol, 1 eq), triethylene glycol (TEG, 2 mL, 15 mmol, 4.3 eq), and methanol (MeOH, 5 mL).

#### 2.2.2. Reaction, work-up and purification procedures

The freshly prepared homogeneous mixtures were allowed to react with CO<sub>2</sub> following 4 different procedures:



**Fig. 1.** Synthesis of styrene carbonate in microdroplets generated by ultrasonic nebulization (UN).

- no-stirred bulk reaction
- stirred bulk reaction
- sonicated bulk reaction
- microdroplets (aerosol) reaction.

All data were acquired in triplicates, and averaged values have been reported.

Accordingly, the homogeneous reaction mixtures were, case by case, transferred into the proper reactor and, upon three vacuum/CO<sub>2</sub> cycles, the gas-liquid reactions were performed at ambient CO<sub>2</sub> pressure and at the specified temperature (RT or 50 °C), following the highlighted specific conditions (Table 1).

After 3 h, the solvent was evaporated under reduced pressure. The crude was then partitioned between ethyl acetate/water (1:1 mixture, 20 mL overall volume), and the residual organics were extracted with ethyl acetate (3 × 10 mL) from the aqueous phase. The collected organic phases were evaporated at reduced pressure. Products were then isolated by medium pressure preparative chromatography, eluting the obtained residue with a cyclohexane (Cy) / ethyl acetate (EtOAc) gradient on silica gel. (Chromatographic method: CombiFlash RF 200 LC system; stationary phase: silica 120, CV = 192 mL; flow rate: 85 mL/min; elution method: 1 CV isocratic 100% Cy, 1 CV gradient to 10% EtOAc, 3 CV isocratic 10% EtOAc, 1 CV gradient to 20% EtOAc, 3 CV isocratic 20% EtOAc, 5 CV gradient to 100% EtOAc, 2 CV isocratic 100%

**Table 1**

Procedure's specific reactors and conditions.

Procedure	Reactor	Specific conditions
a)	25 mL single-neck round-bottom flask, connected to a 1 L chromatography reservoir equipped with a gas connector.	Without stirring.
b)		Stirring at 600 rpm.
c)		The single-neck round-bottom flask was dipped into the water bath of a Yuwell 402B ultrasonic nebulizer, therein centering the flask to avoid the reaction mixture nebulization. The reaction mixture was sonicated at the specified temperature, in turn regulated by an external circulation water bath.
d)	The homogeneous reaction mixture was transferred into the custom-made aerosol reactor (detailed description in <a href="#">Section 2.4</a> ).	The reaction mixture was nebulized and maintained at the specified temperature (see <a href="#">Section 2.4</a> for temperature regulation procedures of both the ultrasonic nebulizer water bath and the nebulized reaction mixture).

EtOAc).

### 2.3. Products characterization

With an Agilent DD2 NMR system, equipped with a 11.7 T (500 MHz) PremiumCompact+ superconducting magnet and an Agilent OneNMR probe, all isolated products were fully characterized by NMR spectroscopy through <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>13</sup>C HMBC experiments performed on CDCl<sub>3</sub>-dissolved samples.

Kinetic data were acquired by NMR spectroscopy, sampling all reaction mixtures at pre-defined reaction times, and performing pre-saturated quantitative <sup>1</sup>H NMR experiments.

#### 2.3.1. Styrene oxide

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.39–7.30 (m, 5 H, AR), 3.88 (dd, 1 H, CH,  $J_{\text{CH-CH}_2}$  = 3.96 Hz,  $J_{\text{CH-CH}_2'}$  = 2.67 Hz), 3.16 (dd, 1 H, CH<sub>2</sub>,  $J_{\text{CH}_2\text{-CH}_2'}$  = 5.46 Hz,  $J_{\text{CH}_2\text{-CH}}$  = 4.16 Hz), 2.82 (dd, 1 H, CH<sub>2</sub>',  $J_{\text{CH}_2'\text{-CH}_2}$  = 5.50 Hz,  $J_{\text{CH}_2'\text{-CH}}$  = 2.58 Hz).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 137.55 (AR<sub>ipso</sub>), 128.42 (AR<sub>meta</sub>), 128.10 (AR<sub>para</sub>), 125.42 (AR<sub>ortho</sub>), 52.27 (CH), 51.11 (CH<sub>2</sub>).

#### 2.3.2. Styrene carbonate

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.46–7.36 (m, 5 H, AR), 5.68 (t, 1 H, CH,  $J_{\text{CH-CH}_2}$  =  $J_{\text{CH-CH}_2'}$  = 8.01 Hz), 4.81 (t, 1 H, CH<sub>2</sub>,  $J_{\text{CH}_2\text{-CH}_2'}$  =  $J_{\text{CH}_2\text{-CH}}$  = 8.40 Hz), 4.35 (t, 1 H, CH<sub>2</sub>',  $J_{\text{CH}_2'\text{-CH}_2}$  =  $J_{\text{CH}_2'\text{-CH}}$  = 8.29 Hz).

<sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 154.77 (OCOO), 135.76 (AR<sub>ipso</sub>), 129.68 (AR<sub>meta</sub>), 129.18 (AR<sub>para</sub>), 125.82 (AR<sub>ortho</sub>), 77.94 (CH), 71.11 (CH<sub>2</sub>).

### 2.4. Aerosol reactor

The homemade ultrasonic nebulizer ([Fig. 2](#)), adapted from the Heated Ultrasonic Nebulization (HUN) system reported by Zare and co-workers, [20] consisted of a 25 mL bottom-threaded cylindrical nebulization chamber ( $\Phi$  = 25 mm) that was bottom-capped with 0.20 mm thick aluminum foil, and thereupon sealed with a plastic screw cap. On the upper end, the nebulization chamber was connected to the aerosol reaction chamber (adapted from 1 L dry solvents reservoir), in turn equipped with a three-way valve for vacuum/CO<sub>2</sub> cycles, CO<sub>2</sub> feed, and crude collection. The nebulization chamber was dipped into the water bath of a Yuwell 402B ultrasonic nebulizer, and centered on the piezo-electric transducer allowing a vigorous nebulization of the reaction mixture. The temperature of the ultrasonic nebulizer water bath was

regulated at the specified temperature (RT or 50 °C) with an external circulation water bath, while, in the case of 50 °C reactions, the nebulized reaction mixture was maintained at that temperature using two 100 W IR lamps to warm the nebulized mixture. The apparatus was reverted upside-down at the end of the reaction time, and the crude was recovered in the collection round-bottom flask, in turn cooled at 0 °C.

### 2.5. Monitoring of reactions temperature

Temperature of all reactions were monitored and measured using a Testo thermal imaging camera model: Testo 890 Thermal Imager, allowing a 0.04 °C (40 mK) thermal sensitivity in the temperature measuring range of 0 to + 650 °C, and featuring a SuperResolution option 960 pixels accounting for overall 1228800 pixels). Thermographic analyses were performed with Testo IRSoft software (version 4.8).

## 3. Results and discussion

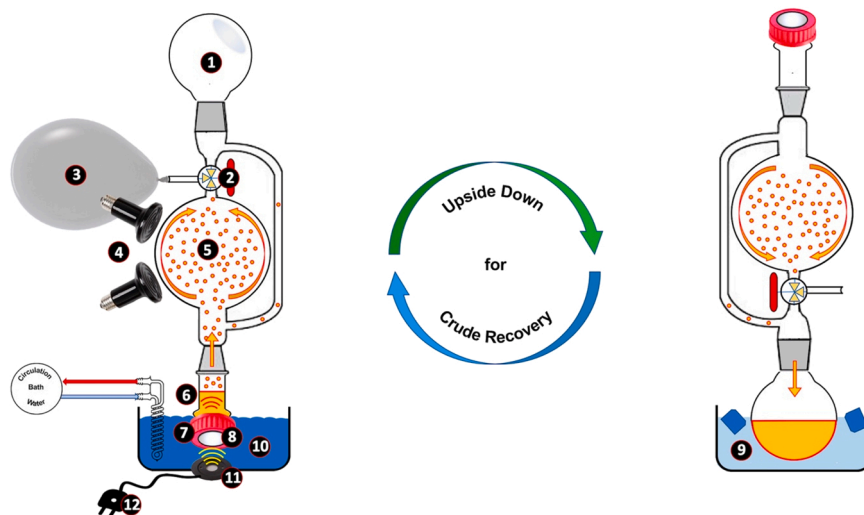
As anticipated, the direct carbonation of **SO** (1) with CO<sub>2</sub> to produce **SC** (2) was selected as the model reaction for our study on CO<sub>2</sub>-utilization in microdroplet conditions. Many different homogeneous and heterogeneous catalytic systems have been developed for this transformation performed with ordinary methodologies often requiring, however, harsh reaction conditions to reach satisfactory levels of conversion efficiency (pressure >10 atm, temperature >100 °C). [21] Guided by the previously mentioned criteria of chemical efficiency, the study of an effective CO<sub>2</sub>-utilization strategy [6a] based on the microdroplet synthesis of **SC** has been approached with a catalytic system belonging to the more restricted class of soluble promoters capable to activate the target carbonation under mild reaction conditions (atmospheric pressure, temperature ≤50 °C). [6c] The triethylene glycol-potassium iodide (TEG/KI, **3**) complex reported by Kaneko and Shirakawa [22] ([Scheme 1](#)) appeared well-suited to the objectives of our research due to its low-cost, practicality, recyclability, sustainability, and good catalytic activity through a bifunctional activation mechanism. [23] Furthermore, this catalytic complex can be easily prepared without any synthetic effort from cheap and readily available commercial chemicals.

Our first modification to the reported in-bulk procedure (1:1 TEG/KI [10 mol%], CO<sub>2</sub> atmospheric pressure, neat **SO**, 25 °C, 24 h: 67% **SC** yield) [22] entailed the variation of the TEG/KI ratio to obtain a fully homogeneous reaction mixture and, consequently, an efficient ultrasonic nebulization. Unfortunately, the 1:1 TEG/KI complex initially obtained as a homogeneous solution, resulted in a heterogeneous slurry upon **SO** addition. Further stepwise additions of TEG favourably reduced the amount of precipitate, thus resulting in a clear and homogeneous solution at the optimized 4.3 TEG/KI ratio.

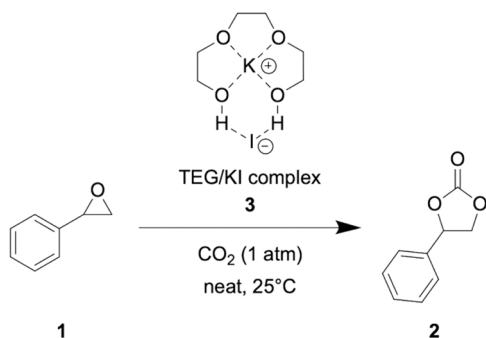
From this point forward, a three-hour reaction time was arbitrarily considered in our kinetic study, matching the need for both fast screening and reliable data acquisition. Next, the achievement of mass-transfer limited conditions was explored by gradually increasing the amount of the TEG/KI complex vs **SO** ([Table 2](#)). Actually, when the CO<sub>2</sub> transfer across the gas-liquid interface becomes the rate limiting step, the rate of **SC** formation is no longer controlled by chemical mechanisms and/or variation of extrinsic reaction parameters such as the catalyst loading.

After some experimentation (entries 1–4), it resulted that the yield of **SC** (52%) remained almost unchanged with the optimized 4.3 TEG/KI complex at KI loadings higher than 50 mol%; nonetheless, equimolar KI/**SO** was utilized in the continuation of the study to definitively ensure the operation under a mass transfer limited regime (entry 4). Disappointingly, any attempt to nebulize the identified reaction mixture failed with our homemade ultrasonic nebulizer ([Section 2.4](#)), thus making necessary dilution with a suitable solvent to obtain an appropriate viscosity of the nebulizing solution. Methanol was selected to this purpose,





**Fig. 2.** Ultrasonic nebulization apparatus for the microdroplet synthesis of styrene carbonate. In details: 1) collection flask; 2) three-way valve; 3) CO<sub>2</sub> balloon; 4) IR lamps; 5) aerosol reaction chamber; 6) bottom-threaded nebulization chamber; 7) plastic screw cap; 8) aluminum foil; 9) melting ice bath; Yuwell 402B ultrasonic nebulizer consisting of the following key elements: 10) water bath; 11) piezoelectric transducer, and 12) plug for power supply.



**Scheme 1.** The model reaction and the selected catalyst, as reported by Kaneko and Shirakawa [22].

**Table 2**

Propaedeutic bulk experiments for subsequent microdroplet synthesis of styrene carbonate (SC) under mass transfer limited conditions.<sup>a</sup>

SO CO<sub>2</sub> (1 atm) TEG/KI (4.3:1) neat or MeOH-diluted 25 °C, 3 h SC

Entry	KI (mol%)	MeOH/TEG (v/v)	SC yield (%) <sup>b</sup>	UN <sup>c</sup>
1	25	–	36	–
2	50	–	52	–
3	75	–	51	–
4	100	–	49	–
5	100	1.25	26	no
6	100	2.50	23	yes
7	100	5.00	15	yes
8	100	7.00	9	yes

<sup>a</sup> SO (3.50 mmol), 4.3 TEG/KI optimized ratio, MeOH/TEG ratio as reported.

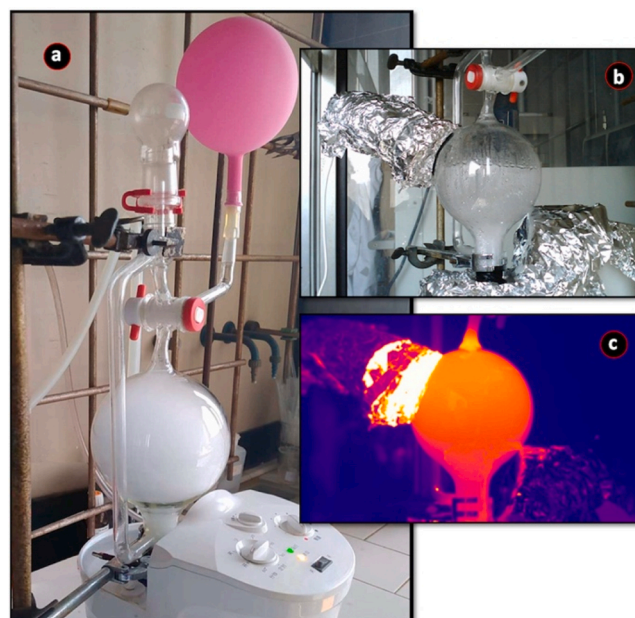
<sup>b</sup> Detected by pre-saturated quantitative <sup>1</sup>H NMR experiments on the crude reaction mixture.

<sup>c</sup> Effective ultrasonic nebulization (UN) in the homemade aerosol reactor.

because of its good environmental acceptability, [24] easy recyclability (distillation), and high CO<sub>2</sub> absorption capability. [25] The optimal compromise between effective nebulization and SO conversion was

found with the 2.5:1 MeOH/TEG volumetric ratio, being the yield of SC unavoidably reduced to 9% (at 7.0:1 MeOH/TEG volumetric ratio) due to dilution effects (entries 5–8). The comparative study on styrene oxide carbonation in bulk and microdroplet conditions was performed utilizing the prototype reactor described in Section 2.4., and sketched in Fig. 2. Inspired by the design of Zare and co-workers, [20] our home-made aerosol apparatus was fabricated from readily available commercial components ensuring an easy experimental reproducibility. Our reactor setup can also be integrated with one (or two) infrared (IR) lamps placed perpendicularly to the nebulization chamber for microdroplet heating and with a thermographic camera for the real-time monitoring of the reaction temperature (Fig. 3).

As planned, the effect of the specific surface area of reactant solution on SC yield was examined in bulk and microdroplet experiments under



**Fig. 3.** Ultrasonic nebulization apparatus for the microdroplet synthesis of styrene carbonate. In detail: a) the apparatus nebulizing the crude at 25 °C; b) the nebulized mixture warmed at 50 °C with one 100 W IR lamp; c) real-time monitoring of the reaction temperature with a thermographic camera.

mass transfer limited conditions. Accordingly, the ratio between the CO<sub>2</sub>-liquid surface area and the liquid volume (SA/V ratio) was progressively increased conducting the carbonation reaction in a conventional batch reactor with and without magnetic stirring and in the homemade UN apparatus. While the SA/V value of 130 m<sup>2</sup>/m<sup>3</sup> can be easily calculated for the non-stirred batch reactor used herein,<sup>2</sup> previous reports indicate SA/V data of ca. 10<sup>3</sup> m<sup>2</sup>/m<sup>3</sup> and 10<sup>4</sup>-10<sup>6</sup> m<sup>2</sup>/m<sup>3</sup> for biphasic gas-liquid reactions run under stirred batch [26] and UN conditions, [15b,20] respectively. For a better comparison with the microdroplet synthesis of SC, sonication was also investigated in bulk experiments to normalize the effect on reaction efficiency of the complex physico-chemical phenomena that may occur in the liquid phase when applying this technique. The kinetic plots of the planned four experiments were readily acquired by monitoring (pre-saturated quantitative <sup>1</sup>H NMR analysis) the yield of SC with time (Fig. 4). Of note, in the case of microdroplet reaction the kinetic profile was obtained by performing different UN experiments with the same feed composition but with different reaction times.

As expected, without magnetic stirring, the reaction yield after 180 min slightly decreased from 23% to 18% (blue-dotted and orange-dashdotted lines), whereas sonication (water bath regulated at 25 °C) produced a small increase to 29% yield (grey-dashed line). Quite satisfyingly, the product yield of the microdroplet reaction was 54% (red-solid line), corresponding to an apparent acceleration factor (AAF) of 1.9 in respect with the bulk reaction under sonication. The AAF was calculated by the ratio between the values of product yield in microdroplet and bulk reactions carried out for the same period of time (180 min; AAF = [SC]<sub>droplet</sub>/[SC]<sub>bulk</sub>). It is important to emphasize that the determined AAF should not be intended as a quantitative measure because of the many kinetic variables involved moving from bulk to microdroplet experiments; however, this simple method of approximating the AF clearly shows that the synthesis of styrene carbonate is significantly accelerated in microdroplet conditions. The productivity of the UN setup was also investigated after 6 h detecting an increased SC yield to 73%. On the other hand, not all reactions undergo dramatic

acceleration in microdroplets, [20a,27] being the mechanism behind this phenomenon strictly dependent on the intrinsic features of the reaction under investigation. In the case of carbonation of styrene oxide, it can be speculated that the enhanced mass transfer of CO<sub>2</sub> in microdroplets can improve the catalyst turnover and so increase the reaction efficiency.

It is well known that the reaction of epoxides with CO<sub>2</sub> to give the corresponding cyclic carbonates is deeply affected by temperature. [5] Therefore, the synthesis of styrene carbonate was next investigated at 50 °C in the bulk with sonication and in microdroplet conditions (Fig. 5).

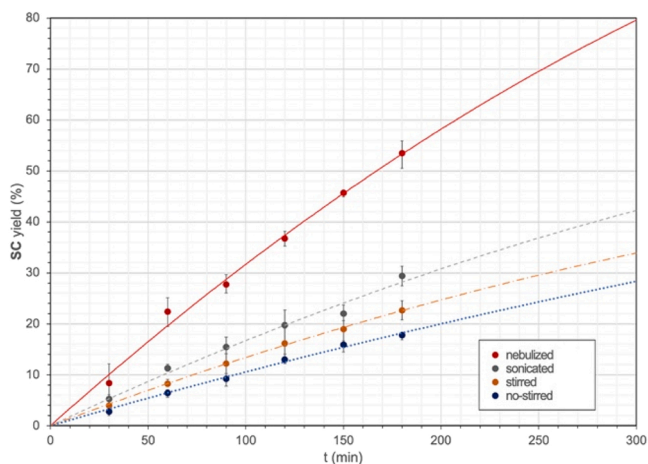
This thermal study was greatly facilitated by our experimental setup integrated with one IR lamps and the thermographic camera for a precise determination of the operating temperature (Fig. 6).

Satisfyingly, the bulk experiment proceeded smoothly at 50 °C affording SC with an increased 40% yield and complete reaction selectivity (reaction time: 180 min). To our delight, also the UN reaction selectively produced SC in higher yield (78%), compared to the experiment at ambient temperature. In light of this outcome, the corresponding AAF resulted 1.95, thus confirming also at 50 °C, a twofold acceleration of the UN reaction vs the bulk counterpart performed under sonication.

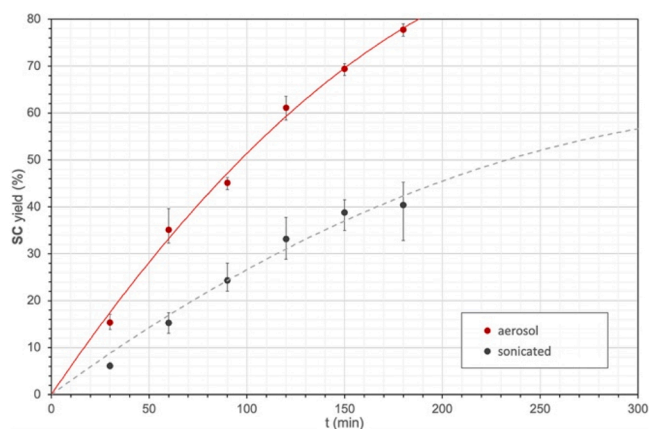
All results obtained in this study were in full agreement with the mechanistic hypothesis proposed by the groups of Shirakawa and Butera, [22,23] herein sketched in Scheme 2, in which is clearly highlighted the CO<sub>2</sub> insertion step.

#### 4. Conclusions

Herein we demonstrated for the first time the beneficial effect of an innovative enabling technology on the styrene oxide to styrene carbonate conversion, selected as a case study in the realm of CO<sub>2</sub>-utilization strategies. The ultrasonic nebulization herein implemented at the preparative scale caused a twofold acceleration of the identified model reaction in very mild conditions, offering an innovative and powerful tool in the continuous efforts toward the efficient exploitation of CCU approaches. The learned lesson is also of great general value, being straightforwardly extendible to all gas-liquid two-phase reactions plagued by mass-transfer limitation phenomena. A batch approach has been adopted in this study, allowing the minimal CO<sub>2</sub> consumption, in sharp contrast with continuous flow operations that, in the case of pneumatic nebulization using CO<sub>2</sub> as sheath gas, would have required unacceptable amounts of CO<sub>2</sub> and apparatus size.

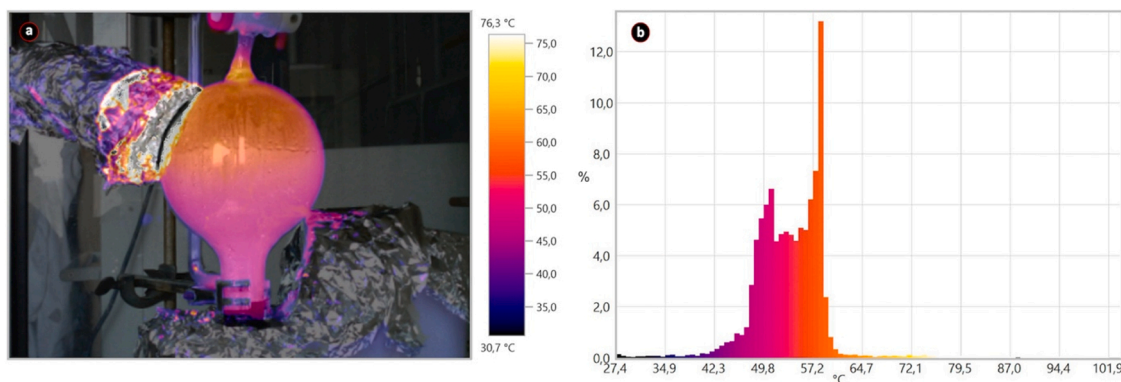


**Fig. 4.** Kinetic profiles of styrene carbonate synthesis at 25 °C in non-stirred (blue-dotted line), stirred (orange-dashdotted line), sonicated (grey-dashed line) bulk experiments and microdroplet conditions (red-solid line) using the homemade aerosol reactor. All reactions were performed in triplicates. Error bars were represented as min-max range of measured values. Averaged experimental data were fitted with a 2nd grade polynomial curve embedded in Microsoft Excel for MAC (version 16.16.27 (201012)).

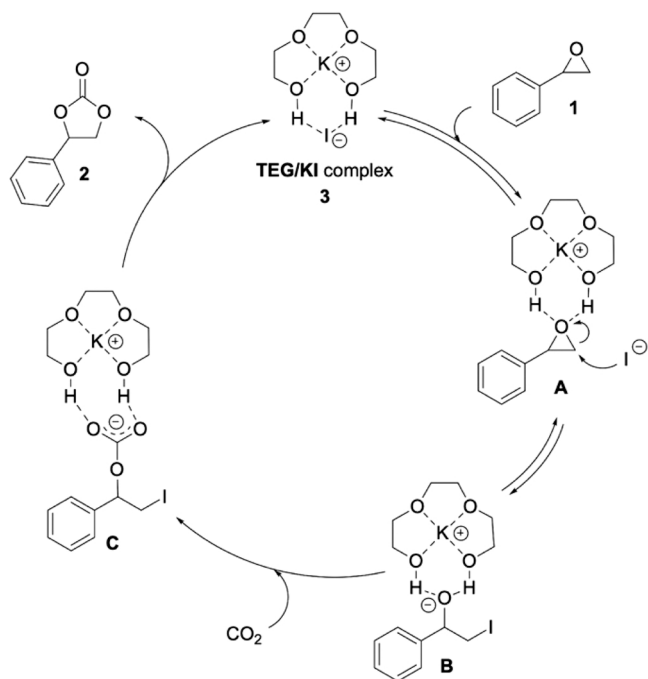


**Fig. 5.** Kinetic profiles of styrene carbonate synthesis at 50 °C in sonicated (grey-dashed line) bulk experiment and microdroplet conditions (red-solid line) using the heated aerosol reactor. All reactions were performed in triplicates. Error bars were represented as min-max range of measured values. Averaged experimental data were fitted with a 2nd grade polynomial curve embedded in Microsoft Excel for MAC (version 16.16.27 (201012)).

<sup>2</sup> calculated considering the 3.5 cm diameter circular surface of a 7.4 mL reaction solution in a 25 mL round-bottomed flask



**Fig. 6.** Real-time monitoring of reaction temperature in the nebulization chamber by thermographic camera. In detail: a) thermo-image of the aerosol warmed at 50 °C (averaged temperature); b) temperature profile within the nebulization chamber.



**Scheme 2.** The proposed reaction mechanism, in accordance with those proposed by Kaneko/Shirakawa [22] and Butera. [23].

These results pave the way for further studies in this field, and we are currently exploring additional exploitation opportunities of the ultrasonic nebulization. At the same time, new challenges need new solutions, and we are constantly involved in the improvement of the ultrasonic nebulization apparatus setup. The novel methodological paradigm herein introduced deserves further studies aimed at identifying key physico-chemical and aerosol-phase composition parameters causing the reported acceleration. [28] Although literature speculations largely assign the temperature-dependent kinetic performances to the reduced droplets size registered at higher temperatures, [20a] the effect on the reaction kinetic of aerosol phase molar composition and catalyst/reactant molar ratio, CO<sub>2</sub> solubility and solvent evaporation should be taken into account to deeply clarify ongoing phenomena. Results of these investigations will be reported in due course.

#### Credit authorship contribution statement

**Daniele Urbani** and **Caterina Rovegno** equally contributed to this research. **Daniele Urbani:** Aerosol reactor manufacturing, Aerosol and

bulk reactions experiments, Data curation. **Caterina Rovegno:** Bulk reactions experiments, Data curation. **Alessandro Massi:** Conceptualization, Methodology, Writing. **Mumin Enis Leblebici:** Methodology, Supervision. **Emine Kayahan:** Data analysis, Writing – review & editing. **Eleonora Polo:** Writing – review & editing. **Paolo Dambruoso:** Project coordination, Conceptualization, Methodology, Supervision, Writing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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