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Cycloaddition of Carbon Dioxide to 1,2-Epoxypropane Catalyzed by Tetra-*t*-butylphthalocyaninatoaluminium(III) Hydroxide

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Carbon dioxide was fixed as propane-1,2-diol carbonate (PDC) with 1,2-epoxypropane (EP) catalyzed by Al(OH){pc(*t*-Bu)$_4$} in the presence of such a quaternary ammonium halide (HAX) as [HO(CH$_2$)$_2$N(CH$_3$)$_2$(C$_4$H$_9$)]X (X = Cl, Br, I). Although the yield was scarcely affected by the structure of HAX, it was dependent on the kind of halide ion. While PDC was formed in chloroform or dichloromethane, the yield decreased extremely in DMSO or pyridine, and PDC was not prepared in methanol. Although halohydrin was formed in a chloroform solution of EP, Al(OH){pc(*t*-Bu)$_4$}, and HAX, it was not an intermediate.

The formation of a hexa-coordinate complex of Al(OH){pc(*t*-Bu)$_4$} with HAX and EP was spectroscopically confirmed, and the complex catalyzed the preparation of PDC from carbon dioxide and EP.

The chemical fixation of carbon dioxide has received intense attention from the viewpoints of a carbon source in industry and an environmental problem.[1—3] There are four important industrial fixation processes of carbon dioxide: the syntheses of urea, cyclic carbonates, salicylic acid, and methanol.[4,5] The syntheses of cyclic carbonates were performed using such catalyst as ZnEt$_2$,[6] Ph$_3$SnI,[7] or Me$_2$TeI$_2$.[7] With the catalysts, however, a high temperature and/or high pressure of carbon dioxide were required for the fixation. It was further reported that cycloaddition was carried out with epoxide at room temperature under carbon dioxide using tetraphenylporphyrinatoaluminium(III), Al(L)tpp (L = chloro, alkoxy, or alkyl ligand) as the catalyst.[8—11]

It is of interest to fix carbon dioxide using metal complexes of phthalocyanine, a macrocyclic homologue of porphyrin. We have previously reported that propane-1,2-diol carbonate (PDC) was obtained by bubbling carbon dioxide through a chloroform solution of 1,2-epoxypropane (EP) and Al(Cl){pc(*t*-Bu)$_4$} (Fig. 1) in the presence of 1-methylimidazole (MeIm).[12] The fixation was carried out via the insertion of EP and carbon dioxide between the aluminium(III) and axial ligand; of which the bonding was weakened by the sixth coordination of MeIm to the aluminium(III), as shown in the fixation of carbon dioxide catalyzed by Al(L)tpp.[8—10]

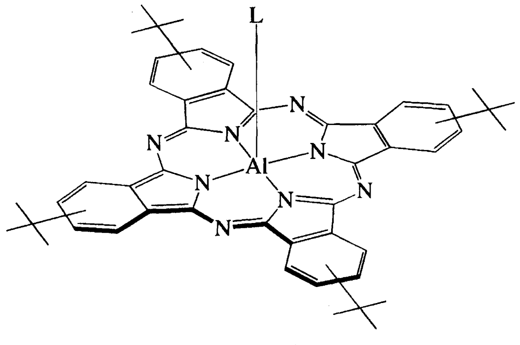


Fig. 1. Al(L){pc(*t*-Bu)$_4$}: L = Cl, OH.

When Al(OH){pc(*t*-Bu)$_4$} was used as the catalyst, the yield of PDC was extremely low, because MeIm did not coordinate to the hydroxide complex. On the other hand, considerable amounts of PDC were obtained by bubbling carbon dioxide through a chloroform solution of EP and Al(OH){pc(*t*-Bu)$_4$} in the presence of triethylamine under irradiation with visible light.[12] This was strange, because no coordination of triethylamine to the aluminium(III) was confirmed spectroscopically. It was thus assumed that fixation in the presence of triethylamine was catalyzed by a complex axially coordinated by triethyl(2-hydroxypropyl)ammonium chloride formed by the reaction of triethylamine and EP in the presence of hydrogen chloride (produced by the decomposition of chloroform under irradiation).[12] To elucidate the fixation mechanism, we prepared triethyl(2-hydroxypropyl)ammonium halide, and its derivatives, HAX (Table 1), and also investigated the fixation of carbon dioxide with EP catalyzed by Al(OH){pc(*t*-Bu)$_4$} in the presence of HAX.

Experimental

Materials. Al(OH){pc(*t*-Bu)$_4$} and Ni{pc(*t*-Bu)$_4$} were prepared according to a literature method.[12—14] Fe(OH){pc(*t*-Bu)$_4$}

Table 1. Quaternary Ammonium Halides

HAX	Rational formula
1	[HOCH(CH$_3$)CH$_2$N(C$_2$H$_5$)$_3$]I
2	[HO(CH$_2$)$_2$N(C$_2$H$_5$)$_3$]I
3	[HO(CH$_2$)$_2$N(C$_2$H$_5$)$_3$]Br
4	[HO(CH$_2$)$_3$N(C$_2$H$_5$)$_3$]I
5	[HO(CH$_2$)$_2$N(CH$_3$)$_2$(C$_4$H$_9$)]I
6	[HO(CH$_2$)$_2$N(CH$_3$)$_2$(C$_4$H$_9$)]Br
7	[HO(CH$_2$)$_2$N(CH$_3$)$_2$(C$_4$H$_9$)]Cl

was prepared as follows: After a mixture of 4-*t*-butylphthalonitrile (920 mg, 5.0 mmol) and anhydrous iron (III) chloride (243 mg, 1.5 mmol) was refluxed for 1 h in 1-pentanol (5 cm^3), the solution was evaporated to dryness under reduced pressure. The solid mass was then dissolved in concentrated sulfuric acid (5 cm^3), and crude products were reprecipitated upon pouring the solution into 150 cm^3 of water, being washed with an aqueous solution saturated by sodium hydrogencarbonate and subsequently with water. The obtained dark-blue complex was then chromatographed over activated alumina using chloroform as an eluent. Yield 187 mg (19%). Found: C, 71.48; H, 6.01 N, 13.94%. Calcd for $C_{48}H_{48}FeN_8O$: C, 71.19; H, 6.11; N, 13.83%. UV/vis (dichloromethane) 286, 338, 610^{sh}, and 668 nm. Epoxides, 1-methylimidazole, and 1-bromo-2-propanol were used without further purification.

Preparation of HAX. HAX **1** was prepared by heating a mixture of 1-diethylamino-2-propanol (1.5 cm^3, 10 mmol) and ethyl iodide (0.8 cm^3, 10 mmol) at ca. 70 °C for 30 min. After filtration of the solution, white powders were obtained and washed with hexane, being dried in vacuo. Yield: 94 mg (3%). Found: C, 37.22; H, 7.84; N, 4.74%. Calcd for $C_9H_{22}INO$: C, 37.64; H, 7.72; N, 4.88%. ^{1}H NMR ($CDCl_3$) $\delta = 1.35$ (m, 12H, CH_3), 3.08—3.13 (m, 2H, CH_2), 3.43—3.70 (m, 6H, CH_2), 4.38 (s, 1H, CH), 4.66 (s, 1H, OH). The other compounds were prepared from various alcohols and alkyl halides in a similar manner described for that of HAX **1**.

HAX **2**. Yield: 450 mg (16%). Found: C, 35.60; H, 7.31; N, 5.16%. Calcd for $C_8H_{20}INO$: C, 35.18; H, 7.38; N, 5.13%. ^{1}H NMR $\delta = 1.40$ (t, 9H, CH_3), 3.55 (m, 8H, CH_2), 4.17 (m, 2H, CH_2), 4.39 (s, 1H, OH).

HAX **3**. Yield: 40 mg (2%). Found: C, 42.26; H, 8.70; N, 6.21%. Calcd for $C_8H_{20}BrNO$: C, 42.49; H, 8.91; N, 6.19%. ^{1}H NMR $\delta = 1.39$ (t, 9H, CH_3), 3.57 (m, 8H, CH_2), 4.16 (m, 2H, CH_2), 5.31 (s, 1H, OH).

HAX **4**. Yield: 722 mg (25%). Found: C, 37.80; H, 7.60; N, 4.85%. Calcd for $C_9H_{22}INO$: C, 37.64; H, 7.72; N, 4.89%. ^{1}H NMR $\delta = 1.42$ (t, 9H, CH_3), 2.00—2.11 (m, 2H, CH_2), 3.40 (q, 6H, CH_2), 3.57—3.63 (m, 2H, CH_2), 3.81 (m, 2H, CH_2).

HAX **5**. Yield: 1.58 g (58%). Found: C, 35.32; H, 7.36; N, 5.03%. Calcd for $C_8H_{20}INO$: C, 35.18; H, 7.38; N, 5.13%. ^{1}H NMR $\delta = 1.02$ (t, 3H, CH_3), 1.46 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 3.38 (s, 6H, CH_3), 3.58 (br. s, 2H, CH_2), 3.80 (t, 2H, CH_2), 4.19 (br. s, 2H, CH_2).

HAX **6** (deliquescent white crystals). Yield: 1.44 g (64%). Found: C, 41.72; H, 9.00; N, 5.97%. Calcd for $C_8H_{20}BrNO \cdot 0.25H_2O$: C, 41.66; H, 8.96; N, 6.07%. ^{1}H NMR $\delta = 1.01$ (t, 3H, CH_3), 1.43 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 3.38 (s, 6H, CH_3), 3.58 (t, 2H, CH_2), 3.77 (t, 2H, CH_2), 4.14 (br. s, 2H, CH_2), 5.04 (br. s, 1H, OH).

HAX **7** (deliquescent white crystals). Yield: 520 mg (29%). Found: C, 51.24; H, 10.99; N, 7.33%. Calcd for $C_8H_{20}ClNO \cdot 0.25H_2O$: C, 51.60; H, 11.10; N, 7.52%. ^{1}H NMR $\delta = 1.00$ (t, 3H, CH_3), 1.43 (m, 2H, CH_2), 1.75 (m, 2H, CH_2), 3.36 (s, 6H, CH_3), 3.56 (t, 2H, CH_2), 3.72 (t, 2H, CH_2), 4.11 (m, 2H, CH_2), 5.82 (br. s, 1H, OH).

Fixation of Carbon Dioxide. A chloroform solution (0.5 cm^3) of EP (0.5 mmol), Al(OH){pc(*t*-Bu)$_4$} (5×10^{-4}—2.5×10^{-3} mmol), and HAX (5×10^{-4}—1×10^{-2} mmol) was kept to stand under carbon dioxide at room temperature for 6 h. The yield of PDC was estimated by means of a ^{1}H NMR spectrometer or gas chromatography using *p*-chlorobenzaldehyde or naphthalene as the internal standard, respectively.

Measurements. UV-vis and IR spectra were recorded on Shimadzu UV-3100 and Hitachi 260-50 spectrophotometers, respectively. ^{1}H NMR spectra were measured with a JEOL GX270 spectrometer at 270 MHz. The chemical shifts were determined in ppm using TMS as an internal standard. Gas chromatograms were measured with a Hewlett Packard 5890 Series II gas chromatography. Elemental analyses were carried out using Yanako CHN Corder MT-5.

Results and Discussion

The ^{1}H NMR spectrum of a deuterated chloroform solution of the complex and triethyl(2-hydroxypropyl)ammonium iodide (HAX **1**) was measured (Fig. 2). The signals at 0.6—0.9 (br. d, 8H, CH_2), −0.3 (br. s, 9H, CH_3), −0.9 (br. 1H, CH), and −2.5 (m, 3H, CH_3) ppm were assigned to the protons of methyl (a), methine (b), methyl (c), and methylene (d, e) of the axial ligand of complex **1**, respectively; they shifted upfield due to a ring-current effect of phthalocyanine. That is, HAX **1** was coordinated to the aluminium(III) by dehydration between the hydroxo ligand of the complex and the hydroxy group of quaternary ammonium iodide in a similar way as that described for the reaction of phthalocyaninatoaluminium(III) hydroxide and various phenols.[15)]

PDC was obtained by bubbling carbon dioxide through a chloroform solution of EP, Al(OH){pc(*t*-Bu)$_4$}, and HAX. During the fixation of carbon dioxide with HAX **3**, the formation of 1-bromo-2-propanol was confirmed by a gas chromatography or ^{1}H NMR spectrum; the proton signals characteristic of halohydrin appeared at 3.4 (br. m, 2H, CH_2) and 3.9 (br. m, 1H, CH) ppm in accordance with those for commercially available 1-bromo-2-propanol. The amounts of halohydrin yielded did not exceed the concentration of the complex. Furthermore, PDC was not obtained by bubbling carbon dioxide through a chloroform solution of the complex, HAX **3**, and 1-bromo-2-propanol, showing that halohydrin was not an intermediate for the preparation of PDC from EP.

With the formation of halohydrin, the hexa-coordinate complex was simultaneously formed (Scheme 1), as confirmed by the ^{1}H NMR and absorption spectra. The proton signal (−3.6 ppm) for the axial methyl group of complex

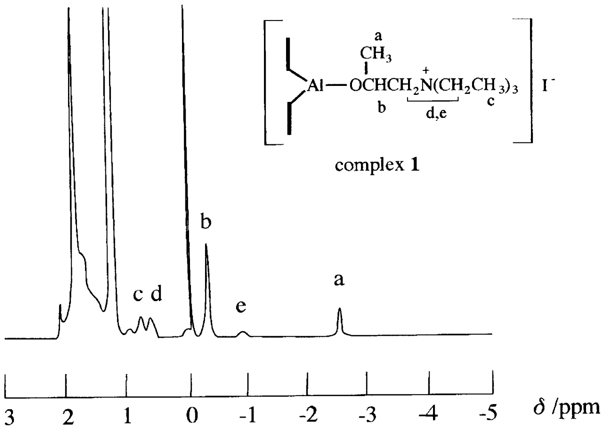
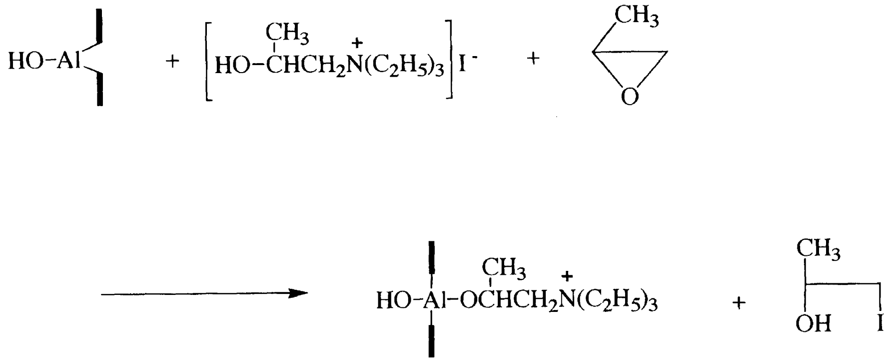


Fig. 2. The ^{1}H NMR spectrum of the $CDCl_3$ solution of Al(OH){pc(*t*-Bu)$_4$} and HAX **1**: [complex] = 5×10^{-3} mol dm^{-3}, [HAX **1**] = 5×10^{-2} mol dm^{-3}.



complex **2**

Scheme 1. Formation of the hexa-coordinate complex.

2 was shifted upfield compared with that (−2.5 ppm) of complex **1**, due to the strong ring-current effect caused by the attraction of the aluminium(III) into the phthalocyanine ring. The formation of complex **2** was also supported by the absorption spectral changes, as shown in Fig. 3. With the addition of EP, the absorption bands at 294, 344, 623, and 690 nm immediately decreased those intensities, and new bands appeared at 280, 360, 609, 641, and 676 nm with accompanying isosbestic points at 290, 350, 617, 632, and 683 nm. It has been reported that the intense Q bands of the phthalocyanine complexes of aluminium(III) in the region from 600 to 700 nm were blue-shifted by the formation of a hexa-coordinate complex.[16] The Q band of Al(OH){Pc(*t*-Bu)$_4$} was blue-shifted from 697 to 676 nm upon the addition of EP, resulting in the formation of a hexa-coordinate complex. An absorbance at the Q band (676 nm) increased in the order of the chloride, the bromide, and the iodide (Fig. 4), showing that HAX with a polar halide easily formed complex **2**. Furthermore, the hexa-coordinate complex was not formed from Al(OH){pc(*t*-Bu)$_4$} and tetraethylammonium iodide in the presence of ethanol. That is, such a ligand as HAX, having both the hydroxy and quaternary ammonium groups, formed only complex **2**.

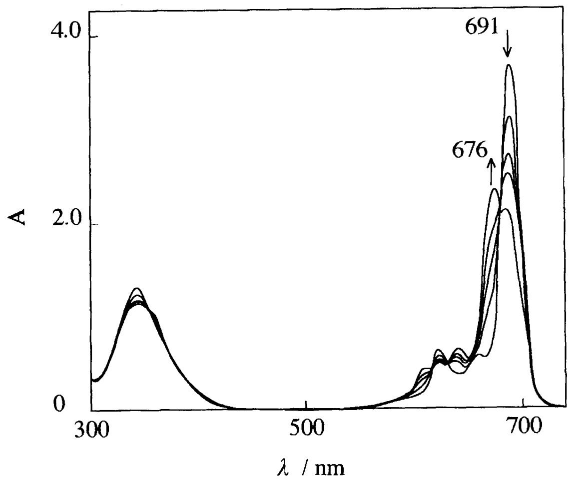


Fig. 3. Absorption spectral changes of a chloroform solution of Al(OH){pc(*t*-Bu)$_4$} with the addition of EP: [complex] = 1.5×10^{-4} mol dm^{-3}, [HAX **1**] = 1.5×10^{-3} mol dm^{-3}, [EP] = 1.5×10^{-4}—1.5×10^{-1} mol dm^{-3}. The cell with 1 mm of light-path length was used.

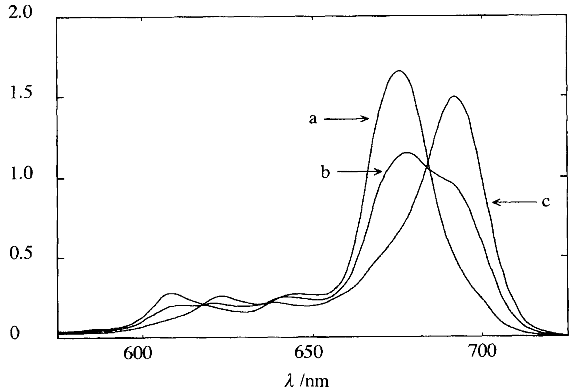


Fig. 4. Effect of the halide ions of HAX on the absorption spectra of a chloroform solution of Al(OH){pc(*t*-Bu)$_4$}: a) HAX **5**, b) HAX **6**, c) HAX **7**; [complex] = 1.5×10^{-4} mol dm^{-3}, [HAX] = 1.5×10^{-3} mol dm^{-3}, [EP] = 7.5×10^{-2} mol dm^{-3}. The cell with 1 mm of light-path length was used.

While the yield of PDC scarcely increased upon the addition of H$_2${pc(*t*-Bu)$_4$} or Ni{pc(*t*-Bu)$_4$} to the solution, the addition of Fe(OH){pc(*t*-Bu)$_4$} or Al(OH){pc(*t*-Bu)$_4$} increased the yield (Runs 1—5 in Table 2). Especially, the yield with an aluminium(III) complex was ca. 60-times that without the complex. These facts show that the formation of the hexa-coordinate complex with HAX is important for fixation, as previously reported by Inoue et al.[17,18] Tetraphenylporphyrinatoaluminium(III) carboxylate formed a hexa-coordinate complex with tetraalkylammonium carboxylate or a mixture of secondary amine and carbon dioxide. Then, the hexa-coordinate complex catalyzed the formation of cyclic carbonate or carbamic ester from carbon dioxide and epoxide.

Furthermore, although the yield was scarcely affected by the structural differences of HAX, it was affected by the kind of halide ions (Runs 6—11), resulting from the dependence of the amounts of complex **2** on the kind of halide ion of HAX (Fig. 4). While PDC was formed in chloroform or dichloromethane, the yield of PDC decreased extremely in

Table 2. Effects of the Complexes, HAX, and Solvents on the Yield of PDC[a)]

Run		Yield/10^{-3} mmol	Run		Yield/10^{-3} mmol
1	Al(OH){pc(*t*-Bu)$_4$}	13	9	HAX **5**	10
2	Fe(OH){pc(*t*-Bu)$_4$}	3.8	10	HAX **6**	6
3	Ni{pc(*t*-Bu)$_4$}	0.3	11	HAX **7**	2
4	H$_2${pc(*t*-Bu)$_4$}	0.2	12	Dichloromethane	11
5	None	0.2	13	DMSO	0.5
6	HAX **2**	12	14	Pyridine	0.3
7	HAX **3**	9	15	Methanol	0
8	HAX **4**	8			

a) [complex] = 5×10^{-3} mol dm^{-3}, [EP] = 1 mol dm^{-3}, [HAX] = 1×10^{-2} mol dm^{-3}. In Runs 1—5 and 12—15, HAX **1** was used, respectively. In Runs 6—15, Al(OH){pc(*t*-Bu)$_4$} was used.

Table 3. The Fixation of Carbon Dioxide with Epoxides[a)]

Epoxides	Yield/10^{-3} mmol
1,2-Epoxypropane	5
1,2-Epoxyethylbenzene	4
1,2-Epoxy-3-methoxypropane	6
1,2-Epoxy-1-methoxy-2-methylpropane	1
1,2-Epoxycyclohexane	—

a) [Al(OH){pc(*t*-Bu)$_4$}]=1×10^{-3} mol dm^{-3}, [HAX **1**] = 1×10^{-2} mol dm^{-3}, [epoxide] = 5×10^{-1} mol dm^{-3}.

such a polar solvent as DMSO or pyridine, and PDC was not formed in such a protic solvent as methanol (Runs 12—15). The hexa-coordinate complex was formed in chloroform, but not formed in DMSO or methanol. That is, the decrease of the yield in the polar solvents results from a depression of the formation of the hexa-coordinate complex. The yield of cyclic carbonate was low with such an epoxide as 1,2-epoxy-1-methoxy-2-methylpropane or 1,2-epoxycyclohexane, having substituents on both carbon atoms in the epoxide ring, probably due to a steric hindrance in their ring-opening reactions (Table 3).[12)]

Although the coordination of MeIm on the aluminium(III) of Al(Cl){pc(*t*-Bu)$_4$} in chloroform required a few days, HAX **1** immediately coordinated to the aluminium(III) of Al(OH){pc(*t*-Bu)$_4$} in the presence of EP. Although the insertion of carbon dioxide or EP between the aluminium(III) and the axial ligand of the hexa-coordinate complex was not spectroscopically confirmed, PDC might be prepared via the insertion mechanism reported previously.[8—10,12,18)]

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