Electronic Supplementary information

The unprecedented catalytic activity of alkanolamine CO_2 scrubbers in the cycloaddition of CO_2 and oxiranes: A DFT endorsed study

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Materials used

All the alkanolamines and epoxides were purchased from Sigma Aldrich with 99.5% purity. Methanol was purchased from TCI chemicals Korea holding a purity of 99.5% and the water was of double distilled quality. CO_2 was obtained from MS Gas Corporation, Korea.

Coupling reaction

All the reactions were carried out in a 25 mL stainless-steel batch reactor with a magnetic stirrer at 500 rpm. In a typical batch reaction process, a pre-decided amount of the catalyst was charged into the reactor containing 42.8 mmol of PO. The reaction was carried out under a preset pressure of carbon dioxide at different temperatures. After the completion of the reaction, the reactor was cooled to zero degree and the products were identified by a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionized detector. The product was confirmed by identifying with the peak of authentic sample and the yield was determined by using an internal standard method with toluene as the standard. The synthesized cyclic carbonates were further purified by column chromatography and the proton NMR chemical shift values were authenticated with literature data and are produced in S5 of this ESI.

S 1

Reaction parameter study of PO-CO_2 cycloaddition with N,N-dimethylaminopropanol (DMPA) as catalyst.

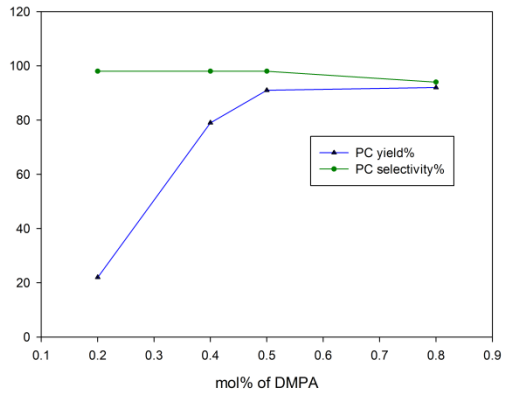


Fig. S1 a) *Catalyst amount study*
42.8 mmol PO, 120 °C, 1 MPa CO_2 initial pressure, 3 h

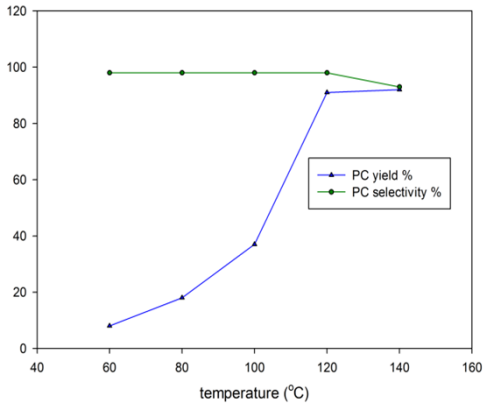


Fig. S1 b) *Temperature study*
42.8 mmol PO, 0.8 mol% DMPA, 1 MPa CO_2 initial pressure, 3 h

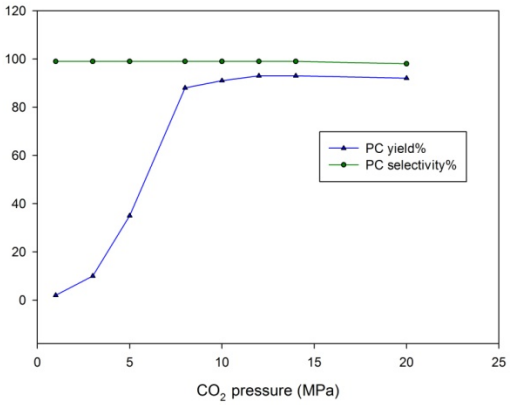


Fig. S1 c) *Pressure study*
42.8 mmol PO, 120 °C,
0.8 mol% DMPA, 3 h

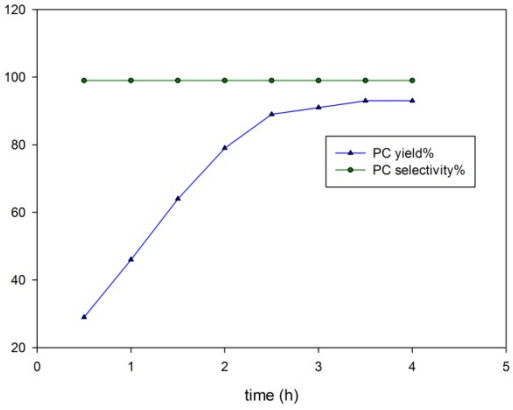


Fig. S1 d) *Time study*
42.8 mmol PO, 120 °C,
0.8 mol% DMPA, 3 h

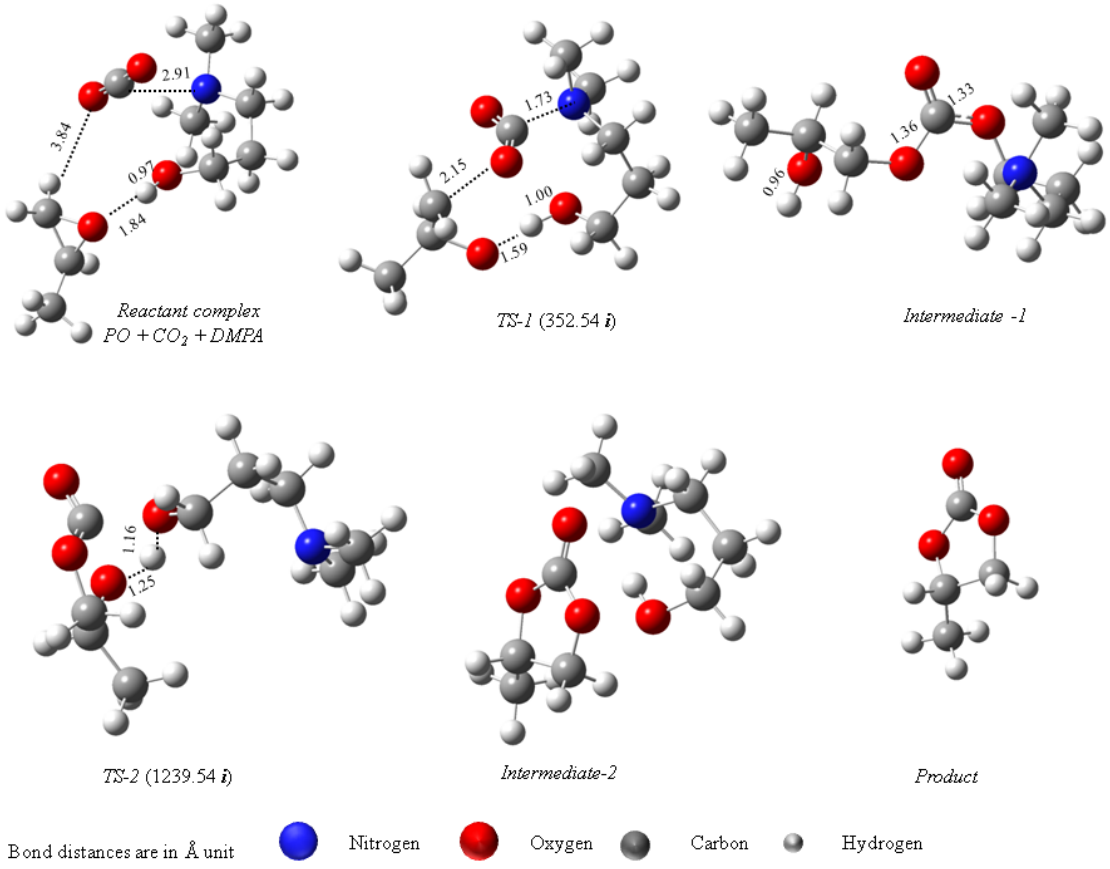
S 2

Comparative activities of various homogeneous ionic liquids and alkanolamines in propylene carbonate synthesis from CO_2 and propylene oxide

Catalyst		Reaction conditions		PC Yield (%)	TON	TOF	Ref.
		Catalyst amount	Temperature/CO_2 pressure/time				
Ammonium salts	$[Bu_4N]Br$	1.6 mol%	125 °C / 2 MPa / 1 h	73.1	45	45	3(b)
	$[Bu_4N]Br$	0.5 mol%		55.7	111	111	
	$[Bu_4N]Cl$			63.3	126	126	
	$[Bu_4N]I$			26.6	53	53	
Imidazolium ILs	[EMIm]Br			82.4	51	51	
	[BMIm]Br			52	104	104	
	[BMIm]Cl			45	90	90	
	[BMIm]I			52.6	105	105	
Phosph -onium ILs	$[PPh_3Bu]Br$			54	108	108	
	$[PPh_3Bu]Cl$			64.6	129	129	
	$[PPh_3Bu]I$			24	49	49	
	$[PPh_3Et]Br$			50	100	100	
	$[PPh_3He]Br$			60.5	121	121	
Hydroxyl functional -ized ILs	HEMImB			99	62	62	
	HETBAB			95	59	59	
	HETEAB			87.1	54	54	
Acid-base functional -ized Imidazolium ILs	$[(CH_2COOH)_2im]Br$			77	77	77	
	$[(CH_2COOH)_2im]Cl$			11	11	11	
	$[\{(CH_2)_3COOH\}im]Br$			98	98	98	
	$[\{(CH_2)_3COOH\}im]Cl$			29	29	29	
Alkanol -amines	DMPA	0.5 mol%	125 °C / 2 MPa / 1 h	60	120	120	Present work
	DMEA			58	116	116	
	MEA			49	98	98	
	MDEA			49	98	98	
	DMPA	0.8 mol%	120 °C / 1 MPa / 3 h	91	114	38	
	DMEA			82	102	34	
	MEA			71	89	30	
	MDEA			76	95	32	

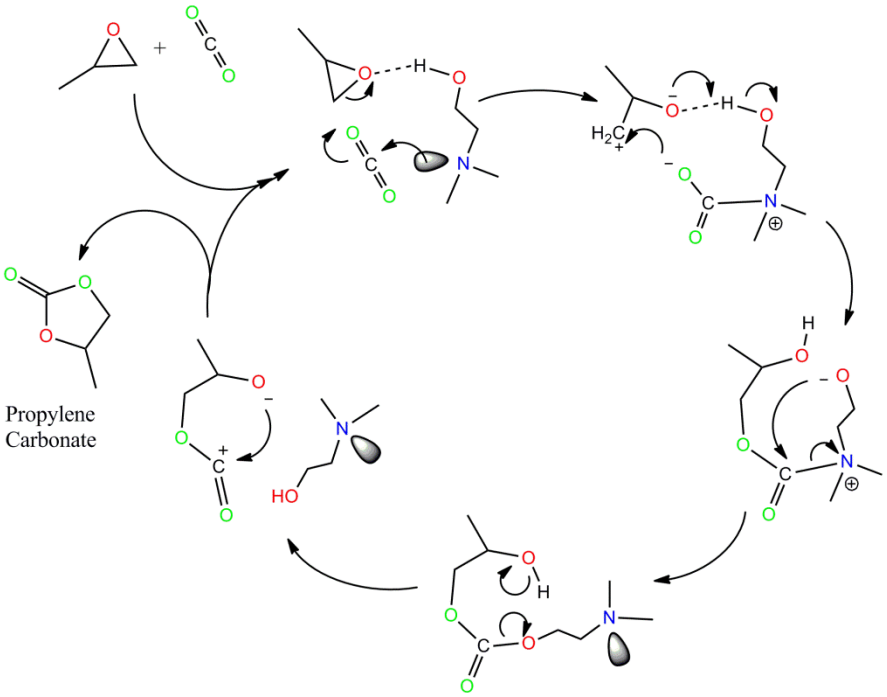
S 3

DFT figures of DMPA catalyzed cycloaddition of PO with CO_2



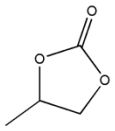
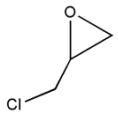
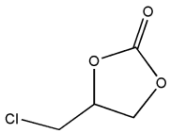
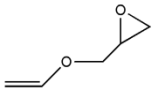
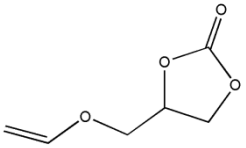
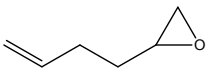
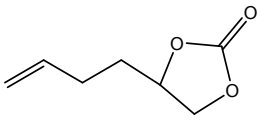
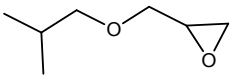
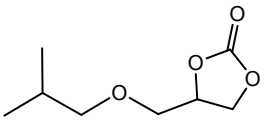
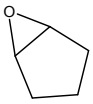
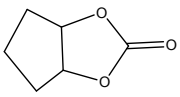
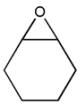
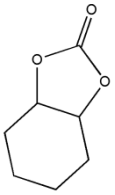
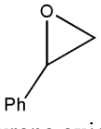
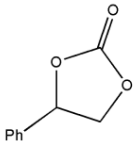
S 4

A plausible mechanism of the alkanolamine catalyzed cycloaddition of PO and CO_2, illustrated using DMEA catalyst utilizing the results of DFT simulations.



S 5

Activity of DMPA in the conversion of various epoxides to its corresponding cyclic carbonates

		Epoxide	Product	Yield(%)	Selectivity (%)
1	Terminal Epoxides	 Propylene oxide		91	>99
2		 Epichlorohydrin		92	>99
3		 Allylglycidyl ether		87	>98*
4		 1,2-epoxy-5-hexene		82	>95
5		 Glycidyl isobutyl ether		88	>96*
6	Internal Epoxides	 Cyclopentene oxide		19	96
7		 Cyclohexene oxide		6	98
8	Aromatic Epoxide	 Styrene oxide		83	94*

Reaction conditions: Epoxide 42.8 mmol, 0.8 mol% DMPA, 120 ^{o}C, 1 MPa initial pressure, 3 h (yield and selectivity calculated from GC/GCMS.*the main by-products were corresponding 1,2-diols.

(1) 4-methyl-1,3-dioxolan-2-one (propylene carbonate) : δH ($CDCl_3$, 400 MHz) : 1.50 (d, 3H, CH_3), 4.04 (d, 1H, OCH_2), 4.57 (t, 1H, OCH_2), 4.8–4.9 (m, 1H, OCH).

(2) 4-chloromethyl-1,3-dioxolan-2-one (epichlorohydrin carbonate) : δH ($CDCl_3$, 400 MHz) : 4.9 (m, 1H, OCH), 4.62 (dd, 1H, OCH_2), 4.47 (dd, 1H, OCH_2), 3.78–3.72 (m, 2H, $ClCH_2$).

(3) 4-allyoxymethyl-1,3-dioxan-2-one (allyl glycidyl carbonate) : δH ($CDCl_3$, 400 MHz): 5.84–5.77 (m, 1H, $CH=CH_2$), 5.38–5.26 (m, 2H, $CH=CH_2$), 4.84–4.80 (m, 1H, OCH), 4.49 (t, 1H, OCH_2), 4.36 (t, , 1H, OCH_2), 4.01–3.97 (m, 2H, OCH_2), 3.63 (m, 2H, OCH_2).

(4) 4-(but-3-en-1-yl)-1,3-dioxolan-2-one : δH ($CDCl_3$, 400 MHz) : 4.36 (m, 1H, $-OCH_2$), 4.12 (m, 1H, $-OCH_2$), 4.26 (m, 1H, -OCH), 1.63 (m, 2H, $-CH-CH_2$), 1.96 (m, 2H, $-CH=CH_2$), 5.73 (m, 1H, $-CH=CH_2$), 4.99 (dd, 1H, $=CH_2$), 4.96 (dd, 1H, $=CH_2$)

(5) 4-(isobutoxymethyl)-1,3-dioxolan-2-one (glycidyl isobutyl carbonate) : δH ($CDCl_3$, 400 MHz) : 4.36 (m, 1H, $-OCH_2$), 4.12 (m, 1H, $-OCH_2$), 4.56 (m, 1H, -OCH), 3.70 (dd, 1 H, $-OCH_2$), 3.51 (dd, 1 H, $-OCH_2$), 3.6 (d, 2H, $-OCH_2$), 1.92 (m, 1H, $-CH(CH_3)_2$), 1.10 (d, 6H, $-CH(CH_3)_2$).

(6) *cis*-1,2-cyclohexene carbonate : δH ($CDCl_3$, 400 MHz) : 4.71–4.66
(m, 2H, OCHCHO), 1.9–1.86 (m, 4H, CH_2), 1.44–1.36 (m, 2H, CH_2), 1.70–1.64 (m, 2H, CH_2),

(7) *cis*-1,2-cyclopentene carbonate : δH ($CDCl_3$, 400 MHz) : 5.19
(m, 2H, OCHCHO), 2.25-2.19 (m, 2H, CH_2), 1.80–1.62 (m, 4H, CH_2).

(8) 4-phenyl-1,3-dioxolan-2-one (styrene carbonate) : δH ($CDCl_3$, 400 MHz): δ 7.48–7.41
(m, 3H, Ar-H), 7.38–7.36 (m, 2H, Ar-H), 5.68 (t, 1H, OCH), 4.81 (t,
1H, OCH_2), 4.35 (t, 1H, OCH_2).