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Direct Synthesis of Cyclic Carbonates in the Presence of Organometallic Compounds. Catalyses by Systems from IVA, VA, and VIA Group Compounds and Lewis Base

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In the cycloaddition of carbon dioxide to oxiranes to form cyclic carbonates in the presence of organometallic halides of group IVA, VA, and VIA, catalytic activities of organometallic halides are in the order Sb>Te>Sn≫Bi, Ge, and Si. An improvement of their catalytic activities is achieved by addition of an equimolar amount of Lewis base. In binary catalyst systems, the order of catalytic activities is in the order Sn>Te>Sb≫Bi, Ge, and Si. Organotin halide–base systems show the highest catalytic activity.

In our previous papers, we reported that pentavalent organoantimony halides such as Ph_4SbBr and Ph_3SbBr_2 are highly effective catalysts for the cycloaddition reaction of carbon dioxide (CO_2) to oxiranes to afford corresponding cyclic carbonates (1,3-dioxolan-2-ones).[1] The striking feature of organoantimony catalysts in the cycloaddition is attributable to the covalent nature of the antimony-halogen bonds[1] in contrast with ammonium halides such as tetraethylammonium chloride.[2]

In the present study, we carried out cycloadditions catalyzed by triphenyl derivatives of Sn^{IV}, Ge^{IV}, Si^{IV}, and Bi^{V} and by dimethyl and diphenyl derivatives of Te^{IV}, expecting a similar effect of metal-halogen bonds as in the pentavalent organoantimony halide-catalyzed cycloaddition. Further, an attempt was made to improve the catalytic activity of the organometallic halides by incorporation of an equimolar amount of Lewis base such as triethylamine (TEA), pyridine (Py), and triphenylphosphine (TPP) to the organometallic halides and it was found that the binary catalysts effectively enhance the catalytic activity, especially in the case of the organotin halides.

Some recent papers have claimed good catalytic activities of pairs of heavy metal halide and Lewis base[3] but do not explain the effect of added bases in detail. Therefore, we also attempted to discuss the effect of added bases.

Results and Disscussion

Catalytic Activities of Organometallic Halides of Groups IV, V, and VI. The cycloaddition of CO_2 to methyloxirane (propylene oxide, PO) was carried out in a stainless-steel autoclave at 100 °C under a fixed initial pressure of CO_2, 50 kg/cm^2, to compare catalytic activities of organometallic halides with one another,

TABLE 1. RELATIVE CATALYTIC ACTIVITIES OF THE ORGANOMETALLIC HALIDES–BASE SYSTEMS IN THE CYCLOADDITION REACTION OF CO_2 TO METHYLOXIRANE AT 100 °C

Catalyst	Relative rate constant[b]			
	No base	TEA[c]	Py[d]	TPP[e]
Ph_3SnCl	>0.01[f] (0.001)	0.22	0.20	0.20
Ph_3SnBr	>0.01[f] (0.01)	6.0	6.6	6.4
Ph_3SnI	>0.01[f] (0.09)	6.0	6.0	5.8
Ph_3GeBr	0[g]	>0.01[f] (0.16)	>0.01[f] (0.08)	>0.01[f] (0.16)
Ph_3SiBr	0[g]	>0.01[f] (0.26)	>0.01[f] (0.11)	>0.01[f] (0.22)
Ph_3SbBr_2	1.0[h]	1.1	1.4	0.74
Ph_4SbBr	5.0	—	—	—
Ph_3BiBr_2	0[g]	>0.01[f] (0.10)	>0.01[f] (0.07)	>0.01[f] (0.04)
Me_2TeCl_2	0[g]	—	—	—
Me_2TeBr_2	0.20	—	—	—
Me_2TeI_2	0.64	2.4	2.2	0.89
Tol_2TeCl_2[i]	0.02	0.08	0.08	0.02
—	—	>0.01[f] (9.7×10^{-4})	>0.01[f] (7.7×10^{-4})	>0.01[f] (7.6×10^{-4})

a) Methyloxirane: 50 mmol, base/organometallic halides: 1.0, initial pressure of CO_2: 50 kg/cm^2. b) Relative rate constant based on Ph_3SbBr_2; see h). c) TEA: Triethyl amine. d) Py: Pyridine. e) TPP: Triphenylphosphine. f) Relative rate constants measured at 120 °C are indicated in parentheses. g) No cycloaddition occurred even at 120 °C. h) 3.4×10^{-1} M^{-1} min^{-1} (1 M=1 mol dm^{-3}). i) Tol: p-$CH_3C_6H_4$–.

and relative rate constants are summarized in Table 1 for the catalysts employed. The catalytic activities of the organometallic halides are in the order

$$Sb > Te > Sn \gg Bi,\ Ge,\ Si. \qquad (1)$$

Only the organotellurium compounds compare with the organoantimony catalysts in activity under the conditions examined. However, the reaction mixture became red-brown as reaction proceeded. Although organotin halides could not cause the cycloaddition at 100 °C, they gave 4-methyl-1,3-dioxolan-2-one (propylene carbonate, PC) at a significant rate, when reaction was carried out at 120 °C.[4]

The dependence of the catalytic activities of the organometallic halides on the polarity of the metal-halogen bonds may be expected, since the organometallic halides used in this study are considered to have relatively covalent metal-halogen bonds similarly to the organoantimony halides.[1] With regard to Sn, Sb, and Te compounds, the length of the metal-chlorine bond was reported to be in the order $Sb^{V} > Te^{IV} > Sn^{IV}$,[5,6] and it can be seen that the catalytic activity of the organometallic halides decreases with decrease in the bond length.

If the organometallic catalyst can be formed *in situ*, some simplification of the process for synthesis of the cyclic carbonate may be achieved. Among the organometallic halides examined, Me_2TeI_2 can be prepared by heating a mixture of tellurium powder and methyl iodide at 80 °C.[7] We attempted a cycloaddition reaction with a mixture of methyl iodide and tellurium which is expected to afford Me_2TeI_2 *in situ*. When methyl iodide and tellurium were added in a mole ratio of more than two, a quantitative yield of PC was obtained as shown in Table 2. However, the question whether Me_2TeI_2 is really formed *in situ*[8] and catalyzes the reaction remains to be solved. We also attempted the cycloaddition with combinations of tin metal-butyl[9] or -methyl iodide and antimony metal-methyl iodide, but they were not effective at all even at 120 °C.

Improvement of the Catalytic Activities of the Organometallic Halides by Addition of Lewis Bases. Generally, group IV organometallic halides are found to be less active for the cycloaddition reaction than organoantimony and organotellurium compounds. Thus, in order to improve the catalytic activity of the organometallic halides, an equimolar amount of Lewis base such as TEA, Py, and TPP was added to the organometallic compounds.[10] A marked rate enhancement was observed as shown in Table 1, *e.g.*, relative rate constants for Ph_3SnBr (or Ph_3SnI)–base systems are obviously larger than those for Ph_3SnBr (or Ph_3SnI) by a factor of $>10^2$. The order of the catalytic activities for the binary catalyst systems changed from (1) to

$$Sn > Te > Sb \gg Bi,\ Ge,\ Si. \qquad (2)$$

Table 2. The cycloaddition reaction of CO_2 to PO in the presence of tellurium and methyl iodide[a)]

Te(mmol)	MeI(mmol)	Temp/°C	Time/h	Yield/%
5	10	100	8	68
5	50	100	6	91
5	10	80	8	3
—	10	100	6	0
5	—	100	6	0

a) PO: 50 mmol, initial pressure of CO_2: 50 kg/cm.²

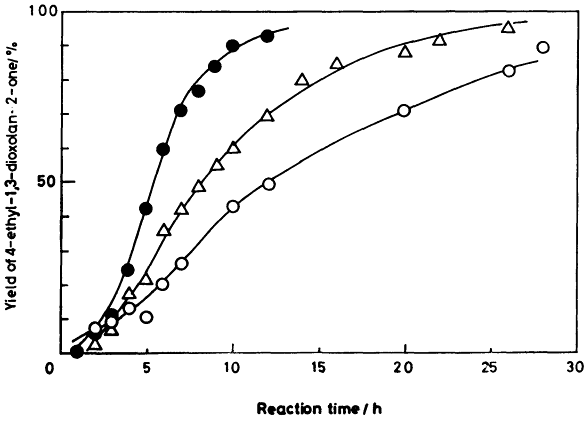


Fig. 1. Cycloaddition reaction under atmospheric pressure of CO_2 at 60 °C.
Ethyloxirane: 50 mmol, organometallic halides: 0.15 M (0.5 mmol). ○: Ph_4SbBr, ●: Ph_3SnBr–TEA (1/1), △: Me_2TeI_2–TPP (1/1), molar ratio in parentheses.

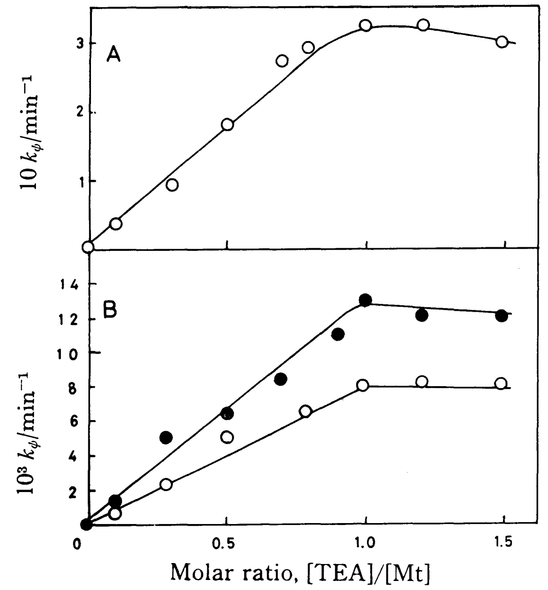


Fig. 2. Relation between k_ψ and molar ratio of [TEA]/[Mt].
Methyloxirane: 50 mmol, organometals [Mt]: 0.15 M, initial pressure of CO_2: 50 kg/cm². A: Ph_3SnBr–TEA at 100 °C. B: Ph_3SiBr–TEA (●) and Ph_3GeBr–TEA (○) at 120 °C.

The most active binary systems, such as Ph_3SnBr–TEA and Me_2TeI_2–TPP, surpassed Ph_4SbBr which is the most effective among the organoantimony compounds,[1] and could give the cyclic carbonate quantitatively even under atmospheric pressure of CO_2 at 60 °C, as shown in Fig. 1.

Effect of Added Bases. Tertiary amines or phosphines themselves have been known to show catalytic activity for the cycloaddition reaction,[11] but their catalytic activity is low as shown in Table 1 under the relevant conditions. Consequently, the enhanced catalytic activity of the binary systems can be said to result from a cooperative effect of the organometallic halide with the base.

In order to understand the synergic effect of the organometallic compound with the base, the Ph_3SnBr–TEA system, showing a high rate enhancement, was examined in detail. Pseudo-first-order rate constant k_ψ was plotted against the molar ratio of [TEA]/[Ph_3SnBr] as shown in Fig. 2. It can be seen from Fig. 2 that k_ψ linearly increases with molar ratio, reaches a maximum value at molar ratio 1.0, and follows a gradual decrease. This characteristic curve indicates that the effective enhancement of the catalytic activity results from a 1 : 1 complexation between Ph_3SnBr and TEA.[5,12] Consequently, in the binary systems the pseudo-first-order rate constant k_ψ may be divided into the respective contributions of organometallic halides alone, of bases alone, and of the organometallic halide–base complex and k_ψ can be expressed as in Eq. 5 by using the equilibrium constant K shown in Eq. 3:

$$\mathrm{Mt} + \mathrm{base} \overset{K}{\rightleftarrows} \mathrm{Mt{-}base(complex)}, \tag{3}$$

$$k_\psi = k_{\psi\,\mathrm{Mt}} + k_{\psi\,\mathrm{base}} + k_{\psi\,\mathrm{complex}} \tag{4}$$

$$= k_{\psi\,\mathrm{Mt}} + k_{\psi\,\mathrm{base}} + k_{\mathrm{complex}}\,K[\mathrm{Mt}][\mathrm{base}], \tag{5}$$

$$k_{\psi\,\mathrm{complex}} = k_{\mathrm{complex}}[\mathrm{complex}], \tag{6}$$

where Mt denotes the organometallic halide. From the results shown in Table 1, the contribution from base alone is negligible, and then Eqs. 7 and 8 can be introduced:

$$k_\psi = k_{\psi\,\mathrm{Mt}} + k_{\mathrm{complex}}\,K[\mathrm{Mt}][\mathrm{base}] \tag{7}$$

$$= k_{\psi\,\mathrm{Mt}} + [\mathrm{Mt}]^2 k_{\mathrm{complex}} K([\mathrm{base}]/[\mathrm{Mt}]). \tag{8}$$

These equations indicate that the catalytic activity of the complex, $k_{\mathrm{complex}}K$, can be calculated from the increment, $\Delta k_\psi/\Delta[\mathrm{base}]$, in the linear part of the curve in Fig. 2.

Similar curves were also obtained for Ph_3GeBr– and Ph_3SiBr–TEA systems at 120 °C, as illustrated in Fig. 2, and for Ph_3SbBr_2–TEA and Me_2TeI_2–TPP systems at 100 °C. The calculated values of $k_{\mathrm{complex}}K$ for each organometallic halide–base system are listed in Table 3. It is found that the value for Ph_3SnBr–TEA system is larger than those for the other binary systems, and that the value for Ph_3SbBr_2–TEA system is negligibly small.

Tetravalent organotin halides are known to react with bases such as amines or phosphines to give a pentacoordinated trigonal bipyramidal complex.[12,13] Such complexation would increase the polarity of the Sn-halogen bonds; in other words, it activates the Sn-halogen bonds. Further, there remains one active coordination site in the complexed tin atom because tin atom can generally uses six coordination sites.[12]

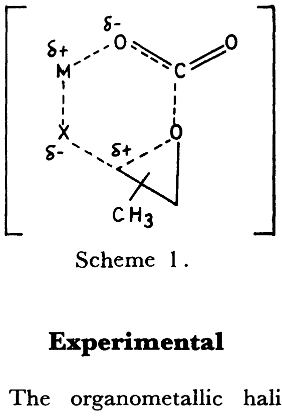
Pentavalent organoantimony compounds are also known to afford a hexacoordinated complex with bases.[10] However, their electron acceptability has been reported to be smaller than that of tetravalent tin compounds.[1,14] In addition, such a hexacoordination may result in a decrease of the polarity of the Sb-halogen bonds in contrast with pentacoordination.[5,12,15] Thus, the complexation is suggested to play a less significant role in the catalytic activity of the Ph_3SbBr_2–base systems than with the Ph_3SnBr–base systems.

On the basis of the results obtained, a reaction pathway as indicated by the set of Eq. 3 and the following two equations

$$\mathrm{CO_2} + \mathrm{PO} \rightleftarrows \mathrm{CO_2{-}PO}, \tag{9}$$

$$\mathrm{CO_2{-}PO} + \mathrm{Mt(or\ Mt{-}base)} \longrightarrow$$
$$\mathrm{PC} + \mathrm{Mt(or\ Mt{-}base)}, \tag{10}$$

is tentatively proposed. The intervention of the CO_2–PO complex has been deduced on the basis of appearance of a new absorption band in UV spectrum of the saturated solution of CO_2 in PO,[16] similarly to the CO_2–phenylaziridine systems.[19] A plausible intermediate is also shown in Scheme 1.



Scheme 1.

Table 3. The catalytic activity of the complexes in the cycloaddition reaction of CO_2 to PO[a)]

Binary system Mt–Base	$k_{\mathrm{complex}}K/\mathrm{M^{-2}\,min^{-1}}$ [b)]
Ph_3SnBr–TEA	160[c)]
Ph_3GrBr–TEA	0.38[d)]
Ph_3SiBr–TEA	0.43[d)]
Ph_3SbBr_2–TEA	0.24[c)]
Ph_3BiBr_2–TEA	0.24[d)]
Me_2TeI_2–TPP	4.3[c)]

a) The catalytic activity of the complexes is defined in Eq. 8. b) The value of $k_{\mathrm{complex}}\,K$ was calculated from the linear relation between k_ψ and molar ratio (base/Mt) shown in Fig. 2. c) Obtained at 100 °C. d) Obtained at 120 °C.

Experimental

Materials. The organometallic halides, Ph_3SnCl,[20] Ph_3SnBr,[21] Ph_3SnI,[21] Ph_3GeBr,[22] Ph_3SiBr,[23] Ph_3SbBr_2,[1] Ph_4SbBr,[1] Ph_3BiBr_2,[24] Me_2TeCl_2,[7] Me_2TeBr_2,[7] and (p-$CH_3C_6H_4)_2TeCl_2$[25] were prepared by the reported methods and checked by elemental analysis. Methyloxirane (PO) and ethyloxirane (1,2-butylene oxide, BO) was dried and stored over calcium hydride. The Lewis bases used as additive were distilled or recrystallized before use. The solvents were used after rectification.

Analysis. Analytical gas chromatography (GC) was performed on a Shimadzu GC-4BPTF gas chromatograph with an FID detector and on a GC-3BT with a TCD detector.

Reaction Procedures. *Under a Pressure of CO_2:* The cycloaddition reaction of CO_2 to PO was carried out in a 50 ml stainless-steel autoclave under the conditions as described previously.[1] The initial pressure of CO_2 was always 50 kg/cm^2.

Under Atmospheric Pressure of CO_2: The cycloaddition reaction of CO_2 to ethyloxirane was carried out under atmospheric pressure of CO_2 at 60 °C. The organometallic halides (0.5 mmol), the base (if solid (TPP)) and a magnetic stirring bar was placed in a 50 ml three-necked flask equipped with a condenser, a CO_2 inlet connected to a 1000 cm^3 balloon filled with CO_2, and a rubber septum (SGA Scientific Inc.) through which sample for GC analysis was taken. The flask was evacuated and flashed by CO_2 three times, and then 50 mmol of ethyloxirane and 0.5 mmol of the base (if liquid (TEA and Py)) was introduced through the septum by the syringe technique. The reaction was monitored by GC. The only detectable product was 4-ethyl-1,3-dioxolan-2-one (1,2-butylene carbonate).

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