Russian Chemical Bulletin, International Edition, Vol. 69, No. 6, pp. 1076—1079, June, 2020

The use of a diammonium salt in the synthesis of organic carbonates from epoxides and CO_2: promoting effect of support*

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Onium salt, N^1,N^1,N^1,N^5,N^5,N^5-hexaethylpentane-1,5-diammonium dibromide, was used as a catalyst for the addition of CO_2 to epoxides. An influence of insoluble supports on the rate of the process as well as possibility of recycling of the catalytic system are described. In addition, the effects of temperature and CO_2 pressure on the yields of products are discussed.

Key words: diammonium salt, carbon dioxide fixation, epoxides, cyclic carbonates, catalytic support.

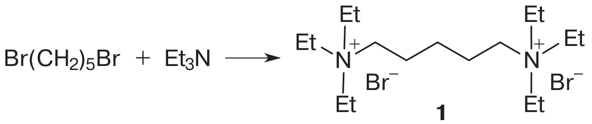
Carbon dioxide is of great interest for use in various reactions and processes due to its availability, low cost, renewability, incombustibility, and safety compared to many other gases.[1] In addition, the possibility of its use is a direct solution to the environmental problem associated with an increasing excess of CO_2 in nature due to widespread consumption of raw materials.[2] One of the effective and practical directions for using CO_2 is its addition at α-epoxides with the formation of organic carbonates.[3,4] The products of this reaction are widely used as fuel additives, electrolytes for lithium-ion batteries, polar solvents, anti-caking agents, monomers for the production of polycarbonates and polyurethanes.[5] Various catalysts including complexes of transition and non-transition metals, derivatives of Sc, Sm, Y, La, Re, modified carbon nanotubes, complexes of crown ethers, modified molecular sieves, ionic liquids based on ammonium, imidazolium, and phosphonium salts, as well as a number of other compounds have been tested for this reaction at present.[6] The development of catalytic systems that combine low cost, the ability to work at low temperatures and low CO_2 pressures, the possibility of easy separation from reaction products, and repeated use is of considerable interest today.

In this work, the use of readily available diammonium salt as a catalyst for the reaction of CO_2 addition to epoxides is considered. Positive effect of using a number of supports on the conversion in this reaction is described. The effect of temperature and CO_2 pressure on the yield of products is studied, and the possibility of recycling of this available catalyst system is demonstrated.

Results and Discussion

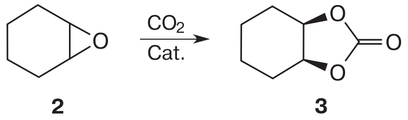
Quaternization of triethylamine with 1,5-dibromopentane (110 °C, 24 h) yielded N^1,N^1,N^1,N^5,N^5,N^5-hexaethylpentane-1,5-diamonium dibromide (**1**, Scheme 1). Note that this approach does not include the use of a solvent and is faster in comparison with other methods known in the literature.[7—9]

Scheme 1



Preliminary testing of diammonium salt **1** was carried out in the reaction of addition of CO_2 (56 atm) to cyclohexene oxide (**2**) (Scheme 2) at various molar catalyst loadings. The conversion reached 65% with an increased loading of the catalyst **1** (1.2 mol%). The yields

Scheme 2



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* Dedicated to Academician of the Russian Academy of Sciences I. L. Eremenko on the occasion of his 70th anniversary.

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1076—1079, June, 2020.

Table 1. Addition of CO_2 to cyclohexene oxide (**2**)[a]

Run	Catalyst **1**/mmol	Additive/mg	*T*/°C	Conversion **2** (%)
1	0.012	—	110	47
2	0.024	—	110	65
3	0.012	TiO_2	110	74
4	0.024	TiO_2	110	92
5	0.012	Al_2O_3	110	89
6	0.024	Al_2O_3	110	91
7	0.024	PVA 80000	110	83
8	0.012	SiO_2	110	85
9	0.024	SiO_2	110	100
10[b]	0.024	SiO_2	110	94
11[c]	0.024	SiO_2	110	92
12	0.024	SiO_2	100	95
13	0.024	SiO_2	80	12

Reaction conditions: [a]support (0.2 mmol), additive (30 mg), 24 h, 56 atm; [b] 20 atm; [c] 10 atm.

of product **3** decrease with a decrease in catalyst amount (0.6 mol%) (Table 1, Runs *1* and *2*).

Given the potential positive effect of the support on the conversion in this reaction,[4,6,10] we decided to test a series of compounds insoluble in organic media in order to heterogenize the catalyst. The use of titanium dioxide as a solid support (see Table 1, Runs *3* and *4*) with constant loading of diammonium salt **1** allowed us to increase the conversion in both cases by about a factor of 1.5. Alumina showed a similar effect, namely, the conversion increased from 47 to 89% when 0.6 mol% of the ammonium salt was used. Increased catalyst loading provides better results (see Table 1, Runs *5* and *6*). The conversion increases to 83% when polyvinyl alcohol (M_w = 80000) is used as a support (Run *7*). Quantitative conversion was achieved using silica gel for column chromatography as a support at 1.2 mol% of the catalyst. A reduced loading caused a natural decrease in the conversion (see Table 1, Runs *8* and *9*). Reduction of carbon dioxide pressure from 56 to 10 atm caused a slight decrease in the conversion (*cf.* Runs *9—11*). We also conducted a small series of experiments to study the effect of temperature on the course of the reaction. So, it was shown that the reaction proceeds only by 12% at 80 °C. Raising the temperature to 100 °C provided 95% conversion while the reaction reached completion at 110 °C (see Table 1, *cf.* Runs *9*, *12*, *13*).

Based on our results using diammonium salt **1** and silica gel, we can propose the reaction mechanism comprising the process acceleration (Scheme 3), being in accord with those proposed for more complex systems, and which can be extended to other supports used here.[5,11] The residual hydroxy groups of silica gel interact with the oxirane to "loosen" the bonds, which contributes to the subsequent addition of the bromine ion coming from the ammonium salt. The presence of a partial positive charge on the oxygen atom promotes the activation of CO_2 and

Scheme 3

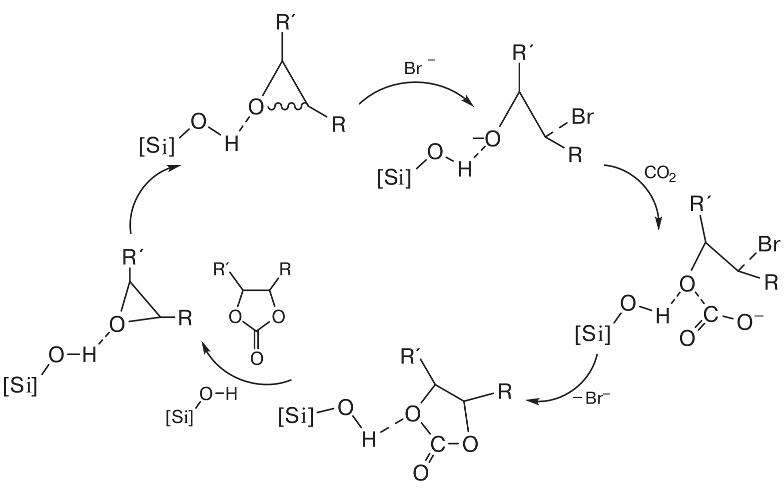


Table 2. Catalyst reuse results

Cycle	Conversion (%)
1	100
2	100
3	100
4	96
5	87
6	77

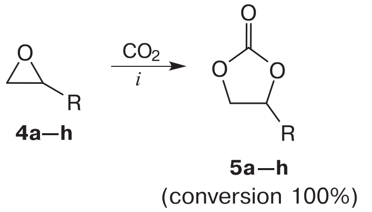
Reaction conditions: support (0.4 mmol), catalyst (0.048 mmol), SiO_2 (60 mg), 24 h.

its addition. The subsequent formation of a stable five-membered carbonate cycle leads to the release of the bromine anion and its return to the dicationic salt.

We also conducted a series of experiments to examine the possibility of catalyst reusing. It turned out that the catalytic system provided quantitative conversion over three cycles. Starting from the fourth cycle, there is a slight decrease in the conversion (Table 2), which can be attributed either to the gradual leaching of the catalyst by a polar organic carbonate, or to the gradual thermal decomposition of the ammonium salt.

We studied the addition of CO_2 to various epoxides **4a—h** (Scheme 4) under optimized reaction conditions. The corresponding carbonates **5a—h** were obtained in quantitative yields in all cases regardless of electronic and steric effects.

Scheme 4

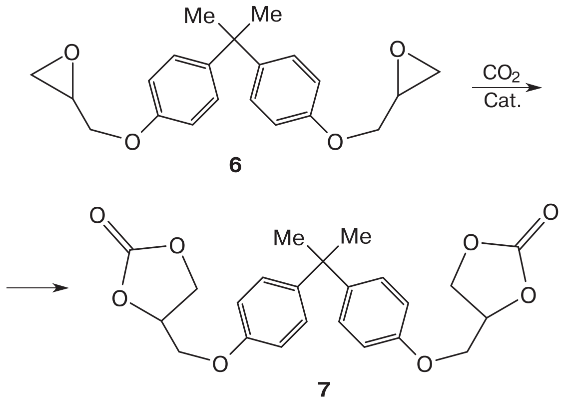


R = CH_2Cl (**a**), CH_2F (**b**), CH_2CF_3 (**c**), $CH_2C_6F_5$ (**d**), CH_2OPh (**e**), CH_2NEt_2 (**f**), morpholin-4-ylmethyl (**g**), Ph (**h**)

Reagents and reaction conditions: *i*. 1.2 mol% **1**, 30 mg SiO_2, 24 h.

Diammonium salt **1** was also used to convert industrial bis-epoxide **6** (ED-22 resin)[12—14] to biscarbonate **7** (Scheme 5). Biscarbonate **7** is used in the synthesis of macromolecular compounds with enhanced thermal and mechanical properties, highly resistant adhesive materials, and hydrophilizing agents. Complete conversion is achieved at a temperature of 110 °C and a pressure of 56 atm using 1.2 mol% of the catalyst in just 3 h both with and without silica gel. The latter, possibly, is associated with the cooperative effect of diammonium salt, simultaneously affecting two reaction centers of epoxide **6**.

Scheme 5



To conclude, long chain diammonium dibromide was used as a catalyst for the reaction of CO_2 addition to epoxides. Supports are able to accelerate the passage of the reaction. The best catalytic performance is provided by the diammonium salt in combination with silica gel giving the possibility of using it three times without a drop in the conversion. It was shown that the process is very sensitive to temperature, while the pressure of carbon dioxide has little effect on the reaction rate of the process.

Experimental

^1H, ^{13}C, and ^{19}F NMR spectra were registered using a Bruker Avance 400 (400.13, 100.61, 376.5 MHz) spectrometer. Silica gel (0.06—0.2 mm, 60 Å, Acros Organics), TiO_2, Al_2O_3, polyvinyl alcohol (M_w = 80000), 1,5-dibromopentane, triethylamine, 7-oxabicyclo[4.1.0]heptane (**3**), 2-(chloromethyl)oxirane (**4a**), 2-(phenoxymethyl)oxirane (**4e**), 2-phenyloxirane (**4h**), 2,2′-[4,4′-(propane-2,2-diyl)bis(4,1-phenylene)]bis(methylene) bis(oxy)dioxirane (**6**, resin ED-22) are commercially available compounds. 2-(Fluoromethyl)oxirane (**4b**), 2-(2,2,2-trifluoroethyl)oxirane (**4c**), 2-(pentafluorophenylmethyl)oxirane (**4d**), *N*,*N*-diethyl-2-oxiranemethaneamine (**4f**), 4-(oxirane-2-ylmethyl)morpholine (**4g**) were obtained according to literature procedures.[15—19]

N^1,N^1,N^1,N^5,N^5,N^5-Hexaethylpentane-1,5-diamonium dibromide (1). Freshly distilled 1,5-dibromopentane (460 mg, 2 mmol) and triethylamine (1.12 mL, 8 mmol) were loaded in a 10 mL autoclave. The mixture was kept at 110 °C for 24 h, washed with acetone (2×3 mL), and dried *in vacuo*. Yellowish powder, yield 0.553 g (64%). ^1H NMR (D_2O) δ: 1.15 (t, 18 H, $CH_2C\underline{H}_3$, J = 8.0 Hz); 1.28—1.39 (m, 2 H, CH_2); 1.59—1.71 (m, 4 H, CH_2); 3.05—3.11(m, 4 H, CH_2N^+); 3.17 (q, 12 H, $N^+C\underline{H}_2CH_3$, J = 8.0 Hz). ^{13}C NMR (D_2O), δ: 6.6 (CH_3), 20.8 (2 CH_2), 22.7 (CH_2), 52.6 (6 CH_2N^+), 56.1 (2 CH_2N^+).

Preparation of carbonates 3, 5a—h, 7 from epoxides (general procedure). Salt **1** (5 or 10 mg, 0.012 or 0.024 mmol, respectively) and the corresponding support (30 mg) were loaded in a 10 mL autoclave, and epoxide (2 mmol) was added. Carbon dioxide (10, 20, and 56 atm) was fed into the autoclave and heated to 110 °C in a thermostat for the required time. After completion of the reaction, the autoclave was cooled to ~20 °C,

CO_2 was evacuated, and dichloromethane (2 mL) was added to the residue. The slurry was filtered through a thin layer of silica gel, and the solvent was evaporated. The reaction mass was analyzed by NMR spectroscopy. The spectral characteristics of carbonates **3**, **5a—h**, **7** correspond to the data presented in the literature.[10,13,17,20—22]

Reuse of the catalyst. Salt **1** (20 mg, 0.048 mmol), silica gel (60 mg) were loaded in a 10 mL autoclave, and cyclohexene oxide (**2**) (0.4 mL, 4 mmol) was added. Carbon dioxide (56 atm) was introduced into the autoclave and the autoclave was heated to 110 °C in a thermostat. The autoclave was cooled after the reaction, CO_2 was discharged, diethyl ether (2 mL) was added to the residue, the mixture was filtered through a Schott filter, the autoclave and the precipitate were further washed with diethyl ether (2 mL). The catalyst from the filter was transferred to the autoclave, cyclohexene oxide (**2**) was added, CO_2 was fed, and the process was repeated. After removal of diethyl ether *in vacuo*, the reaction product was analyzed by NMR spectroscopy.

The work was financially supported by the Russian Science Foundation (Project No. 19-43-02031).

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Received January 14, 2020;
in revised form March 17, 2020;
accepted March 20, 2020