



Title	有機アンチモン化合物の触媒としての利用に関する研究
Author(s)	野村, 良紀
Citation	大阪大学, 1982, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/2390
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

7-2795

Studies on Utilization of
Organoantimony Compounds as Catalyst

1982

RYOKI NOMURA

Studies on Utilization of
Organoantimony Compounds as Catalyst

(有機アニモニ化合物の触媒としての
利用に関する研究)

1982

RYOKI NOMURA

Preface

The work of this thesis has been done under the guidance of Professor Haruo Matsuda at the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, during 1978-1982.

The author would like to express his grateful acknowledgement to Professor Haruo Matsuda for his invaluable guidance and constant encouragement throughout this work.

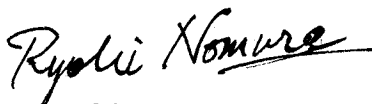
The author is deeply grateful to Associate Professor Akira Ninagawa for his helpful suggestion and discussion. The author wishes to express a grateful gratitude to Dr. Akira Uchida and Dr. Akio Baba for their valuable discussion. Much thanks are due to Mr. Masao Kawazoe for his helpful suggestion. The author wishes to acknowledge to Mr. Tetsuo Tsuchida, Mr. Masahiro Kimura, Mr. Hitoshi Hisada, Mr. Hirohiko Katayama, and Mr. Satoshi Teshima for their active collaboration. The author also wishes to thank to Mrs. Kyoko Tsuchida and all the members of Matsuda Laboratory for their constant assistance and friendship.

Grateful acknowledgment is due to Mr. late Seizo Nakajima, Mr. Hiroshi Moriguchi, and Mr. Seiji Nakajima for their kindly encouragement.

Finally the author wishes to thank his father Kohei Nomura and his mother Kazuko Nomura for their heartfelt encouragement.

Suita, Osaka

January 1982


Ryoki Nomura

List of Publications

The content of this thesis is composed of the following papers:

1. Reaction of Carbon Dioxide with Ethylene Oxide in the presence of Organotin Compounds.
H. Matsuda, A. Ninagawa, R. Nomura, and T. Tsuchida,
Chem. Lett., 1979, 573.
2. Reaction of Carbon Dioxide with Epoxides in the Presence of Pentavalent Organoantimony Compounds.
H. Matsuda, A. Ninagawa, and R. Nomura,
Chem. Lett., 1979, 1261.
3. Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides in the Presence of Organoantimony Compounds as Novel Catalysts.
R. Nomura, A. Ninagawa, and H. Matsuda,
J. Org. Chem., 45, 3735 (1980).
4. Polymerization of Ethylene Oxide Catalyzed by Organoantimony Compounds.
R. Nomura, H. Hisada, A. Ninagawa, and H. Matsuda,
Makromol. Chem., Rapid Commun., 1, 135 (1980).
5. Polymerization of Ethylene Oxide Catalyzed by Triphenylantimony Dibromide-Lewis Base Systems.
R. Nomura, H. Hisada, A. Ninagawa, and H. Matsuda,
Makromol. Chem., Rapid Commun., 1, 705 (1980).
6. Polymerization of Ethylene Oxide. A Novel Binary Catalyst System Consisted of Triphenylantimony Dibromide and Triphenylphosphine.
R. Nomura, H. Hisada, A. Ninagawa, and H. Matsuda,
Makromol. Chem., in press.

7. Kinetics and Mechanism of the Direct Synthesis of Cyclic Carbonates Catalyzed by Pentavalent Organoantimony Compounds.
R. Nomura, A. Ninagawa, and H. Matsuda,
Bull. Chem. Soc. Jpn., in contribution.
8. Direct Synthesis of Cyclic Carbonates in the Presence of Organometallic Compounds. Catalyses of IV_A, V_A and VI_A Group Compounds and Lewis Base Systems.
R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, and H. Matsuda,
Bull. Chem. Soc. Jpn., in contribution.

The Supplementary Treatise is as following:

The Acid-Catalyzed Reactions of 4-Chromanones with Formaldehyde.

A. Ninagawa, R. Nomura, and H. Matsuda,
Bull. Chem. Soc. Jpn., 52, 1169 (1979).

Contents

Preface	i
List of Publications	ii
Contents	iv
General Introduction	1
PART ONE ORGANOANTIMONY CATALYZED SYNTHESIS OF CYCLIC CARBONATES DIRECTLY FROM CARBON DIOXIDE AND OXIRANES	
Chapter I Catalytic Activities of Organoantimony Compounds	4
Chapter II Kinetics and Mechanism	12
Chapter III Catalytic Activities of Group IV _A , V _A and VI _A Organometallic Compounds and Effect of Adding Base	29
PART TWO ORGANOANTIMONY CATALYZED POLYMERIZATION OF OXIRANE	
Chapter IV Activities of Organoantimony Compounds	44
Chapter V Enhancement of Catalytic Activities of Organoantimony Compounds by Addition of Bases	50
Chapter VI Kinetics of Polymerization of Oxirane Catalyzed by Ph ₃ SbBr ₂ -Ph ₃ P system	58
Conclusion	72
References	74

General Introduction

In present time, it is not too much to say that synthetic chemistry can not be done without metal catalysts, because the theoretical and applied chemistry of the catalyst has been remarkably progressed. Consequently, a current research for more effective catalysts is vigorously doing around the world and much interest is given to the field of the transition metal compounds. However, the use of typical metal organometallic compounds is limiting and most of them still remains unexploitable with few exception.

Antimony(Sb) is at fifth row belonging to V_A group in the periodic table. Alchemist long ago knew antimony as typical metal element and isolated it. Nowadays, it is widely utilized for alloy *etc.* The other hand, the chemistry of organoantimony compounds began at the very early stage of the organometallic chemistry and some basic organoantimony derivatives was already synthesized in the last century. Although the long history of the chemistry of organoantimony compounds, in contrast to that of organotin compounds as the members of the same row as the antimonies, effective application of organoantimony compounds as catalyst is not established yet. The present study has been done with the aim of developing a novel catalytic use of the organoantimony compounds, especially of the pentavalent derivatives.

There has been much attention given to synthetic utilization of carbon dioxide(CO_2) as raw material along with various organometallic compounds.¹ Recently, it has been

reported that alternating copolymers of CO_2 and oxiranes are given by the use of organozinc² and aluminum compounds³ and that organotin alkoxides afford alkylcarbonates.⁴ In relation to these reactions, for the direct synthesis of cyclic carbonates from CO_2 and oxiranes which was begun in 1943 by Vierling,⁵ many types of the catalysts have been surveyed and the synthesis has been done on an industrial scale⁶: *e.g.* ammonium or phosphonium salts,⁷ bases,⁸ Lewis acid-base systems⁹ and previous transition metal complexes¹⁰ are typical catalysts, however, it is known that most of them requires severe conditions and is accompanied by problems in purification of the resulting cyclic carbonates by coloring. Thus the development of a stable catalyst which are effective even under mild conditions not to color the products has been desired.

Consequently, in PART ONE of this study organoantimony catalyzed synthesis of cyclic carbonates from CO_2 and oxiranes aiming at exploitation of novel catalytic uses of them is investigated. In Chapter I the catalytic activities of the organoantimony compounds are examined and it is found that the pentavalent organoantimony halides are superior catalysts to those already reported. Chapter II deals with kinetics of the direct synthesis of the cyclic carbonates catalyzed by the pentavalent organoantimony halides and discussion on the mechanism is also described. Further, in Chapter III, as intending to obtain more active catalysts than the pentavalent organoantimony halides, the objective organometallic halides are extended from Sb to IV_A group such as Sn, Ge and Si, V_A

such as Bi and VI_A such as Te, and the adding effect of the bases to these organometals is investigated.

Meanwhile, many organometallic compounds have been employed as catalysts for ring-opening polymerization of oxiranes.¹¹

Organotin halides, which was used for the synthesis of cyclic carbonates as described in Chapter III, are besides known to be useful for the polymerization of oxiranes.¹²

In comparison to the organotin halides, it is interesting to investigate whether the organoantimony compounds should polymerize oxiranes or not. Consequently, PART TWO deals with the ring-opening

polymerization of oxirane catalyzed by the organoantimony compounds. In Chapter IV the activities of the

organoantimony halides are investigated and triorganoantimony dihalides are found to be able to give poly(ethylene oxide) in good yields. Thus, in Chapter V enhancement of the

catalytic activities of them, especially of triphenylantimony dibromide(Ph_3SbBr_2) by addition of bases such as triethylamine, tributylamine, pyridine, tributylphosphine and triphenylphosphine is attempted.

Further, Chapter VI describes on kinetics of the polymerization of oxirane induced by Ph_3SbBr_2 - Ph_3P system in order to reveal the adding effect of the bases schematically.

PART ONE

**ORGANOANTIMONY CATALYZED SYNTHESIS OF CYCLIC
CARBONATES DIRECTLY FROM CARBON DIOXIDE AND
OXIRANES**

Introduction

Many catalysts or catalyst systems have been reported for the direct synthesis of cyclic carbonates from CO_2 and oxiranes,⁵⁻¹⁰ no example of the use of typical-metal organometallic compounds is known. Thus in this chapter, with an aim to establish a novel catalytic use of organoantimony compounds, the synthesis of cyclic carbonates in the presence of them is attempted and the catalytic activities of the following organoantimony compounds are compared: pentavalent compounds, pentaphenylantimony (Ph_5Sb), tetraphenylstibonium chloride and bromide (Ph_4SbCl and Ph_4SbBr), triphenylantimony dichloride and dibromide (Ph_3SbCl_2 and Ph_3SbBr_2), trimethylantimony dichloride, dibromide and diiodide (Me_3SbCl_2 , Me_3SbBr_2 and Me_3SbI_2), and triphenylstibine oxide (Ph_3SbO), and trivalent compounds, triphenylstibine (Ph_3Sb), chlorodiphenylstibine (Ph_2SbCl) and antimony trichloride. The reactions were generally carried out in a stainless-steel autoclave under pressure of CO_2 unless otherwise noticed. Then the abbreviations for oxiranes and cyclic carbonates as shown in Table I-1 will be used throughout this thesis.

Scheme I-1.

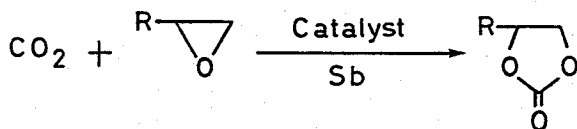


Table I-1. List of Abbreviations

R	oxiranes	cyclic carbonates
H	EO	EC
CH ₃	PO	PC
CH ₂ Cl	ECH	ECHC
C ₄ H ₉	BO	BC
C ₆ H ₅	SO	SC

Results and Discussion

The results of the reaction of CO₂ with PO catalyzed by organoantimony compounds to afford PC are summarized in Table I-2. The yields of PC were quantitative and no byproduct was detected in the reaction catalyzed by the pentavalent organoantimony halides, but the reaction time* was strongly dependent on the catalysts employed, 8-150 min in the presence of 1.0 mol% of catalyst as 120°C. Among the pentavalent compounds, Ph₄SbBr and Ph₃SbBr₂ exhibited the highest catalytic activity. The reactions of CO₂ with PO which had been previously heated with catalysts (preheating reaction) were carried out, but no significant differences in the yield of PC or the reaction time were apparent in comparison with the reactions in Table I-2. The trivalent compounds did not seem to catalyze the reaction.

*After equilibrium of the temperature in the autoclave, the reaction time was clocked until the pressure fell to a constant value.

Table I-2 Organoantimony Catalyzed Synthesis of PC^a

Catalyst(concn) ^b		T, °C	t, min ^c	yield of PC ^d , %
Ph ₅ Sb	(1.0)	120	130	87 ^e
Ph ₄ SbCl	(1.0)	100	220	90 ^{e,f}
Ph ₄ SbBr	(1.0)	120	8	92 ^f
	(1.0) ^g	120	9	93 ^f
	(1.0) ^h	120	9	93 ^f
	(1.0)	100	20	98 ^f
	(1.0)	80	60	93 ^f
	(1.0)	60	120	93 ^f
	(1.0)	k	3600	90 ^f
	(0.5)	120	40	99 ^f
	(0.1)	120	480	88 ^f
Ph ₃ SbCl ₂	(1.0)	120	150	96 ^f
Ph ₃ SbBr ₂	(1.0)	120	16	97 ^f
	(1.0)	100	50	92 ^f
	(1.0)	80	100	96 ^f
	(1.0)	60	390	97 ^f
	(1.0) ^g	60	390	95 ^f
	(1.0)	k	7200 ^j	95 ^f
	(1.0)	100	360 ^j	3 ^{e,f}
Me ₃ SbCl ₂	(1.0)	100	60	94 ^{e,f}
Me ₃ SbBr ₂	(1.0)	100	80	94 ^{e,f}
	(1.0)	100	35	91 ^{e,f}
Me ₃ SbI ₂	(1.0)	100	35	91 ⁱ
Ph ₃ SbO ₂	(1.0)	120	120 ^j	94 ⁱ
Ph ₃ Sb	(1.0)	120	360 ^j	7
Ph ₂ SbCl	(1.0)	120	360 ^j	5 ^e
SbCl ₃	(1.0)	120	360 ^j	4 ⁱ

^aPO, 0.1mol; CO₂, 50kg/cm². ^bMole% with respect to PO.

^cThe time, t, was clocked until the pressure fell on to a constant. ^dWith respect to PO. ^eThe crude products

were light brown. ^fThe catalysts were able to be recovered in good yields. ^gPO and catalysts were

preheated at 120°C for 2h prior to the reaction.

^hRecovered Ph₄SbBr was employed. ⁱThe crude products were light yellow. ^jDecreasing of pressure was not

observed. ^kRoom temperature.

Table I-3 Organoantimony Catalyzed Synthesis of
Cyclic Carbonates at 120°C^a

Catalyst	<u>1</u>	t, ^b min	yield of <u>2</u> ^c , %
Ph ₅ Sb	EO	330	82 ^d
Ph ₄ SbBr	EO	15	96
	BO	10	94
	ECH	24	97 ^e
	SO	15	91 ^{e,f}
	EO	180	99
Ph ₃ SbCl ₂ Ph ₃ SbBr ₂	EO	40	95
	BO	20	93
	ECH	80	94 ^e
	SO	24	82 ^{e,g}
	EO	15	72 ^h
Me ₃ SbBr ₂	EO	960	74 ^{d,i}
Ph ₃ SbO ₂ Ph ₃ Sb	EO	540	86
	ECH	240 ^j	34 ^e
	SO	600 ^j	0 ^k

^a1, 0.1mol; CO₂, 50kg/cm²; catalyst, 1.0mol% with respect to 2. ^bThe time, t, is defined in Table I-2.

^cWith respect to 1. ^dThe crude product

was light brown. ^eYields after distillation.

^fA trace amount of poly(styrene oxide) was obtained.

^gPoly(styrene oxide) was obtained in ca.10% yield besides SC. ^hThe crude product was light yellow.

ⁱA trace amount of poly(ethylene oxide) was confirmed by NMR analysis. ^jDecreasing of pressure

was not observed. ^kSO was recovered nearly quantitatively.

Stibonium salt Ph_4SbBr showed a large catalytic effect which was superior to the ammonium and phosphonium salts⁷ in 8 min, a 92% yield of PC was obtained at 120°C in the presence of 1.0 mol% of Ph_4SbBr ; quantitative yields were obtained at low reaction temperature or at lower concentration of Ph_4SbBr . More covalent Ph_3SbBr_2 is found to almost have same activity as Ph_4SbBr and it is interesting that no halogen containing Ph_5Sb and Ph_3SbO are also active (see Chapter II). Thus the increasing order of catalytic activities was as follows:
 $\text{Ph}_4\text{SbBr} > \text{Me}_3\text{SbI}_2, \text{Ph}_3\text{SbBr}_2 > \text{Me}_3\text{SbBr}_2 \gg \text{Ph}_5\text{Sb}, \text{Ph}_3\text{SbCl}_2, \text{Ph}_3\text{SbO} \gg \text{Ph}_4\text{SbCl}, \text{Me}_3\text{SbCl}_2$ and the trivalent compounds. Catalysts of high activity were recovered in good yields from the crude products. However, Ph_5Sb and Ph_3SbO could not be recovered, and the crude products were light brown and light yellow, respectively. These phenomena might be due to instability of these catalysts.

The reactions of CO_2 with other substituted oxiranes were carried out, and the corresponding cyclic carbonates were obtained in good yields as shown in Table I-3. In these runs, Ph_4SbBr and Ph_3SbBr_2 also showed good catalytic activities, but in the reaction with SO small amounts of poly(styrene oxide) were obtained as a byproduct which may be resulted from thermal polymerization of SO. In addition a trace of poly(ethylene oxide) was formed in the reaction with EO catalyzed by Ph_3SbO , which was considered to be resulted from its specific activity for polymerization of EO (see Chapter IV). In addition, the higher catalytic activity of Ph_4SbBr enables

the synthesis of the cyclic carbonates even under atmospheric CO_2 at 60°C as shown in Fig. I-1.

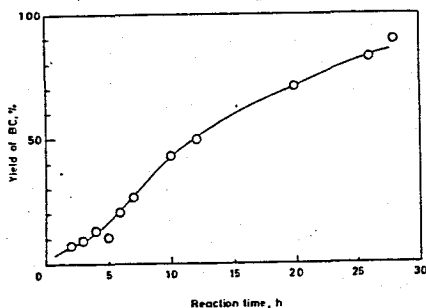


Fig. I-1. Cycloaddition reaction under atmospheric pressure of CO_2 catalyzed by Ph_4SbBr at 60°C . BO : 50mmol, Ph_4SbBr : 0.15M(0.5mmol).

As can be seen from Table I-3, it was found that the catalytic behavior of trivalent compounds, Ph_3Sb , is very much lower than that of the pentavalent compounds. It should be noted that Ph_3Sb also does not promote the reaction of the more sensitive oxiranes, PO and SO, in cationic reactions. On the other hand, oxiranes that opened easily in anionic reactions EO and ECH could capture CO_2 to afford the corresponding cyclic carbonates in 86 and 34 % yields, respectively. Overall, the catalytic activity of Ph_3Sb and other trivalent compounds was inferior to that of pentavalent compounds and it is found that they behave as base in the reaction.

Pentavalent organoantimony halides, especially Ph_4SbBr and Ph_3SbBr_2 are found to be more effective than the catalysts already reported⁵⁻¹⁰ and they successfully enable the direct synthesis of the cyclic carbonates even under mild conditions in quantitative yields.

Experimental Section

General Methods. IR spectra were recorded on a Hitachi EPI-G2 spectrophotometer and ^1H -NMR spectra on a JEOL Model Ps-100 spectrometer with tetramethylsilane as an internal standard. Gas-chromatographic analyses(GC) were performed on a Shimadzu GC-4BPTF gas chromatograph with a FID detector connected to an Apiezon L grease coated 30m x 0.25mm column.

Materials. The organoantimony compounds used as catalysts, pentaphenylantimony(Ph_5Sb)¹³, tetraphenylstibonium chloride and bromide(Ph_4SbCl ¹⁴ and Ph_4SbBr ¹⁵), triphenylantimony dichloride and dibromide(Ph_3SbCl_2 and Ph_3SbBr_2)¹⁶, trimethylantimony dichloride, dibromide and diiodide(Me_3SbCl_2 , Me_3SbBr_2 and Me_3SbI_2)¹⁷, triphenylstibine oxide(Ph_3SbO)¹⁸, triphenylstibine(Ph_3Sb)¹⁹ and chlorodiphenylstibine(Ph_2SbCl)²⁰ were prepared from commercial SbCl_3 (Wako Junyaku Kogyo, Ltd., extra pure grade) as reported in the literature and confirmed by elemental analysis.

Oxiranes were purified and dried by the general procedures.

Reaction of CO_2 with Oxiranes Under Pressure of CO_2 . (a)
General Reaction Procedure. Only a typical procedure for using of PO as substrate is described. Measured quantities of PO and the catalyst were placed in a 100ml stainless-steel autoclave, and CO_2 was then introduced under a pressure of ca. 50kg/cm^2 (initial pressure). After the pressure in the autoclave fell to a constant value, the reaction was discontinued by cooling and decompression of the autoclave.

The crude reaction product was found to consist of PC and the catalyst from the results of ^1H -NMR, GC and IR. Catalysts Ph_4SbCl , Ph_4SbBr , Ph_3SbCl_2 , Ph_3SbBr_2 , Me_3SbCl_2 , Me_3SbBr_2 and Me_3SbI_2 could be recovered in good yields by crystallization from crude PC. Fractional distillation under reduced pressure was necessary for the runs of ECH and SO because of their high boiling points, and in the case of SO, a poly(strene oxide)²¹ was obtained from the distillation residue.

(b) Preheated Reactions. After a mixture of measured quantities of PO and the catalyst sealed in a glass ampule was heated at 120°C for 2h, the ampule was placed in the autoclave and CO_2 was then introduced. The reaction was then carried out as described in part a. Significant effect by such a preheating on the reaction time can not be observed.

Reaction of Atmospheric CO_2 with BO catalyzed by Ph_4SbBr .

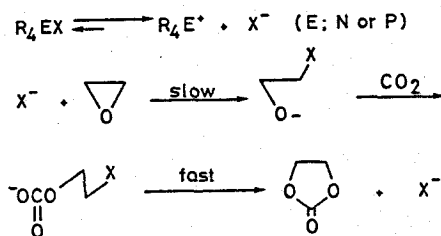
Into a 50ml three-necked round-bottomed flask equipped with a condenser and a CO_2 inlet which was connected to a ca. 1-l balloon filled with CO_2 was placed 0.5mmol of Ph_4SbBr and a magnetic stirring bar. The flask was evacuated and flashed by CO_2 three times and then 50mmol of BO was introduced through a rubber septum by syringe technique. The reaction mixture was heated in a temperature controlled oil bath and the reaction was monitored by GC. The only detectable product was BC.

Introduction

Since Vierling claimed in 1943 that cyclic carbonates could be synthesized directly from CO_2 and oxiranes under severe conditions,⁵ the catalysts have been surveyed for the cycloaddition.^{6-10,22} The catalysts can be tentatively classified into three groups; the salts which include alkali or alkali earth metal halides²² and the onium salts,⁷ the strong Lewis acid-base systems,⁹ and the transition metal complexes.¹⁰ However, the catalytic use of stable organometallic compounds was not known before the pentavalent organoantimony halides were found to be very effective for the cycloaddition even under mild conditions as described in Chapter I.

Meanwhile, it has been stated that the onium salts such as ammonium halides release halides anions which cause the oxirane ring cleavage to capture CO_2 ⁷ as shown in Scheme II-1.

Scheme II -1.



Though the pentavalent organoantimony halides may be regarded formally as a salts, they have covalent antimony-halogen bonds²³ and their poor electrolytical property even in polar solvents

has been reported.²⁴ Consequently, it is very interesting that such organoantimony compounds are more active catalysts for the cycloaddition than the onium salts.

In Chapter II, aiming at a reasonable explanation of the reaction pathway of the cycloaddition catalyzed by the pentavalent organoantimony halides, especially by Ph_3SbBr_2 , kinetic studies and investigation of solvent effect by using PO were carried out.

Results and Discussion

Kinetics. Kinetic investigation was carried out by using of pseudo-order treatment,²⁵ and otherwise noticed the reaction was generally performed at 100°C under 50kg/cm^2 of initial pressure of $\text{CO}_2(\text{Pi}_{\text{CO}_2})$. A typical time-yield curve in the cycloaddition of CO_2 to PO to afford PC catalyzed by Ph_3SbBr_2 is shown in Fig. II-1. In very early stage of the reaction there can be observed an induction period which may point out that the cycloaddition may be proceed *via* consecutive processes.²⁵ Thus the pseudo-order treatment was adopted to the reaction after the induction.

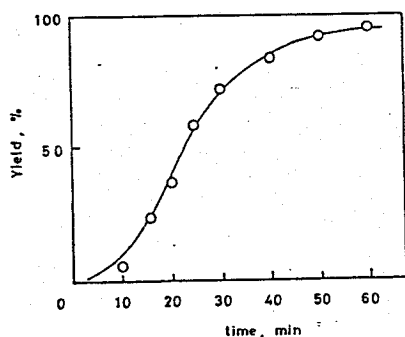


Fig. II-1. Time-yield curve in the cycloaddition catalyzed by Ph_3SbBr_2 at 100°C . Pi_{CO_2} : 50kg/cm^2 , $[\text{Ph}_3\text{SbBr}_2]$: 1.5×10^{-1} M.

Pseudo-first-order rate constant (k_ψ) was obtained from the slopes in the semi-logarithmical plots as shown in Fig. II-2. Then k_ψ was plotted against the concentration of the organoantimony catalysts and well linear relations were obtained as shown in Fig. II-3. The second-order rate constant (k_{obs}) was obtained from the slopes. Under fixed Pi_{CO_2} the cycloaddition was turned out to be first order in $[\text{PO}]$ and $[\text{catalyst}]$ each and the same relations were also obtained for other organoantimony catalysts with exceptions of Me_3SbCl_2 and Ph_3SbCl_2 which cannot cause the cycloaddition under the conditions.

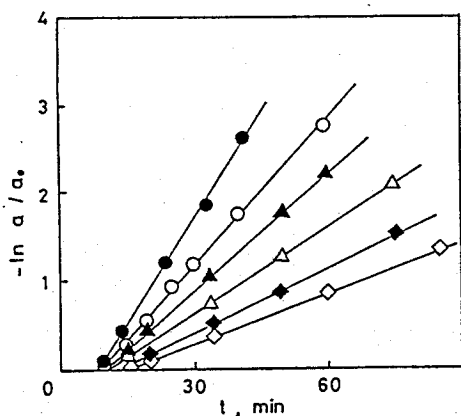


Fig. II-2. First-order plots for the cycloaddition catalyzed by Ph_3SbBr_2 at 100°C . Pi_{CO_2} : $50\text{kg}/\text{cm}^2$. $[\text{Ph}_3\text{SbBr}_2]$: $\bullet$; 1.8 , $\circ$; 1.5 , $\blacktriangle$; 1.2 , $\triangle$; 0.9 , $\blacklozenge$; 0.6 , $\diamond$; $0.3 \times 10^{-1}\text{M}$, respectively. a denotes $[\text{PO}]$ at time, a_0 that at initial one.

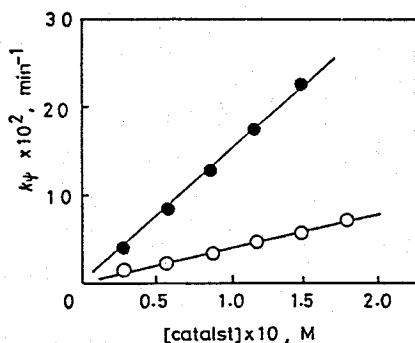


Fig. II-3. Linear relation between k_ψ and $[\text{catalyst}]$ at 100°C . Pi_{CO_2} : $50\text{kg}/\text{cm}^2$. Catalyst: $\circ$; Ph_3SbBr_2 , $\bullet$; Ph_4SbBr .

The relative catalytic activities of the pentavalent organoantimony halides estimated from k_{obs} are summarized in Table II -1. It is found that the catalytic activities, as noticed to the halogen species in the catalysts, fall off in the following order, $I > Br > Cl$. This order is opposite from that reported for the ammonium halides.⁷ Thus the order suggests that the active species of the cycloaddition catalyzed by the organoantimony compounds is different from free halide ions such as that by the onium salts.⁷

Table II -1. Relative Catalytic Activity at 100°C^a

Catalyst	relative rate
Ph_3SbCl_2	0.01
Ph_3SbBr_2	1.00 ^b
Me_3SbCl_2	0.01
Me_3SbBr_2	0.97
Me_3SbI_2	4.40
Ph_4SbCl	0.31
Ph_4SbBr	5.00

^a Pi_{CO_2} : 50kg/cm², PO: 3.4ml(50mmol).

^b $k_{obs} = 3.4 \times 10^{-1} (M^{-1}min^{-1})$.

Then the cycloaddition was carried out under several Pi_{CO_2} and k_{ψ} plotted against Pi_{CO_2} as shown in Fig. II -4.

The linear relations indicate that the reaction rate also depends on $[\text{CO}_2]$ in first order. Same relations were obtained for other pentavalent organoantimony halides.

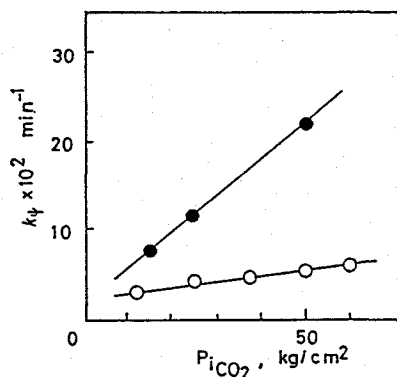


Fig. II-4. Linear relation between k_ψ and $P_{i\text{CO}_2}$ at 100°C.
 $\circ$; Ph_3SbBr_2 , $\bullet$; Ph_4SbBr .
 $[\text{catalyst}]$: $1.5 \times 10^{-1} \text{ M}$.

Table II-2. Reactivities of Oxiranes^a

Oxiranes	T, °C	k_{obs} , $\text{M}^{-1}\text{min}^{-1}$
PO	120	1.9
	100	0.34
BO	100	0.39
SO	120	0.65
EO	120	0.54
ECH	120	0.22

^a Oxiranes: 50 mmol, catalyst(Ph_3SbBr_2):
0.5 mmol, $P_{i\text{CO}_2}$: 50 kg/cm².

Kinetic investigations of the cycloaddition of CO_2 to other substituted oxiranes were also carried out and k_{obs} obtained for each oxiranes are summarized in Table II-2. Substituent effect is remarkable and the reactivity of the

Table II -3 Solvent Effect on the Cycloaddition
Catalyzed by Ph_3SbBr_2 at 100°C^a

Solvent ^b	$k_\psi \times 10^2 \text{ (min}^{-1}\text{)}$
PC	3.3
Dimethyl sulfoxide	c
Acrylonitrile	4.2
Acetonitrile	4.4
Methyl ethyl ketone	2.4
Acetophenone	3.7
1,2-Dichloroethane	1.9
Dichloromethane	2.2
Tetrahydrofuran	2.1
Ethyl acetate	1.2
Chlorobenzene	2.2
Diethyl carbonate	1.8
Benzene	1.6
1,4-Dioxane	2.5
n-Hexane	1.5
Ethanol	slow ^d
Benzyl alcohol	slow ^d

^aSolvent: 10ml, Pi_{CO_2} : 50kg/cm^2 , $[\text{PO}]$: 3.7M, $[\text{Ph}_3\text{SbBr}_2]$: $3.7 \times 10^{-2}\text{M}$. ^bThese 2 aprotic solvents are arranged in the order of their dielectric constant. ^c Ph_3SbBr_2 was decomposed. ^dThese solvents gave only trace amounts of PC and no increase of the yields of PC with time was observed.

oxiranes falls off in following order: BO, PO > SO > EO > ECH. Thus it is found that electron donor ability of the oxiranes²⁶ is followed by the reactivity of them: the oxiranes of more strong donor are more reactive.

Solvent Effect. In the reaction between ions and polar, but neutral molecules in a solution, the rate of the reaction will be faster in the medium of lower dielectric constant.²⁵ This theory has been well documented in the cycloaddition catalyzed by ammonium or phosphonium salts.⁷ The other hand, in the reaction between neutral dipoles, the rate constant contrary increases with dielectric constant of the solvents if the activated intermediate is more polar than the reactants.²⁵ Table II-3 exhibits k_ψ given when the cycloaddition was carried out in several aprotic solvents and it is obvious that the reaction proceeds faster in more polar solvents such as acetonitrile and PC itself and slower in non-polar solvents such as benzene and hexane. Unusually large k_ψ observed in dioxane in spite of its low dielectric constant may be attributable to the high solubility of CO₂ as shown in Fig. II-5 (see Experimental Section).

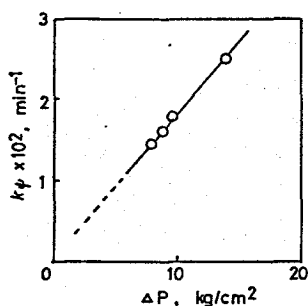


Fig. II-5. Linear relation between k_ψ and ΔP . PiCO_2 : 50 kg/cm², [PO]: 3.7M, $[\text{Ph}_3\text{SbBr}_2]$: $3.7 \times 10^{-2}\text{M}$, temp.: 100°C. Solvents (top to bottom): dioxane, diethyl carbonate, benzene, hexane.

Effective acceleration of the cycloaddition by adding protic solvents to the reaction medium has been reported in the cycloaddition catalyzed by the ammonium or phosphonium salts.⁷ This acceleration may be considered to be affected by push-pull mechanism caused by hydrogen bonding. However, protic solvents such as ethanol are recognized to prevent the cycloaddition in the organoantimony catalyzed reaction.

Lewis Acid Strength of the Organoantimony Halides. Since it was important to investigate the interaction between oxiranes and the catalysts to reveal the reaction path, the measurement of their Lewis acid strength was carried out to obtain information about the electronacceptability of the organoantimony compounds.²⁷ The pKa values of the pentavalent organoantimony compounds are summarized in Table II -4 and found to be more than 4.8 based on the Hammett indicator and those of organotin halides between 4.8 and 4.0.¹² The shift of $\nu_{C=O}$ of xanthone caused by the complexation with the catalysts²⁷ were so small as to be undetectable. The ring-opening polymerization of PO and SO catalyzed by Ph_4SbBr and Ph_3SbBr_2 was also carried out and these organoantimony halides are found to be inactive for the polymerization as shown in Table II -5. These facts indicate the weak electron acceptability of the central antimony atoms in the organoantimony halides.

Table II-4. Lewis Acid Strength of Organoantimony Compounds by Hammett Indicators

Catalyst	indicators and their color ^{a,b}				pKa
	I	II	III	IV	
Ph ₅ Sb	B	B	B	B	~ 6.0
Ph ₄ SbBr	B	B	B	B	~ 6.0
Ph ₃ SbCl ₂	A	B	B	B	6.0-4.8
Ph ₃ SbBr ₂	A	B	B	B	6.0-4.8
Me ₃ SbBr ₂	A	B	B	B	6.0-4.8
Ph ₃ SbO	B	B	B	B	~ 6.0
Ph ₃ Sb	B	B	B	B	~ 6.0

^aA represents acidic color and B basic color.

^bIndicators used here are as follows(pKa at color change area): I: netral red(6.0), II: methyl red(4.8), III: naphtyl red(4.0), IV: butter yellow(3.3).

Table II-5. Ring-Opening Polymerization of PO and SO^a

Catalyst	T, °C	t, h	yield ^b , %	
			poly-PO	poly-SO
Ph ₄ SbBr	120	5	5	5
	80	24	3	
Ph ₃ SbBr ₂	120	5	8	12
	80	24	4	

^aOxiranes, 0.1mol; catalyst, 1.0mol% with respect to oxiranes.

^bWith respect to oxiranes. Poly-PO and poly-SO are the polymerized compounds.

CO₂-PO Adduct. These organoantimony halides were inactive for the polymerization of PO at 120°C or lower temperature, however, once CO₂ coexists with PO they display very large catalytic activities. Thus behavior of CO₂ in the reaction system was so interesting to investigate. In visible and near-UV regions, neither CO₂²⁸ nor PO²⁹ have absorption bands. However, a new absorption band at ca. 260nm, which suggests the formation of an adduct CO₂-PO, appeared when CO₂ was saturated into PO as shown in Fig. II -6. A similar complexation has been reported in the copolymerization of CO₂ with aziridine³⁰. The formation of such a CO₂-PO adduct may be supported by an exotherm when CO₂ was introduced into the reactor which contained of PO in the actual reaction.

Essentially, CO₂ itself easily accepts electron followed by transformation of its molecular structure: namely from a linear to a bent form.³¹ In other words, CO₂ can be

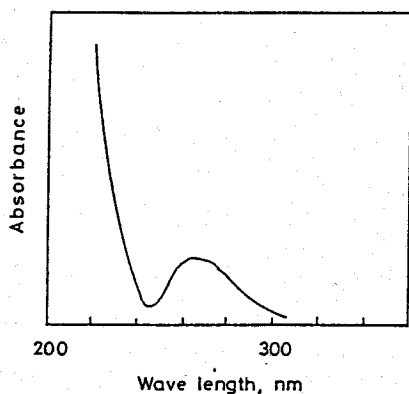


Fig. II -6. UV spectrum of the saturated solution of CO₂ in PO.

activated by acceptance of electron. In fact, it is known that CO_2 can afford a C-T complex with some polar and electron donating solvents when CO_2 is introduced into them.³² Therefore, it can be said that CO_2 may be activated by the formation of the adduct with PO in the course of the cycloaddition. Although such a complexation has been neglected in the chemistry of the reaction of CO_2 with oxiranes, further interest should be given.

Plausible Reaction Path. From the kinetic plots shown in Figures II -2 and -3, the following rate expression under fixed Pi_{CO_2} can be introduced as,

$$-d[\text{PO}]/dt = k_{\psi} \cdot [\text{PO}] \quad \text{II -1}$$

$$-d[\text{PO}]/dt = k_{obs} \cdot [\text{PO}] [\text{catalyst}] \quad \text{II -2}$$

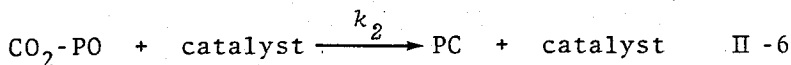
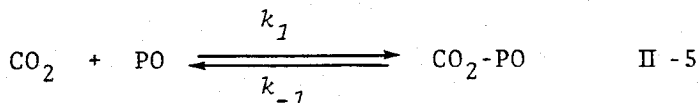
and eq. II -2 can be rewritten by using of the results indicated in Fig. II -4,

$$-d[\text{PO}]/dt = k' \cdot k_{\text{CO}_2} \cdot \text{Pi}_{\text{CO}_2} \cdot [\text{PO}] [\text{catalyst}] \quad \text{II -3}$$

where k_{CO_2} denotes a coefficient related to Pi_{CO_2} . If Henry's law is obeyed for the reaction system under the conditions, $k_{\text{CO}_2} \cdot \text{Pi}_{\text{CO}_2}$ can be correlated to $[\text{CO}_2]$ ^{30,33} and eq. II -4 is obtained as the apparent rate expression.

$$-d[\text{PO}]/dt = k \cdot [\text{PO}] [\text{catalyst}] [\text{CO}_2] \quad \text{II -4}$$

Meanwhile, elementary processes for the cycloaddition may be given as following, with regard to the solvent effect and UV measurement.



Using the steady state approximation, the consecutive reaction can be resolved and the theoretical rate expression may be introduced as eq. II -7.

$$-d[\text{PO}]/dt = \frac{k_1 k_2}{k_{-1} + k_2 \cdot [\text{catalyst}]} \cdot [\text{CO}_2][\text{PO}][\text{catalyst}] \quad \text{II -7}$$

Suppose $k_{-1} \gg k_2 \cdot [\text{catalyst}]$, eq. II -7 can be rewritten as,

$$-d[\text{PO}]/dt = \frac{k_1 k_2}{k_{-1}} \cdot [\text{CO}_2][\text{PO}][\text{catalyst}] \quad \text{II -8}$$

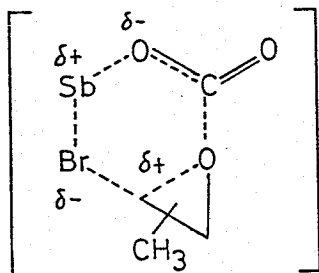
and eq. II -8 may be equal to eq. II -4.

It is known that the CO_2 -aziridine complex interact with the catalyst in the copolymerization of CO_2 with aziridine.³⁰ Consequently, an expectance of the interaction between the CO_2 -PO adduct and the organoantimony catalysts may be considered to be reasonable.

From the results of the solvent effect investigation, it may be deduced that the antimony-halogen dipoles promote the cycloaddition and the order of the catalytic activities on the halogen species seems to support the above assumption.

Since electron donor ability of the oxiranes²⁸ may affect the formation of the CO₂-oxiranes complexes: using of the more basic PO or BO makes (k_1/k_{-1}) larger but the use of less basic ECH smaller, the order of the reactivities of the oxiranes is agreed with the donor ability of them. Further it is tentatively proposed that the cycloaddition may proceed via the intermediate shown in Scheme II -2, where the antimony-halogen dipoles may behave as an acceptor and a donor, respectively. However, no evidence to justify the presence of such an intermediate can not be obtained and the scheme is one rather than convenience.

Scheme II -2. Tentative Intermediate



Experimental Section

General Method. IR, UV and ^1H NMR spectra were recorded on a Hitachi EPI-G2 spectrophotometer, on a Shimadzu UV-200S spectrometer using of a 1cm quartz cell and on a JEOL Model PS-100 spectrometer with tetramethylsilane as internal standard in deuterochloroform solution, respectively. Analytical gas chromatography(GC) was performed on a Shimadzu GC-4BPTF gas chromatograph with a FID detector connected to an Apiezon L grease coated 30m x 0.25mm Golay type capillary column.

Materials. The organoantimony halides used as the catalysts, triphenylantimony dichloride and dibromide(Ph_3SbCl_2 and Ph_3SbBr_2), trimethylantimony dichloride, dibromide and diiodide(Me_3SbCl_2 , Me_3SbBr_2 and Me_3SbI_2) were prepared by direct halogenation of corresponding stibines,^{16,17} and tetraphenylstibonium chloride and bromide(Ph_4SbCl and Ph_4SbBr) by addition of corresponding halobenzene to triphenylstibine in the presence of aluminum trichloride.^{14,15} They were confirmed by elemental analysis.

Methyloxirane(PO) was refluxed over potassium hydroxide pellets and calcium hydride(CaH_2), successively, then rectified over CaH_2 . Other oxiranes were also dried and rectified over CaH_2 before use.

Solvents employed in the investigation of the solvent effect were used after distillation with a exception. Acrylonitrile was used as received(Wako Junyaku Kogyo, Ltd., extra pure grade). Hammett indicators and xanthone were

used as received(Wako Junyaku Kogyo, Ltd., extra pure grade).

Reaction of CO_2 with Oxiranes. (a) General Reaction

Procedure for Kinetic Investigation. All the reaction was carried out in a 50ml stainless-steel autoclave. Into the autoclave containing of 3.4ml(50mmol) of PO and measured quantities of the catalysts, CO_2 was introduced under an initial pressure and then it was heated in temperature regulated oil bath with stirring by a magnetic stirring bar. Resulted product was treated as described in Chapter I. An exotherm was observed when CO_2 was introduced into the autoclave to be mixed with PO. By NMR, GC ca. 100% selectivity was confirmed in every case.

(b) Solvent Effect Investigation. In the autoclave containing 10ml of the solvents was carried out the cycloaddition as described above. From analysis of the resulting product by IR, NMR and GC, no other reaction was found to occur and PC was selectively obtained.

Ring-Opening Polymerization of PO and SO. The polymerization of PO and SO were carried out in the autoclave at 120°C or in glass ampule at 80°C . The polymers obtained were purified by reprecipitation(benzene/ether) and identified as poly(propylene oxide)³⁴ and poly(styrene oxide)²¹, respectively, by their IR spectra.

Measurement of Lewis Acid Strength. (a) Measurement with

Hammett Indicator.^{12,27} To 1-5 wt% solution of organoantimony compounds in benzene was added 1 drop of a 0.1 wt% solution of indicator in benzene, and the color change of the indicator

was observed.

(b) Measurement with IR Spectra.¹² According to the method reported in the literature, an attempt was made to observe the lower wave-number shift of $\nu_{C=O}$ of xanthone caused by complexation with the organoantimony compounds, but no shift was detected.

Measurement of UV Spectrum of CO_2 -PO Adduct. Into the autoclave containing of PO, CO_2 was introduced under a pressure of 50kg/cm^2 and then it was degassed immediately. The resulting saturated solution was placed into a quartz cell which was tightly stoppered with rubber septum(Aldrich Chemical, Co.).

Measurement of CO_2 Solubility. The autoclave containing of 10ml of the solvents was introduced with CO_2 under a pressure of 50kg/cm^2 at room temperature. After equilibrium of the inner pressure of CO_2 , it was heated in the oil bath. The pressure was read by a pressure-guage equipped to the autoclave at every ten degrees from 80 to 120°C , repeatedly, and the linear relations as shown in Fig. II-7 were obtained by least-square treatment for the solvents of which dielectric constants are nearly 2. The solubility parameter ΔP is then defined as the differences between the lines a and b in Fig. II-7, which was obtained for the solvents and blank, respectively. Values of ΔP for the solvents was obtained as follows, (ΔP , kg/cm^2 at 100°C): benzene(8.6), hexane(8.0), diethyl carbonate(9.8), and 1,4-dioxane(13.6). The solubility parameter for benzene is well corresponded to the

reported solubility coefficient of CO_2 to benzen.³³

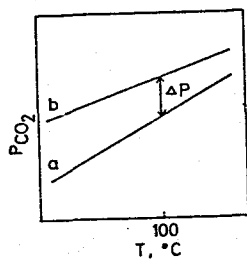


Fig. II -7 Definition of ΔP .

a; in the presence of the solvents, b; in the absence of the solvent(blank).

Chapter III Catalytic Activities of Group IV_A, V_A and VI_A
Organometallic Compounds and Effect of Adding
Base

Introduction

The striking feature of the organoantimony catalysts for the cycloaddition was found to be attributable to the covalent nature of antimony-halogen bonds, in contrast to the onium salts catalysts.⁷ Where the antimony-halogen dipoles may be tentatively considered to interact with CO₂-oxirane adduct, which synergically play as an acceptor and a donor, respectively. In Chapter III the organometallic halides are extended to IV_A, V_A and VI_A Groups, expecting the similar effect of their metal-halogen bonds as the antimony-halogen bonds in the pentavalent organoantimony halides and the catalytic activities of triphenyl derivatives of Sn^{IV}, Ge^{IV}, Si^{IV} and Bi^V and of dialkyl or diaryl derivatives of Te^{IV} were investigated.

While the organotellurium halides are found to be as active as the organoantimony compounds among these series of organometallic compounds, the IV_A compounds showed very inferior ones to the organoantimony compounds. An attempt to improve their activities was therefore made and addition of an equimolar amount of Lewis base such as triethylamine (TEA), pyridine (Py) and triphenylphosphine (TPP) to the organometallic halides is found to enhance their own catalytic activities. Especially, in the case of triphenyltin halides used as organometallic component the most large enhancement of the

catalytic activity is achieved, and the catalytic activities of Ph_3SnBr or Ph_3SnI and base systems exceed that of Ph_4SbBr which is the most active among the pentavalent organoantimony catalysts. Some recent publications⁹ have claimed good catalytic activities of pairs of heavy metal halides and Lewis bases but do not state the effect of the adding bases at all. Therefore, it is also attempted to explain the effect of the adding base to improve the catalytic activities of the organometallic halides reasonably.

Results and Discussion

Catalytic Activities of Organometallic Halides of Groups

IV_A , V_A and VI_A . The second-order rate constant (k_{obs}) was obtained for the cycloaddition catalyzed by the organometallic halides or the binary catalyst systems of the organometallic halides and bases, which will be described below, as for the organoantimony halides (see Chapter II). It was indeed found that the cycloaddition catalyzed by Me_2TeI_2 , Me_2TeI_2 -TPP and Ph_3SnBr -TEA was kinetically equivalent to that by Ph_3SbBr_2 which were treated with in Chapter II: namely, the rate is found to depend on the initial pressure of CO_2 in first order, respectively. In order to compare the catalytic activity, the cycloaddition was generally carried out at 100°C by using PO as substrate and the relative rate constants which were measured for the catalysts and the binary catalysts based on Ph_3SbBr_2 are summarized in Table III-1.

The catalytic activities of the organometallic halides,

Table III -1 Relative Catalytic Activities of the Organometallic Halides-Base Systems at 100°C^a

Catalyst	Relative rate constant ^b			
	no base	TEA ^c	Py ^d	TPP ^e
Ph ₃ SnCl	< 0.01 ^f (0.001)	0.22	0.20	0.20
Ph ₃ SnBr	< 0.01 ^f (0.01)	6.0	6.6	6.4
Ph ₃ SnI	< 0.01 ^f (0.09)	6.0	6.0	5.8
Ph ₃ GeBr	0 ^g	< 0.01 ^f (0.16)	< 0.01 ^f (0.08)	< 0.01 ^f (0.16)
Ph ₃ SiBr	0 ^g	< 0.01 ^f (0.26)	< 0.01 ^f (0.11)	< 0.01 ^f (0.22)
Ph ₃ SbBr ₂	1.0 ^b	1.1	1.4	0.74
Ph ₄ SbBr	5.0	-	-	-
Ph ₃ BiBr ₂	0 ^g	< 0.01 ^f (0.10)	< 0.01 ^f (0.07)	< 0.01 ^f (0.04)
Me ₂ TeCl ₂	0 ^{g,h}	-	-	-
Me ₂ TeBr ₂	0.20 ^h	-	-	-
Me ₂ TeI ₂	0.64 ^h	2.4 ^h	2.2 ^h	0.89 ^h
Tol ₂ TeCl ₂ ⁱ	0.02 ^h	0.08 ^h	0.08 ^h	0.02 ^h

^aMethyloxirane: 50mmol, base/organometallic halides: 1.0, initial pressure of CO₂: 50kg/cm². ^bRelative rate constant based on

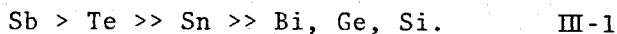
Ph₃SbBr₂, $k_{obs} = 3.4 \times 10^{-1} \text{M}^{-1} \text{min}^{-1}$. ^cTEA: triethylamine.

^dPy: pyridine. ^eTPP: triphenylphosphine. ^fThe relative rate constants measured at 120°C are indicated in parentheses

^gNo cycloaddition occurred even at 120°C. ^hThe reaction mixture

became red-brown as the reaction proceeded. ⁱTol: $p\text{-CH}_3\text{C}_6\text{H}_4\text{-}$.

as seen from the table , fall off in the following order,



Only the tellurium compounds can compare with the antimony catalysts and the less effective compounds from Sn in this order can cause no cycloaddition reaction under the standard condition followed by recovery of PO. When the reaction temperature was risen to 120°C, the organotin derivatives became to afford PC in significant rates.

When the tellurium compounds were used as catalyst, the reaction mixture gradually became red-brown as the reaction proceeded. This phenomena may be resulted from the easiness of decomposition of such organotellurium compounds derived from the labile Te-C bondings.* Since Me_2TeI_2 can be directly prepared by heating a mixture of powdery tellurium and methyl iodide at 80°C³⁶, it was attempted to promote the cycloaddition reaction by the pair of powdery tellurium and methyl iodide which may be expected to form Me_2TeI_2 *in situ*. When methyl iodide and tellurium were added in the molar ratio of more than two, quantitative yield of PC could be obtained as shown in Table III-2. However, the question whether Me_2TeI_2 is really formed *in situ* was remained unresolved.³⁵ By the way, other pairs of metals and alkyl iodides which can give a certain organometallic iodide such as tin foil and butyl

*The diorganotellurium dihalides are known to gradually decompose to a complicated mixture in polar aprotic solvents. See ref. 35.

iodide³⁷ were not effective at all under the reaction conditions.

Table III-2. The Reaction 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

^aMethyloxirane: 50mmol, initial pressure of CO₂: 50kg/cm².

Improvement of the Catalytic Activities of the Organometallic Halides by Addition of Lewis Bases. In order to improve the catalytic activities, an equimolar amount of Lewis bases such as triethylamine (TEA), pyridine (Py) and triphenylphosphine (TPP) was added to the organometallic halides. A marked rate enhancement was observed as shown in Table III-1: *e.g.*, relative rate constants measured in Ph₃SnBr or Ph₃SnI and base systems are obviously larger than those in the sole uses of the organotin halides in the magnitude of more than 10².

Tertiary amines or phosphines have been known to show catalytic activity for the cycloaddition reaction⁸ but the activity is as low as shown in Table III-3. The enhanced

catalytic activity can be said to be derived from synergism of the organometallic halides with the bases. The largest enhancement effect was observed in organotin halides-bases systems. In comparison with the activity of Ph_4SbBr which is the most effective among the organoantimony compounds, the binary systems consisted of Ph_3SnBr or Ph_3SnI surpassed it. In contrast with Sn, there observed no successful enhancement effect by addition of the bases to Ph_3SbBr_2 .

Table III-3. The Catalytic Activities of the Bases^a

Base ^b	rate constant, $10^4 \cdot \text{M}^{-1} \text{min}^{-1}$	
	100°C	120°C
TEA	very slow	9.7
Py	very slow	7.7
TPP	very slow	7.6

^aMethyloxirane: 50mmol, initial pressure of CO_2 : 50 kg/cm^2 .

^bSee footnotes c-e in Table III-1.

In order to reveal the synergic effect of the organotin compounds with the bases, being focussed in the Ph_3SnBr -TEA system in which one of the largest enhancement of the activity was achieved, pseudo-first-order rate constant (k_ψ) was plotted against the molar ratio of $[\text{TEA}]/[\text{Ph}_3\text{SnBr}]$ as shown in Fig. III-1. It can be read that k_ψ linearly increases with

the molar ratio and reaches its maximum at 1.0 followed by a gradual decrease. This curve clearly indicates that the effective enhancement of the catalytic activities may be resulted from a 1 : 1 complexation between the Ph_3SnBr and TEA.

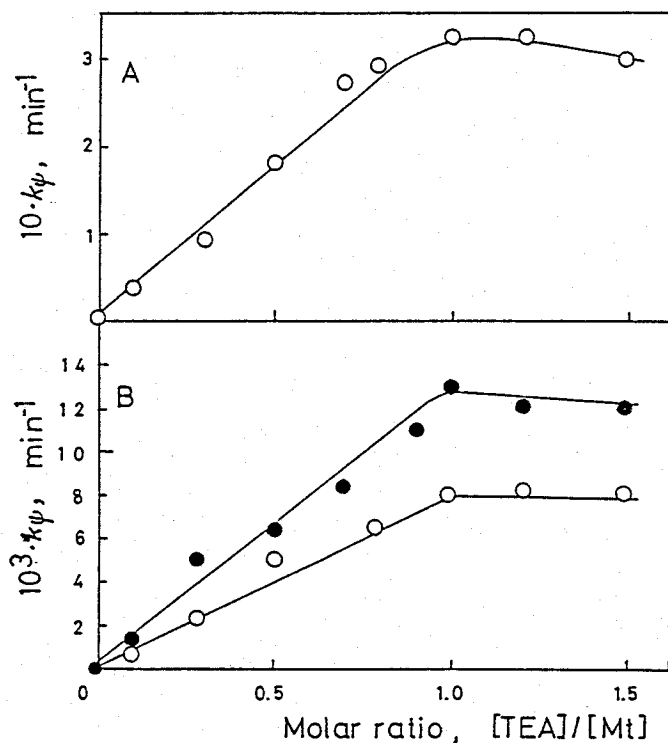
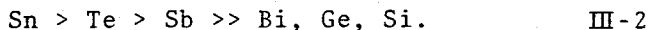


Fig. III-1. Relation between k_ψ and molar ratio of $[\text{TEA}]/[\text{Mt}]$. PO: 50mmol, organometallic compounds, $[\text{Mt}]$: 0.15M, initial pressure of CO_2 : 50kg/cm^2 .
A; Mt: Ph_3SnBr at 100°C . B; Mt: ●; Ph_3SiBr , ○; Ph_3GeBr at 120°C .

The similar curves were also obtained in Ph_3GeBr - or Ph_3SiBr -TEA systems at 120°C , which are also displayed in Fig. III-1, and in Ph_3SbBr_2 -TEA and Me_2TeI_2 -TPP systems at 100°C .

Again the order of the catalytic activities of the binary systems consisting of the organometallic halides and the bases are rearranged as following,



Further, the binary catalyst systems consisting of Ph_3SnBr or Me_2TeI_2 as organometallic components could give cyclic carbonates quantitatively under atmospheric pressure of CO_2 at 60°C and typical runs are indicated in Fig. III-2. It is

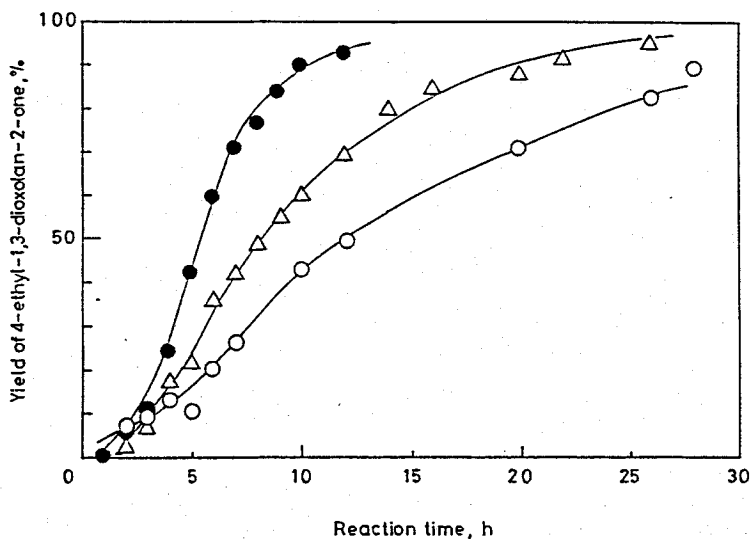
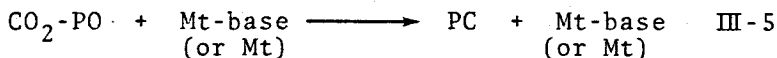
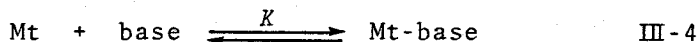
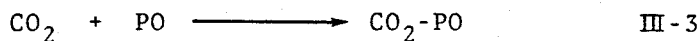


Fig. III-2. Cycloaddition under atmospheric pressure of CO_2 at 60°C . Ethyloxirane: 50mmol, organometallic halides: 0.15M. ○; Ph_4SbBr , ●; Ph_3SnBr -TEA(1/1) △; Me_2TeI_2 -TPP(1/1), molar ratio in parentheses.

clear that the reactions catalyzed by the Ph_3SnBr -TEA and Me_2TeI_2 -TPP systems proceed faster than that by Ph_4SbBr .

Adding Effect of Bases to Organometallic Halides. Since all the organometallic halides regarded here have covalent metal-halogen bonds as well as the organoantimony halides,³⁸ the reaction pathway digested in eq. III-3, III-4 and III-5 may be expected to be adopted to the reaction catalyzed by the binary catalyst systems and the organometallic halides.



, where Mt denotes organometallic halides.

This anticipation may be justified by the same kinetic behavior of organometallic halides and the binary catalyst systems as those of the organoantimony catalysts, and also by the order of the catalytic activities which can well correspond with the order of the length of metal-halogen bonds in the organometallic halides: in other words, polarity of the metal-halogen bonds, as shown in Table III-4³⁹⁻⁴²: the catalytic activities roughly increase with the length of metal-halogen bonds.

Table III-4. Reported Values of Metal-Halogen Bond
Distance

Metal	r_{M-Cl} , Å		
	tetrahedral	TBP ^a	octahedral
Sn ^b	2.37	2.42	2.39
Ge	2.08 ^c	-	-
Si	2.03 ^d	-	-
Sb	-	2.49 ^e 2.34 ^g	2.26-2.38 ^f
Te	-	2.48 ^h	-

^aTBP: trigonal bipyramidal. ^bValues for Me_3SnCl , see ref. 43.

^cValues for $GeCl_4$, see ref. 40. ^dValues for Me_3SiCl , see ref.

40. ^eValues for Me_3SbCl_2 , see ref. 39. ^fValues for

$SbCl_5$ -base complexes, see ref. 41. ^gValues for $SbCl_5$, see

ref. 42. ^hValues for Me_2TeCl_2 , see ref. 39, Te^{IV} compounds

have TBP structure because of the presence of non-bonding
electron pair.

The large enhancement effect of the activity shown in the binary systems of the organotin halides-bases may be deduced to be resulted from a complexation between the organotin halides and the bases. It is well known that Sn^{IV} compounds and Lewis bases must give a trigonal bipyramidal pentacoordinated complex,⁴³ where the bond distance of tin-halogen becomes longer than that in tetrahedral compounds as shown in Table III-4, and the nucleophilicity of the halogen atom bonding to tin atom may be increased. Although there must occur an equilibrium in the reaction mixture as indicated in eq. III-4 and all the component in this equilibrium can promote the cycloaddition, there exists very large gaps among the catalytic activities of the respective components as shown in Tables III-1 and -3. Consequently, it is clear that the high catalytic activities of the binary systems of triphenyltin halides-bases may be predominantly attributed to the formation of the 1 : 1 complex of the tin-base *in situ*.

In the binary systems, the pseudo-first-order rate constant may be divided into the respective contribution of organotin halides, bases and the complexes and can be rewritten by using the equilibrium constant (K) as,

$$k_{\psi} = (k_{\psi\text{Mt}} + k_{\psi\text{base}} + k_c \cdot K \cdot [\text{Mt}][\text{base}]) \quad \text{III-6}$$

, where Mt denotes the organotin halides and $k_{\psi} = k \cdot [\text{catalyst}]$. From the results shown in Table III-3, the contribution from base can be negligible, then eqs. III-7 and -8 may be introduced.

$$k_{\psi} = (k_{Mt} + k_e \cdot K \cdot [\text{base}]) [Mt] \quad \text{III-7}$$

$$k_{\psi} = k_{\psi Mt} + [Mt]^2 \cdot k_e \cdot K \cdot ([\text{base}] / [Mt]) \quad \text{III-8}$$

Eqs. III-7 and -8 indicate that the activity index of the complexation, $k_e \cdot K$, can be calculated from increment, $\Delta k / \Delta [\text{base}]$: namely the slopes of the linear relation as in Fig. III-3.

The similar complexation may be considered to affect the activity of other binary systems³⁹ and the activity index, $k_e \cdot K$, was also calculated for other binary systems. The obtained values of the index for each organometallic halides and base systems are summarized in Table III-5 and it is found that

Table III-5. The Catalytic Activity of the Complexes

Binary system Mt - Base	$k_e \cdot K, \text{M}^{-2} \text{min}^{-1}$
$\text{Ph}_3\text{SnBr-TEA}$	160 ^a
$\text{Ph}_3\text{GeBr-TEA}$	0.38 ^b
$\text{Ph}_3\text{SiBr-TEA}$	0.43 ^b
$\text{Ph}_3\text{SbBr}_2\text{-TEA}$	0.24 ^a
$\text{Ph}_3\text{BiBr}_2\text{-TEA}$	0.24 ^b
$\text{Me}_2\text{TeI}_2\text{-TPP}$	4.3 ^a

^aObserved at 100°C.

^bObserved at 120°C.

the value for Ph_3SnBr is conspicuously larger than those for other binary systems.

The effect of addition of the bases to Ph_3SbBr_2 , in contrast with Ph_3SnBr , is somewhat negligibly small. This is considered to be resulted from the necessity of the formation of a hexacoordinated complex⁴⁴ in the system if the complex really formed. The negligibly small enhancement in the system may be considered to be ascribed to the low activity of the Ph_3SbBr_2 -base complex expected from consideration of the following points: 1) the reactivity of the antimony-halogen dipoles in the complex may be diminished as the coordination number increases from five to six as shown in Table III-4,^{39,41} similarly to the organotin-base complex,⁴³ and 2) it may be difficult for the hexacoordinated organoantimony complex to interact with the CO_2 -PO adduct because of the saturated coordination site⁴⁴ and the large steric hindrance.

Thus the novel binary catalyst systems for the synthesis of cyclic carbonates, such as Ph_3SnBr -TEA and Me_2TeI_2 -TPP, is clarified.

Experimental Section

Materials. The organometallic halides, triphenyltin chloride, bromide and iodide(Ph_3SnCl ,⁴⁵ Ph_3SnBr ⁴⁶ and Ph_3SnI ⁴⁶), triphenylgermanium bromide(Ph_3GeBr),⁴⁷ triphenylsilicon bromide(Ph_3SiBr),⁴⁸ triphenylantimony dibromide(Ph_3SbBr_2),¹⁶ tetraphenylstibonium bromide(Ph_4SbBr),¹⁵ triphenylbismuth dibromide(Ph_3BiBr_2),⁴⁹ dimethyltellurium dichloride, dibromide and diiodide(Me_2TeCl_2 , Me_2TeBr_2 and Me_2TeI_2)³⁶ and bis(*p*-tolyl)tellurium dichloride($(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{TeCl}_2$)⁵⁰ were prepared by the reported methods and checked by elemental analysis.

Methyl- and ethyloxirane(PO and BO, respectively) was dried and stored over calcium hydride. Lewis bases as additives were distilled(triethylamine and pyridine) or recrystallized(triphenylphosphine) before use. Solvents were used after rectified. Tellurium metal powder(Mitsuwa Kagaku Yakuhin Co. Ltd.) and methyl iodide(Wako Junyaku Ltd.) were used as received.

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

Reaction Procedures. (a) Under Pressure of CO_2 . The reaction was carried out in 50ml stainless-steel autoclave as described in Chapter I. Initial pressure of CO_2 when the catalytic activities were investigated was 50kg/cm^2 .

(b) Under Atmospheric Pressure of CO_2 . As the reactivity of BO has been found to be as well as that of PO which was

described in Chapter II, and the higher boiling point of BO was preferable for treatment, BO was employed. Into a 50ml three-necked round bottomed flask equipped with a condenser and CO₂ inlet which was connected to a ca. one l balloon filed with CO₂ was placed 0.5mmol of the organometallic halides, the base if solid(TPP) and a magnetic stirring bar. The flask was exacuated and flashed by CO₂ three times and then 50mmol of BO and 0.5mmol of the base if liquid(TEA or Py) was introduced through a rubber septum by syringe technique. The reaction mixture was heated in a temperature controlled oil bath and the reaction was monitored by GC. The only detectable product was BC.

PART TWO

ORGANOANTIMONY CATALYZED POLYMERIZATION OF
OXIRANE

Introduction

Many organometallic compounds have been employed as catalysts for ring-opening polymerization of oxiranes.¹¹ It has been reported that organotin compounds, as one of the organometallic series, such as mono- or diorganotin halides are useful for the polymerization of oxirane(EO) and its substituted derivatives.¹² In the meantime these organotin compounds are also effective catalysts for the direct synthesis of the cyclic carbonates from CO₂ and oxiranes as described in Chapter III.

While the pentavalent organoantimony compounds are more active for the synthesis of the cyclic carbonates than the organotin compounds, however, no attempt to polymerize oxiranes in the presence of the organoantimony compounds has been known. Therefore, it is interesting to investigate whether oxirane can be polymerized by the organoantimony compounds or not. In Chapter IV, the catalysis of the polymerization of EO by the organoantimony compounds is described.

Results and Discussion

The results of the polymerization of EO catalyzed by the organoantimony compounds are summarized in Table IV-1. The data show that triorganoantimony dihalides, R₃SbX₂ (R: phenyl or methyl, X: Cl or Br) are active catalysts to give poly(ethylene oxide)(PEO) in good yields. However, the

Table IV -1 Polymerization of EO Catalyzed by Organoantimony Compounds at 120°C

Run No.	Catalyst ^a	Time in h	Yield ^b in %	Elemental analysis ^c			Appearance	[η] ^d in dl g ⁻¹
				C	H	Br	Cl	
1	Ph ₅ Sb	5	Trace	-	-	-	-	Yellow oil
2	Ph ₄ SbBr	5	Trace	-	-	-	-	Yellow oil
3	Ph ₃ SbCl ₂	5	77	52.17	8.16	-	1.23	White powder
4	Ph ₃ SbBr ₂	5	32	48.21	5.56	0.72	-	White wax
5	Ph ₃ SbBr ₂	7	73	51.49	8.22	2.20	-	White powder
6	Me ₃ SbBr ₂	5	27	46.27	7.58	11.18	-	Colorless paste
7	Me ₃ SbBr ₂	9	96	51.31	8.83	4.00	-	White powder
8	Ph ₃ SbO	5	66	53.47	9.10	-	-	White powder
9	Ph ₃ Sb	5	Trace	-	-	-	-	Yellow paste

^aPh: C₆H₅; Me: CH₃. ^bBased on EO. ^c(C₂H₄O)_n (44.1)_n Calc. C 54.53 H 9.15.
^dMeasured in benzene at 30°C.

molecular weight of the resulting PEO are rather low based on their inherent viscosities and on their IR spectra which coincide with those of low molecular weight PEO already reported.⁵¹ On the other hand, the stibonium salt Ph_4SbBr and both pentavalent and trivalent compounds containing no halogen atom, Ph_5Sb and Ph_3Sb , respectively, were found to be inactive for the polymerization. The following order of catalytic activity may be appraised from the polymer yields after a period of 5h as,

$\text{Ph}_3\text{SbCl}_2 > \text{Ph}_3\text{SbBr}_2 > \text{Me}_3\text{SbBr}_2 \gg \text{Ph}_4\text{SbBr}, \text{Ph}_5\text{Sb}$ and Ph_3Sb .

IV-1

This order seems to be affected by the electron acceptability of the central metal atoms of the catalysts: *i.e.*, by their

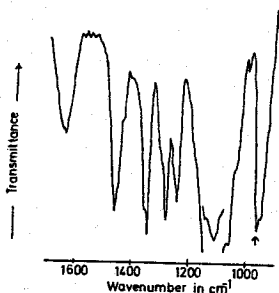


Fig. IV-1. IR spectrum(KBr) of the poly(ethylene oxide) (Table IV-1, Run No. 8).

Lewis acid strength which has been discussed in Chapter II .
 The pKa values of active Ph_3SbCl_2 , Ph_3SbBr_2 and Me_3SbBr_2 are
 between 4.8 and 6.0, but those of the other three >6.0 .

With the oxide-type compounds, Ph_3SbO , about the same
 yield was obtained as with the halides, however, the molecular
 weight of the resulting PEO was twice as high as those obtained
 with other catalysts. The IR spectrum of PEO is shown in
 Fig. IV-1. The absorption band belonging to the crystalline
 part of PEO can be observed at 960cm^{-1} .⁵² The mechanism of
 the catalysis with Ph_3SbO may be considered as a coordinated
 anionic polymerization. Ph_3SbO itself has a polymeric
 structure consisting of an Sb-O chain¹⁸ as shown in Fig. IV-2,
 similar to organostannoic acids, which are known to polymerize
 EO *via* a coordinated anionic mechanism.

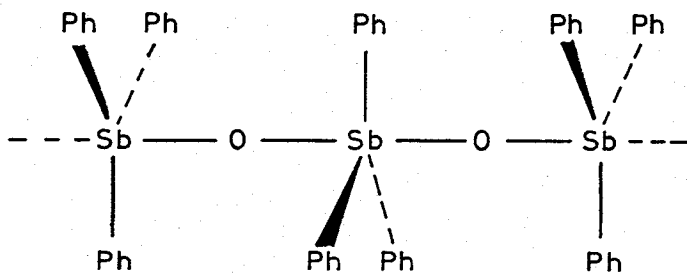


Fig. IV-2. Polymerized chain structure of Ph_3SbO .

Thus the catalytic activity for the polymerization of EO by organoantimony compounds was found to depend strongly upon their Lewis acidity, but they show an opposite tendency to catalyzed the cycloaddition of CO_2 to oxiranes, similarly to the catalytic activity of organotin compounds both in the polymerization of EO and in the cycloaddition. And the activities of the organoantimony compounds seems to be inferior to those of the organotin compounds which are considered to be resulted from their Lewis acidity.

Experimental Section

General. The IR spectrum was recorded on a Hitachi EPI-G2 spectrophotometer. The viscosities of poly(ethylene oxide) samples were determined in benzene at 30°C . Organoantimony compounds, pentaphenylantimony(Ph_5Sb),¹³ tetraphenylstibonium bromide(Ph_4SbBr),¹⁵ triphenylantimony dichloride and dibromide(Ph_3SbCl_2 and Ph_3SbBr_2),¹⁶ trimethylantimony dibromide(Me_3SbBr_2),¹⁷ triphenylstibine oxide (Ph_3SbO)¹⁸ and triphenylstibine(Ph_3Sb)¹⁹ were prepared by the reported methods and checked by elemental analysis.

EO(from the Nippon Shokubai Co., Osaka) was purified by the methods previously reported.¹² Solvents were purified by usual methods followed by distillations.

Polymerization. A mixture of 100mmol of EO and 1 mol% (related to EO) of catalysts sealed in a glass ampule was placed into a stainless-steel autoclave(100ml). Then the ampule was broken under nitrogen. After completion of the

reaction, the polymerization product was dissolved in methanol. The methanol solution was filtered to separate the catalysts and the filtrate was evaporated *in vacuo* to dryness. The resulting product was purified by reprecipitation(benzene/ether).

Chapter V Enhancemant of Catalytic Activities of Organoantimony Compounds by Addition of Bases

Introduction

In the course of studies on the utilization of organoantimony compounds as catalysts, it has been found that pentavalent organoantimony halides catalyze the cycloaddition of CO_2 to oxiranes and that they are also active in polymerization of EO as described in the last chapters. Chapter V describes the effect of adding Lewis bases, such as triethylamine (TEA), tributylamine (TBA), pyridine (Py), tributylphosphine (TBP) and triphenylphosphine (TPP) on the catalytic activity of triphenylantimony dibromide (Ph_3SbBr_2) in the polymerization of oxirane (EO).

Results and Discussion

The results of the polymerization of EO catalyzed by Ph_3SbBr_2 -Lewis base systems at 120°C are listed in Table V-1. The polymerization catalyzed by Ph_3SbBr_2 alone gave a wax-like poly(ethylene oxide) (PEO) in a 32% yield. When the Lewis base was added to Ph_3SbBr_2 , the yield of PEO was remarkably increased to ca. 90%, in contrast to the cases of the cycloaddition reaction as indicated in Chapter III. However, the basicity of the Lewis bases seems not to affect the yield of PEO.

The PEO samples obtained by Ph_3SbBr_2 -Lewis base systems were white powders. The IR spectra of them coincide with

Table V - 1 Polymerization of EO Catalyzed by Ph_3SbBr_2 -Base Systems at 120°C^a

Base ^b	Molar ratio base/ Ph_3SbBr_2	Yield ^c in %	$[\eta] \cdot 10^2$ d in dl·g ⁻¹	$\bar{M}_v \cdot 10^{-3}$ e	Elemental analysis ^f			α ^g
					C	H	Br	
None	-	32	-	-	48.21	5.56	0.72	-
TEA	1.0	92	8.2	2.4	51.75	8.82	3.30	1.7
	0.1	99	7.4	2.0	52.10	8.69	2.51	2.1
	0.01	90	7.6	2.1	52.48	8.71	1.93	1.9
TBA	1.0	86	7.5	2.1	52.97	8.84	1.35	1.8
	0.4	88	7.2	2.0	53.34	8.74	2.02	2.0
Py	1.0	92	6.1	1.5	52.57	8.80	2.44	2.6
	0.1	83	6.4	1.6	52.23	8.77	2.25	2.2
	0.01	90	6.7	1.8	51.92	8.49	3.47	2.2
TBP	1.0	84	6.1	1.5	53.39	9.04	1.82	2.4
	0.3	87	6.7	1.8	52.89	8.71	1.68	2.2
TPP	1.0	94	6.8	1.8	52.48	8.82	0.77	2.3
	0.5	87	7.0	1.9	52.54	8.78	2.03	2.1
	0.1	92	7.0	1.9	52.04	8.62	2.46	2.1
	0.05	91	7.6	2.1	52.28	8.80	2.42	1.9
	0.01	87	6.5	1.7	52.68	8.71	3.41	2.2

^aEO: 100mmol; Ph_3SbBr_2 : 1.0mmol; temp: 120°C; time: 5h. ^bTEA: triethylamine; TBA: tributylamine; Py: pyridine; TBP: tributylphosphine; TPP: triphenylphosphine. ^cBased on EO. ^dMeasured in benzene at 25°C. ^eCalc. from the following eq.:

$$[\eta] = 3.97 \cdot 10^{-4} (\bar{M}_v)^{0.686} \cdot f(C_2H_4O)_n \text{ calc. C 54.53 H 9.15.}$$
^fCatalytic efficiency α =(mole of obtained PEO)/(mole of Ph_3SbBr_2 initially added). ^g

those already reported,^{51,52} and the absorption band belonging to the crystalline part of PEO can be observed at 960cm^{-1} .⁵² The molecular weight of PEO appears to increase with increasing basicities of the Lewis bases, but are not so significant. Since the presence of bromine is revealed by elemental analysis and the absorption band belonging to the C-Br bonding can be observed at $530\text{-}540\text{ cm}^{-1}$ in the IR spectrum of the obtained PEO samples, it may be deduced that bromine is attached to the polymer chains as end group.

To investigate the effect of the adding bases, the polymerization of EO by the Lewis base alone was also carried out at 120°C for 5h using of 1.0 mol% of base related to EO. Only trace amounts of oily PEO samples were obtained with one exception. The strongest base among the Lewis bases employed in this chapter, TEA, gave powdery PEO in 41% yield, however, the molecular weight of the PEO sample was lower than that obtained by the Ph_3SbBr_2 -TEA system.

The catalytic activity of all Ph_3SbBr_2 -base systems was found to be independent of the concentration of the adding bases in the range of mole ratio $[\text{base}]/[\text{Ph}_3\text{SbBr}_2]$ between 1.0 and 0.01. Addition of the Lewis base, even in small amounts, enhance greatly the catalytic activity of Ph_3SbBr_2 . The catalytic efficiency, α , which is defined as number of obtained PEO molecules per catalyst molecules, was estimated to be nearly equal to two, regardless of the mole ratio of the catalyst systems, and it agrees with the numbers of Sb-Br bonds of Ph_3SbBr_2 .

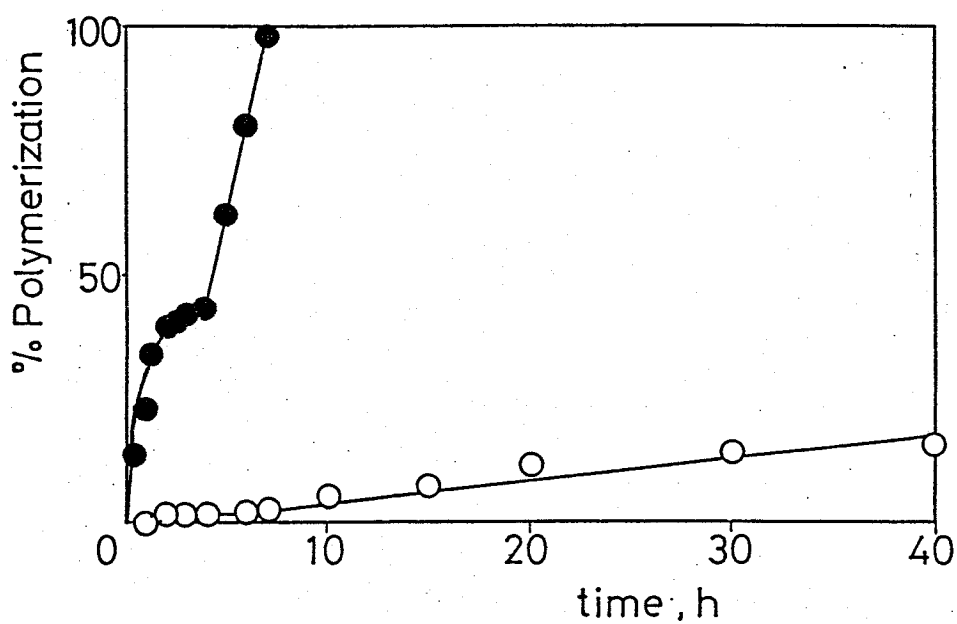


Fig. V - 1. Typical time-polymerization curve at 80°C.
 Concn. of catalyst: 0.204M.

○; Ph₃SbBr₂.

●; Ph₃SbBr₂/TPP(1.0).

The polymerization of EO by Ph_3SbBr_2 seemed to undergo a dual successive step, since there appeared the inflection point, which might not be so clear as to be regarded as an induction, in the time-polymerization curve at 80°C shown in Fig. V-1.

When molar equivalent of TPP was added to Ph_3SbBr_2 , the inflection point also appeared but shifted to higher conversion area than in the polymerization catalyzed by Ph_3SbBr_2 alone as shown in Fig. V-1, and the polymerization induced by Ph_3SbBr_2 -TPP system was greatly accelerated both in the first and the second steps. The increase of the molecular weight with polymerization was linear after the inflection point, and the catalytic efficiency, α , which was calculated from average molecular weight of the resulting PEO, increased rapidly from one to two in the first step and then remained a constant at about two in the second step as shown in Fig. V-2. Further, during the first step polymerization, a formation of 1,4-dioxane as general byproduct in cationic polymerization of EO,¹¹ which increases with the polymerization, was detected by GC analysis as well as in the polymerization of EO by the dialkyltin dihalides such as dibutyltin diiodide.¹²

In the field of the chemistry of ring-opening polymerization, few reports have described on the binary catalyst systems which are consisted of organometallic compounds and Lewis bases,⁵³ although addition of water as "modifier" and of chelating agents such as acetylacetone is well known.⁵⁴ It has been also reported that tertiary amines play rather

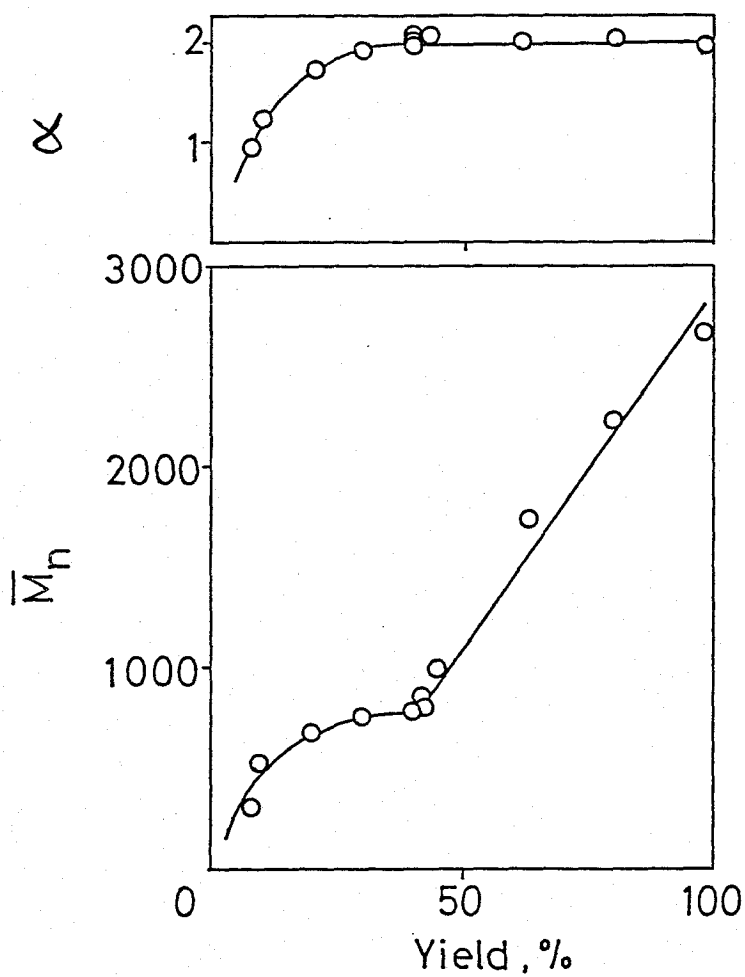


Fig. V - 2. Increase of $\overline{M}_n$ and catalytic efficiency with polymerization at 80°C.

as a poison in polymerization of EO catalyzed by organostannoic acids.^{12b} Therefore the enhancement effect of the catalytic activity of Ph_3SbBr_2 by addition of Lewis bases can be said to be unusual.

In addition, these results obtained in this chapter may be considered to suggest that the polymerization of EO catalyzed by Ph_3SbBr_2 -TPP system may proceed *via* dual step of cationic-coordinated anionic polymerization course.^{11,12}

Experimental Section

General. The IR spectra were recorded on a Hitachi EPI-G2 spectrophotometer. Gas chromatographic analysis (GC) to detect the formation of 1,4-dioxane during the course of the polymerization was performed on a Shimadzu GC-3BT gas chromatograph with the use of Silicon SE-30 as liquid phase, and on a Shimadzu GC-4BPTF gas chromatograph with a FID detector connected to an Apiezon L grease coated 30m x 0.25mm Golay type capillary column. The viscosities of PEO samples were determined in benzene at 25°C with an Ubbelohde type viscometer, and viscosity-average molecular weight ($\bar{M}_v$) was calculated for the PEO using the following equation,⁵⁵ $3.97 \cdot 10^{-4} (\bar{M}_v)^{0.686}$. Number-average molecular weight of the PEO samples was obtained in chloroform solution with a osmometric method using a Hitachi 116 type vapor pressure osmometer and was calibrated by dibenzyl.

Triphenylantimony dibromide (Ph_3SbBr_2)¹⁶ was prepared by the reported method. Oxirane (EO) (from the Nippon Shokubai

Co., Osaka) was purified by the method previously reported.¹² Solvents and the Lewis bases as additives were purified carefully by usual methods.

Polymerization. (a) Polymerization at 120°C. A mixture of 100mmol of EO, 1.0 mole-%(related to EO) of Ph_3SbBr_2 , and 0.01-1.0 mole-%(related to EO) of the Lewis base, sealed in a glass ampule, was placed into a stainless-steel autoclave (100ml). The ampule was broken under nitrogen in the autoclave, and the reaction was carried out at 120°C for 5h. After completion of the polymerization, the polymerization product was dissolved in benzene solution containing ca. 40% methanol. The solution was filtered to separate the catalyst, and the filtrate was evaporated *in vacuo* to dryness. The resulting solid material was purified by reprecipitation (benzene/ether).

(b) Polymerization at 80°C. The polymerization was carried out in a glass ampule which contained EO(100mmol) and 1mmol of the catalyst: Ph_3SbBr_2 or Ph_3SbBr_2 -TPP(1/1). The ampule was sealed off under vacuum after degassing the content of the ampule by usual freezing and thawing method. After completion of the polymerization the ampule was cooled with acetone-Dryice bath then the content of it was dissolved in benzene containing methanol. Resulting PEO was treated as described in part (a).

Chapter VI Kinetics of Polymerization of Oxirane Catalyzed
by $\text{Ph}_3\text{SbBr}_2\text{-Ph}_3\text{P}$ system

Introduction

The polymerization of oxirane(EO) catalyzed by the binary system consisted of triphenylantimony dibromide-triphenylphosphine($\text{Ph}_3\text{SbBr}_2\text{-Ph}_3\text{P}$) has been found to have a characteristic inflection point in the time-polymerization curve as shown in Fig. V - 1, which divided the polymerization into two different courses.

It is well known that oxiranes can be polymerized by metal halides such as ferric chloride through a dual clearly defined stage.¹¹ The initial reaction gives ferric dialkoxide which contains less than five units of oxiranes and the reaction vigorously takes place even at room temperature. The resulting ferric dialkoxide then initiate the polymerization in the later step but slowly: namely coordinated anion mechanism.⁵⁶

Similar two steps polymerization has been observed in the case of the polymerization catalyzed by dialkyltin dihalides such as dimethyltin diiodide.¹² A characteristic time-polymerization curve is reported, accordingly a clear inflection point divides the polymerization into different parts. In the first step, the formation of an intermediate tin dialkoxide which is required to proceed at higher temperature than that in the ferric chloride induced polymerization occurs, however, monomer units contained in the

tin alkoxide is much greater than that in the ferric dialkoxide. The mechanism of the two steps polymerization has been certified as successive cationic-coordinated anionic polymerization.¹² The inflection point has been considered to show the completion of the termination of the initial cationic polymerization by halogen displacement from the central tin atom to the growing polymer chains.

Chapter VI describes kinetic investigation of the polymerization of EO catalyzed by Ph_3SbBr_2 - Ph_3P system, supposing that the dual step polymerization mechanism can be adoptable because of the appearance of the inflection point,¹² the similar tendency of the increase of molecular weight of obtained poly(ethylene oxide) (PEO) and catalytic efficiency, α , and the formation of 1,4-dioxane during the first step polymerization as described in Chapter V. Then the adding effect of Ph_3P (TPP) to Ph_3SbBr_2 is discussed in detail.

Results and Discussion

First Step Polymerization. The amount of reacted EO per Ph_3SbBr_2 in the inflection point, $[\text{EO}]_{\text{reacted}}/[\text{Ph}_3\text{SbBr}_2]$, was plotted against the molar ratio of $[\text{TPP}]/[\text{Ph}_3\text{SbBr}_2]$ as shown in Fig. VI-1. About 45 units of monomers per Ph_3SbBr_2 molecules are found to be consumed during the first step polymerization, being independent of the concentration of the catalyst system and of its molar ratio. This consumption of monomer in the inflection point is much greater than that reported for ferric chloride¹¹ and obtained for the sole use

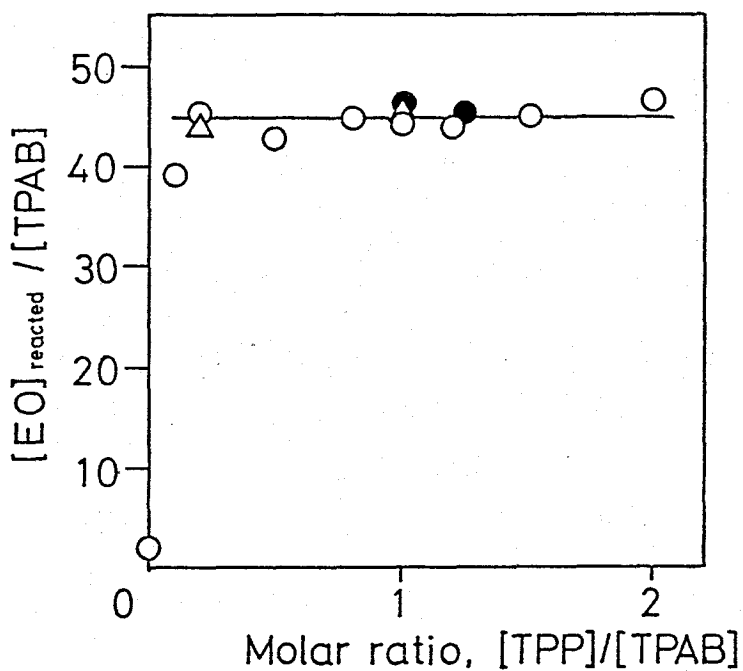


Fig. VI-1. Unity of consumption of EO per Ph_3SbBr_2 in the inflection point against the molar ratio.at 80°C . TPAB; Ph_3SbBr_2 : $\circ$; 0.204, $\bullet$; 0.163, $\triangle$; 0.102 M.

of Ph_3SbBr_2 and is similar to that reported for dimethyltin dihalides,^{12a} and these are listed in Table VI -1. The unity

Table VI - 1. Consumed Monomer per Catalyst in the Inflection Point

Catalyst	Amounts of consumed EO per catalyst	ref.
FeCl_3	5	56
Me_2SnCl_2	22	13
Me_2SnBr_2	24	13
Me_2SnI_2	46	13
Ph_3SbBr_2	2	This work
$\text{Ph}_3\text{SbBr}_2\text{-TPP}$	45	This work

in the plots of the amount of the consumption of EO against the molar ratio in the inflection point may indicate that the polymerization in the second step must take place after all Br was displaced by the growing polymer chains in the first cationic polymerization. Thus the kinetic investigation was carried out, considering that the first step polymerization may be cationic and the second coordinated anionic.

Initial rate of the first step polymerization was investigated as reported,¹² considering that the decrease of the monomer concentration may be ignorable and that eq. VI-1 can be adopted within a low conversion of EO.¹²

$$R_1 = k_1 \cdot [\text{Ph}_3\text{SbBr}_2]$$

VI-1

As shown in Fig. VI - 2, the initial rate constant, k_1 ,

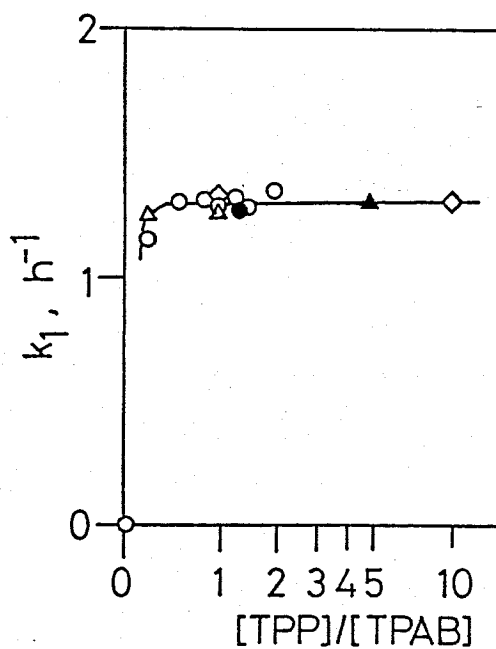


Fig. VI - 2. Unity of the initial rate against the molar ratio in the first step polymerization at 80°C. TPAB; Ph_3SbBr_2 : ○; 0.204, ●; 0.163, △; 0.102, ▲; 0.0408, ◇; 0.0204 M.

stayed uniquely against a wide range of the molar ratio of $[TPP]/[Ph_3SbBr_2]$, which indicate that the rate of the polymerization might be independent of the molar ratio but dependent on the concentration of the catalyst system.

Second Step Polymerization. In the second step, kinetics were investigated with an assumption that all the Ph_3SbBr_2 initially added was converted completely into the antimony dialkoxide.¹² As shown in the time-polymerization curve shown in Fig. V-1, the conversion increased linearly with time, consequently, the consumption rate of the monomer, R_2 , was obtained from the slope directly and then R_2 was plotted against the concentration of Ph_3SbBr_2 as shown in Fig. VI-3, which indicates a linear relation between them, when the molar ratio was settled. Then following equation was obtained as the rate expression in the second step polymerization,

$$R_2 = k_2 \cdot \alpha \cdot [Ph_3SbBr_2] \quad VI-2$$

, where α was defined as catalytic efficiency of Ph_3SbBr_2 and was decided to be two for the Ph_3SbBr_2 -TPP system in Chapter V. The polymerization rate constant, k_2 , was then calculated from eq. VI-2 and listed in Table VI-2 with those for the organotin halides already reported.¹²

In order to reveal the effect of the adding TPP, k_2 was plotted against the molar ratio of $[TPP]/[Ph_3SbBr_2]$ as shown in Fig. VI-4. In contrast to the first step polymerization, there can be observed a dependency on the molar ratio.

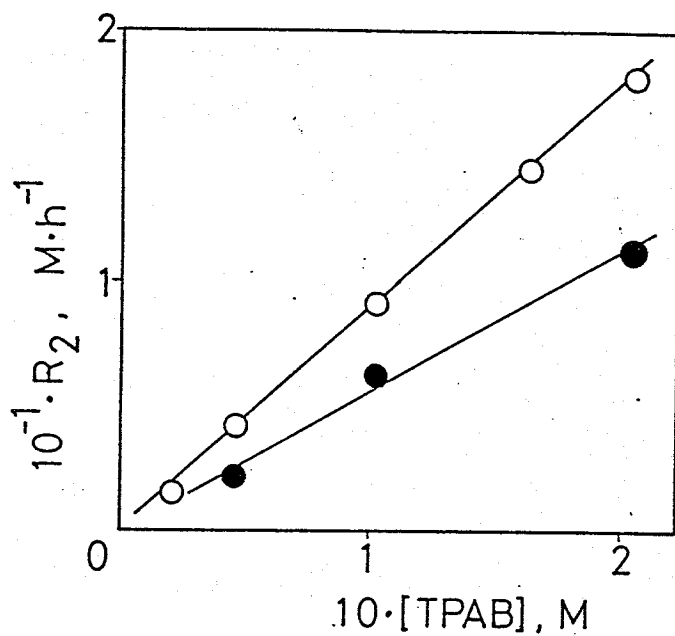


Fig. VI-3. Linear relation of R_2 against the concentration of catalyst system in the second step polymerization at 80°C . TPAB: Ph_3SbBr_2 . Molar ratio of $[\text{TPP}]/[\text{Ph}_3\text{SbBr}_2]$: ○; 1.0, ●; 0.5.

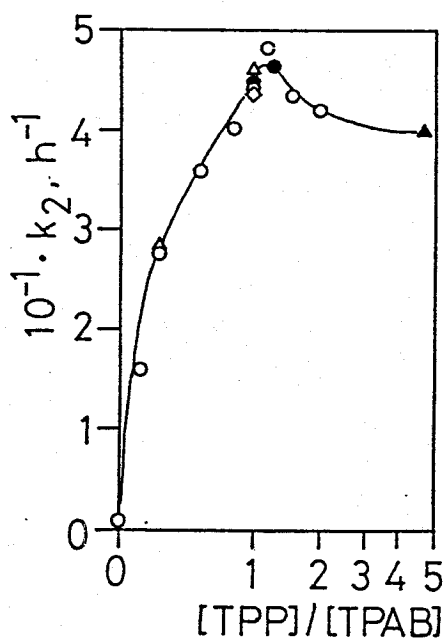


Fig. VI - 4. Variation of k_2 with the molar ratio of TPP/ Ph_3SbBr_2 at 80°C . TPAB; Ph_3SbBr_2 : ○; 0.204, ●; 0.163, △; 0.102, ▲; 0.0408, ◇; 0.0204 M.

Table VI - 2. Relative Catalytic Activity in the Second Step Polymerization at 80°C

Catalyst(molar ratio)	k_2, h^{-1}	ref.
Me_2SnCl_2	0.088	12
Me_2SnBr_2	1.5	12
Me_2SnI_2	3.8	12
Ph_3SbBr_2	0.79	This work
$\text{Ph}_3\text{SbBr}_2\text{-TPP}(1/1)$	45.0	This work

The value of k_2 seemed to be more sensitive to the molar ratio than that of k_1 and to take a maximum at molar ratio 1.0.

Hammett Plot. Investigation of the effect of *p*-substituent in Ph_3SbBr_2 on the polymerization was carried out using of tris(*p*-tolyl)antimony dibromide and tris(*p*-chlorophenyl)antimony dibromide together with Ph_3SbBr_2 . Hammett plots for both the first and the second steps are shown in Fig. VI-5, and the values of ρ was obtained as +1.7 and +1.0, respectively.

Such positive values of ρ indicate that nucleophilic attack to the central antimony atom significantly takes place during the polymerization. In general, stronger Lewis acidity is claimed for the cationic polymerization than for the coordinated anionic polymerization.¹¹ Consequently, the first step polymerization may be more sensitive to a fine varying of the electron acceptability of the central antimony than the second step.

Effect of Adding TPP. It is reasonably concluded that the polymerization of EO catalyzed by Ph_3SbBr_2 -TPP system may undergo a dual stage, which is consisted of preceding cationic polymerization course in the first step and the following coordinated anionic polymerization course in the second, as well as in the polymerization induced by organotin halides,¹² because of the results described above. And then polymerization catalyzed by Ph_3SbBr_2 may be induced to bear

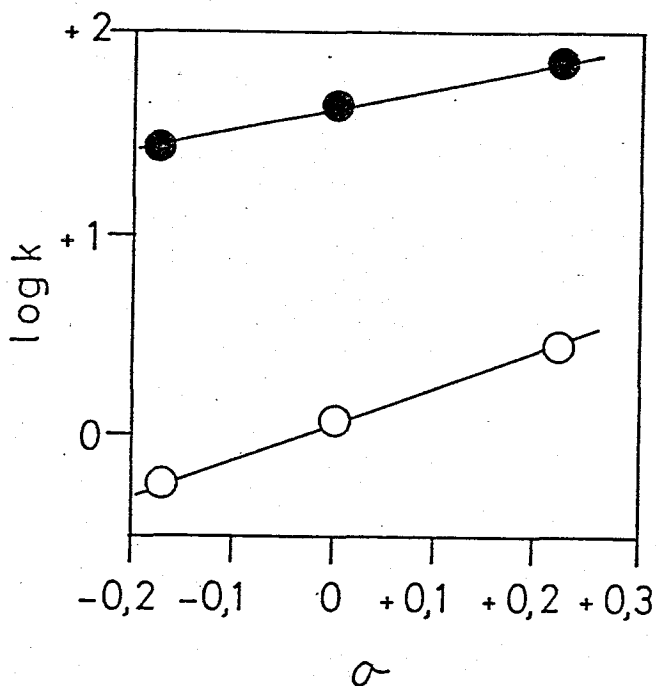


Fig. VI-5. Hammett plots. The polymerization was carried out at 80°C. Polymerization rate constant, h^{-1} (value of ρ): $\bigcirc$; $k_1(+1.7)$, $\bullet$; $k_2(+1.0)$.

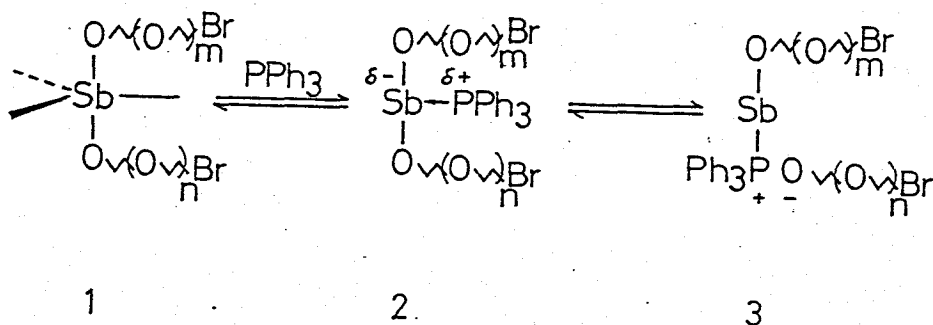
such a dual character.

It is clearly found that the addition of TPP to Ph_3SbBr_2 results in the acceleration of the polymerization both in the first and the second step. It is well known that the "modifier" should convert the organometallic compounds to an active form.¹¹ Further, the chelating agents occupy the strong acid site of the organometallic compounds as catalysts by coordination and the use of the higher energy orbitals which are suitable for the coordinated polymerization,^{11,53} becomes possible. In this study, TPP may be recognized to play as donor as well as the chelating agents. However, the effect of TPP, especially in the first step, is so complicated that it could not be schematically expressed. Consequently, it is attempted to discuss on the effect of TPP in the second step which may be considered to be treated more simply.

Pentavalent organoantimony halides or pseudohalides which contain alkoxides are known to react with bases to form a hexacoordinated complex, some are bearing the displacement of halides or pseudohalides species and others are not.⁴⁴ Therefore it may be reasonable to expect that the intermediate antimony dialkoxide(1) may react with TPP to form an adduct (2): in general hexacoordinated conformation, as shown in Scheme VI -1. When such a coordination occurs, the weakened antimony-oxygen bonds might result in the substitution of one of the alkoxide moiety by TPP to form a complex salt(3),⁵⁷ and

then EO can coordinate to 3. Where the reactivity of the alkoxide moiety should be enhanced to attack on oxirane ring. Then the propagation may be deduced to proceed under pseudo-cyclic intermediate as reported for $\text{AlEt}_3\text{-H}_2\text{O}$ system.¹¹ While the tendency of the polymerization rate in the second step on the molar ratio of $[\text{TPP}]/[\text{Ph}_3\text{SbBr}_2]$ supports the activation by such a complexation.

Scheme VI -1.



Experimental Section

General. Number-average molecular weight of the poly(ethylene oxide) (PEO) samples was obtained in a chloroform solution with osmometric method using a Hitachi 116 type vapor pressure osmometer and was calibrated by dibenzyl.

Materials. Oxirane (EO) (from Nippon Shokubai Co., Osaka) was dried and stored over calcium hydride. Solvents were purified and dried by the usual methods. Triphenylantimony dibromide (Ph_3SbBr_2),¹⁶ tris(*p*-tolyl)antimony dibromide⁵⁸ and tris(*p*-chlorophenyl)antimony dibromide⁵⁹ were synthesized as reported in the literature and confirmed by elemental analysis.

Triphenylphosphine (TPP) (Wako Junyaku, extra pure grade) was used without further purification.

Polymerization. The polymerization was carried out in a glass ampule which contained EO (100 mmol) and prescribed amounts of Ph_3SbBr_2 and TPP. The ampule was sealed off under vacuum after degassing from the content in the ampule by the usual freezing and thawing method. After completion of polymerization the ampule was cooled with acetone-Dryice then the content of it was dissolved in benzene solution of methanol. The solution was filtered, and the filtrate was evaporated *in vacuo* to dryness and weighed. The yield was regarded as a difference between the weight of the product after the evaporation and that of the catalyst system initially added. PEO samples for the measurement of $\overline{M}_n$ was purified with reprecipitation from benzene/ether after hydrolysis by

acidified methanol.

Conclusion

The results obtained from the present work may be summarized as follows;

In Chapter I, direct synthesis of cyclic carbonates from CO_2 and oxiranes catalyzed by organoantimony compounds is described. It is clarified that the use of pentavalent organoantimony halides such as Ph_4SbBr and Ph_3SbBr_2 enables the synthesis of the cyclic carbonates even under mild conditions in quantitative yields.

In Chapter II, kinetic investigation on the synthesis of the cyclic carbonates catalyzed by pentavalent organoantimony halides is carried out. It is found that the reaction rate depends on the concentrations of oxiranes, the catalysts and CO_2 each in first order. It is shown that CO_2 might form a complex with oxiranes in the reaction system by UV measurement. It is also proposed that the reaction may proceed *via* an interaction between CO_2 -oxiranes complex and antimony-halogen dipoles in the catalysts.

In Chapter III, along with the organoantimony catalysts, the binary systems consisted of IV_A , V_A and VI_A metal organometallic halides and Lewis bases are found to be effective for the synthesis of the cyclic carbonates as novel catalysts. It is also clarified that these high catalytic activities of the binary systems may be resulted from complexation of the organometallic halides and the bases.

In Chapter IV, the pentavalent organoantimony halides are found to be catalysts for the ring-opening polymerization of oxirane.

In Chapter V, it is shown that the catalytic activity of the pentavalent organoantimony halides can be effectively improved by addition of bases to them.

In Chapter VI, it is clarified that the polymerization of oxirane catalyzed by Ph_3SbBr_2 - Ph_3P system proceeds *via* a characteristic dual step. It is indicated that in the first step cationic polymerization induced by Ph_3SbBr_2 itself, which is followed by a formation of an intermediate antimony dialkoxide, is predominant. In the second step, it is also proved that the polymerization is catalyzed by a complex salt between the antimony dialkoxide and Ph_3P as a coordinated anionic catalysts.

References

- (1) (a) Y. Yoshida and S. Inoue, *Kagaku Zokan*, 90, 85 (1981).
(b) S. Inoue, *ibid.*, 63, 29 (1974).
- (2) S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B*, 7, 287 (1969); *Makromol. Chem.*, 130, 210 (1969).
- (3) (a) H. Koinuma and H. Hirai, *Makromol. Chem.*, 178, 1283 (1977).
(b) Y. Yoshida and S. Inoue, *Polymer J.*, 12, 763 (1980).
- (4) S. Sakai, T. Fujinami, T. Yamada and S. Furusawa, *Nippon Kagaku Kaishi*, 1975, 1789.
- (5) K. Vierling, *Ger. Patent*, 740,366; *Chem. Abstr.*, 39, 2294 (1945).
- (6) (a) W.J. Pepple, *Ind. Eng. Chem.*, 50, 767 (1958).
(b) Y. Taneda, *Yuki Gosei Kagaku Kyokaishi*, 17, 783 (1959).
- (7) (a) A.L. Shapiro, I.S. Lyubovskii and S.Z. Levin, *Zh. Org. Khim.*, 6, 1366 (1970).
(b) B. Vorobyov, V. Skop and A.L. Shapiro, *Org. React. (Tartu)*, 14, 444 (1977); *Chem. Abstr.*, 89, 128931j (1978).
- (8) (a) *Ital. Patent* 499,185; *Chem. Abstr.*, 57, 9681h (1957).
(b) Y. Fujita, T. Morimoto and T. Nakanouchi, *Japan* 73 22,702; *Chem. Abstr.*, 79, 146007k (1973).
(c) C. Neri and G. Cipriani, *Ger. Offen.* 2,611,087; *Chem. Abstr.*, 86, 29791v (1977).
- (9) (a) F. Ota and S. Tobita, *Japan* 73 27,314; *Chem. Abstr.*, 79, 136527r (1973).
(b) M. Ratzenhofer and H. Kisch, *Angew. Chem.*, 92, 303

- (1980).
- (10)(a) R.J. DePasquale, J. Chem. Soc., Chem. Commun., 1973, 157.
- (b) T. Tsuda, Y. Chujo and T. Saegusa, *ibid.*, 1976, 415; J. Am. Chem. Soc., 102, 431 (1980).
- (c) J.-E. Baeokoall and O. Karlsson, Tetrahedron Lett., 21, 4985 (1980).
- (11)(a) J. Furukawa and T. Saegusa, "Polymerization of Aldehyde and Oxides", Wiley, New York (1963), Chapter III.
- (b) T. Saegusa, "Ring-Opening Polymerization", Kagaku Dojin, Kyoto (1971), Chapter 2.
- (c) P. Sigwalt, Angew. Makromol. Chem., 94, 161 (1981).
- (12)N. Iwamoto, A. Ninagawa, H. Matsuda and S. Matsuda, Kogyo Kagaku Zasshi, 72, 1847, 2329 (1969).
- (13)G. Wittig and K. Clauss, Justus Liebigs Ann. Chem., 577, 35 (1952).
- (14)H.H. Wilard, L.R. Perkins and F.F. Blicke, J. Am. Chem. Soc., 70, 737 (1948).
- (15)J. Chatt and F.G. Mann, J. Chem. Soc., 1940, 1195.
- (16)A. Michaelis and A. Reese, Justus Liebigs Ann. Chem., 233, 50 (1886).
- (17)H. Hibert, Ber. Dtsch. Chem. Ges., 39, 160 (1906).
- (18)D.L. Venzky, C.W. Sink, B.A. Nevett and W.F. Fortescue, J. Organomet. Chem., 35, 131 (1972).
- (19)G.T. Morgan and F.M.G. Mickleitwait, J. Chem. Soc., 1911, 2286.
- (20)Netherlands Patent, 6,505,216; Chem. Abstr., 64, 9766d

- (1966).
- (21) J. Furukawa, T. Tsuruta, R. Sakata and T. Saegusa, Makromol. Chem., 32, 90 (1959).
- (22) (a) T. Zhesko, G.N. Mishenkova, V.S. Moshchenko, G.S. Lyubovskii and A.L. Shapiro, Reacts. Sposonost Org. Soedin, 10, 299 (1973); Chem. Abstr., 89, 42314y (1978).
(b) T.A. Dolgopyatova, Neftpuerab. Neftekhim. (Moscow), 1978, 33; Chem. Abstr., 89, 42314y (1978).
- (23) (a) K.A. Jansen, Z. Anorg. Allgem. Chem., 250, 257 (1943).
(b) L. Kolditz, M. Gitter and E. Roesel, ibid., 316, 270 (1962).
(c) G.G. Long, G.O. Doak and L.D. Freedman, J. Am. Chem. Soc., 86, 209 (1964).
- (24) A.D. Beveridge, G.S. Harris and F. Inglis, J. Chem. Soc. (A), 1966, 520.
- (25) A.A. Frost and R.G. Pearson, "Kinetics and Mechanism", 2nd ed., Wiley, New York (1961), Chapters 7-9.
- (26) S. Searles, M. Tamres and E.R. Lippincott, J. Am. Chem. Soc., 75, 2775 (1953).
- (27) (a) G.A. Olah, "Friedel-Crafts and Related Reactions", Wiley, New York (1973), Chapter V.
(b) H.A. Beneji, J. Am. Chem. Soc., 78, 5490 (1956).
(c) D. Cook, Can. J. Chem., 41, 522 (1963).
- (28) (a) Y. Tanaka, A.S. Jursa and F.J. LeBlanc, J. Chem. Phys., 32, 1199 (1960).
(b) J.W. Rablis, J.M. McDonald, V. Schnerr and S.P. McGlynn, Chem. Rev., 71, 73 (1971).

- (29) G. Fleming, M.M. Anderson, A.J. Harrison and L.W. Pickett, J. Chem. Phys., 30, 351 (1959).
- (30) T. Kagiya and T. Matsuda, Polymer J., 2, 398 (1971).
- (31) (a) D. Rappe and D.D. Briglia, J. Chem. Phys., 43, 1480 (1965).
- (b) M.J.W. Boness and G.J. Schultz, Phys. Rev. Letters, 21, 1031 (1968).
- (32) G.P. Naletova, Tr. Nauch.-Issled. Inst. Neftekhim. Proizd., 1970, 121; Chem. Abstr., 74, 105059g (1971).
- (33) S.-W. Wan and B.F. Dodge, Ind. Eng. Chem., 32, 95 (1940).
- (34) A. Kawasaki, J. Furukawa, T. Tsuruta, T. Saegusa and G. Kakogawa, Kogyo Kagaku Zasshi, 63, 871 (1960).
- (35) R.H. Irgoloic, "The Chemistry of Tellurium", Gordon and Breach, New York (1974), Chapter VII.
- (36) R.H. Vernon, J. Chem. Soc., 1920, 86.
- (37) H. Matsuda and S. Matsuda, Kogyo Kagaku Zasshi, 63, 114, 1958 (1960).
- (38) E.G. Rochow, D.T. Hurd and R.N. Lewis, "The Chemistry of Organometallic Compounds", Wiley, New York (1957) Chapters 7-9.
- (39) E.L. Muetterties and R.A. Shunn, Quart. Rev., 20, 245 (1966).
- (40) H.J.M. Bowen, "Tables of Interatomic Distances and Configuration in Molecules and Ions", Chemical Society, London (1958).
- (41) M. Webster, Chem. Rev., 66, 87 (1966).
- (42) S.M. Ohlberg, J. Am. Chem. Soc., 81, 811 (1959).

- (43) G.P. Van der Kelen, E.V. Van den Berghe and L. Verdonk, "Organotin Compounds", A.K. Sawyer, ed., Marcel Dekker, New York (1971), Chapter 3.
- (44) (a) H.A. Meinema and J.G. Noltes, J. Organomet. Chem., 16, 257 (1969).
(b) H.A. Meinema, E. Riverola and J.G. Noltes, *ibid.*, 17, 71 (1969).
(c) N. Nishii, Y. Matsumura and R. Okawara, *ibid.*, 30, 59 (1970).
(d) N. Bertazzi, M. Airolidi and L. Pelleritto, *ibid.*, 97, 399 (1975).
(e) H. Matsuda, T. Isaka and N. Iwamoto, Makromol. Chem., 179, 539 (1978).
- (45) H. Gilman and H.W. Melvin, J. Am. Chem. Soc., 71, 4050 (1949).
- (46) R.F. Chambers and P.J. Scherer, J. Am. Chem. Soc., 48, 1054 (1926).
- (47) C.A. Krause and L.S. Foster, J. Am. Chem. Soc., 49, 457 (1927).
- (48) C. Eaborn, J. Chem. Soc., 1952, 2849.
- (49) P. Pfeiffer, Ber. Dtsch. Chem. Ges., 37, 4621 (1904).
- (50) J. Bergman, Tetrahedron, 28, 3323 (1972).
- (51) (a) P.E. Ebert and C.C. Price, J. Polym. Sci., 46, 455 (1960).
(b) Y. Kuroda and M. Kubo, *ibid.*, 26, 323 (1957).
- (52) W.H.T. Davison, J. Chem. Soc., 1955, 2431.
- (53) (a) J. Furukawa, N. Kawabata and A. Kato, J. Polym. Sci.,

- Part A-1, 5, 3139 (1967).
- (b) M. Nakaniwa, I. Kameoka, K. Ozaki, H. Ohashi and J. Furukawa, J. Polym. Sci., Part B, 8, 131 (1970).
- (54) E.J. Vandenberg, J. Polym. Sci., Part A-1, 7, 525 (1969).
- (55) G. Allen, C. Booth, S.J. Hurst, M.M. Jones and C. Price, Polymer, 8, 391 (1967).
- (56) (a) A.B. Borkovec, J. org. Chem., 23, 828 (1958).
(b) R.O. Colclough, G. Gee, W.C.E. Higginson, J.B. Jackson and M. Litt, J. Polym. Sci., 34, 171 (1959).
- (57) (a) Y. Takashi, Bull. Chem. Soc. Jpn., 40, 1194 (1967).
(b) Y. Takashi and I. Aishima, J. Organomet. Chem., 8, 209 (1967).
- (58) K. Shen, W.E. McEwen, S.J.L. Place, W.C. Hamilton and A.P. Wolf, J. Am. Chem. Soc., 90, 1718 (1968).
- (59) J.I. Harris, S.T. Bowden and W.J. Jones, J. Chem. Soc., 1947, 1568.