CO_2 utilization in a micellar system: synthesis of cyclic carbonates

Wojciech J. Depa,[1] Souvik Majumder,[1] Mariana Nadirova,[1] Piotr Cmoch,[1] Wojciech Chaładaj,[1,*] Martin P. Andersson,[2,**] and Dorota Gryko,[1,3,***]

[1]Institute of Organic Chemistry Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[2]Center for Integrative Petroleum Research, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

[3]Lead contact

*Correspondence: wojciech.chaladaj@icho.edu.pl

**Correspondence: martin.andersson@kfupm.edu.sa

***Correspondence: dorota.gryko@icho.edu.pl

Abstract

Fixation of carbon dioxide from its waste streams into value added products, in organic synthesis processes, whilst challenging, would lead to great ecological benefits. To this end, a CO_2 cycloaddition to epoxides seems most promising as it is a 100% atom economic reaction leading to valuable cyclic carbonates. However, many of the reaction systems utilized for their synthesis employ organic solvents, high temperatures, and high pressure. Thus, the micellar conditions reported here achieve a metal and organic solvent free approach, giving access to not only carbonates but also carbamates without the need for pressurization or heating. Extensive studies of interactions between micelles and carbon dioxide opens up pathways to use this gaseous reagent in aqueous media.

Carbon dioxide, micelles, micellar catalysis, surfactants, cyclic carbonates, carbon disulfide, epoxides, aziridines, carbamates

INTRODUCTION

The development of sustainable processes and methods for the synthesis of organic molecules represents one of the key challenges of modern chemistry articulated by the principles of the Green Chemistry.[1] While preventing waste generation highly beneficial from an environmental point of view, it is not always possible within the current state of the art. Organic solvents constitute more than 60% by mass in pharmaceutical industries, which are then often burnt, emitting CO_2 to the atmosphere.[2] In recent years, a 'greener' alternative, water, has received considerable attention. Until now, many transformations utilizing water based systems,[3–13] with micellar solutions at the forefront, have been developed and, more importantly, industrially applied, as they often allow to 1) minimize cumulative process mass intensities (PMIs), 2) lower catalyst loadings, or 3) run reactions under milder conditions.[14–16] The astonishing progress made

would not be possible without designer surfactants, for example TPGS-750-M[17] that allows solubilization of various substance, that would otherwise be non-miscible in water.

Furthermore, to adhere to the green principles, carbon feedstocks should, if possible, be recovered and recycled. Along this line, waste streams of carbon dioxide that heavily impact the global carbon cycle, are increasingly available, and they should be utilized as renewable resources, in accordance with circular economy where waste products are transformed into value added chemicals. CO_2 has already proven as a valuable C1 feedstock in synthetic chemistry. While there are many reactions that employ carbon dioxide,[18–20] formal cycloaddition to epoxides is attractive as it omits the challenging reduction of CO_2 and is 100% atom economy efficient.[21] It is also one of the most promising for the consumption of large amounts of this greenhouse gas, which adheres to the goals of a carbon capture and utilisation strategy (CCU).[22,23] The resulting cyclic carbonates themselves, have many uses across many industries.[24–27] They are commonly used as solvents in electrolytes for lithium-ion batteries, as monomers in the production of polycarbonates, and are employed in cleaning, coatings, and adhesives processes.

The synthesis of cyclic carbonates can be realized using various methods. For example, in aqueous systems where water acts as a solvent[28] or a dispersing phase in "on water"[29] and "around water"[30] media, where the hydrogen bonding increases its efficacy.[31–39] Although the micellar environment, in particular, the hydrophobic core, appears suitable for capturing highly nonpolar CO_2, it has been rarely utilized for this purpose. In general, reactions with gaseous reagents remain an underdeveloped niche in the micellar catalysis field. Some reported methods use heterogeneous catalysts, for example carbon nitride for oxidative cleavage of 1,2-diols[40] or lignin processing[41] with O_2 under visible light irradiation (Fig. 1A). Other reactions with gases include reductions of various nitro compounds, or double/triple bonds with H_2 in the presence of Pd/C[42] or nickel nanoparticles (Fig. 1B, 1C),[43] carbonylation with CO generated from $W(CO)_6$.[44] C-H insertion into gaseous alkanes with diazo-compounds is also possible in micellar media.[45]

With our own quest to pursue greener methodologies, and in the effort to understand both micellar catalysis employing gaseous reagents, we aim to develop an attractive CO_2 utilisation strategy boosting the sustainability of valuable carbonate synthesis. Quaternary ammonium salts, such as TBAB, are known surface active agents and they have been reported to catalyse the cycloaddition of CO_2 to epoxides.[46] However, traditionally these reactions are performed in organic solvents under high temperature and pressure, and often require metal catalysts combined with quaternary ammonium or phosphonium salts. With this in mind, we wondered whether cationic surfactants such as DTAC or DTAB would allow the synthesis of carbonates, from epoxides, under aqueous conditions. *Indeed, here we present a micellar approach to formal CO_2 cycloaddition that allows access not only to cyclic organic carbonates, but, for the first time, also to oxazolidinones and/or their sulphur analogues under mild conditions* (Figure 1D).

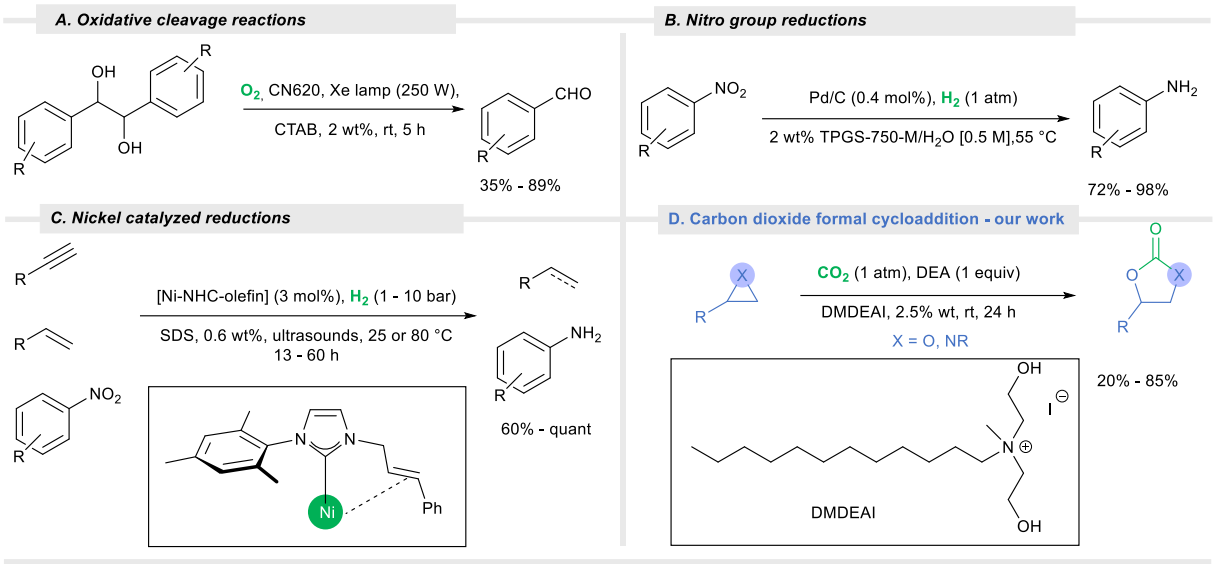


Figure 1. Reactions involving gaseous reagents in a micellar environment.

RESULTS AND DISCUSSION

As a proof of concept, we initiated our studies using styrene oxide (**1**) and CO_2 as benchmark substrates alongside surfactants as solubilizing agents, as both molecules are hydrophobic. Although CO_2 is slightly soluble in water (0.144 g/100 mL H_2O), its concentration is too low for the cycloaddition to proceed with reasonable rate and efficacy, so commonly used CO_2 binding agenst, namely amines[47] and pressure of a 3 bar was initially applied. Preliminary studies showed that among the surfactants tested, only quaternary ammonium salts enabled the efficient reaction (for details, see SI 4.1.1 and 4.1.15). The iodide counter anion proved crucial, which is on par with previous studies,[29,30,48] eg, both Crespy and D'Elia groups observed that TBACl does not catalyse the formation of carbonates from epoxides, while TBAB gives a decreased yield compared to TBAI. The same was observed in our micellar system, where reactions in the presence of DTAI (**5**), DTAB (**6**), and DTAC (**7**) gave the desired product **2** in 50%, 15%, and 0% yield, respectively. On the contrary, both anionic and non-ionic surfactants were ineffective. Further optimization of the reaction parameters included altering the length of the hydrocarbon chain of surfactants, modification of the chemical structure of surfactants, concentration and quantities of all reactants, different amines, CO_2 pressure, co-solvents, and the reaction time (Fig. 2B) (for full description see SI 4.1.2 – 4.1.16). Importantly, the reaction does not require pressurized CO_2 nor heating. The optimised conditions are as follows: DMDEAI (**10**) as surfactant, diethanolamine (**11**) as a CO_2 binding agent, and a balloon of CO_2. Of note is the fact that our designer DMDEAI surfactant not only proved the most productive but also has increased affinity to water phase, in comparison to the simple methylated derivatives, which facilitates the isolation of products from the reaction mixture.

During the reaction, an epoxide **A** is opened by the iodide, giving an iodoalkoxylate intermediates **B** and **C**, which further reacts with CO_2 leading to intermediate **D**, which upon iodide intramolecular substitution results in the formation of the desired cyclic carbonate **E** (Fig. 2C).

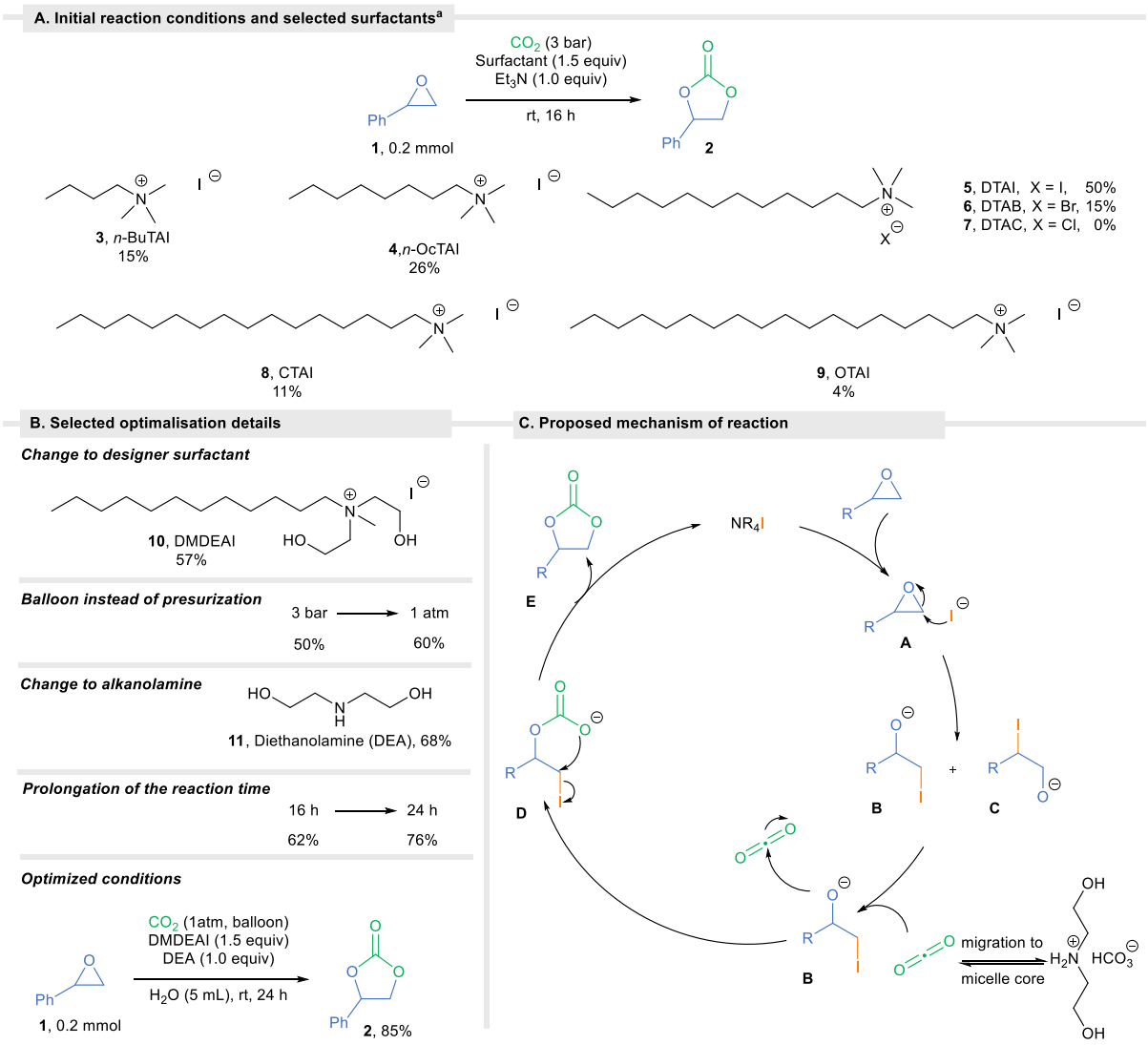


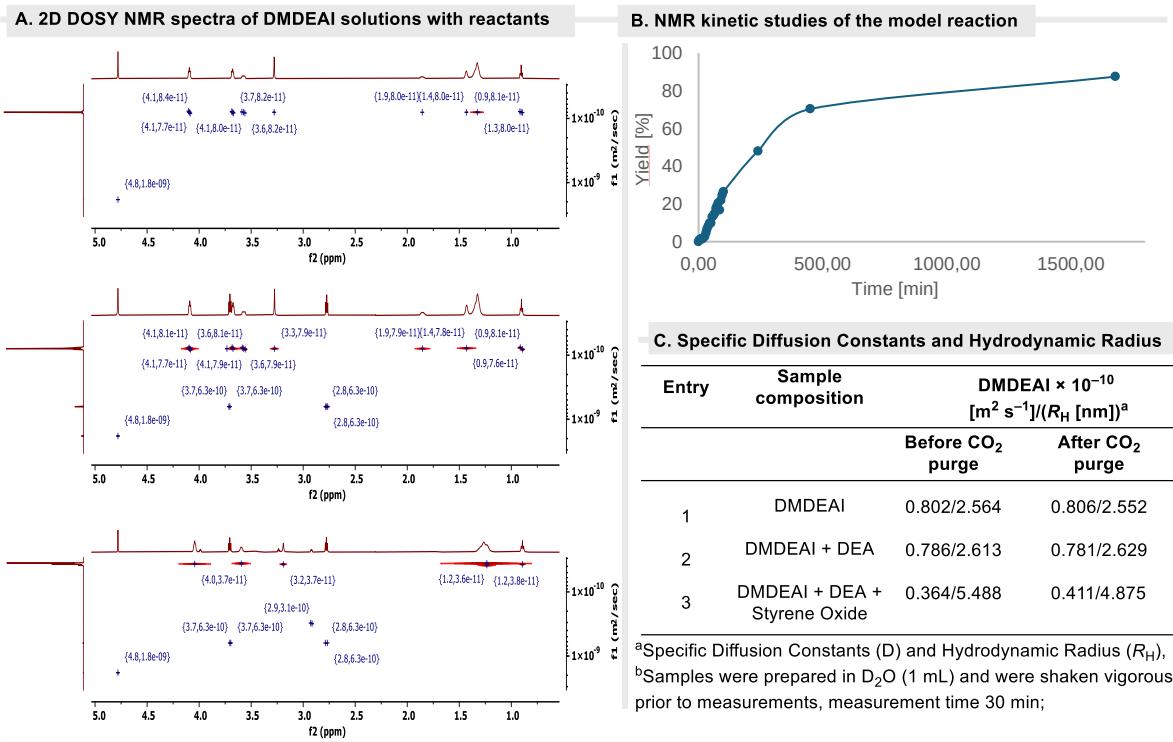
Figure 2. Preliminary studies on the reaction system

a) Preliminary screening of surfactants for the cycloaddition of CO_2 to epoxide in micellar solution. Reaction conditions: styrene oxide (0.20 mmol), NEt_3 (1.0 equiv.), surfactant (1.5 equiv.), H_2O (5 mL), CO_2 (3 bar), 16 h, rt.

Mechanistic investigations

To shed light on the catalytic system developed, mechanistic investigations using both theoretical calculations and NMR measurements, were conducted, which, as we have previously shown, are excellent tools for studying micellar systems.[49,50] One key aspect of reactions in heterogeneous systems, such as micellar solutions, is the necessary prerequisite for reactants, intermediates, and catalysts involved in each elementary-reaction step to be co-located, either in the micellar cores or the micellar interface region. Density functional theory (DFT) with the COSMO-RS implicit solvent model studies addressed this aspect.

Critical micelle concentration (CMC) is an important characteristic of a surfactant, which tells the surfactant concentration at which micelle formation is first seen in the solution. Therefore, in the first instance, the CMC of our designer DMDEAI surfactant was predicted based on the COSMO-RS calculations.[51] The calculated concentration, ~0.3 mM, is similar to the experimental value measured for the analogous bromide salt.[52,53] This value is significantly below the experimentally used surfactant concentration (60 mM) in our studies, which implicated, that the model reaction occurs indeed in the micellar regime. Indeed, two-dimensional diffusion-ordered experiments (2D DOESY NMR) measured for DMDEAI solutions in D_2O at the concentration corresponding to its concentration in the model reaction indicates formation of the aggregates (Fig. 3A). The kinetics of the reaction (Fig. 3B) shows the expected behavior of micellar catalysis, with almost linear rise of yield with time until the plateau. This is consistent with a small reaction volume and a reservoir of reactants outside the micelles, keeping the concentration in the reaction volumes constant.[54] At the surfactant concentration in the reaction mixture (60 mM), micelles of 2.564 nm hydrodynamic radius are formed (Fig. 3C). Dynamic light scattering (DLS) measurements of the surfactant solution in water also show aggregation signals (See SI 4.1.15). Upon the addition of styrene oxide and saturation with CO_2 the size of the aggregates increases from 2.564 to 4.475 nm. The addition of styrene oxide had the biggest impact on the size of the micelle, which shows that it is incorporated into the micelles upon addition.



C. Specific Diffusion Constants and Hydrodynamic Radius

Entry	Sample composition	DMDEAI × 10^{-10} [m^2 s^{-1}]/(R_H [nm])[a]	
		Before CO_2 purge	After CO_2 purge
1	DMDEAI	0.802/2.564	0.806/2.552
2	DMDEAI + DEA	0.786/2.613	0.781/2.629
3	DMDEAI + DEA + Styrene Oxide	0.364/5.488	0.411/4.875

[a]Specific Diffusion Constants (D) and Hydrodynamic Radius (R_H), [b]Samples were prepared in D_2O (1 mL) and were shaken vigorously prior to measurements, measurement time 30 min;

Figure 3. NMR studies of the reaction system

A. 2D DOSY NMR spectra, samples were shaken vigorously before measurement; I) DMDEAI; II) DMDEAI + DEA; III) DMDEAI + DEA + styrene oxide.

B. Reaction kinetics of styrene carbonate formation were studied based on ^{1}H NMR, 1,2-dimethoxyethane was used as an internal standard for full experimental description see SI (8.2).

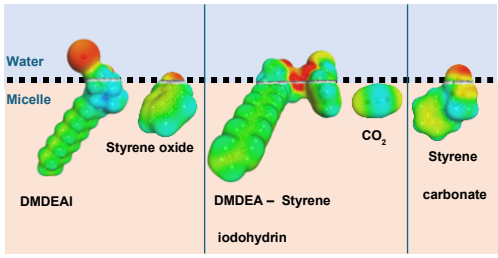
C. Specific Diffusion Constants and Hydrodynamic Radius Measured for reaction components and the designer surfactant DMDEAI with the ONE-SHOT sequence.

Furthermore, the most favorable location/orientation at the micelle interface (Fig. 4A) and the partition of all components in the aqueous part versus the micellar core region or the micellar interfacial region (Fig. 4B) were calculated COSMO-RS. The initial amounts of various components for the calculation can be found in Table S6.1 in the SI. Both styrene oxide and CO_2, as hydrophobic molecules, are indeed, localized in the micellar core, while more hydrophilic styrene carbonate occupies the interfacial region. ^{1}H NMR spectra were recorded for all components of the reaction (styrene oxide, iodohydrin, carbonate and styrene) in neat D_2O and within a surfactant solution, which exhibited a small but evident difference in chemical shift values (0.1 – 0.2 ppm). Such behavior is usually attributed to interaction of the surfactant with the studied molecule. For example, styrene oxide characteristic ^{1}H NMR shifts are as follows: a) pure D_2O: 4.08, 3.29, 3.11 b) in D_2O with DMDEAI: 4.00, 3.25, 2.93; (for full table with comparison of

chemical shifts and stacked spectra please SI 8.1). However, there are no differences in the chemical shifts for diethanolamine, which resides outside of the micelle.

Based on the predicted mole fractions, hence co-locations of reactants, a sequence of events involved in the designed reaction system can be envisaged (Fig 4. B). Firstly, because the counterion (I^-) of the DMDEAI surfactant is crucial for the activity, the initial step should involve a halide ion-assisted ring opening of styrene oxide. The epoxide, while most stable in the micelle core, also has a significant concentration at the micelle interface (0.06), where the surfactant is located. Hence, upon reaction with nucleophilic I^-, an iodohydrin (both regioisomers) is formed in less than 30 minutes, as corroborated by ^1H NMR experiments (See SI 8.3).

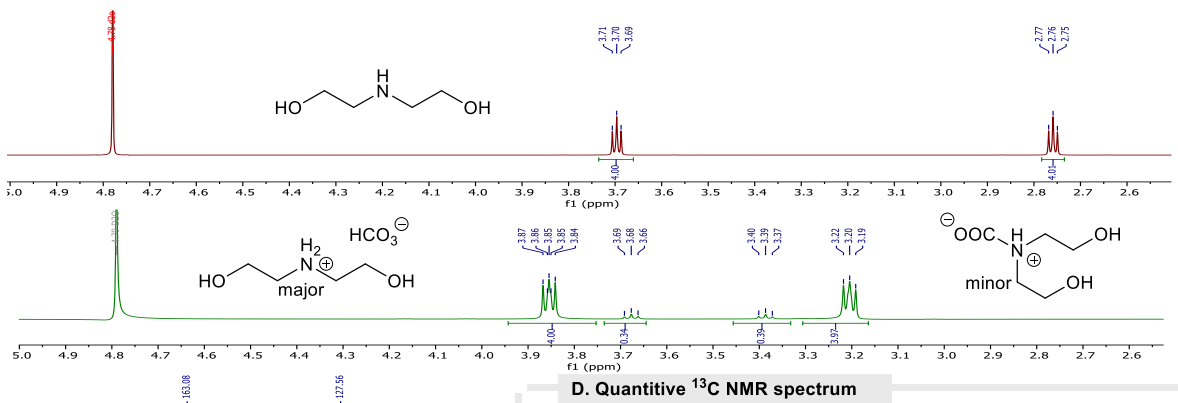
A. Collocations of reactants in the aqueous system



B. Mole fractions of reactants in the studied system

Compound	Mole fraction (in water)	Mole fraction (at interface)	Mole fraction (micellar cores)	Most stable location
DEA-CO_3H_2	0.000376	3.40E-06	2.09E-11	water
DEA	0.000375	6.37E-05	1.16E-06	water
Styrene carbonate	**0.000875**	**0.373**	**0.196**	**interface**
CO_2	1.60E-06	0.000103	0.000362	core
Styrene oxide	0.000151	0.0602	0.196	core
DMDEA-Iodohydrine	**8.02E-10**	**0.000330**	**3.27E-05**	**interface**

C. NMR spectra of DEA before and after CO_2 purge; spectrum of reaction mixture with ^{13}C CO_2



D. Quantitive ^{13}C NMR spectrum

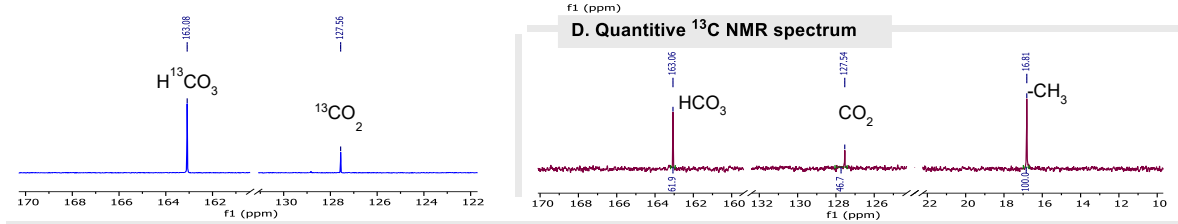


Figure 4. Mechanistic investigations

A. Molecular structures and COSMO surfaces of reactants calculated using COMSO-RS.

B. Mole fractions of the compounds in the system calculated using COSMO-RS at the surfactant CMC concentration for a current conversion of 50%. The entries are ordered according to the increasing micelle core/water partition coefficient. The compounds that are most stable at the micelle interface are shown in bold.

C.NMR spectra of I) DEA; II) DEA after CO_2 purge; III) Spectrum of reaction mixture with $^{13}CO_2$.

D. Quantitative NMR measurement of free and bind CO2 in surfactant solution; DMDEAI in used as an internal standard, methyl group integration set as 100.

It was modelled as DMDEA-iodohydrin neutral complex (Figure 4B, analogously to DMDEAI). The resulting complex, like DMDEAI, mostly remains at the micelle interface and, as such, assumingly, reacts with electrophilic CO_2.

Carbon dioxide is almost as stable at the interface as in the micellar core (Fig. 4A, 0.000103 vs. 0.000362, respectively). However, its concentration is quite low, and therefore any reaction would reduce it even further, which would then significantly reduce the reaction rate, unless CO_2 is being resupplied to the micelles fast enough. Because the free energy of CO_2 is in the order: water>micelle interface > core, there is no energetic barrier to diffusion based on the relative stability of CO_2 in the various locations. It should be noted that the concentration of CO_2 in the aqueous phase is significantly lower than in the micelle core (Fig. 4B, 1.60E-6 vs 0.000362 respectively), so CO_2 located in water on its own would not be sufficient to replenish CO_2 in the micellar core. That is why the addition of diethanolamine to capture CO_2 is crucial for an efficient reaction. Once CO_2 is introduced to the reaction mixture, a quick acid-base reaction takes place and the amine, is fully transformed into bicarbonate and carbamate.[55] In the ^{1}H NMR spectra of diethanolamine in D_2O, the two triplets corresponding to the amine -CH_2 groups (3.70, 2.76) disappear instead, two sets of triplets (3.85 and 3.20, 3.68 and 3.39, ratio above 10:1) after purging the solution with CO_2, assigned to bicarbonate and carbamate, respectively, are observed. In the ^{13}C spectra, one peaks is present in the carbonyl region ~163.1 ppm, characteristic for the HCO_3^- signal. With a much longer acquisition time, signals corresponding to both carbamate ~167.1 ppm and CO_2 127.6 ppm can be detected. The CO_2-amine equilibrium greatly increases the total amount of CO_2 in the aqueous phase and therefore allows the aqueous concentration of it to be constant during the reaction. The bicarbonate salt formed serves as a large reservoir of CO_2 in the reaction mixture. Furthermore, by employing quantitative ^{13}C NMR spectroscopy, the CO_2 concentration in the system was estimated (Figure 4D C; for the full spectrum and pulse program please see SI 8.4). For that, we have used the surfactant as an internal standard. Setting the integration of the methyl group in the alkyl chain to 100 allowed us to determine integral values of 62 and 47 for bicarbonate and free CO_2 respectively. Therefore, the molar fractions are close to 0.57 and 0.43 respectively assuming that in the studied system CO_2 exists in these two forms only.

The obtained results corroborate that, indeed, amine bound to CO_2 provides a large surplus of the reagent, however free CO_2 is also present and, presumably, in this form reacts with iodohydrin to give intermediate **D** at the water/micelle interface. Subsequent intramolecular substitution leads to the cyclic carbonate. ^{13}C NMR studies using $^{13}CO_2$ indicate that the reaction of iodohydrin with

CO_2 is rather slow, which at least in part could stem from the low concentration of CO_2 at the interface (Fig. 4B).

DFT calculations of reaction pathways

To provide a better picture of the underlaying reaction mechanism regarding the formal addition of CO_2 to epoxides, the model reaction of propylene oxide was studied computationally at the M06/def2-TZVPP level of theory. The solvation by water (blue paths) and toluene (green paths), which resembles the lipophilic environment of the micelle core, was included with the SMD model. Ring-opening of propylene oxide by iodide was found to be associated with high barriers (**TS2**, $\Delta G^{\ddagger}$= 113.3 and 117.4 kJ/mol in water and toluene, respectively; pale colored paths in Figure 5).

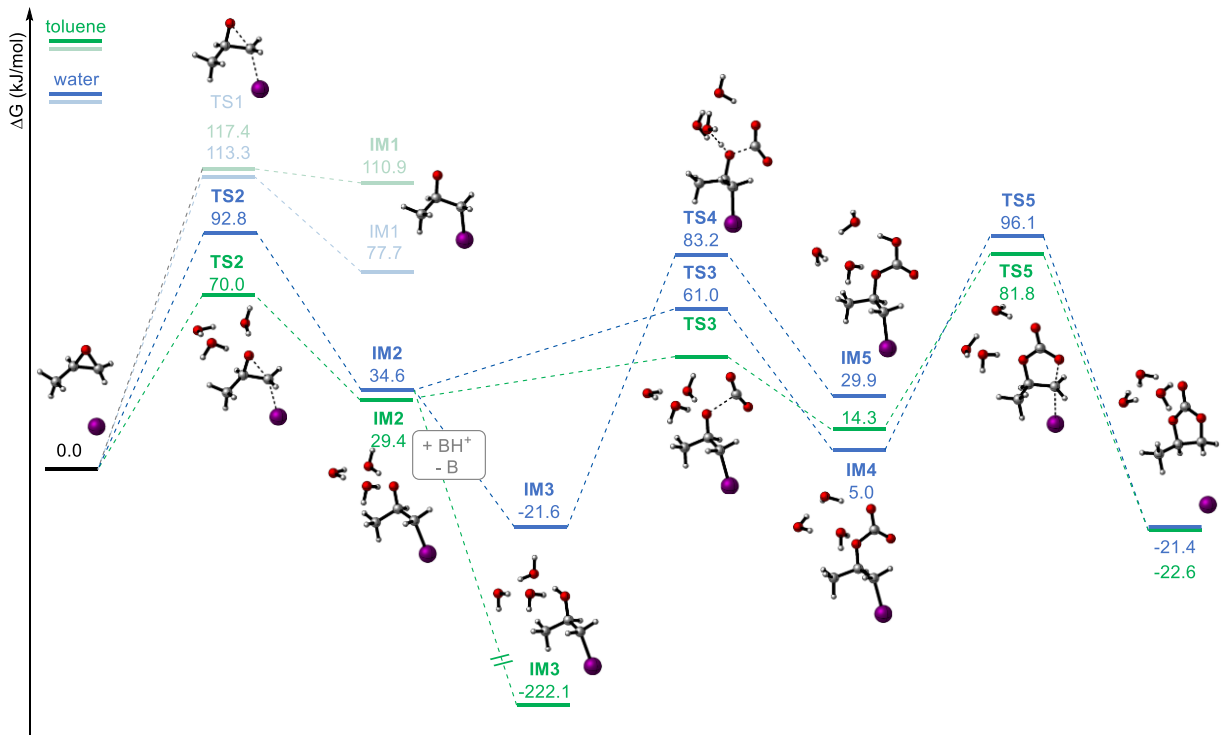


Figure 5. Gibbs free energy profile for the CO_2 addition to epoxides. Calculated at M06/def2-TZVPP/SMD(solvent).

Stabilization of the transition states and intermediates by hydrogen bondings could play a crucial role in facilitation of the process, in particular through stabilization of the negative charge developing on the oxygen. In fact, an interaction with a small cluster of three molecules of water considerably lowers the barrier for the opening of epoxide (**TS3**, $\Delta G^{\ddagger}$= 92.8 and 70.4 kJ/mol in water and toluene, respectively). The effect is particularly pronounced in less polar media, which

supports the observation that the fission of the epoxide takes place at the interface or inside the micelle within minutes; notably, ring opening of the epoxide was considered a rate limiting step for halide-mediated formal cycloaddition of CO_2 in water.[56] The subsequent facile fixation of CO_2 by alkoxide **IM2** is followed by cyclization through intramolecular S_{N2} substitution of iodide (**TS5**). The latter, presumably a rate limiting step, proceeds with Gibbs free energies of activation of 91.1 and 67.5 kJ/mol in water and toluene, respectively. It must be considered that under a relatively low concentration of CO_2, the alkoxide can undergo cyclization back to the epoxide (through **TS2**), or protonation providing iodohydrin **IM3**, which is a "resting state" of the epoxide. Direct reaction of **IM3** with CO_2 through **TS4** is associated with $\Delta G^{\ddagger}$=104.8 kJ/mol in water, which is more than 20 kJ/mol higher than an alternative pathway involving prior deprotonation by secondary amine (through **IM2** and **TS3**).

Scope and limitations

With the optimized reaction conditions and full understanding of the micellar system developed, we examined the synthesis of cyclic carbonates from various epoxides. In micellar systems, the efficacy of a certain reaction is strongly influenced by the alignment of the reaction's components in the micellar environment. 4-Fluorostyrene oxide afforded the desired product (**12**, 50%), but an electron rich 4- methoxy derivative (**16**, 0%) hydrolyzed under the developed aqueous conditions (Fig. 6). The substitution pattern on the phenyl ring influences the reaction yield; both 2- (**13**) and 3-tolyl (**14**) derivatives worked similarly (63% and 62% of yield, respectively), while for 4-tolyl (**15**), the yield diminishes to 31%. We have previously reported that, for reaction involving alkyl bromides, the carbon chain length has strong impact on the reaction yield, as collocation of substrates inside micelle is a key factor determining outcome of the reaction.[49,57] Herein the effect for alkyl epoxides is less pronounced, 1,2-epoxyoctane (**17**) gave better results than 1,2-epoxydecane (**18**) (81% vs. 71% respectively). Furthermore, functional groups can influence the organization of substrates in the micellar environment and therefore change the reaction rate.[58] Indeed, our attempts of the reaction with oxiranes substituted with glycidyl ethers (**19** – **25**) performed much slower than other substrates. After 24 hours, the iodohydrin was almost exclusively formed, thus precluding subsequent CO_2 addition, in contrast to aliphatic or styrene oxide derivatives for which only traces of the corresponding iodohydrins were detected. However, after prolonging the reaction time (48 h), the desired product formed in synthetically useful yields. For example, for the glycidyl ether with a PMP (**23**, 4-MeO-C_6H_4-) group, the yield increased to 78%, which is comparable to the result for the styrene carbonate (**1**, 85%). However, some other glycidyl ethers such as propargyl glycidyl ether (**22**) react even slower with CO_2 and large quantities still remained in the postreaction mixture; similar behavior was observed for the estrone (**25**) and bisphenol A (**24**) derivatives. We also explored the utility of epoxyamines (**26** – **29**), typically these substrates, require higher pressure and temperature, as well as utilization of metal complexes, with organic solvents for the CO_2 addition to proceed effectively.[59–61] Therefore, their synthesis in a more ecological manner would be beneficial. The aniline derivative (**28**) furnished the desired carbonate in 67% yield after 48 h. The introduction of a steric hindrance in the phenyl group, with a 2,6-diisopropylphenyl (**29**, DIPP-) derivative, only slightly decreased the yield of the carbonate to 52%. The introduction of electron rich phenyl (**27**) or alkyl (**28**) substituents diminished the reaction yield. As for the limitations of the developed methodology,

disubstituted epoxides remained unreactive (for all unsuccessful examples, please see SI 5.2). Such compounds usually require elevated pressure and temperature for the cycloaddition reaction to occur, and we, by principle, limited ourselves to room temperature and atmospheric pressure to ensure that our methodology remains as mild as possible. Furthermore, the presence of alkene, halogen or perfluorinated motifs are not tolerated.

2-Oxazolidiones are an important motif in medicinal chemistry, as it constitutes a bioisostere ofcarbamates, thiocarbamates, ureas, or amides.[62] Moreover, market approved drugs such as Linezolid, Tedizolid, or Rivaroxaban contain an oxazolidione moiety as the pharmacophore group and other molecules are being currently evaluated in clinical trials as potential drug candidates for example for breast cancer. Thus, we also investigated the feasibility of the cycloaddition of carbon dioxide to aziridines a highly atom economic approach to these valuable molecules. Effectively all tested aziridines (**30** – **36**) lead to the desired product except the *N*-Ts-aziridine (**35**), which underwent the ring opening reaction. However, the formed iodohydrin did not react with CO_2 presumably because of the decreased nucleophilicity of the nitrogen atom in the sulfonamide group that prevents an effective reaction with carbon dioxide under such mild conditions (Figure 3).

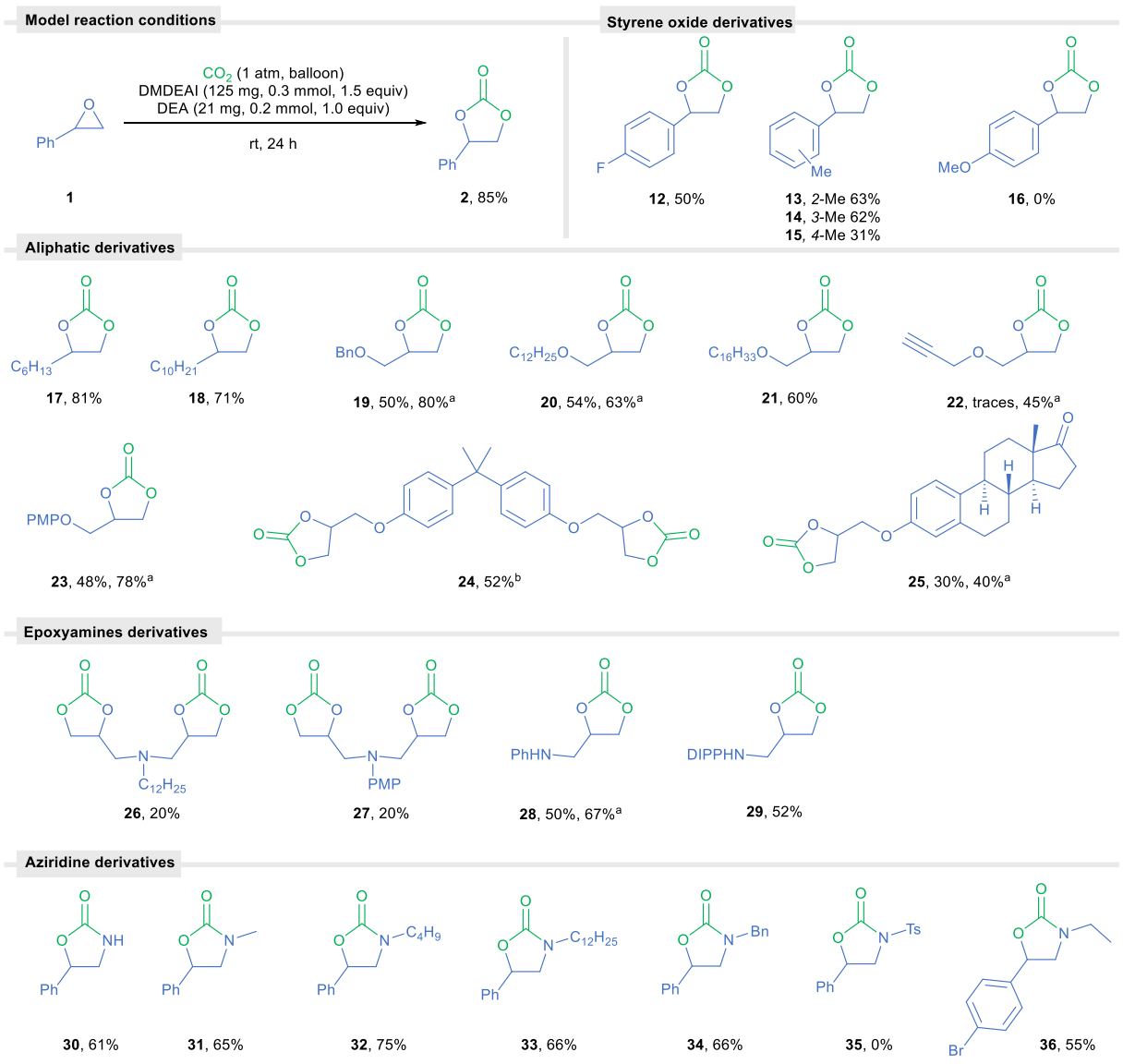


Figure 6. Formal cycloaddition of CO_2 to epoxide in micellar solution – scope and limitations studies

Reaction conditions: epoxide/aziridine (0.20 mmol), DMDEAI (1.5 equiv), DEA (1.0 equiv), H_2O (5 mL) Isolated yields. [a]Reaction time 48 h. [b]Reaction time 7 days. PMP – 4-MeO-C_6H_4-; DIPP – 2,6-di*iso*propylphenyl

Beyond CO_2, a formal CS_2 cycloaddition to epoxides/aziridines

Carbon disulfide shares similar properties as to carbon dioxide in that they are both planar and nonpolar molecules. However, while the cycloaddition of CO_2 to epoxides is one of the most thoroughly studied reactions in organic chemistry, cycloaddition of carbon disulfide to epoxides has been largely neglected by the community.[63] Nonetheless, CS_2 is commonly used in e.g.

viscose fiber manufacturing or the cellophane film industry. Unfortunately, CS_2 can leak into the atmosphere where it decomposes to COS and SO_2 causing harm to the environment.[64] One of the potential solutions to this problem could be the capture and utilization strategy centered around the cycloaddition to epoxides leading to valuable cyclic thiocarbonates which can be further used, eg, in the polymer industry as monomers.

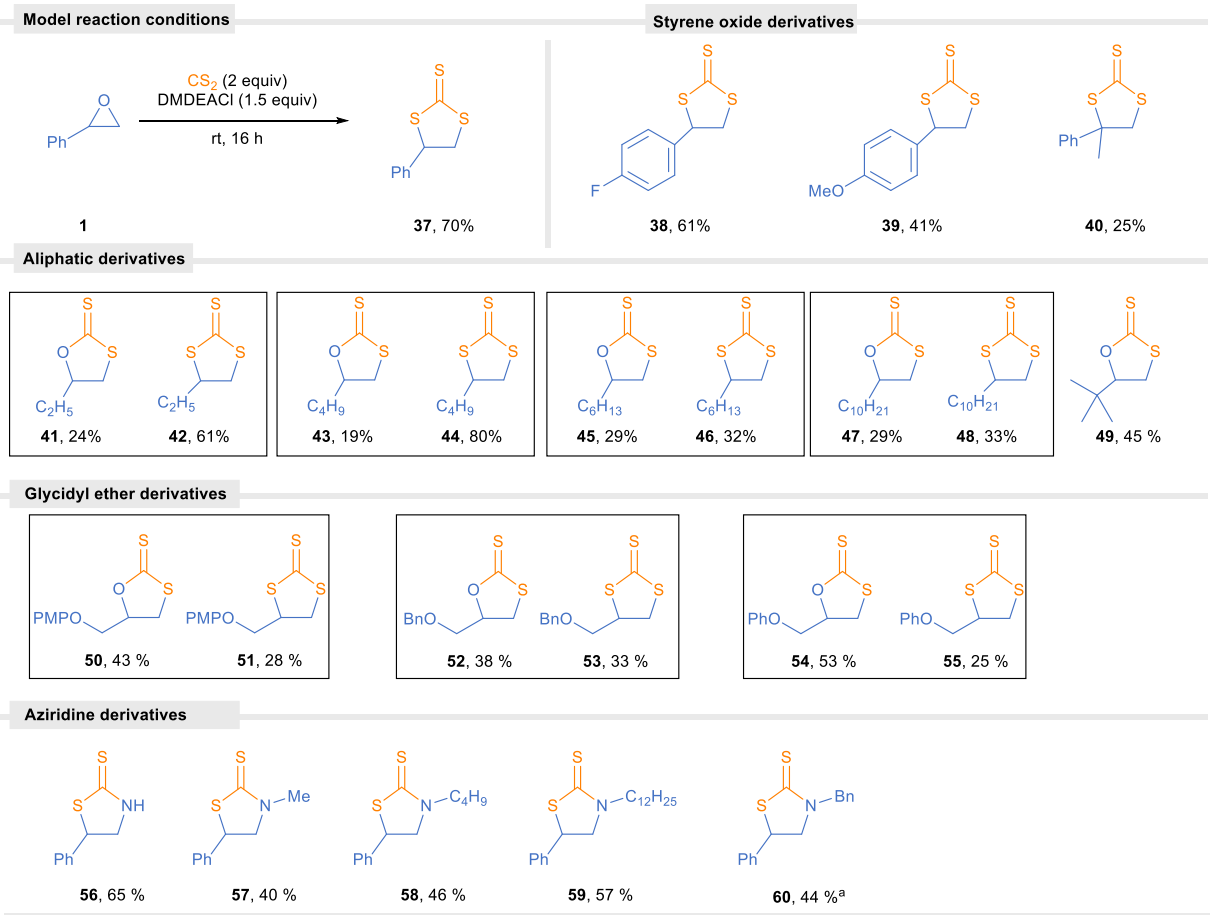


Figure 7. Formal cycloaddition of CS_2 to epoxides and aziridines in micellar solution – scope and limitations studies

Reaction conditions: epoxide/aziridine (0.20 mmol), DMDEAC (2.0 equiv), CS2 (2.0 equiv), H_2O (5 mL). Isolated yields.

Initially, the reaction of epoxides with CS_2 was carried out under the conditions optimized for CO_2. However, we quickly found out that neither amine nor strong nucleophilic iodide is required for the reaction to proceed efficiently. CS_2, unlike CO_2, is a liquid at room temperature, and will therefore preferentially partition into the micelles and give a high local concentration without the need for the amine to act as a reactant reservoir. Thus, DMDEAI was replaced with the respective chloride salt as a counter anion of lower molecular weight (Figure 4). In contrast to the selective CO_2 addition, with CS_2 a mixture of 1,3-oxathiolane-2-thiones and 1,3-dithiolane-2-thiones usually formed in good yields. This is on par with previous findings, where the ratio of products

depended on the substrate used,[65–67] although a proper choice of base/Lewis acid/temperature enables a selective transformation.[68] In our case, styrene oxide and its analogues (**37** – **40**) selectively reacted giving cyclic trithiocarbonates, though as previously described for substituted styrene oxide and CO_2, the yield was diminished. Aliphatic epoxides (**41** – **49**) were less selective. The amount of dithiocarbonates formed stayed relatively constant regardless of the length of the alkyl chain, while the yield of trithiocarbonates varied and was the highest for 1,2-epoxyhexane (80% for **44**, trisulfuric derivative and 19% for disulfuric **45**). In contrast to previous findings, for these starting materials, the reaction was more efficient for substrates with shorter alkyl chain.[49,57] This phenomenon, in general, requires further studies. 2-(*tert*-Butyl)oxirane was the only substrate that exclusively gave dithiocarbonate (**49**) in 45%yield. Intriguingly, for glycidyl ether derivatives (**50** – **55**), a reverse of the chemoselectivity was observed where dithiocarbonates predominated.

Furthermore, aziridines (**56** – **60**) were also compatible with the reaction with CS_2 under the developed conditions furnishing desired the products in 44-65% yield. The unsubstituted aziridine (**56**) proved to be the most reactive (65% yield), whilst for *N*-alkyl derivatives a slight increase in yield was observed as the hydrophobic chain length of the surfactant increases.

To the best to our knowledge no effort to study the CS_2 formal cycloaddition with epoxides using DFT calculation has been previously made. The calculated Gibbs free energy profile for fixation of CS_2 is analogues to that of CO_2 (see SI for details). An interesting issue, however, is the formation of 1,3-dithiolane-2-thiones It was originally theorized that the halide could attack the thiocarbonyl group of 1,3-oxathiolane-2-thiones leading to a thiirane intermediate.[65]S The calculated barrier for this process was found to be associated with very high energy (**TS6**, $\Delta G^{\ddagger}$= 169.1 kJ/mol), and thus it is highly unfavorable. We postulate that cleavage of the 1,3-dithiolane-2-thione system could proceed through a SN2 attack of the halide on the C-O bond in **IM6**, proceeding through a relatively low-lying transition state TS7 ($\Delta G^{\ddagger}$= 82.1 and 69.5 kJ/mol in water and toluene, respectively). The resulting **IM8** can easily lose CSO (**TS8**, $\Delta G^{\ddagger}$= 68.1 kJ/mol) ultimately leading to thiirane, which can react with another CS_2 molecule leading to the desired products.

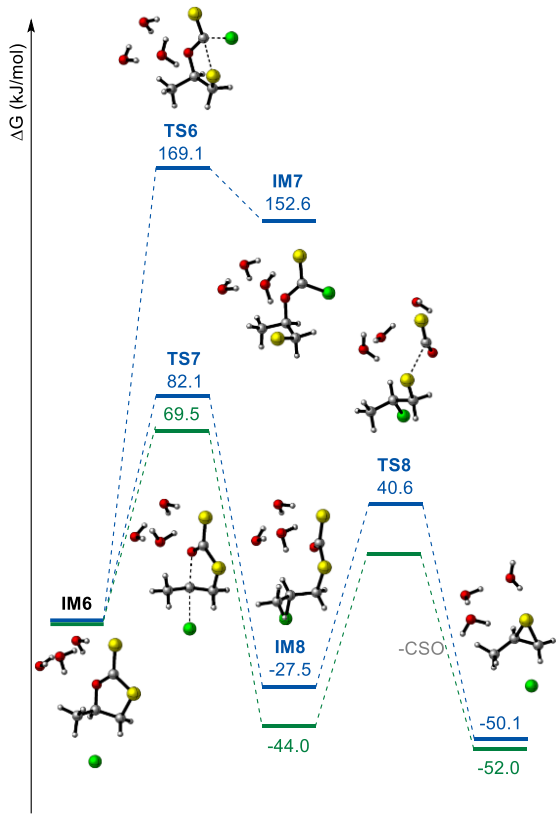


Figure 8. Gibbs free energy profile for plausible opening of dithiolane-2-thiones. Calculated at M06/def2-TZVPP/SMD(solvent).

CONCLUSIONS

In conclusion, micellar system can be effectively utilized in CO_2/CS_2 formal cycloadditions with both epoxides and aziridines. The designed system gives access to a broad group of products in reasonable yields under very mild conditions. Furthermore, our COSMO-RS calculations and NMR experiments not only helped to elucidate the role of the amine in the studied reaction but also underlined the importance of co-location of the reactants. This prerequisite is a key difference between micellar catalysis and conventional organic solvent-based synthesis, and reliable modelling of the concept, as shown in this work, can be used to design similar reactions using for example gaseous CO_2 as a reagent.

Lead contact

Requests for further information and raw data should be directed to and will be fulfilled by the lead contact, Dorota Gryko (Dorota.Gryko@icho.edu.pl).”

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