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Activation of Carbon Dioxide by Tetraphenylporphinatoaluminium Methoxide. Reaction with Epoxide

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α,β,γ,δ-Tetraphenylporphinatoaluminium methoxide reacts reversibly with carbon dioxide in the presence of 1-methylimidazole, and this carbon dioxide is activated to react with propylene oxide to produce propylene carbonate under atmospheric pressure and at room temperature.

In the course of our studies on the reaction of carbon dioxide with organometallic compounds,[1-3] we have found that carbon dioxide reacts with tetraphenylporphinatoaluminium ethyl in the presence of 1-methylimidazole only in visible light, but not in the dark.[4] Further studies on the reaction of porphinatoaluminium complex with carbon dioxide have led to an interesting finding that tetraphenylporphinatoaluminium methoxide can be a carrier of carbon dioxide which is activated enough to easily react with propylene oxide.

Experimental

Materials. α,β,γ,δ-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid.[5-6] Propylene oxide was purified by refluxing over potassium hydroxide, then fractional distillation. 1-Methylimidazole (Im) was purified by distillation over calcium hydride under reduced pressure. Dichloromethane was washed with sulfuric acid followed by water, dried over calcium chloride and then calcium hydride, and distilled over calcium hydride in a nitrogen atmosphere.

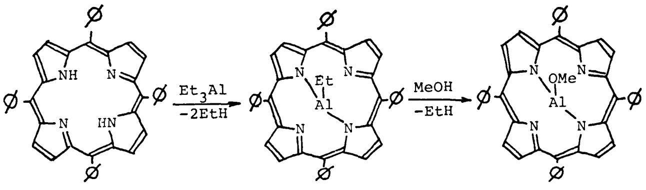
Carbon dioxide was purified by passing through a series of columns packed with copper(II) sulfate, potassium hydrogen carbonate, reduced copper, phosphorus pentaoxide and activated copper(II) oxide. Triethylaluminium was purified by distillation in a nitrogen atmosphere under reduced pressure (111 °C/24 mmHg).

Measurement. Infrared spectra were measured in a fixed cell (0.1—1.0 mm) using a Hitachi EPI-G3 spectrophotometer. Ultraviolet and visible spectra were measured in a quartz cell of length 0.1 cm using Shimadzu RSP-7B spectrophotometer. ^1H NMR spectra were measured using a JEOL 4H-A type spectrometer.

Gas chromatographic analysis was carried out using a Yanagimoto Model G80 gas chromatograph with the column of 1—1.5 m packed with silica gel with helium as the carrier gas. The composition of propylene oxide–carbon dioxide copolymer was determined by the ^1H NMR spectrum of its chloroform solution.[7]

Average molecular weight of the polymer was measured by using Toyo Soda HLC-802UR high speed liquid chromatograph.

Procedure. *Formation of Tetraphenylporphinatoaluminium Methoxide (TPPAlOMe) by the Reaction of Tetraphenylporphinatoaluminium Ethyl (TPPAlEt) with Methanol*: A 200 ml two-necked Pyrex flask containing tetraphenylporphine ($TPPH_2$; 3.07 g, 5.0 mmol) was purged with nitrogen, and dichloromethane (150 ml) was added to dissolve $TPPH_2$. Triethylaluminium (0.69 ml, 5.0 mmol) was added slowly to the solution in a nitrogen stream at room temperature to give a solution of TPPAlEt in a few minutes.[4] The solvent was removed under reduced pressure from this system, the purple residue was dissolved in methanol (100 ml), and the solution was refluxed for three hours in a nitrogen atmosphere. After removing most of methanol under reduced pressure, remaining trace of methanol was removed as benzene azetrope. The resulting product was dark reddish-purple powder (about 3.3 g). Found C, 80.18; H, 4.81; N, 8.15%. Calcd for $C_{45}H_{31}N_4OAl$: C, 80.58; H, 4.66; N, 8.35%.



When dry hydrogen chloride was bubbled in the dichloromethane solution of the resulting product, the liberation of an equivalent amount of methanol to aluminium was detected in the solution by gas chromatography.

Reaction of Carbon Dioxide with TPPAlOMe: Reactions of tetraphenylporphinatoaluminium methoxide (TPPAlOMe) with carbon dioxide were carried out in a 20 ml quartz cell at 20 °C. The cell containing TPPAlOMe (0.168 g, 0.25 mmol), synthesized by the aforesaid method, was purged with nitrogen, and dichloromethane (20 ml) was added to dissolve TPPAlOMe. After the addition of 1-methylimidazole (0.033 g, 0.40 mmol), carbon dioxide was bubbled in the solution for one minute, and the reaction was followed by the infrared spectral measurement of the reaction mixture.

Reaction of Carbon Dioxide and Propylene Oxide with TPPAlOMe: *Reaction in Dichloromethane*: Carbon dioxide was bubbled into the dichloromethane solution (20 ml) of TPPAlOMe (0.168 g, 0.25 mmol) with 1-methylimidazole (0.033 g, 0.40 mmol), and after two hours propylene oxide (0.35 ml, 5.0 mmol) was added to the solution in a carbon dioxide stream.

The solvent was removed from the solution after 45 h under reduced pressure at room temperature, followed by the addition of 5% hydrochloric acid (about 30 ml). After the insoluble materials were filtered off, sodium chloride (about 1 g) and diethyl ether (about 100 ml) were added to the aqueous filtrate, and the reaction product was extracted into the ether layer. After the evaporation of diethyl ether, the product was isolated by distillation under reduced pressure as a colorless oily liquid (0.2 g), which was identified as propylene carbonate by infrared spectral measurement and gas chromatography. The yield was directly determined by gas chromatography of the reaction mixture.

Reaction in Propylene Oxide in the Presence of 1-Methylimidazole: The cell containing TPPAlOMe (0.168 g, 0.25 mmol) was purged with nitrogen and propylene oxide (8.3 g, 140 mmol) was added to dissolve TPPAlOMe. After the addition of 1-methylimidazole (0.033 g, 0.40 mmol), carbon dioxide was bubbled in the solution for one minute every 24 h.

After 96 h the reaction product was isolated by the same procedure as described above. In this case, about 1.2 g of propylene carbonate was obtained.

Reaction in Propylene Oxide in the Absence of 1-Methylimidazole: Carbon dioxide was bubbled in the propylene oxide solution (10 ml) of TPPAlOMe (0.12 or 0.25 mmol) for 1 min every 24 h. After 11 days, unreacted propylene oxide was removed from the reaction mixture under reduced pressure at room temperature. Diethyl ether was added to the residual viscous product, and the solvent was removed from the ether soluble part to obtain 9.3 g of propylene oxide–carbon dioxide copolymer.

Results and Discussion

Reaction of Carbon Dioxide with Tetraphenylporphinatoaluminium Methoxide (TPPAlOMe). When carbon dioxide was bubbled in a dichloromethane solution of TPPAlOMe in the presence of 1-methylimidazole (Im), a new carbonyl absorption band immediately appeared at 1697 cm^{-1} in the infrared spectrum of the reaction mixture (Fig. 1). If nitrogen gas was bubbled in this reaction mixture, this absorption band disappeared, and it appeared again by the introduction of carbon dioxide in the solution, indicating carbon dioxide reversibly reacted with TPPAlOMe in the presence of Im. In the absence of Im, no carbonyl absorption band was observed in the spectrum, in the reaction in 1 atm CO_2 at 20 °C for 120 h as well as in the reaction in 40 atm CO_2 at 60 °C for 20 h. No remarkable effect of irradiation of visible light was recognized in this reaction.

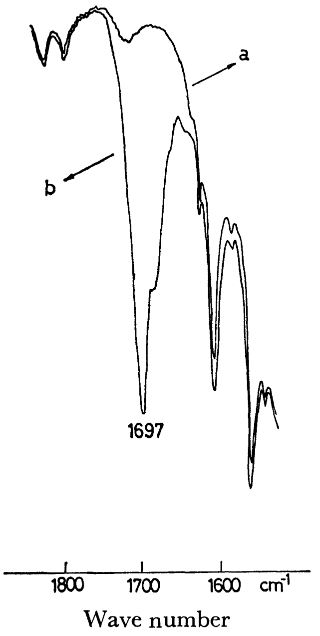


Fig. 1. Infrared spectra of the reaction mixture of tetraphenylporphinatoaluminium methoxide (TPPAlOMe) with carbon dioxide (CO_2) in the presence of 1-methylimidazole, TPPAlOMe; 0.25 mmol, 1-methylimidazole; 0.40 mmol, CH_2Cl_2; 20 ml, temp; 20 °C, a: before bubbling of CO_2, b: 20 min after bubbling of CO_2.

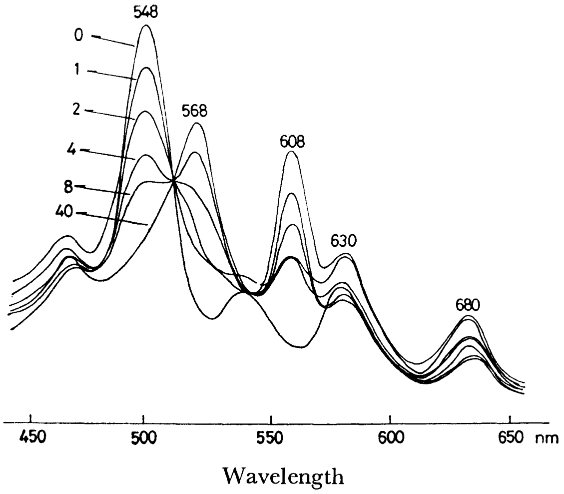


Fig. 2. Visible spectra of tetraphenylporphinatoaluminium methoxide (TPPAlOMe) and tetraphenylporphinatoaluminium methoxide–1-methylimidazole system in dichloromethane, TPPAlOMe; 7.0×10^{-3} mmol, CH_2Cl_2; 20 ml, 1-methylimidazole; 0, 7.0×10^{-3}, 1.4×10^{-2}, 2.8×10^{-2}, 5.6×10^{-2}, 2.8×10^{-1} mmol. The number in the figure represents the mole ratio of 1-methylimidazole to TPPAlOMe.

Figure 2 shows the visible spectra of TPPAlOMe and TPPAlOMe–Im (1 : 0.5—1 : 40) systems in dichloromethane at room temperature. The absorption maximum of the TPPAlOMe spectrum shifted from 548 to 568 nm in the presence of a sufficient amount of Im, and an isosbestic point was observed at 557 nm, which indicates the coordination of Im to TPPAlOMe probably as an axial ligand on the opposite side of methoxyl group with respect to the porphine ring.

As to the reactivity of other aluminium alkoxides with carbon dioxide, diethylaluminium ethoxide does not react with carbon dioxide even at 100 °C in the presence of several tertiary amines.[8] Thus, the reversible reaction with carbon dioxide at room temperature and under atmospheric pressure is very characteristic of the present system.

Reaction of Carbon Dioxide and Propylene Oxide with TPPAlOMe. Reaction in Dichloromethane in the Presence of 1-Methylimidazole: When the solution of TPPAlOMe with 1-methylimidazole (Im), saturated with carbon dioxide, was added by propylene oxide, the absorption at 1697 cm^{-1}, which was already observed in the TPPAlOMe-Im-CO_2 system, increased immediately (Fig. 3(A)). After three hours, a new carbonyl absorption band centered at 1805 cm^{-1} appeared, assigned to C=O stretching vibration of cyclic carbonate (propylene carbonate). And then after about 25 h other carbonyl absorption bands appeared at 1675 and 1750 cm^{-1}, which did not disappear by bubbling nitrogen gas or by removing the solvent. The band at 1750 cm^{-1} is considered due to linear carbonate as mentioned in the latter part of this paper, but the assignment of the band at 1675 cm^{-1} is not made at present.

The behavior of the absorption band at 1697 cm^{-1} is particularly interesting as shown in Fig. 3(B). As long as sufficient carbon dioxide existed in the solution as indicated by the absorption at 2340 cm^{-1}, the band at

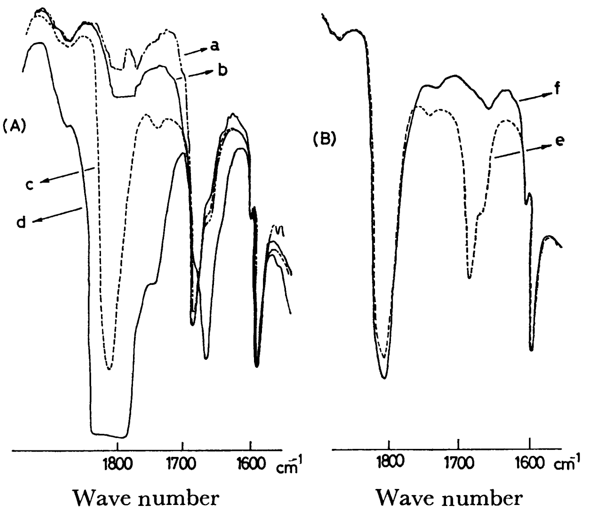


Fig. 3. Infrared spectra of the reaction mixture of tetraphenylporphinatoaluminium methoxide (TPPAlOMe), carbon dioxide (CO_2) and propylene oxide in the presence of 1-methylimidazole, TPPAlOMe; 0.25mmol, 1-methylimidazole; 0.40 mmol, PO; 5.0 mmol, CO_2; bubbling, (A); a: before addition of propylene oxide, b: 3 h after addition c: 25 h, d: 43 h, (B); e: when free CO_2 exists in the reaction mixture, f: when there remains no free CO_2 in the system.

1697 cm^{-1} did not change its intensity. When the solution became deficient in carbon dioxide, it diminished rapidly, while the absorption band at 1805 cm^{-1} increased. Supply of carbon dioxide here in the solution made absorption band at 1697 cm^{-1} strong again. Thus, the absorption band at 1697 cm^{-1} is due to carbon dioxide activated by the TPPAlOMe-Im complex, which reacts immediately with propylene oxide to produce propylene carbonate at room temperature and under atmospheric pressure.

The formation of propylene carbonate proceeded catalytically with respect to TPPAlOMe: for example, 2.7 equivalent in dichloromethane and 4.0 equivalent in propylene oxide under 1 atm CO_2 at 20 °C, after 2.5 h, respectively.

As to other amines than Im, pyridine behaved similarly, showing a reversible absorption band at 1695 cm^{-1} in the infrared spectrum of the reaction system TPPAlOMe-pyridine-CO_2. In contrast, no new carbonyl absorption band was observed when carbon dioxide was bubbled in the TPPAlOMe-triethylamine system. However, when propylene oxide was added to the solution, a reversible absorption band appeared at 1697 cm^{-1}. Similar results were obtained in the case of *N*,*N*-dimethylbenzylamine or *N*,*N*-dimethylaniline. Nevertheless, propylene carbonate could be produced from propylene oxide and carbon dioxide under mild reaction conditions by using TPPAlOMe coupled with amine, such as 1-ethylimidazole, pyridine, picolines, *N*,*N*-dimethylbenzylamine, triethylamine, tributylamine, triethylenediamine and hexamethylenetetraamine.

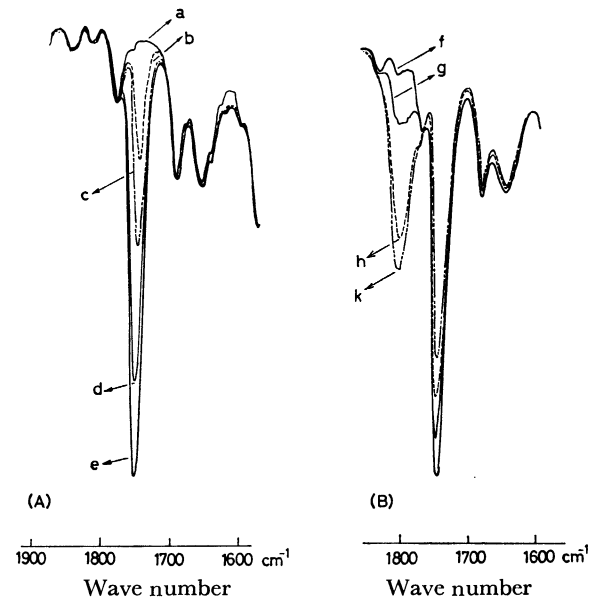


Fig. 4. Infrared spectra of the reaction mixture of tetraphenylporphinatoaluminium methoxide (TPPAlOMe), carbon dioxide (CO_2) and propylene oxide, (A); TPPAlOMe; 0.25 mmol, propylene oxide; 10 ml, CO_2; bubbling every 24 h, a: before bubbling of CO_2, b: 18 h after bubbling of CO_2, c: 44 h, d: 92 h, e: 167 h, (B) when there exists no free CO_2. Added 1-methylimidazole; 0.40 mmol, f: 20 min after addition of 1-methylimidazole, g: 2 h, h: 33 h, k: 49 h.

However, under atmospheric pressure and at room temperature, a mixture of only carbon dioxide, propylene oxide and tertiary amine, without TPPAlOMe, could not produce propylene carbonate.

Reaction in Propylene Oxide in the Absence of 1-Methylimidazole: When TPPAlOMe, carbon dioxide and propylene oxide reacted in the absence of amine, the infrared spectra of the reaction mixture showed a carbonyl absorption band only at 1750 cm^{-1} (Fig. 4(A)) which was assigned to C=O stretching vibration of linear carbonate. In fact, from this reaction mixture was obtained 9.3 g of propylene oxide-carbon dioxide copolymer, which consisted of 15 mol % of oxycarbonyl and 85 mol % of oxy(2-methylethylene) units, and the average molecular weight was about 4000.[9]

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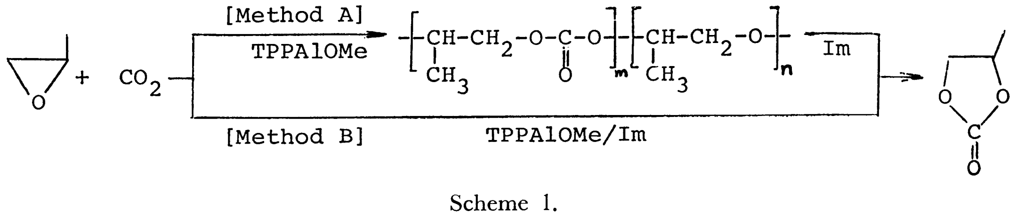
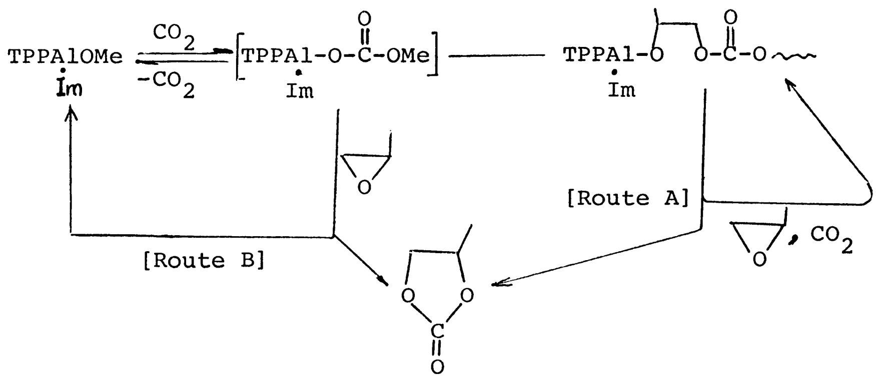


Scheme 1.



Scheme 2.

system, followed by the addition of Im or *N*,*N*-dimethylbenzylamine, the intensity of the absorption band at 1750 cm^{-1} decreased and an absorption at 1805 cm^{-1} appeared (Fig. 4(B)).

Therefore, propylene carbonate may be formed from the cyclization of carbon dioxide–propylene oxide copolymer (linear polyether-carbonate) by the effect of amine (Scheme 1).

However, as the formation reaction of propylene carbonate (PC) in the TPPAlOMe–Im–CO_2–propylene oxide system (Method B; 2.7 mol PC/mol TPPAlOMe/2.5 h) proceeds much faster than that *via* carbon dioxide–propylene oxide copolymer (Method A; 0.1 mol PC/mol TPPAlOMe/2.5 h), there seems to be another route than that *via* the copolymer, in which TPPAlOMe–Im–CO_2 complex reacts with propylene oxide to produce propylene carbonate directly.

Conclusion

Possible routes for the reaction in TPPAlOMe–Im–CO_2–propylene oxide system are shown in Scheme 2. In route A, carbon dioxide inserts between Al–OMe bond reversibly, propylene oxide reacts into the Al-carbonate bond thus formed, and the repeating reaction of propylene oxide and CO_2 results in the formation of copolymer. This copolymer may be gradually cyclized to propylene carbonate in the presence of amine, as actually confirmed. However, there still remains the possibility of the existence of another direct route, B, because of the difference in the rates of the formation of propylene carbonate in two methods of Scheme 1 (directly from TPPAlOMe–amine–CO_2–propylene oxide system, and *via* copolymer). Although TPPAlOMe–Im–CO_2 complex, having infrared absorption at 1697 cm^{-1}, would be an aluminium alkyl carbonate as shown in Scheme 2, the structure has not yet been confirmed, because of its highly reversible, unstable nature.

As the conclusion, TPPAlOMe–1-methylimidazole complex is a carrier of activated carbon dioxide which is able to react readily with propylene oxide to give propylene carbonate even under atmospheric pressure of carbon dioxide and at room temperature.

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