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Catalytic Activity of Various Salts in the Reaction of 2,3-Epoxypropyl Phenyl Ether and Carbon Dioxide under Atmospheric Pressure

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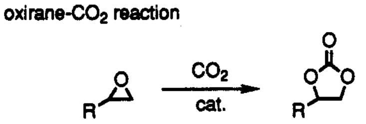
Reaction of 2,3-epoxypropyl phenyl ether (**1**) with carbon dioxide was carried out under atmospheric pressure in *N*-methylpyrrolidinone (NMP) at 100 °C in the presence of 5 mol % of various salts to obtain a five-membered cyclic carbonate, 4-(phenoxymethyl)-1,3-dioxolan-2-one (**2**), selectively. Only halide salts showed high catalytic activity, and the order of intrinsic activity was found to be as follows: chloride > bromide > iodide which is the order of nucleophilicity of the anion. Furthermore, the order of the activity was found to be lithium salt > sodium salt > benzyltrimethylammonium salt, which is in accord with the order of Lewis acidity of the cation. Kinetic analyses show that the reaction rate can be represented by $-d[\mathbf{1}]/dt=k[\mathbf{1}][\text{cat.}]$, where the carbon dioxide pressure shows no effect on the reaction rate. The reaction proceeds *via* nucleophilic attack of halide to oxirane to form β-haloalkoxide **4** which reacts with CO_2 followed by cyclization. The presence of key intermediate **4** was indirectly proved by the reaction of **1** with 1 equiv of LiBr in the absence of CO_2 at 100 °C for 2.5 h in NMP which leads to 1-phenoxy-2-propanone (**6**) in 20 % yield as the rearrangement product of **4**.

Recently, the chemistry of carbon dioxide has received much attention,[1] and its reaction with oxiranes leading to five-membered cyclic carbonates (oxirane–CO_2 reaction, Scheme I) is well-known among many examples.[2] These carbonates can be used as aprotic polar solvents[3] and sources for polymer synthesis.[4-10]

Many organic and inorganic compounds including amines,[11] phosphines,[11] quaternary ammonium salts,[2,11] alkali metal salts,[2,12,13] halostannanes,[14,15] antimony compounds,[16] and porphyrin[17,18] and transition-metal complexes[19-21] are known to catalyze the oxirane–CO_2 reaction. Alkali metal salts have been used not only alone but also in combination with crown ether[12] or inorganic supports[22] because they have been thought to be less active in comparison with lipophilic catalysts.[12] Although many catalysts have been reported, the structure–activity relationship of the catalyst based on a reaction mechanism have not been fully understood.[12,18,23]

Scheme I



In the oxirane–CO_2 reaction, high pressure of CO_2 has been thought to be necessary.[2,12] The oxirane–CO_2 reactions under atmospheric pressure have been reported only recently. Reaction of vinyloxirane with CO_2 under atmospheric pressure in the presence of a palladium complex was reported by Fujinami *et al.*,[20] and Takeda *et al.* reported a porphyrin complex-catalyzed oxirane–CO_2 reaction under atmospheric pressure,[17] where the polymerization of oxirane occurs simultaneously. Brindöpke[11] reported in a patent a quantitative oxirane–CO_2 reaction under atmospheric pressure in the presence of ammonium salts, amines, or phosphines. He also reported, however, that alkali metal salts can be used as cocatalysts although they were not recommended as main catalysts. On the basis of the report, Rokicki *et al.*[24] demonstrated the reaction of an oxirane having an ammonium substituent with CO_2 under atmospheric pressure. Very recently, Nishikubo *et al.* reported that polymer-supported ammonium salts catalyzed the oxirane–CO_2 reaction under atmospheric pressure.[25]

Recently, we have described the reaction of CO_2 and poly(glycidyl methacrylate) as polymeric oxirane in *N,N*-dimethylformamide (DMF) under atmospheric pressure.[26]

[•] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Inoue, S. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha Ltd.: Tokyo, 1982.

(2) Peppel, W. J. *Ind. Eng. Chem.* **1958**, *50*, 767.

(3) Johnson, P. H. Report **1985**, LBL-19886, Order No. DE85016526.

(4) Whelan, J. M., Jr.; Hill, M.; Cotter, R. J. U.S. Patent 3072613, 1963.

(5) Nomura, R.; Kori, M.; Matsuda, H. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 739.

(6) Rokicki, G. *Makromol. Chem.* **1985**, *186*, 331.

(7) Rokicki, G.; Pawlicki, J.; Kuran, W. *Polym. J.* **1985**, *17*, 509.

(8) Rokicki, G.; Jezewski, P. *Polym. J.* **1988**, *20*, 499.

(9) Sakai, S.; Suzuki, M.; Aomo, T.; Hasebe, K.; Kanbe, H.; Hiroe, M.; Kakei, T.; Fujinami, T.; Takemura, H. *Kobunshi Ronbunshu* **1984**, *41*, 151.

(10) Mikheev, V. V.; Svetlakov, N. V.; Sysoev, V. A.; Brus'ko, N. V. Deposited Doc. **1982**, SPSTL 41 Khp-D82.

(11) Brindöpke, G. German Patent DE 3529263, 1987.

(12) Rokicki, G.; Kuran, W.; Marciniak, B. P. *Monat. Chem.* **1984**, *115*, 205.

(13) Sàndescu, F.; Scurtu, M. *Mater. Plast.* **1985**, *22*, 226.

(14) Baba, A.; Nozaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552.

(15) Matsuda, H.; Ninagawa, A.; Nomura, R.; Tsuchida, T. *Chem. Lett.* **1979**, 573.

(16) Matsuda, H.; Ninagawa, A.; Nomura, R. *Chem. Lett.* **1979**, 1261.

(17) Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3564.

(18) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304.

(19) Pasquale, R. J. D. *J. Chem. Soc., Chem. Commun.* **1973**, 157.

(20) Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. *Chem. Lett.* **1985**, 199.

(21) Aresta, M.; Quaranta, E.; Ciccarese, A. *J. Mol. Catal.* **1987**, *41*, 355.

(22) Andreozzi, R.; Annesini, M. C.; Chiarotti, M.; Pochetti, F. *Chim. Ind. (Milan)* **1985**, *67*, 481.

(23) Annesini, M. C.; Fumasoni, S.; Giona, A. R.; Pochetti, F. *Chim. Ind. (Milan)* **1983**, *65*, 149.

(24) Rokicki, G.; Czajkowska, J. *Polimery (Warsaw)* **1989**, *34*, 140.

(25) Nishikubo, T.; Kameyama, A.; Yamashita, I.; Tomoi, M.; Fukuda, W. *J. Polym. Sci., A: Polym. Chem.* **1993**, *31*, 939.

0022-3263/93/1958-6198$04.00/0

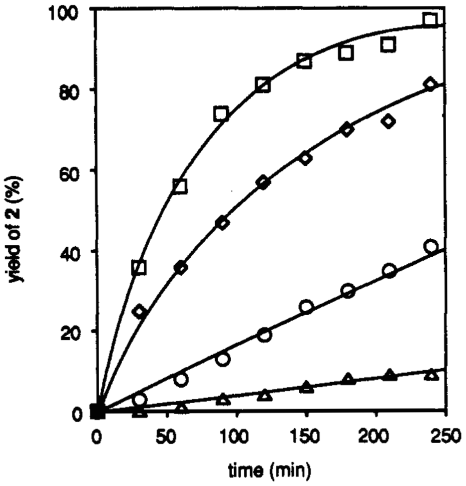
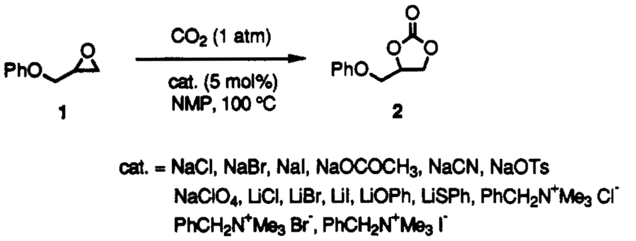


Figure 1. Yield of 2 *vs* reaction time for the reaction of 1 with carbon dioxide under atmospheric pressure at 100 °C using NaBr (□), NaI (◇), NaCl (○), and NaOAc (△) as catalysts.

Scheme II



cat. = NaCl, NaBr, NaI, $NaOCOCH_3$, NaCN, NaOTs $NaClO_4$, LiCl, LiBr, LiI, LiOPh, LiSPh, $PhCH_2N^+Me_3\ Cl^-$ $PhCH_2N^+Me_3\ Br^-$, $PhCH_2N^+Me_3\ I^-$

Although alkali metal salts had been thought to be not so active catalysts, we found for sodium iodide a higher activity than for triphenylphosphine or benzyltrimethylammonium iodide. We assumed that in homogeneous systems, such as in DMF solution, the intrinsic activity of alkali metal salts may be higher compared with phosphines or ammonium salts. Thus, we undertook detailed studies on the catalytic activity of various salts on the oxirane–CO_2 reaction using 2,3-epoxypropyl phenyl ether as model oxirane in an aprotic dipolar solvent under atmospheric pressure.

In this paper, we wish to report our findings: (1) only halides show high catalytic activity under atmospheric pressure, (2) alkali metal halides are more effective catalysts than onium salts, (3) the pressure of CO_2 does not affect the reaction rate, and (4) establishment of reaction mechanism.

Results

2,3-Epoxypropyl phenyl ether (1) was used as oxirane, and the reaction was carried out in NMP at 100 °C under 1 atm of CO_2 in the presence of 5 mol % of the salts. The conversion of 1 and the yield of a five-membered cyclic carbonate, 4-(phenoxymethyl)-1,3-dioxolan-2-one (2), were monitored by HPLC (Scheme II).

First of all, the reaction of 1 and CO_2 was carried out using sodium salts, including iodide, bromide, acetate, cyanide, *p*-toluenesulfonate, and perchlorate, as catalysts. In these cases, the yield of 2 corresponded to the conversion of 1, and no byproduct could be detected by HPLC analysis. Typical time–yield curves are shown in Figure 1. To describe the activity of the catalyst, eq 1 was assumed:

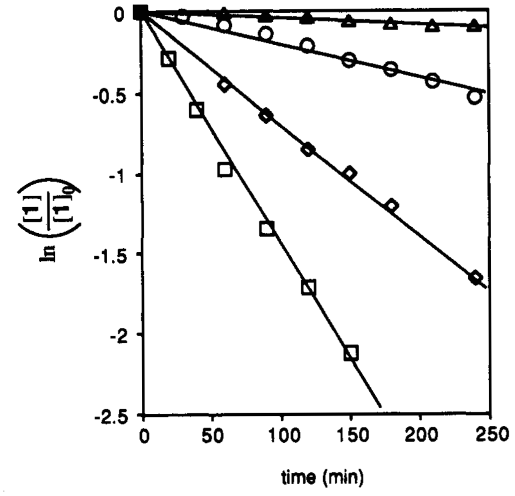


Figure 2. $\ln([1]/[1]_0)$ *vs* reaction time for the reaction of 1 with carbon dioxide under atmospheric pressure at 100 °C using NaBr (□), NaI (◇), NaCl (○), and NaOAc (△) as catalysts.

Table I. Apparent Rate Constant (k') and Yield of 2 of the Reaction of 1 and Carbon Dioxide under Atmospheric Pressure

catalyst (mol %)	k' (min^{-1}) × 10^4 [a]	yield of 2 (%)[b]
NaCl (5)[c]	20.2	41
NaBr (5)	155	98
NaBr (1)	27.4	48
NaBr (3)	95.2	88
NaBr (10)	217	100
NaI (5)	68.9	81
AcONa (5)	3.98	9
NaCN (5)	0	0
TsONa (5)	<1.0	1
$NaClO_4$ (5)	0	0
NaCl (5) + 3 (7.5)[c]	14.9	30
NaBr (5) + 3 (7.5)	141	96
LiCl (5)[c]	45.2	66
LiBr (5)	296	100
LiI (5)	101	91
LiOPh (5)	<1.0	1
LiSPh (5)	<1.0	2
$PhCH_2N^+Me_3\ F^-$ (5)	8.34	19
$PhCH_2N^+Me_3\ Cl^-$ (5)	176	100
$PhCH_2N^+Me_3\ Br^-$ (5)	31.9	57
$PhCH_2N^+Me_3\ I^-$ (5)	7.12	17

[a] In NMP at 100 °C. [b] Yield of 2 in the reaction for 4 h estimated from HPLC. [c] Catalyst was suspended.

$$-\frac{d}{dt}[1] = k'[1] \qquad (1)$$

where [1] is the concentration of 1, t is reaction time, and k' is the apparent rate constant of the reaction. Integration of eq 1 gave eq 2:

$$\ln\left(\frac{[1]}{[1]_0}\right) = k't \qquad (2)$$

where $[1]_0$ is initial concentration of 1. $\ln([1]/[1]_0)$ was plotted a function of t in Figure 2. Since a linear relationship was observed in every case, the oxirane–CO_2 reaction seems to be first order with respect to the concentration of oxirane as expressed in eq 1, and k' can be a parameter of activity of a catalyst. k' values were estimated from the slope of the lines in Figure 2 and are summarized in Table I. Sodium halide (bromide and iodide) exhibited higher activity, while other sodium salts were found to show only a very low activity. Thus, sodium chloride was also examined as catalyst in spite of its

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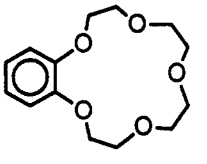
(26) Kihara, N.; Endo, T. *Macromolecules* **1992**, *25*, 4824.

insolubility in NMP. Indeed, a simple first order kinetic was observed, and it showed a medium activity depicted in Table I.

Since crown ethers are known to enhance the solubility of alkali metal salts in organic solvents, 7.5 mol % (1.5 equiv to NaCl) of benzo-15-crown-5 (**3**), which exhibits a high affinity to sodium ion,[27] was added to the system with sodium chloride. However, sodium chloride did not dissolve completely in NMP (*N*-methylpyrrolidinone) in the presence of **3**, and k' decreased. Furthermore, **3** was added to the system with sodium bromide although k' also decreased. Thus, it can be concluded that crown ether acted as deactivator of the catalyst.



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To evaluate the role of the cation part of the catalysts, a series of lithium compounds including iodide, bromide, chloride, phenolate, and thiophenolate was examined. In each case, the yield of **2** corresponded to the conversion of **1**, and no byproduct could be detected by HPLC analysis. A linear relationship between $\ln([1]/[1]_0)$ and t was observed, and the values of k' are summarized in Table I. Lithium salts showed higher activity in comparison with the corresponding sodium catalysts. Only halides showed a considerable catalytic activity, and bromide was more active than iodide, as in the case of the sodium salts. Unfortunately, lithium chloride precipitated during the reaction. Although simple first-order kinetics were observed for lithium chloride and the apparent activity was lower than that of bromide and iodide, its intrinsic activity could not yet be exactly determined.

Since quaternary ammonium salts dissolve in NMP, a series of benzyltrimethylammonium halides, including fluoride, chloride, bromide, and iodide, was used as catalyst to demonstrate the intrinsic order of the halide activity. In every case, the reaction system remained homogeneous during the reaction. The yield of **2** corresponded to the conversion of **1**, and no byproduct could be detected by HPLC analysis. A linear relationship between $\ln([1]/[1]_0)$ and t was observed, and the values of k' were calculated and are summarized in Table I. The catalytic activity of ammonium salts is rather low compared with the corresponding alkali metal salts.[2] It can be clearly shown that the intrinsic order of activity of the catalysts is chloride > bromide > iodide ~ fluoride.

To evaluate the kinetic order with respect to the catalyst, $\ln(k')$ obtained from an NaBr-catalyzed system was plotted as function of $\ln([\mathrm{NaBr}])$ as shown in Figure 3. Since the slope of the line is 1.0, the oxirane–CO_2 reaction seems to be first order with respect to the concentration of the catalyst. On the other hand, the carbon dioxide pressure showed no effect on the yield of **2** at all, as shown in Figure 4. Consequently, the reaction rate can be expressed by following equation:

$$-\frac{d}{dt}[1] = k[1][\mathrm{cat.}] \qquad (3)$$

where [cat.] is the concentration of the catalyst and the reaction rate is independent of the carbon dioxide pressure.

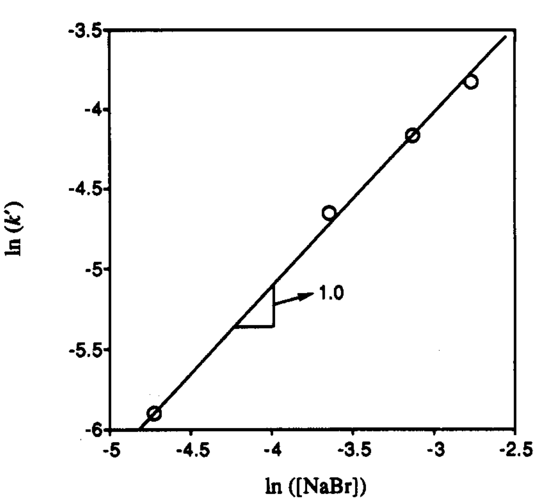

Figure 3. Plot of the rate constant (k') at 100 °C for the reaction of **1** with carbon dioxide under atmospheric pressure catalyzed by NaBr as a function of concentration of NaBr.

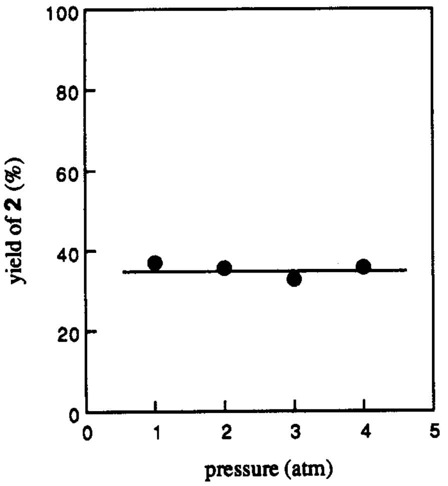

Figure 4. Yield of **2** *vs* pressure of carbon dioxide for the reaction of **1** with carbon dioxide at 100 °C for 30 min using NaBr as a catalyst.

Discussion

Structure–Activity Relationship of the Catalyst. The counter anion of the salts significantly affects the catalytic activity. Essentially, only halides showed a considerable activity, probably because halide anions exhibit moderate nucleophilicity and high leaving ability. Salts with nonnucleophilic anions, such as *p*-toluenesulfonate and perchlorate, showed no activity in spite of higher leaving ability. Furthermore, salts with higher nucleophilic anions, such as acetate, cyanide, phenolate, and thiophenolate, showed very low activity probably because of low leaving ability. Rokicki *et al.* reported that potassium phenolate and acetate exhibited considerable catalytic activity at 40 atm,[12] indicating that such highly nucleophilic anions can catalyze the oxirane–CO_2 reaction via a different reaction mechanism under higher pressure.

The order of the activity of halides can be estimated to be chloride > bromide > iodide ~ fluoride. The apparently lower activity of sodium and lithium chloride may arise from the low solubility of these salts. Although the nucleophilicity of an anion depends on the solvent used, the order of the nucleophilicity of halides in S_N2-type reactions in aprotic solvents, such as NMP, is known to

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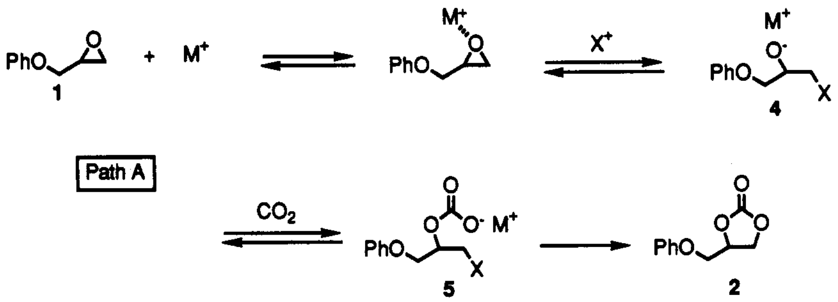
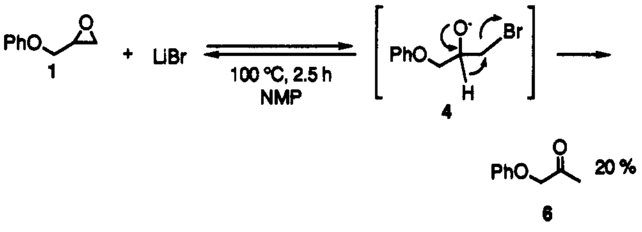
[27] Weber, E.; Vögtle, F. *Top. Curr. Chem.* **1981**, *98*, 1.

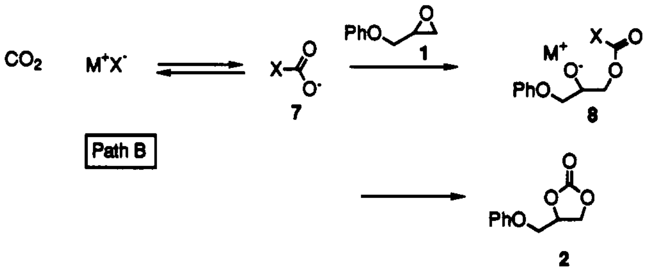
Scheme III



Scheme IV



Scheme V



be $Cl^- > Br^- > I^-$.[28-30] Thus, the order of activity of halide anions is consistent with the order of nucleophilicity. The low activity of fluoride can be explained by its low leaving ability.[22] The importance of anion nucleophilicity indicates that the rate-determining step of the oxirane–CO_2 reaction involves nucleophilic attack of an anion to oxirane, which is consistent with the kinetic analyses (eq 3).

Furthermore, the role of the catalyst cation is notable. In both series of bromide and iodide, the order of the activity is lithium salt > sodium salt > benzyltrimethylammonium salt. This order is in accord with the order of Lewis acidity of the cation,[31] indicating the cation acted as Lewis acid to activate the oxirane.[32,33] Since the Lewis acidity of cation decreases in the presence of a strong ligand, the catalyst activity decreased by addition of crown ether,[34] although the coordination ability of crown ether in NMP is very low.[35]

Mechanistic Aspects. Although the reaction mechanism shown in Scheme III (path A) has been proposed for the oxirane–CO_2 reaction by many researchers,[12,18,23] no reliable evidence has yet been reported. Path A was, however, clearly confirmed from kinetic analyses made in our simple system. It was found that the rate-determining step is the attack of the anion part of the catalyst to oxirane. The importance of Lewis acidity of the cation part and nucleophilicity of the anion part of the catalyst as described above can be explained by this mechanism.

To prove the reaction of oxirane and salts, the reaction of 1 with 1 equiv of LiBr was carried out in the absence of CO_2 at 100 °C for 2.5 h in NMP. 1-Phenoxy-2-propanone (6) was isolated in 20% yield as the sole product. 4 could not be detected because it cyclized rapidly to 1 and LiBr. Since the formation of 6 is reasonably explained by hydride transfer of 4 as shown in Scheme IV, the presence of key intermediate 4 was proved indirectly. Although the Lewis acid-catalyzed rearrangement of oxirane to aldehyde *via* more the stable carbenium intermediate is well-known,[36,37] the rearrangement of oxirane to ketone is not conventional. Formation of ketone 6 clearly indicates the attack of bromide anion to oxirane on the less substituted carbon regioselectively, which is characteristic of S_N2-type nucleophilic attacks on oxirane ring systems.[37]

Although anions with higher nucleophilicity react with oxiranes more rapidly, acetate, phenolate, and thiophenolate anions may show no catalytic activity based on path A because of their low leaving ability in S_N2-type reaction on sp^3 carbons. However, a small amount of 2 was obtained using these salts, and carboxylate and phenolate are known to catalyze the oxirane–CO_2 reaction in the presence of crown ether under high pressure conditions.[12] These facts indicate the possibility of another reaction mechanism, especially under high pressure. Because the catalytic activity of these highly nucleophilic anions seem to depend on the CO_2 pressure and these anions are good leaving groups in displacement reactions on carbonyl carbon, another possible reaction mechanism can be proposed as represented in Scheme V (path B). Since the equilibrium of the first step of path B with atmospheric pressure of CO_2 lies so far to the left, path B can not be the main reaction path under atmospheric pressure. However, when the pressure of CO_2 increases, the equilibrium may shift to the right so that the oxirane–CO_2 reaction *via* path B may proceed smoothly. At present, it is not clear whether halide salts can catalyze the oxirane–CO_2 reaction *via* path B.

Summary

We demonstrated the structure–activity relationship of the catalyst and a proposed reaction mechanism of the oxirane–CO_2 reaction by which CO_2 can be easily introduced into organic molecules under atmospheric pressure. Alkali metal salts, which have been thought to exhibit

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(28) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(29) Winstein, S.; Savedoff, L. G.; Smith, S.; Stevens, I. D. R.; Gall, J. S. *Tetrahedron Lett.* **1960**, 24.

(30) Liotta, C. L.; Grisdale, E. E. *Tetrahedron Lett.* **1975**, 4205.

(31) Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: Northern Ireland, 1987.

(32) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323.

(33) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(34) Handel, H.; Pierre, J. *Tetrahedron Lett.* **1976**, 741.

(35) Lincoln, S. F.; Brereton, I. M.; Spotswood, T. M. *J. Am. Chem. Soc.* **1986**, *108*, 8134.

(36) Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693.

(37) Smith, J. G. *Synthesis* **1984**, 629.

rather low catalytic activity in comparison with lipophilic onium salts, are more active catalysts for the oxirane–CO_2 reaction because alkali metal cations behave as Lewis acids. Furthermore, halides are the most suitable anion part of the catalyst for the oxirane–CO_2 reaction because of their appropriate nucleophilicity and leaving ability. Consequently, alkali metal halides were the best catalysts examined. A significant feature of the oxirane–CO_2 reaction is that the rate of the reaction is independent of the pressure of CO_2 because the reaction of alkoxide anion with CO_2 is rapid enough. Although we used 1 as a representative oxirane, these structure–activity relationships and reaction mechanism are assumed to be valid for most oxiranes.

The fact that easily available alkali metal salts act as highly active catalysts in nature is very important from an economical and practical viewpoint, although low solubility of alkali metal salts in organic solvents is disadvantageous. Further research of novel catalysts which combine lipophilicity, high Lewis acidity, high nucleophilicity, and high leaving ability is in progress.

Experimental Section

General Method. ^1H and ^{13}C NMR spectra were recorded on a JEOL PMX-60 SI (60 MHz) or on a JEOL EX-90 (90 MHz) spectrometer, using TMS as an internal standard. IR spectra were recorded on a JEOL JIR-5300 instrument. HPLC analyses were made by using UV detector (JASCO UVIDEC-100-V) at 245 nm, utilizing freshly distilled dichloromethane as solvent (elution rate; 1 mL/min, at room temperature), and a Gasukuro Kogyo Unisil Q 60–5 column.

Materials. 2,3-Epoxypropyl phenyl ether (1) and *N*-methylpyrrolidinone (NMP) were distilled from CaH_2 and stored under nitrogen. THF was distilled from sodium–benzophenone ketyl under nitrogen atmosphere before use. Naphthalene was recrystallized from ethanol. Benzo-15-crown-5 was recrystallized from *n*-hexane. Reagent grade phenol and thiophenol were used without further purification. Hydrated benzyltrimethylammonium fluoride was commercially available and was dried under vacuum at 100 °C for 24 h over P_2O_5 followed by crushing and subsequent further drying under vacuum at 100 °C for 24 h over P_2O_5 before use. Other ammonium salts and inorganic chemicals were reagent grade and used after drying under vacuum.

Lithium Phenoxide. To a solution of 2.8 g (30 mmol) of phenol in 60 mL THF was added 18 mL of a 1.62 mol/L hexane solution of butyllithium (30 mmol) dropwise under nitrogen at 0 °C. After 30 min, the volatiles were removed under vacuum to obtain lithium phenoxide as a white powder.

Lithium Thiophenoxide. To a solution of 0.55 g (5 mmol) of thiophenol in 10 mL of THF was added 3.1 mL of a 1.62 mol/L hexane solution of butyllithium (5 mmol) dropwise under nitrogen at 0 °C. After 30 min, the volatiles were removed under vacuum to obtain lithium thiophenoxide as a white powder.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (2). A solution of 1.71 g (11 mmol) of 1 and 75 mg (0.5 mmol) of sodium iodide in 11 mL of NMP was heated at 100 °C for 24 h under a carbon dioxide atmosphere. The reaction mixture was poured into 100 mL of water and precipitates were washed thoroughly with water. The crude cyclic carbonate was recrystallized in ethanol to obtain 1.61 g (73%) of 4-(phenoxymethyl)-1,3-dioxolan-2-one (2). Mp: 98.5–99.5 °C (lit.[38] mp 98–99 °C). NMR: (60 MHz, $CDCl_3$) δ 7.40–6.65 (m, 5H, Ar), 5.24–4.67 (m, 1H, CH), 4.62–3.87 (m, 4H, CH_2). IR: (KBr) 1805, 1167, 1092, and 760 cm^{-1}.

Reaction of 1 and Carbon Dioxide. A mixture of 1.50 g (10 mmol) of 1, 5.0 mmol of catalyst, and 0.128 g of naphthalene was introduced in a two-necked flask equipped with a rubber septum. After the atmosphere was replaced with CO_2, 10.0 mL of NMP was introduced using a syringe through a rubber septum to dissolve the mixture. The total volume of the solution became 11.4 mL. The solution was allowed to stand at 100 °C with continuous stirring. Periodically, a small portion of the reaction mixture was removed out through rubber septum, diluted with dichloromethane, and washed with water. The organic extract was analyzed by HPLC to estimate the conversion of 1 and yield of 2 using naphthalene as an internal standard.

Reaction of 1 and LiBr. A solution of 782 mg (5.2 mmol) of 1 and 449 mg (5.2 mmol) of lithium bromide in 5 mL of NMP was heated at 100 °C for 2.5 h under a nitrogen atmosphere. The reaction mixture was poured into 50 mL of phosphate buffer (pH = 6.8) and extracted with 5 × 10 mL of ether. The organic layer was washed with water and dried with $MgSO_4$ before evaporation. 1-Phenoxy-2-propanone (6) (156 mg, 20%) was isolated as the sole product from the crude mixture by preparative TLC (eluent; CH_2Cl_2). NMR: (60 MHz, $CDCl_3$) δ 7.43–6.61 (m, 5H, Ar), 4.45 (s, 2H, CH_2), 2.20 (s, 3H, CH_3). IR: (NaCl) 1736, 1722, 1599, 1589, 1497, 1228, 1171, 754, and 692 cm^{-1}.

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(38) Nishikubo, T.; Iizuka, T.; Iida, M.; Isobe, N. *Tetrahedron Lett.* 1986, *27*, 3741.