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Reaction of Carbon Dioxide with Tetraphenylporphinatoaluminium Ethyl in Visible Light

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Tetraphenylporphinatoaluminium ethyl reacts with carbon dioxide in the presence of 1-methylimidazole to produce tetraphenylporphinatoaluminium propionate in the presence of visible light but not in the dark.

In the photosynthesis of green plants, carbon dioxide is fixed and reduced by species activated by the energy of light in visible region of the spectrum which is absorbed by and transferred from chlorophylls——a dihydroporphyrin system. In this connection, the reaction of carbon dioxide with species activated by visible light is very interesting.

In the course of the present study on the reaction of carbon dioxide with organometallic compounds and related systems,$^{1-3)}$ it was found that the reaction of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoaluminium ethyl with carbon dioxide was induced by visible light in the presence of 1-methylimidazole.

Experimental

Materials. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid.$^{4)}$ Contaminated $\alpha,\beta,\gamma,\delta$-tetraphenylchlorin was transformed into $TPPH_2$ using 2,3-dichloro-5,6-dicyanobenzoquinone in boiling methylene chloride.$^{5)}$

1-Methylimidazole was prepared by the alkylation of imidazole with methyl iodide in liquid ammonia.$^{6)}$

Carbon dioxide was purified upon passage through a series of columns packed with cupric sulfate, potassium bicarbonate, reduced copper, phosphorous pentoxide and activated cupric oxide.

Methylene chloride 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. Benzene was washed with sulfuric acid and then with water, dried over calcium chloride, and distilled in the presence of sodium wire in a nitrogen atmosphere.

Triethylaluminium was purified by distillation under reduced pressure (111 °C/24 Torr).

Procedure. *Formation of Tetraphenylporphinatoaluminium Ethyl (TPPAlEt) by the Reaction of Tetraphenylporphine ($TPPH_2$) with Triethylaluminium*: The reaction of $TPPH_2$ and triethylaluminium was carried out in a quartz cell having four flat faces (2.5×2.5×4.0 cm) fitted with a three-way cock. The cell containing $TPPH_2$ (0.92 g, 1.5 mmol) was purged with nitrogen and a solvent (20 ml) was added to dissolve the $TPPH_2$. Triethylaluminium (0.21 ml, 1.5 mmol) was added slowly to the solution using a syringe from the three-way cock in a nitrogen stream at room temperature. The reaction of $TPPH_2$ with triethylaluminium was completed within a few minutes under the evolution of two equivalent amounts of ethane (Fig. 1) which was identified by gas chromatography and measured volumetrically by a mercury-sealed gas burette. By adding an excess of hydrochloric acid to this reaction mixture, a stoichiometric amount of ethane to aluminium was evolved, indicating the existence of one ethyl-aluminium bond.

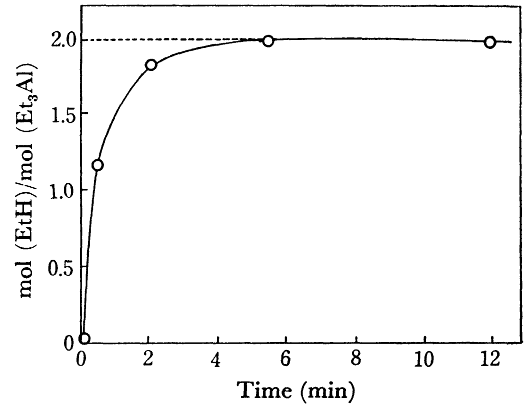


Fig. 1. Reaction of tetraphenylporphine($TPPH_2$) and triethylaluminium(Et_3Al), $TPPH_2$; 1.8 mmol, Et_3Al; 1.8 mmol, CH_2Cl_2; 30 ml, temp; 30 °C.

In the ^{1}H NMR spectra of the reaction mixture, the ratio of phenyl protons ($\delta=8.22$ ppm (ortho) and $\delta=7.85$ ppm (meta and para)) to β-protons on the pyrrole ring ($\delta=9.05$ ppm) of the porphine was found to be 5:2, excluding the possibility of the reaction of triethylaluminium with the C–H protons of the porphine ring. Methylene (-aluminium) and methyl signals are found at $\delta=-6.35$ ppm (quartet) and $\delta=-3.40$ ppm (triplet), respectively, which occur for a much higher magnetic field compared with the methylene ($\delta=0.46$ ppm) and methyl ($\delta=1.26$ ppm) signals of triethylaluminium. This fact clearly indicates that the ethyl group is attached to the aluminium atom as an axial ligand and is affected by the ring current of the porphine ring.

From these results, $TPPH_2$ and triethylaluminium are considered to react to form tetraphenylporphinatoaluminium ethyl (TPPAlEt):

$$TPPH_2 + Et_3Al \longrightarrow TPPAlEt + 2EtH$$

A similar reaction for triethylaluminium with octaethylporphyrin has been reported,$^{7)}$ though a detailed examination of the reaction was not presented.

Reaction of Carbon Dioxide with TPPAlEt: Reactions of tetraphenylporphinatoaluminium ethyl (TPPAlEt) with carbon dioxide were carried out in the quartz cell which was placed in a glass water bath at 25 °C. Several hours after the formation of TPPAlEt, 1-methylimidazole (0.13 ml, 1.5 mmol) was added, followed by carbon dioxide bubbling for 5 min, and the mixture was irradiated for a given period of time by visible light (450—750 nm) obtained from a 500-W xenon lamp placed at a distance of 10 cm outside the water bath. Light of higher and lower wavelength was eliminated using appropriate filters.

Separation of the Reaction Product: In order to obtain the reaction product in an amount sufficient to conduct further examinations, carbon dioxide was bubbled for 10 min at room temperature in a 300 ml two-necked Pyrex flask which

contained $TPPH_2$ (6.14 g, 10 mmol), Et_3Al (1.37 ml, 10 mmol) and 1-methylimidazole (1.00 ml, 10 mmol). After an appropriate period of time, hydrogen chloride gas was bubbled through the above reaction mixture, and the solvent and excess hydrogen chloride were removed under reduced pressure at room temperature giving a solid residue, which was further treated in accordance with the following two procedures: 1) 1-Butanol (5 ml), concd sulfuric acid (1 ml) and sodium sulfate (5 g) were added to the residue, and the mixture was heated at 130 °C for 20 min. The reaction mixture was concentrated and extracted with hexane, then fractionated into several parts employing column chromatography on silica gel using hexane as the eluent. Some fractions which were found to contain butyl propionate by gas chromatography were collected and purified by passage through a column of silica gel using a mixture of hexane and methylene chloride as the eluent, then through another silica gel column using methylene chloride as the eluent. After removing the solvent from the fractions, a liquid was obtained, and its IR spectrum agreed with that of authentic butyl propionate.
2) An ether solution of diazomethane (in great excess with respect to TPPAlEt) was added to the residue at room temperature, and after one day the reaction mixture was concentrated to remove the solvent by evaporation and subjected to gas chromatography.

Measurement. Infrared spectra were measured in a fixed cell (0.1 mm) using a Hitachi EPI-G3 spectrophotometer. Ultraviolet and visible spectra were obtained with the sample in a quartz cell (of length 0.1 cm) using a 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 dioctyl phthalate, silica gel, polyethylene glycol, and with hydrogen as the carrier gas.

Results

Reaction of Tetraphenylporphinatoaluminium Ethyl with Carbon Dioxide. When carbon dioxide was bubbled in a solution of TPPAlEt in methylene chloride in the presence of from one to three equivalent amounts of 1-methylimidazole and irradiated by visible light, a new carbonyl absorption band appeared at 1642 cm^{-1} in the infrared spectrum (Figs. 2 and 3). The figures show that the absorption increased with time fairly rapidly but substantially ceased after about 40 h. On the other hand, absorption due to carbon dioxide at 2340 cm^{-1} decreased as the band at 1642 cm^{-1} increased. In the dark, however, absorption at this frequency was very slight even after 48 h. The temperature in the irradiated case was the same as that for the measurements in the dark. The same effect was also observed when benzene was used as the solvent.

In the absence of 1-methylimidazole, no absorption at 1642 cm^{-1} was present even when the system was irradiated by visible light. Thus, TPPAlEt reacts with carbon dioxide only when irradiated by visible light in the presence of 1-methylimidazole.

Reaction Products. In the reaction of carbon dioxide and TPPAlEt in methylene chloride for 20 h, treatment of the reaction mixture with hydrogen chloride gas followed by 1-butanol gave butyl propionate in a 4% yield based on the amount of porphinatoaluminium ethyl.

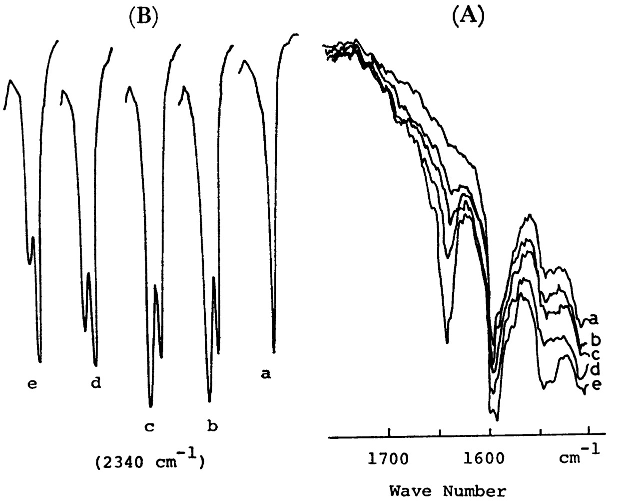


Fig. 2. Infrared spectra of the reaction mixture of tetraphenylporphinatoaluminium ethyl(TPPAlEt) with carbon dioxide(CO_2, bubbling for 5 min) in the presence of 1-methylimidazole.
TPPAlEt; 3mmol, 1-methylimidazole; 3mmol, CH_2Cl_2; 50ml, temp; 25 °C; (A) a; before bubbling of CO_2, b; 20 min, c; 40 min, d, 60 min, e; 14 h; (B) Absorption due to CO_2.

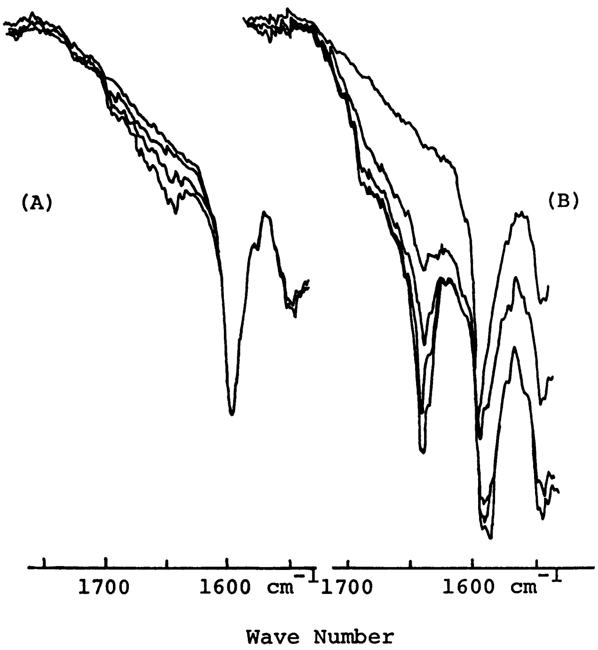
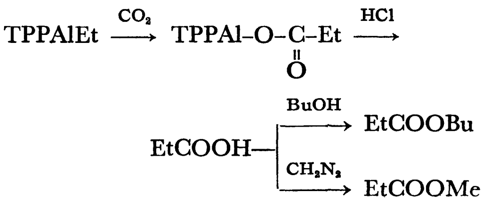


Fig. 3. Infrared spectra of the reaction mixture of tetraphenylporphinatoaluminium ethyl(TPPAlEt) with carbon dioxide(CO_2) in dark(A) and under radiation of visible light(B); TPPAlEt; 1.5mmol, 1-methylimidazole; 1.5mmol, CO_2 bubbling for 5 min.

In another reaction, treatment with diazomethane gave methyl propionate in a 12% yield based on the amount of porphinatoaluminium ethyl. Thus, carbon dioxide was inserted into aluminium-ethyl bond of TPPAlEt to form aluminium propionate.



$$\text{TPPAlEt} \xrightarrow{CO_2} \text{TPPAl-O-}\underset{\overset{\|}{O}}{C}\text{-Et} \xrightarrow{HCl}$$

$$\text{EtCOOH}-\begin{cases} \xrightarrow{BuOH} \text{EtCOOBu} \\ \xrightarrow{CH_2N_2} \text{EtCOOMe} \end{cases}$$

Other expected products, such as 3-ethyl-3-pentanol, 3-pentanol and ethyl formate were not detected in the reaction mixture after treatment with hydrogen chloride.

Attempted direct esterification of the reaction mixture with methyl iodide and ethyl iodide at 130 °C were unsuccessful.

Discussion

As described above, irradiation by visible light in the presence of 1-methylimidazole is necessary for the reaction of TPPAlEt and carbon dioxide. Figure 4 shows the visible spectra of the TPPAlEt and TPPAlEt–1-methylimidazole (1 : 1) system in methylene chloride at room temperature. The absorption maximum of the TPPAlEt spectrum shifted from 548 to 568 nm in the presence of 1-methylimidazole. By changing the ratio of the amount of 1-methylimidazole to that of TPPAlEt, an isosbestic point was observed at 557 nm, and the strength of the absorption maximum at 568 nm remained almost the same when a more than equimolar amount of 1-methylimidazole was added. Therefore, 1-methylimidazole is considered to form an equimolar coordination compound with TPPAlEt in methylene chloride. Such coordination of 1-methylimidazole possibly to the aluminium is considered to increase the nucleophilicity of the ethyl group.

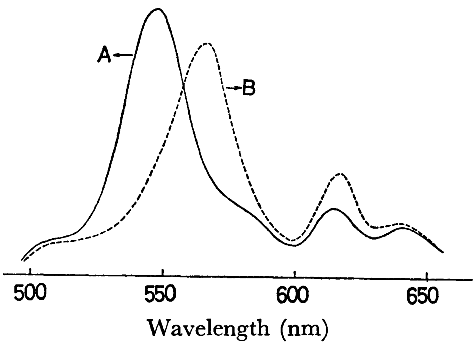


Fig. 4. Visible spectra of tetraphenylporphinatoaluminium ethyl(A) and tetraphenylporphinatoaluminium ethyl-1-methylimidazole(1:1) system(B) in methylene chloride, TPPAlEt; 7.0×10^{-3} mmol, CH_2Cl_2; 20ml, 1-methylimidazole; 7.0×10^{-3} mmol.

However, irradiation by visible light is essential for the reaction. Since neither 1-methylimidazole nor the aluminium-ethyl bond have absorptions in the visible region, it is reasonable to consider that the aluminium-ethyl bond of the TPPAlEt–1-methylimidazole complex was indirectly activated by visible light excitation of the porphine ring.

Such an activation effect by visible light on the reaction of carbon dioxide is very interesting in relation to the electron transfer in photosynthesis.

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