



# A MIXTURE OF TRIETHANOLAMINE AND IODINE AS AN ACCESSIBLE AND EFFECTIVE CATALYST FOR THE FORMATION OF ORGANIC CARBONATES FROM EPOXIDES AND CO<sub>2</sub>

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Cite this: *INEOS OPEN*,  
2022, 5 (1), 7–9  
DOI: 10.32931/io2202a

Received 12 May 2022,  
Accepted 2 June 2022

<http://ineosopen.org>

## Abstract

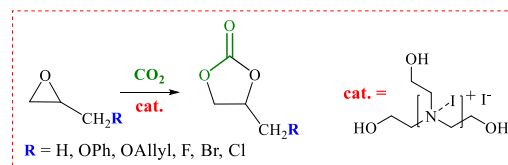
An effective catalyst formed by mixing molecular iodine with triethanolamine is suggested for the addition of CO<sub>2</sub> to epoxides.

**Key words:** triethanolamine, iodine, epoxides, CO<sub>2</sub> fixation.

## Introduction

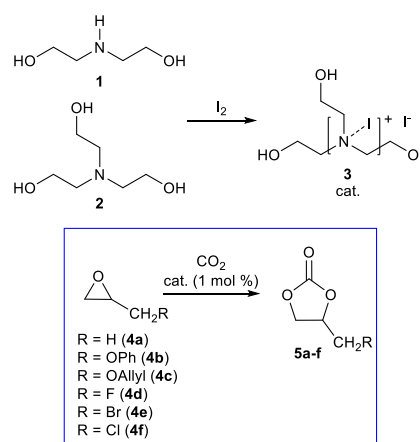
The high available volumes of CO<sub>2</sub>, in particular, largely emitted as an industrial by-product, and the ease of its condensation predetermine the low cost of this gas. Furthermore, carbon dioxide is nonflammable and less toxic than many organic solvents and reagents [1]. However, wide application of CO<sub>2</sub> is hampered by its low solubilizing ability and inertness associated with the zero dipole moment and dielectric permittivity ranging from 1.1 to 1.5 depending on the temperature and pressure [2]. From the synthetic point of view, one of the most efficient and convenient directions of the carbon dioxide utilization is its insertion into organic molecules, resulting in the formation of organic cyclic carbonates [3–6]. This process does not require the use of a solvent since CO<sub>2</sub> serves simultaneously as a reaction medium and reagent. It should be noted that organic carbonates are extensively used as fuel additives, electrolytes for lithium-ion batteries, polar solvents, and monomers for the production of polycarbonates and non-isocyanate polyurethanes [5]. In order to further optimize the process, of particular interest is the development of effective catalysts that would be able to promote the coupling of CO<sub>2</sub> with epoxides and feature maximum affordability. Recently, we have shown that the molecular complexes of [R<sub>3</sub>N]<sup>+</sup>I<sup>-</sup> composition, which result from simple mixing of monoamines or amino acids with molecular iodine, can serve as effective catalysts for this reaction, providing the quantitative conversion [7, 8]. Taking into account the co-catalytic effect of hydroxy groups during the addition of CO<sub>2</sub> to epoxides, which has been previously demonstrated with ammonium salts [9, 10], we decided to obtain the molecular complexes of iodine with di- and triethanolamines and evaluate their activity in this reaction. Of note are the low cost of ethanolamines, which are produced on a large scale, and low toxicity, which stipulates their use in cosmetic products.

Herein, we report on the preparation of the catalysts based on iodine and di- and triethanolamine and their application in the addition of CO<sub>2</sub> to epoxides.



## Results and discussion

The catalysts obtained *in situ* from equimolar mixtures of di- (1) and triethanolamine (2) with iodine (1 mol %) were studied first in the addition of CO<sub>2</sub> to propylene oxide (4a, R = H, Scheme 1).



**Scheme 1.** Addition of CO<sub>2</sub> to epoxides.

It was found that the catalytic system based on triethanolamine, which has a higher content of the hydroxy groups than diethanolamine, provides the higher conversion (Table 1, entries 1, 2). The application of preformed molecular complex 3 led to additional conversion enhancement (entry 3). An increase in the CO<sub>2</sub> pressure almost did not affect the reaction efficiency (entry 4). To optimize the results, we turned to the promoting effect of a silica gel substrate, which was observed earlier with the ammonium salts [4, 11]. For this purpose, two mass equivalents of silica gel were added during the complex formation (see the Experimental section). This simple manipulation allowed us not only to increase the conversion (entries 4, 5) but also to make the catalyst a free-flowing powder and, therefore, more convenient to handle compared to the oily complex lacking the substrate. The

promoting effect of silica gel was also confirmed in the reaction at a higher temperature (130 °C) but for a shorter period of time (entries 6, 7). An increase in the reaction duration to 2 h afforded the quantitative conversion (entry 8); under these conditions, the immobilized catalyst can be reused while keeping the complete conversion; however, the third run afforded a reduction in the conversion to 96%. This is likely to be associated with the partial leaching of the catalyst from the substrate. It should be noted that neither molecular iodine, nor silica gel, nor their mixture does not catalyze the process under consideration.

**Table 1.** CO<sub>2</sub> addition to propylene oxide

Entry	Amine	Additive	Time, h	T, °C	P, atm	Conversion, %
1	1	–	3	105	10	43
2	2	–	3	105	10	52
3	2 <sup>a</sup>	–	3	105	10	61
4	2 <sup>a</sup>	–	3	105	56	63
5	2 <sup>a</sup>	SiO <sub>2</sub>	3	105	10	76
6	2 <sup>a</sup>	–	1	130	10	77
7	2 <sup>a</sup>	SiO <sub>2</sub>	1	130	10	85
8	2 <sup>a</sup>	SiO <sub>2</sub>	2	130	10	100 <sup>b</sup>

<sup>a</sup> preformed catalysts;

<sup>b</sup> 97% yield.

The catalytic system based on triethanolamine and iodine immobilized on silica gel was further tested in the coupling of CO<sub>2</sub> with epoxides **4b–f** (Scheme 1, Table 2).

**Table 2.** CO<sub>2</sub> addition to epoxides **4b–f** (105 °C, CO<sub>2</sub> 10 atm)

Entry	Epoxide	Time, h	Conversion, %	Yield, %
1	4b	3	77	–
2	4b	4	100	95
3	4c	4	100	97
4	4d	4	100	96
5	4e	4	100	97
6	4f	4	100	97

In the case of epoxide **4b** bearing a bulky phenyl substituent, the conversion achieved 77% in 3 h. An increase in the reaction time to 4 h afforded the complete conversion. Under these conditions, substrates **4b–f** were also quantitatively converted to the corresponding carbonates.

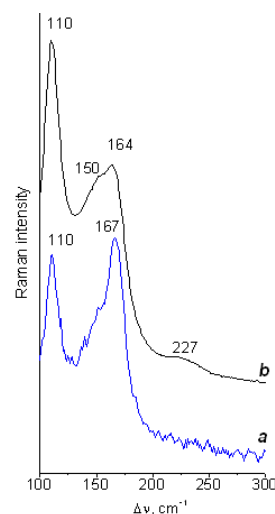
Molecular complex **3** was studied by NMR spectroscopy. The expected shifts of the signals of the CH<sub>2</sub> units relative to those of initial triethanolamine **2** were observed both in the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Table 3), which confirms the formation of the bond between the halogen atom and the amine.

**Table 3.** NMR spectroscopic data for compound **2** and its molecular complex with iodine

	<sup>1</sup> H NMR ((CD <sub>3</sub> ) <sub>2</sub> SO, δ)		<sup>13</sup> C NMR ((CD <sub>3</sub> ) <sub>2</sub> SO, δ)	
	CH <sub>2</sub> N	CH <sub>2</sub> O	CH <sub>2</sub> N	CH <sub>2</sub> O
2	2.54 (t, J = 4.0 Hz)	3.40 (t, J = 4.0 Hz)	57.60	58.72
3	3.30 (t, J = 4.0 Hz)	3.75 (t, J = 4.0 Hz)	55.51	55.55

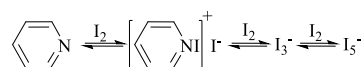
Adduct **3** was also studied by Raman spectroscopy (Fig. 1). At the laser power of 0.01 mW, the resulting spectrum displayed the characteristic lines of I<sub>3</sub><sup>–</sup> and I<sub>5</sub><sup>–</sup> ions [12, 13]. As the laser

power was enhanced to 1 mW, the intensity of the line at 165 cm<sup>–1</sup> corresponding to polyiodide I<sub>5</sub><sup>–</sup> reduced and a new line at 227 cm<sup>–1</sup> appeared that can be attributed to released molecular iodine.



**Figure 1.** Raman spectra of complex **3** at the laser power of 0.01 mW (**a**) and 1 mW (**b**).

Based on the results presented, it can be concluded that molecular complex **3** is analogous to the well-known complexes of iodine with amines, among which an iodine–pyridine complex is the most popular one (Scheme 2) [14–23].



**Scheme 2.** Iodine complex with pyridine.

## Experimental

The NMR spectra were registered on a Bruker Avance 400 spectrometer. The Raman spectra were recorded on a JobinYvon LabRAM 300 spectrometer (He-Ne laser 632.8 nm, 1 mW) in the range of 100–4000 cm<sup>–1</sup>. Epoxides **4a–f** and silica gel 0.06–200 mm, 60 Å were purchased from commercial sources (Sigma-Aldrich and Acros).

### Iodine adduct of triethanolamine

Triethanolamine (149 mg, 1 mmol) and molecular iodine (254 mg, 1 mmol) were dissolved in methanol (5 mL) under stirring for 5 min. Then, the solvent was removed under vacuum (30 Torr). The complex immobilized on silica gel was obtained analogously by the addition of the substrate (806 mg) to a methanol solution of the complex followed by the solvent removal.

### Synthesis of carbonates **5a–f** from the epoxides

A 10 mL autoclave was charged with the corresponding amine (0.06 mmol), iodine (15 mg, 0.06 mmol), and the preformed complex or complex immobilized on silica gel (0.06 mmol). Then, epoxide (6 mmol) was added. The autoclave was filled with CO<sub>2</sub> and heated at the required temperature in a thermostatically controlled chamber. After the reaction completion, the autoclave was cooled to 5 °C, CO<sub>2</sub> was

depressurized, and, after addition of  $\text{CDCl}_3$  (1 mL), the reaction mixture was filtered through a thin layer of silica gel to remove the residual catalyst. The resulting solution was analyzed by NMR spectroscopy. The spectral characteristics of the carbonates were in good agreement with the earlier published data [24–26].

## Conclusions

Hence, we developed an accessible and effective catalyst for the  $\text{CO}_2$  addition to epoxides, which can be formed by simple mixing of triethanolamine with iodine. The efficiency of this catalytic system increases with the immobilization on silica gel. The latter also imparts heterogeneity and recyclability to the suggested catalyst.

## Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00697-22-00) and was performed using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

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## References

1. E. J. Beckman, *J. Supercrit. Fluids*, **2004**, *28*, 121–191. DOI: 10.1016/S0896-8446(03)00029-9
2. A. van Itterbeek, K. de Clippeleir, *Physica*, **1947**, *13*, 459–464. DOI: 10.1016/0031-8914(47)90033-5
3. S. Dabral, T. Schaub, *Adv. Synth. Catal.*, **2019**, *361*, 223–246. DOI: 10.1002/adsc.201801215
4. C. Calabrese, F. Giacalone, C. Aprile, *Catalysts*, **2019**, *9*, 325. DOI: 10.3390/catal9040325
5. A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chem.*, **2019**, *21*, 406–448. DOI: 10.1039/C8GC03086C
6. L. Guo, K. J. Lamb, M. North, *Green Chem.*, **2021**, *23*, 77–118. DOI: 10.1039/D0GC03465G
7. B. Chowdhury, A. A. Zvinchuk, R. R. Aysin, E. A. Khakina, P. V. Cherkasova, S. E. Lyubimov, *Catal. Surv. Asia*, **2021**, *25*, 419–423. DOI: 10.1007/s10563-021-09341-9
8. S. E. Lyubimov, P. V. Cherkasova, R. R. Aysin, B. Chowdhury, *Russ. Chem. Bull.*, **2022**, *71*, 408–411. DOI: 10.1007/s11172-022-3427-0
9. J. Sun, S. Zhang, W. Cheng, J. Ren, *Tetrahedron Lett.*, **2008**, *49*, 3588–3591. DOI: 10.1016/j.tetlet.2008.04.022
10. S. Denizalti, *RSC Adv.*, **2015**, *5*, 45454–45458. DOI: 10.1039/C5RA05384F
11. S. E. Lyubimov, A. A. Zvinchuk, V. A. Davankov, B. Chowdhury, A. V. Arzumanyan, A. M. Muzafarov, *Russ. Chem. Bull.*, **2020**, *69*, 1076–1079. DOI: 10.1007/s11172-020-2869-5
12. J. D. Comins, T. P. Nguyen, M.-A. Pariselle, S. Lefrant, A. M. T. Allen, *Radiat. Eff. Defects Solids*, **1995**, *134*, 437–441. DOI: 10.1080/10420159508227264
13. E. M. Nour, L. H. Chen, J. Laane, *J. Phys. Chem.*, **1986**, *90*, 2841–2846. DOI: 10.1021/j100404a014
14. H. D. Bist, W. B. Person, *J. Phys. Chem.*, **1969**, *73*, 482–489. DOI: 10.1021/j100723a003
15. P. Boule, *J. Am. Chem. Soc.*, **1968**, *90*, 517–518. DOI: 10.1021/ja01004a070
16. S. Kobinata, S. Nagakura, *J. Am. Chem. Soc.*, **1966**, *88*, 3905–3909. DOI: 10.1021/ja00969a003
17. R. S. Mulliken, *J. Am. Chem. Soc.*, **1969**, *91*, 1237. DOI: 10.1021/ja01033a046
18. H. Tsubomura, S. Nagakura, *J. Chem. Phys.*, **1957**, *27*, 819–820. DOI: 10.1063/1.1743845
19. C. Reid, R. S. Mulliken, *J. Am. Chem. Soc.*, **1954**, *76*, 3869–3874. DOI: 10.1021/ja01644a001
20. J. R. Sabin, *J. Mol. Struct.*, **1971**, *7*, 407–419. DOI: 10.1016/0022-2860(71)87011-4
21. S. Aronson, S. B. Wilensky, T.-I. Yeh, D. Degraff, G. M. Wieder, *Can. J. Chem.*, **1986**, *64*, 2060–2063. DOI: 10.1139/V86-340
22. M. Tuikka, M. Haukka, *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, **2015**, *71*, o463. DOI: 10.1107/S2056989015010518
23. E. M. Karlsen, J. Spanget-Larsen, *Chem. Phys. Lett.*, **2009**, *473*, 227–232. DOI: 10.1016/j.cplett.2009.04.005
24. H. Zhou, G.-X. Wang, W.-Z. Zhang, X.-B. Lu, *ACS Catal.*, **2015**, *5*, 6773–6779. DOI: 10.1021/acscatal.5b01409
25. P. A. Carvalho, J. W. Comerford, K. J. Lamb, M. North, P. S. Reiss, *Adv. Synth. Catal.*, **2019**, *361*, 345–354. DOI: 10.1002/adsc.201801229
26. H. Chang, Q. Li, X. Cui, H. Wang, C. Qiao, Z. Bu, T. Lin, *Mol. Catal.*, **2018**, *449*, 25–30. DOI: 10.1016/j.mcat.2018.02.007

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