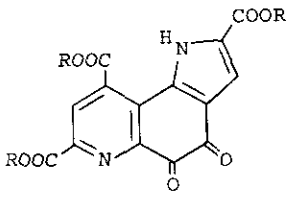
NOVEL FUNCTION OF THE PYRROLOQUINOLINE QUINONE, PQQ, ENHANCED BY MICELLE

Yoshiki OHSHIRO, Toshikazu HIRAO, and Toshio AGAWA
Department of Applied Chemistry, Faculty of Engineering, Osaka University
Yamada-oka 2-1, Suita, Osaka 565, Japan

Several types of alcohol dehydrogenase which is neither NAD nor flavin dependent have been found to contain a unique low molecular weight prosthetic group, which was assigned the pyrroloquinoline quinone 1 (PQQ or methoxatin). The mechanistic role of the coenzyme PQQ in the oxidation process, however, remains uncertain. We demonstrate the novel function of PQQ; oxidation of amines with PQQ is facilitated by the micelle.



1: R=H, PQQ

2: R=Me, PQQTME

Treatment of cyclohexylamine with PQQ in aqueous basic solution (pH 10.7) at room temperature under air gave cyclohexanone in 22% yield (based on 1) as a sole isolable product. The presence of cetyltrimethylammonium bromide (CTAB) in the system drastically enhanced the oxidation reaction, and the yield increased to 386%. This enhancement is assumed to be attributed to the micelle formation, which was ascertained by the measurement of the cmc.

Generation of PQQ was easily realized by the hydrolysis of the trimethyl ester of PQQ (PQQTME, 2), a key intermediate in a total synthesis, with aqueous basic solution. Thus obtained PQQ also exhibited the similar activity in the oxidation function. It should be noted that the present oxidation reaction was strongly influenced by the pH of the starting aqueous solution. The reaction at pH 6.7 gave cyclohexanone in 727% yield.

The present methodology was applied to oxidation of various amines. Benzylamine derivatives and cyclododecylamine were readily converted into the corresponding carbonyl compounds in high yields, respectively. The quinone group adjacent to pyrrole and pyridine rings seems to play an important role in the oxidation reaction. Oxygen is assumed to participate in regeneration of the active species in the catalytic cycle.

Enhancement of oxidation reactions with PQQ in the micellar environment is considered to be correlated with enzymatic reactions.