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REACTION OF CARBON DIOXIDE WITH ETHYLENE OXIDE IN THE PRESENCE OF ORGANOTIN COMPOUNDS

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The reaction of carbon dioxide (CO_2) with ethylene oxide (EO) in the presence of organotin compounds, such as organotin halides (R_nSnX_{4-n}; R=Alkyl, Aryl, X=Br, Cl, n=2,1) or organostannoic acids ($(RSnOOH)_n$; R=Alkyl, Aryl) yielded ethylene carbonate (EC) as a product in fairly good yields at 120°C.

Recently, synthetic utilization of CO_2 has been extensively studied using various organometallic compounds as catalyst. Organozinc catalyst systems$^{1)}$ or group VIII transition metal complexes$^{2,3)}$ have been used for the alternating copolymerization of CO_2 and epoxides, and for the preparation of alkylene carbonates, respectively. And it has been also known that organotin alkoxides are effective for the direct synthesis of alkyl or alkylene carbonates from CO_2.$^{4,5)}$

We tried a direct carbonylation of EO with CO_2 in the presence of organotin halides $\underline{1}$ or organostannoic acids $\underline{2}$, and found that EC is formed in fairly good yields under comparatively mild conditions. We had already reported that these organotin derivatives are effective for the polymerizations of alkylene oxides.$^{6,7)}$ It is interesting to observe the same compounds are also effective for the formation of EC by the reaction of CO_2 with EO.

When mono- or diorganotin halides were used in the reactions, EC was obtained in 28 to 72% yield, and the catalytic activity decreased in the order of n-C_4H_9, CH_3 > n-C_8H_{17} > C_6H_5 derivatives (Table 1). The catalytic activity of $\underline{2}$ seems to have less dependence on the number and the sort of halogen atoms in the molecule of $\underline{2}$ in comparison with those for the polymerization of EO.$^{6)}$

In the presence of methane- or n-buthanestannoic acid as catalyst, EC was also formed in 47 and 74% yield, but two arenestannoic acids were recognized to be less effective (Table 2). However, the heat-treated arenestannoic acids (190-200°C/1.0 mmHg for 2h) were found to become very active for homopolymerization of EO in CO_2-EO system. The rates of the polymerization of EO catalyzed by $\underline{2}$ are perceived to be p-CH_3-C_6H_4 > C_6H_5 > n-C_4H_9 > CH_3, and coordinated anionic character$^{8)}$ of $\underline{2}$ also decreases in the same order. But, in the present results, it can be viewed from Table 2 that catalytic activity in the reaction of CO_2 with EO had a tendency opposite from that in the coordinated anionic polymerization of EO.$^{8)}$

Table 1 Reaction of CO_2 with EO catalyzed by 1

Cat. (1)	Yield of EC (%)
CH_3SnCl_3	69
CH_3SnBr_3	72
$(n\text{-}C_4H_9)_2SnCl_2$	62
$(n\text{-}C_8H_{17})_2SnCl_2$	54
$(C_6H_5)_2SnCl_2$	28

Reaction conditions: EO, 0.1 mol , CO_2, 50 kg/cm^2, Cat., 1.0 mol% to EO, Temp., 120°C, Time, 6h, in a 100 ml stainless steel autoclave.

Table 2 Reaction of CO_2 with EO catalyzed by 2

Cat.; (RSnOOH)n	Products and yields (%)	
R	EC	Poly(ethylene oxide)
CH_3	47	0
$n\text{-}C_4H_9$	74	0
C_6H_5	29	0
C_6H_5 a)	0	59 b)
$p\text{-}CH_3\text{-}C_6H_4$	22	0
$p\text{-}CH_3\text{-}C_6H_4$ a)	0	84 b)

a) Heat-treated before use.

b) White wax was obtained.

Reaction conditions were shown in Table 1.

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