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Coupling Reactions of CO_2 with Neat Epoxides Catalyzed by PPN Salts To Yield Cyclic Carbonates

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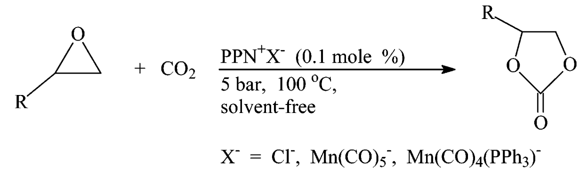
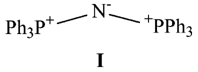


The off-the-shelf reagent PPN^+Cl^- and PPN-manganese carbonylates $[PPN]^+[Mn(CO)_4L]^-$ (L = CO, PPh_3) are good catalysts for the coupling reactions of CO_2 with neat epoxides without the use of organic solvents to afford cyclic carbonates. PPN salts with weak nucleophilic anions such as $PPN^+BF_4^-$ and PPN^+OTf^- are, however, inactive for the coupling reactions.

The utilization of carbon dioxide as a feedstock for the production of chemical products has attracted much attention owing to its economic and environmental benefits.[1] One promising methodology in chemical CO_2 fixation is the reaction of carbon dioxide with epoxides to synthesize cyclic carbonates, which are valuable as aprotic polar solvents, fine chemical intermediates, and sources for polymer and engineering plastic syntheses.[2] Various catalysts have been explored for the CO_2/epoxide coupling reactions.[3] It has been suggested that parallel Lewis base activation of CO_2 and Lewis acid activation of epoxide are important for the success of the coupling reactions.[3a−d] For example, it has been proposed that in the (salen)Cr(III) complex/(4-dimethylamino)pyridine (DMAP)-catalyzed CO_2/epoxide coupling reactions the starting (salen)Cr(III) complex acts as a Lewis acid to activate the epoxide, and the (salen)Cr(III)·DMAP complex, in which the Cr(III) center is rendered more electron-rich by coordination of the DMAP molecule, activates the CO_2 by forming a metallocarboxylate intermediate.[3a] It is also likely that the catalytic activity of the Mg−Al mixed oxides in the coupling of carbon dioxide with epoxides originates from the cooperative actions of the neighboring basic and acidic sites on the surface.[3b]

The bis(triphenylphosphine)immium (PPN) cation is well-known for imparting a high degree of stability to air-sensitive anions and therefore has been extensively used as counterion for anionic mono- and polynuclear metal carbonyls.[4] It is readily available as halide salts and salts containing other simple inorganic anions such as cyanate, thiocyanate, azide, and nitrate. X-ray photoelectron spectroscopic (ESCA) study on PPN salts implied that the phosphorus atoms in PPN^+ carry a degree of positive charge, whereas the nitrogen atom is largely negative in character, suggesting that the ionic structure **I** is the more appropriate description of PPN^+.[5] We study the catalytic activity of some PPN salts in the CO_2/epoxide coupling reactions for the formation of cyclic carbonates because we are of the opinion that proximity of acidic and basic sites on PPN^+ renders the PPN salts potential catalysts for the reactions.



I

The readily available PPN^+Cl^- was found to be active for the catalytic coupling reactions of CO_2 (5 bar) with epoxides at 100 °C to form cyclic carbonates, the results of which are shown in Table 1. However, the tetrafluoroborate and the triflate salts, $PPN^+BF_4^-$ and PPN^+OTf^-, respectively, show no catalytic activity. It is therefore probably true that the catalytic activity of PPN^+Cl^- does not originate from the cooperative actions of the basic and acidic sites on the PPN ion shown in **I**, but the anion might also play an important role in the catalysis. The nucleophilicity of the chloride anion in PPN^+Cl^- is much higher than those of the tetrafluoroborate and triflate anions in $PPN^+BF_4^-$ and PPN^+OTf^-, respectively. We have also studied the catalytic activity of the PPN salts

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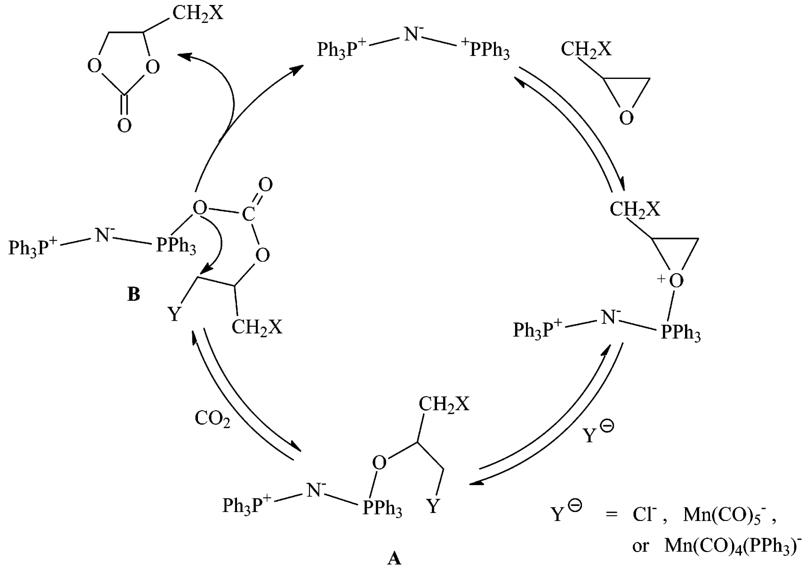
TABLE 1. Coupling of Epoxides with CO_2 Catalyzed by PPN Salts[a]

entry	substrate	time (h)	catalyst	TON[b]	TOF (h^{-1})[c]	entry	substrate	time (h)	catalyst	TON[b]	TOF (h^{-1})[c]
1	epifluorohydrin	1	**1**	867	867	15	propylene oxide	6	**1**	665	111
2	epifluorohydrin	1	**2**	876	876	16	propylene oxide	6	**2**	669	112
3	epifluorohydrin	1	**3**	847	847	17	propylene oxide	6	**3**	624	104
4	epichlorohydrin	1	**1**	846	846	18	propylene oxide	6	**4**	60	10
5	epichlorohydrin	1	**2**	853	853	19[d]	propylene oxide	6	**4**	nil	nil
6	epichlorohydrin	1	**3**	809	809	20	butadiene monoxide	6	**1**	638	106
7	epichlorohydrin	1	**4**	23	23	21	butadiene monoxide	6	**2**	624	104
8	epibromohydrin	1	**1**	828	828	22	butadiene monoxide	6	**3**	642	107
9	epibromohydrin	1	**2**	846	846	23	1,2-epoxyhexane	6	**1**	646	108
10	epibromohydrin	1	**3**	808	808	24	1,2-epoxyhexane	6	**2**	628	105
11	epibromohydrin	1	**4**	19	19	25	1,2-epoxyhexane	6	**3**	634	106
12	styrene oxide	6	**1**	790	132	26	isobutylene oxide	6	**1**	668	111
13	styrene oxide	6	**2**	772	129	27	isobutylene oxide	6	**2**	653	109
14	styrene oxide	6	**3**	783	131	28	isobutylene oxide	6	**3**	627	105

[a] Typical reaction conditions. Catalyst: 3.5 μmol [PPN][Cl] (**1**), [PPN][$Mn(CO)_5$] (**2**), [PPN][$Mn(CO)_4PPh_3$] (**3**), [Li][$Mn(CO)_4PPh_3$] (**4**). Substrates: 3.5 mmol (S/C = 1000), CO_2 pressure 5 bar, 100 °C. [b] Turnover numbers were determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture. [c] Moles of cyclic carbonates products per mole of catalyst per hour. [d] 7.0 μmol of 12-crown-4 added.

SCHEME 1



of manganese carbonylates $PPN^+Mn(CO)_5^-$ [6] (**2**) and $PPN^+Mn(CO)_4(PPh_3)^-$ [7] (**3**) in the coupling reactions. Results of the **2**- and **3**-catalyzed CO_2/epoxide coupling reactions are also included in Table 1. All three PPN salts are able to catalyze the coupling reactions at lower temperature (80 °C), but with much lower activities. It can be seen that the epihalohydrins, which contain electron-withdrawing groups, show higher reactivity (entries 1−6, 8−10, Table 1).

The catalytic reactions were carried out in neat epoxides, and no CO_2/epoxide copolymer was formed in any of the reactions. We monitored the **1**-, **2**-, and **3**-catalyzed CO_2/propylene oxide coupling reactions by high pressure ^{31}P NMR spectroscopy. It was found in each case that the PPN cation was the only phosphorus-containing species throughout the experiment. Scheme 1 shows a possible mechanism for the PPN-salt-catalyzed coupling reactions. Attachment of the epoxide to the phosphorus atom of PPN^+ activates the former toward nucleophilic ring opening by Y^- ($Y^- = Cl^-$, $Mn(CO)_5^-$, or $Mn(CO)_4(PPh_3)^-$). It is widely accepted that coordination of an epoxide to a Lewis acid facilitates nucleophilic ring opening of the former. For example, it has been shown by Jacobsen et al. that coordination of the epoxide to the (salen)Cr(III) complex is a necessary step to activate the former toward nucleophilic ring opening by the (salen)-Cr(III)-azide complex.[8] Insertion of CO_2 into **A** then gives the carbonato species **B**. Although **A** is not exactly a metal-alkoxy complex, its reactivity toward CO_2 is expected to be similar to that of metal alkoxides. Insertion of CO_2 into a metal-alkoxy bond to form metal carbonate species is well-documented.[9] Finally, the S_N2-type ring-closing step gives the cyclic carbonate product. Similar mechanisms have been proposed for the CO_2/epoxide coupling reactions with other catalyst systems.[3g,i,k,n,o,q,r] It was learned that in the coupling reactions catalyzed

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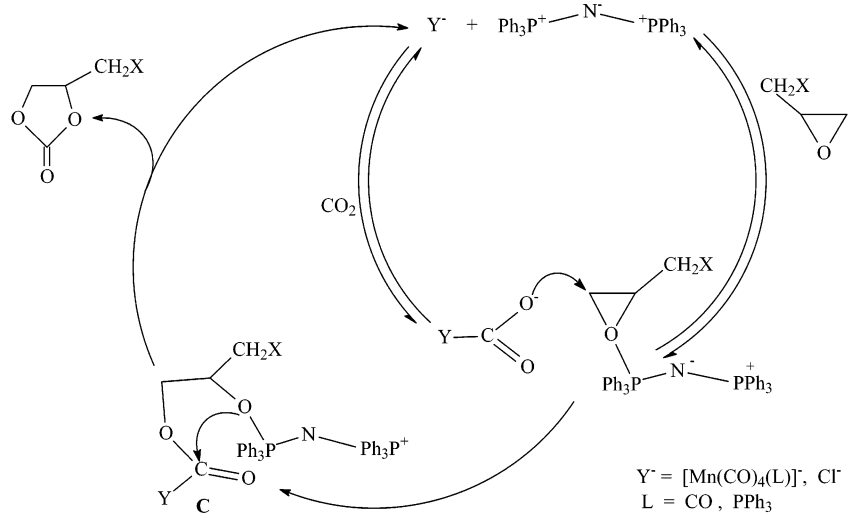
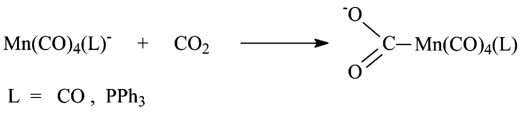
SCHEME 2



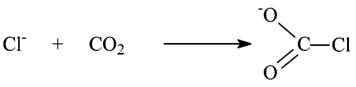
by various salts M^+X^- ($M^+ = Na^+$, Li^+ or $PhCH_2N^+Me_3$), only the halide salts (Br^-, Cl^-, and I^-) showed considerable activity. The salts with nonnucleophilic anions, such as *p*-toluenesulfonate and perchlorate, and salts with higher nucleophilic anions such as acetate, cyanide, phenolate, and thiophenolate showed very low activity. The activity of the halide salts is attributable to their possessing nucleophicity high enough to ring-open the epoxide and good leaving ability essential to the ring closure, which is a S_N2-type reaction on sp^3 carbon.[3k]

An alternative mechanism involving parallel Lewis acid activation of epoxide and Lewis base activation of CO_2 is shown in Scheme 2. This pathway also begins with PPN-activation of the epoxide molecule; in the second step, it is proposed that the anion, instead of ring-opening the epoxide, activates the carbon dioxide molecule by forming the manganese formate (eq 1) or the chloroformate (eq 2). Gibson et al. have proposed the manganese formate $[Mn(CO)_4(PPh_3)(CO_2)]^-$, which has not been isolated, to be the intermediate in the reaction of $K^+[CpFe(CO)(PPh_3)(CO)_2]^-$ with $[Mn(CO)_5(PPh_3)]^+BF_4^-$ followed by addition of CH_3I to afford $[CpFe(CO)_2(PPh_3)]^+BF_4^-$ and $Mn(CO)_4(PPh_3)(CH_3)$.[10] Moreover, since the catalytic reactions were performed in neat substrates, it is therefore conceivable, in the absence of solvating solvent, that the chloride anion (in the case of PPN^+Cl^-) might possess greatly enhanced nucelophilicity and would react with carbon dioxide to generate the chloroformate anion.[11] The manganese formate or chloroformate opens the expoxide forming **C**, and finally ring closure gives the product. A similar mechanism involving haloformate anion opening up the expoxide had been proposed.[3k]



$$Mn(CO)_4(L)^- + CO_2 \longrightarrow {}^-O(O=)C\text{—}Mn(CO)_4(L) \qquad (1)$$

$$L = CO,\ PPh_3$$



$$Cl^- + CO_2 \longrightarrow {}^-O(O=)C\text{—}Cl \qquad (2)$$

At this stage, we are not able to favor one mechanism over the other; much work would have to be done to elucidate the mechanistic details of the catalytic reactions. It is observable that the epihalohydrins react faster than the other epoxides (entries 1−6, 8−10, Table 1); a possible explanation for the enhanced activity of the epihalohydrins might lie in the greater electrophilicity of the epoxide carbons of these compounds facilitating the ring-opening step. Paddock and Nguyen have found the epichlorohydrin to be the most active epoxide among the aromatic and aliphatic epoxides in the Cr(III)salen complex-catalyzed CO_2/epoxide coupling reactions.[3a]

For comparison purpose, we also carried out coupling reactions of CO_2 with some of the epoxides using $Li^+Mn(CO)_4(PPh_3)^-$ (**4**) as catalyst. It was found that the catalytic activity of **4** is much lower than that of **3** under identical conditions (entries 6, 7, 10, 11, 17, 18, Table 1). The fact that addition of 12-crown-4, which is able to encapsulate Li^+, practically quenches the activity of **4** (entries 18, 19, Table 1) indicates that the manganese carbonylate anion $Mn(CO)_4(PPh_3)^-$ by itself is not able to catalyze the coupling reaction.

In conclusion, we have shown that the PPN manganese carbonyls and more interestingly the off-the-shelf reagent PPN^+Cl^- are good catalysts for the coupling reactions of CO_2 (5 atm) with epoxides to yield cyclic carbonates. The reactions are clean with no polycarbonate contamination and are performed in neat substrates with no need of organic solvents. Work aimed at elucidating the mechanistic details of the catalytic reactions is now in progress.

Experimental Section

$[PPN]^+[Mn(CO)_4(PPh_3)]^-$. The complex was synthesized according to a literature method[7] with slight modification. To a solution of $Mn_2(CO)_8(PPh_3)_2$[12] (0.33 g, 0.38 mmol) in 10 mL of THF at 0 °C was added $Li(C_2H_5)_3BH$ (1.0 M THF solution, 0.96 mL, 0.96 mmol). The solution was allowed to warm to room

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temperature and stirred for 2.5 h, after which a solution of PPN^+Cl^- (0.44 g, 0.76 mmol) in dichloromethane (10 mL) was added via a cannula. The resulting solution was allowed to stir overnight at room temperature and then filtered through Celite, and the solvent was removed under vacuum. The residue was washed with diethyl ether (5 mL) and then extracted with 10 mL of toluene. The extract was brought to dryness to afford a yellow solid, which was washed with diethyl ether (2 × 5 mL) and dried in a vacuum. Yield: 0.51 g (70%). Anal. Calcd for $MnC_{46}H_{35}O_4NP_3$: C 69.32, H 4.51. Found: C 68.90, H 4.47. IR (KBr, cm^{-1}): $\nu(C{\equiv}O)$ 1911 (m), 1931 (s), 1947 (s), and 1977 (s). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.45−7.76, (m, H's of PPN^+ and PPh_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 25 °C): δ 189.9 (CO), 195.8 (CO), 201.6 (CO), 230.8 (CO). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25 °C): δ 22.3 (s, 2P of PPN^+), 77.3 (s, 1P of PPh_3).

General Procedure for the Catalytic CO_2/Epoxide Coupling Reactions. The reactions were carried out in a 10 mL stainless steel autoclave equipped with a magnetic stirring bar. In a typical run, 14.3 μmol of the catalyst (PPN salt) was dissolved in the epoxide (~1 mL, 1000 equiv), and the solution was heated with stirring under 5 bar of CO_2 at 100 °C. At the end of the required length of time, the autoclave was cooled rapidly and vented carefully. The yield of cyclic carbonate was determined by ^1H NMR spectroscopy. The set of three signals for the two methylene hydrogen atoms and the hydrogen on the substituted carbon of the substrate epoxide is well-separated from the set of three signals for the corresponding hydrogen atoms in the product cyclic carbonate. The yield of the cyclic carbonate can therefore be determined by comparing the sum of integration of one set of hydrogen atoms with that of the other set. To identify the cyclic carbonate, at the conclusion of the catalytic reaction the unreacted epoxide, which has a much lower boiling point than the cyclic carbonate, was easily removed under reduced pressure, and the cyclic carbonate that remained was identified by comparing its ^1H NMR spectrum with that of the authentic sample.

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