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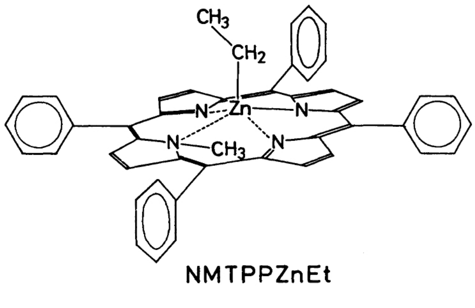
LIGHT-INDUCED FIXATION OF CARBON DIOXIDE WITH ZINC PORPHYRIN

Shohei INOUE,* Masahiro NUKUI, and Fumitoshi KOJIMA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

N-Methyltetraphenylporphinatozinc ethyl reacts with carbon dioxide in the presence of secondary amine or alcohol to form novel metalloporphyrins containing metal carbamate or carbonate group. Some of these reactions are accelerated remarkably upon irradiation with visible light.

Photochemical fixation of carbon dioxide is of much interest in connection with biochemical carbon dioxide fixation such as photosynthesis as well as from the viewpoint of the recycle of carbon resources.1) However, the examples of non-biological photochemical fixation of carbon dioxide have been very limited.2) In the present report is described a novel light-induced fixation of carbon dioxide by alkyl-zinc porphyrin in the presence of secondary amine or alcohol to give zincporphyrin containing zinc carbamate or carbonate group.

A benzene solution (0.7 cm^3) of a secondary amine (0.18 mmol) was added to a benzene solution (6 cm^3) of N-methyltetraphenylporphinatozinc ethyl (NMTPPZnEt)3) (0.16 mmol) in a 30 cm^3 Pyrex flask fitted with a three-way cock and wrapped in aluminum foil to keep the system in the dark. Carbon dioxide was bubbled into the reaction mixture for 1 min, the mixture was stirred for 24 h at room temperature, and the solution was subjected to evaporation under reduced pressure to remove the solvent, excess amine, and carbon dioxide. Obtained purple powder was dissolved in dichloromethane or benzene and subjected to IR, ^1H-NMR, and



NMTPPZnEt

^{13}C-NMR spectroscopy. For example, in the case of diethylamine, the IR spectrum of the product exhibits a new band at 1560 cm^{-1}. This indicates that the resulting product contains a zinc carbamate (ZnO_2CNEt_2) moiety. ^{1}H-NMR spectrum (Fig. 1) shows new resonances at δ1.31(q) and -0.36(t) assigned to the protons of $N-C\underline{H}_2-CH_3$ and $N-CH_2-C\underline{H}_3$, respectively, at much higher magnetic field than those for ethylzinc diethylcarbamate[4)] ($EtZnO_2CNEt_2$, $N-C\underline{H}_2-CH_3$ and $N-CH_2-C\underline{H}_3$ at δ3.30(q) and 1.10(t)). Thus, the carbamate group is bound to the zinc atom in the porphyrin ring and affected by the ring current. Relative intensities of the resonances confirm the equimolar ratio of the carbamate group to N-methyl group of the porphyrin. In the ^{13}C-NMR spectrum of the product, the resonances at δ12.50, 38.59, and 31.34 are assigned to the carbons of $N-CH_2-\underline{C}H_3$, $N-\underline{C}H_2-CH_3$, and N-methyl group of the porphyrin, respectively. When carbon dioxide enriched in ^{13}C was employed in the reaction, the resonance at δ157.2 assigned to the carbonyl carbon of carbamate group was much enhanced. In the IR spectrum of this product, a new band due to carbonyl group appeared at 1540 cm^{-1} instead of 1560 cm^{-1}.

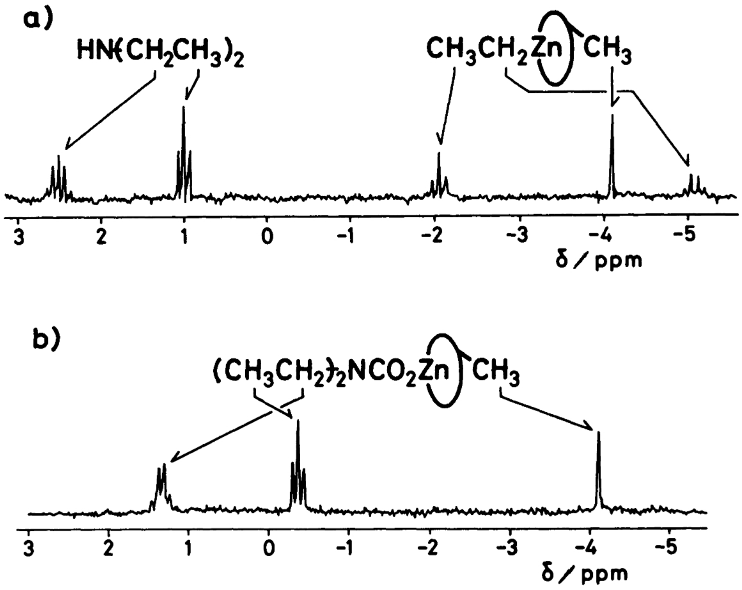


Fig. 1. ^{1}H-NMR spectra in benzene of (a)the mixture of NMTPPZnEt and Et_2NH, (b)$NMTPPZnO_2CNEt_2$.

From these results, it is concluded that NMTPPZnEt reacts with carbon dioxide and diethylamine to give N-methyltetraphenylporphinatozinc diethylcarbamate ($NMTPPZnO_2CNEt_2$) quantitatively. Similarly, NMTPPZnEt was found to react with carbon dioxide in the presence of other secondary amines, such as dipropylamine, diisopropylamine and diisobutylamine, to yield the corresponding porphinatozinc carbamates. The fixation of carbon dioxide on zinc porphyrin was also observed in the system consisting of NMTPPZnEt, ethanol, and carbon dioxide in benzene at room temperature to form N-methyltetraphenylporphinatozinc ethylcarbonate ($NMTPPZnO_2COEt$)(IR, $\nu_{C=O}$ 1664 cm^{-1}).[5,6)]

$$\text{NMTPPZnEt} + \text{HX} + \text{CO}_2 \longrightarrow \text{NMTPPZnO}_2\text{CX} + \text{EtH}$$

$$\text{X=NR}_2\text{;R=Et,Pr}^n\text{,Pr}^i\text{,Bu}^i$$

$$\text{OR ;R=Et,Bu}^t$$

Of particular interest is the accelerating effect of visible light on the reaction of NMTPPZnEt, carbon dioxide, and amine or alcohol. For example, when the reaction of NMTPPZnEt and carbon dioxide in the presence of diisopropylamine was carried out at room temperature in the dark, the conversion of NMTPPZnEt was only about 29% after 196 min, based on the signal intensity of Zn-Et group in the ^{1}H-NMR spectrum of the reaction mixture. On the other hand, in the reaction carried out in a Pyrex water bath and irradiated from outside by Xe lamp (>420nm with a filter), the conversion increased remarkably to 100% after 120 min (Fig. 2). Accelerating effect of visible light, though smaller, was also observed in the reaction of NMTPPZnEt, carbon dioxide, and diethylamine. The photo-acceleration was also observed in the reaction of NMTPPZnEt, carbon dioxide, and tert-butyl alcohol in dichloromethane, to form NMTPPZnO$_2$COBu^t.[7)]

NMTPPZnEt did not react with carbon dioxide under the conditions examined. Neither secondary amine nor alcohol reacted with NMTPPZnEt even upon irradiation in the absence of carbon dioxide. Therefore, NMTPPZnO$_2$CNR$_2$ or NMTPPZnO$_2$COR is considered to be formed <u>via</u> the reaction of NMTPPZnEt with dialkylcarbamic acid or monoalkyl carbonate from amine or alcohol and carbon dioxide, respectively. The zinc-carbon bond of NMTPPZnEt is considered to be activated indirectly <u>via</u> excitation of porphyrin ring upon irradiation with visible light,[8,9)] resulting in the photo-acceleration of the reaction with carbamic acid or monoalkyl carbonate.

Thus, carbon dioxide is fixed to alkylzincporphyrin under mild condition to give porphyrin complexes containing metal carbamate or carbonate group, where the irradiation with visible light exhibits a dramat-

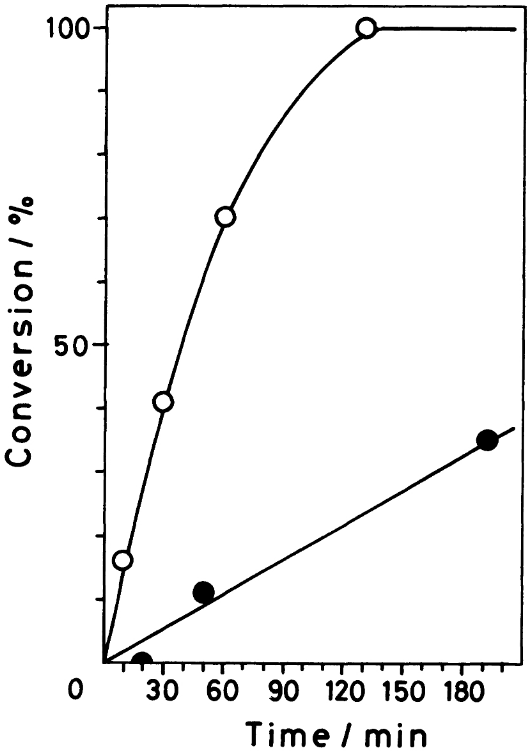


Fig. 2. Reaction of NMTPPZnEt and carbon dioxide in the presence of Pr$^i{}_2$NH in benzene, o: upon irradiation, ●: in the dark.

ic acceleration effect.

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3) NMTPPZnEt was prepared by the reaction between N-methyl-5,10,15,20-tetraphenylporphine and diethylzinc in benzene in the dark and in nitrogen atmosphere.$^{7)}$

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5) ^{1}H-NMR data of NMTPPZnX$^{a)}$ are as follows. X=Et:δ -2.9(3H,t,Zn-CH$_2$-C$\underline{H}_3$), -6.0 (2H,q,Zn-C$\underline{H}_2$-CH$_3$), -4.00(3H,s,N-CH$_3$). X=O$_2$CNEt$_2$:δ 1.31(4H,q,N-C$\underline{H}_2$-CH$_3$), -0.36 (6H,t,N-CH$_2$-C$\underline{H}_3$), -4.10(3H,s,N-CH$_3$). X=O$_2$CNPr$^n{}_2{}^{b)}$:δ 0.11(4H,t,N-C$\underline{H}_2$-CH$_2$-CH$_3$), -0.06(10H,m,N-CH$_2$-C$\underline{H}_2$-C$\underline{H}_3$), -3.92(3H,s,N-CH$_3$), X=O$_2$CNPr$^i{}_2$:δ -0.34(12H,d,N-CH-(C$\underline{H}_3$)$_2$), -4.10(3H,s,N-CH$_3$).X=O$_2$CNBu$^i{}_2$:δ 1.24(4H,d+2H,m,N-C$\underline{H}_2$-C$\underline{H}$-(CH$_3$)$_2$), -0.17 (12H,d,N-CH$_2$-CH-(C$\underline{H}_3$)$_2$), -4.07(3H,s,N-CH$_3$). X=O$_2$COEt:δ 2.19(2H,q,O-C$\underline{H}_2$-CH$_3$), -0.12(3H,t,O-CH$_2$-C$\underline{H}_3$), -4.02(3H,s,N-CH$_3$). X=O$_2$COBu$^{t\ c)}$:δ -0.22(9H,s,O-C-(C$\underline{H}_3$)$_3$), -3.96(3H,s,N-CH$_3$). a)In benzene, b)in CDCl$_3$, c)in CH$_2$Cl$_2$.

6) The elemental analyses of NMTPPZnO$_2$CX recrystallized from benzene/hexane are as follows. X=NEt$_2$: Found:C, 74.40; H, 5.26; N, 8.25%. Calcd for C$_{48}$H$_{38}$N$_5$:C, 74.21; H, 5.11; N, 8.65%. X=NPr$^n{}_2$, Found:C, 74.16; H, 5.69; N, 7.87%. Calcd for C$_{52}$H$_{42}$N$_5$:C, 74.49; H, 5.15; N, 8.52%. X=OEt: Found:C, 74.08; H, 4.16; N, 7.00%. Calcd for C$_{46}$H$_{33}$ON$_4$:C, 73.70; H, 4.64; N, 7.16%.

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