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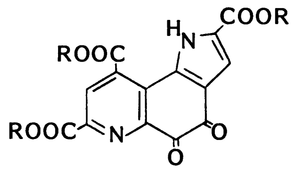
Redox System of Palladium-Trimethyl Ester of Coenzyme PQQ

Toshikazu HIRAO, Toshihide MURAKAMI, Mitsuru OHNO, and Yoshiki OHSHIRO*
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamadaoka, Suita, Osaka 565

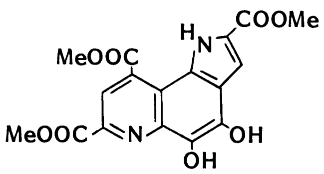
Trimethyl ester of coenzyme PQQ (PQQTME) and $PdCl_2$ constitute an effective redox system on treatment with terminal olefin in DMF-H_2O, which permits the $PdCl_2$-PQQTME catalyzed Wacker oxidation reaction under oxygen.

PQQ (1) is a novel coenzyme of alcohol dehydrogenase, methanol dehydrogenase, aldehyde dehydrogenase, glucose dehydrogenase, amine oxidase, etc.[1] A model system for PQQ-containing enzymes has been recently disclosed in a micelle-enhanced oxidation of amines and amino acids.[2] Quinone function of PQQ is considered to play an important role in the dehydrogenation reactions. We herein describe the first example for the redox system of PQQ derivatives with transition metals.

A large change in UV-VIS spectrum of trimethyl ester of PQQ (PQQTME, 2) was observed on treatment with 1-decene and $PdCl_2$ in DMF-H_2O under argon as shown in Fig. 1. The new species (absorption maximum 330 nm) is assigned to be the reduced



1 R=H
2 R=Me



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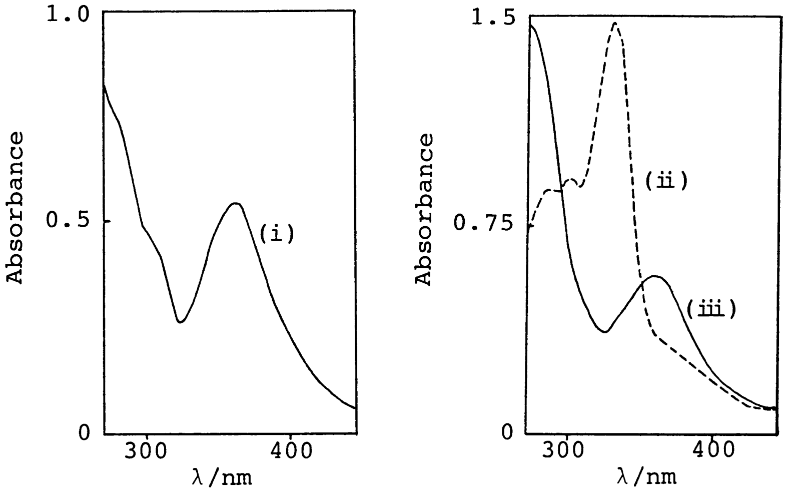
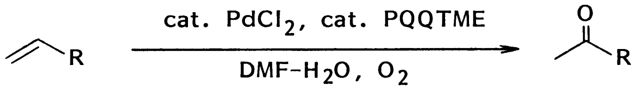


Fig. 1. UV-VIS spectra in the redox process of PQQTME. (i) PQQTME; solvent, DMF; [PQQTME]=4×10^{-5} M. (ii) PQQTME was treated with $PdCl_2$ (1 molar equiv.) and 1-decene (100 molar equiv.) in DMF-H_2O (4:0.1 V/V) at 20 °C for 1 h with bubbling argon to the solution. Thus obtained mixture was diluted with DMF for the spectrum measurement. [PQQTME deriv.]=4×10^{-5} M. (iii) Oxygen was bubbled to the solution in the cell at 20 °C for 3 h.

quinol 3, which was checked by comparison of its spectrum with that of the authentic sample. Only bubbling oxygen to the resultant solution led to reappearance of the PQQTME spectrum. The oxidation of the independently prepared quinol 3 with oxygen was found to be facilitated by the coexistence of $PdCl_2$. An efficent redox system is suggested to be achieved between PQQTME and palladium species.

The Wacker oxidation reaction was tried on these observations. Dropwise addition of terminal olefin to the solution of $PdCl_2$ (0.1 molar equiv.), PQQTME (0.1 molar equiv.) and H_2O (1400 molar equiv.) in DMF followed by stirring under oxygen at 60 °C for 3 h resulted in the formation of 2-alkanone; eg, 2-dodecanone was produced in 62% yield based on 1-dodecene. It should be noted that PQQTME



constitutes a catalytic oxidation-reduction cycle. The orthoquinone function seems to reoxidize the reduced palladium species generated in situ. $PdCl_2$ was superior to $Pd(OAc)_2$ as a catalyst. The yield was not raised even if 0.2 molar equiv. of PQQTME was employed. PQQ did not work well as a cocatalyst. Use of 1,7- or 1,10-phenanthrolinequinone gave a poor result maybe due to the coordination of palladium(II) species towards pyridine moiety opposite to the quinone group.$^{3)}$

Preliminary electrochemical measurement on the present system was done to get further insight. Cyclic voltammetry for the solution of PQQTME and $PdCl_2$ indicated a new high reduction wave (-0.06 V vs. SCE, 0.1 M Bu_4NPF_6/DMF-H_2O 10:1 V/V, platinum working electrode, scan rate 50 mV/s) in addition to the wave of PQQTME (-0.23 V). This finding suggests the in situ formation of the more active species for the oxidation reaction presumably via effective interaction or complexation although a large difference was not observed in UV-VIS spectra only by the addition of $PdCl_2$ to the solution of PQQTME.

Mediation of p-benzoquinone in the palladium-catalyzed oxidation reactions has been recently reported to require electrochemical or cobalt porphyrin catalyzed oxidation of the quinol.$^{4)}$ The above-mentioned results provide an example for efficient redox systems of coenzyme derivatives with transition metals, which is demonstrated to be synthetically useful. Further studies are now in progress.

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