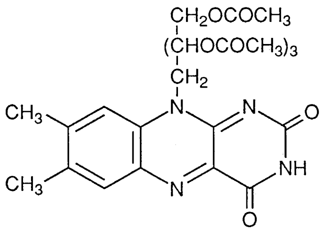
Double Mediatory System Involving a Flavin Analog and a *p*-Benzoquinone Derivative for Photoinduced Electrochemical Oxidation of Benzyl Alcohol to Benzaldehyde in Acetonitrile

Masashi Ishikawa,* Hiroyuki Okimoto, Masayuki Morita, and Yoshiharu Matsuda#
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755

(Received July 25, 1996)

The photoinduced electrochemical oxidation of benzyl alcohol to benzaldehyde in acidic acetonitrile proceeded with practically 100% product selectivity and ca. 100% current efficiency under visible-light irradiation in the presence of riboflavin-2',3',4',5'-tetraacetate (RF) as a mediator. A double mediatory system involving duroquinone as well as RF resulted in remarkable acceleration of the benzaldehyde formation with maintenance of both the high product selectivity and high current efficiency.

The electrochemical behavior of flavin coenzymes and their analogs have been extensively investigated in aqueous media, and flavins have been applied to various aqueous electrochemical systems.[1-3] In marked contrast to the aqueous electrolyte systems, little is known about the utilization of flavins to organic electrolyte systems,[4] mainly because typical flavins lack in solubility in organic electrolytes. On the other hand, in non-electrochemical systems the redox reactions between substrates and some modified flavin analogs soluble in organic solvents have been studied.[5-8] Among them, the effective oxidation of benzyl alcohol ($C_6H_5CH_2OH$) to benzaldehyde (C_6H_5CHO) by the excited state of the flavin analog in acetonitrile (MeCN) was reported.[6] The present study reports the photoinduced electrochemical oxidation of $C_6H_5CH_2OH$ to C_6H_5CHO with excellent product selectivity and with high current efficiency in MeCN utilizing a flavin analog soluble in MeCN, riboflavin-2',3',4',5'-tetraacetate (RF),[9] as a mediator. Especially, we propose herein a simple and effective method to accelerate this reaction with maintenance of both excellent product selectivity and high current efficiency; that is the photoinduced electrochemical double mediatory system involving a *p*-benzoquinone derivative as well as RF.



riboflavin-2',3',4',5'-tetraacetate (RF)

The electrolysis was performed under an argon atmosphere using a divided glass-beaker cell (30 cm^3), where the working electrode was a glassy carbon (GC) plate (1.0 cm^2), the counter electrode was a platinum sheet (8.0 cm^2), and the reference electrode was a silver/silver chloride electrode (Ag/AgCl). The supporting electrolyte was tetraethylammonium perchlorate (TEAP) [0.1 mol dm^{-3} (M)]. The electrochemical oxidation of $C_6H_5CH_2OH$ (1.0 x 10^{-2} M) proceeded at the GC electrode polarized at 0.5 V *vs.* Ag/AgCl in the presence of RF (3.3 x 10^{-3} M) and perchloric acid ($HClO_4$: 6.7 x 10^{-3} M) in MeCN to yield C_6H_5CHO, when the cell system under an argon atmosphere was irradiated with visible light (> 310 nm) as shown in Figure 1 (broken lines).[10] The conversion to C_6H_5CHO reached to ca. 90% in 25 h, and the current efficiency was nearly equal to 100% during the electrolysis. It is worth notable that the product selectivity to $C_6H_5CH_2OH$ was practically 100%. RF is known to be present as the protonated from (RFH$^+$) in MeCN containing the excess amount of $HClO_4$.[8] This RFH$^+$ is easily excited by visible-light irradiation, and the resulting excited species [(RFH$^+$)*] can oxidize $C_6H_5CH_2OH$ to give C_6H_5CHO and the protonated dihydro-RF (RFH$_3^+$) as depicted in Eq. 1.[6] During

$$C_6H_5CH_2OH + (RFH^+)^* \longrightarrow C_6H_5CHO + RFH_3^+ \quad (1)$$

the electrolysis, however, no presence of RFH$_3^+$ was detected, while considerable amount of the radical cation of dihydro-RF (RFH$_2^{+\bullet}$) was observed as shown in Figure 2 (broken lines). It has been known that RFH$_2^{+\bullet}$ is formed by the comproportionation between RFH$^+$ and RFH$_3^+$ in MeCN under an argon atmosphere as indicated in Eq. 2.[8] This process is an

$$RFH^+ + RFH_3^+ \rightleftharpoons 2RFH_2^{+\bullet} \quad (2)$$

equilibrium reaction, and in MeCN containing the excess amount of $HClO_4$ the equilibrium sifts dominantly to RFH$_2^{+\bullet}$.[8] Thus, RFH$_3^+$ formed in Eq. 1 may be immediately converted to RFH$_2^{+\bullet}$ by the comproportionation between RFH$_3^+$ and RFH$^+$

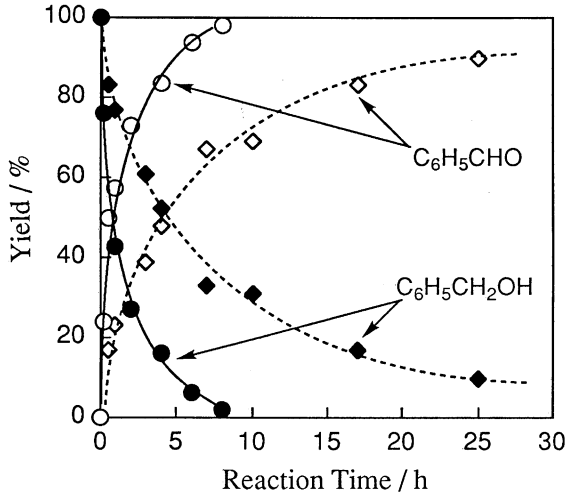


Figure 1. Electrochemical oxidation of $C_6H_5CH_2OH$ (1 x 10^{-2} M) mediated by RF (3.3 x 10^{-3} M) under visible-light irradiation in MeCN containing $HClO_4$ (3.3 x 10^{-2} M) and TEAP (0.1 M), ◆◇: in the absence of DQ; applied potential: 0.5 V (vs. Ag/AgCl), ●○: in the presence of DQ (5 x 10^{-3} M); applied potential: 0.75 V (vs. Ag/AgCl).[11]

(Eq. 2). This reaction, therefore, should decrease the RFH$^+$ concentration as observed in Figure 2 (broken lines). The decrease in RFH$^+$ is undesirable because it should result in a decrease in the rate of the photochemical reaction in Eq. 1. Thus, it is desirable to suppress the RFH$_2^{+\bullet}$ formation in order to accelerate the photochemical reaction. Recently, we found that *p*-benzoquinones, typically duroquinone (tetramethyl-*p*-benzoquinone: DQ), react with RFH$_3^+$ to yield the corresponding hydroquinone (DQH$_2$) and RFH$^+$ as shown in Eq. 3.[8] The

$$\mathrm{RFH_3^+ + DQ \xrightarrow{fast} RFH^+ + DQH_2} \qquad (3)$$

reaction of DQ with RFH$_3^+$ is much faster than the comproportionation between RFH$^+$ and RFH$_3^+$.[8] Therefore, the presence of DQ should suppress the RFH$_2^{+\bullet}$ formation to lead to the acceleration of the photochemical reaction.

In fact, the addition of DQ (5 x 10^{-3} M) to the above electrolysis system resulted in dramatic acceleration of the C_6H_5CHO formation as shown in Figure 1 (solid lines); the 100% conversion to C_6H_5CHO was attained in 8 h, maintaining the current efficiency of ca. 100%. No presence of RFH$_2^{+\bullet}$ was observed at all during the electrolysis, while practically 100% RFH$^+$ was detected as shown in Figure 2. This result strongly suggests that RFH$_3^+$ formed in the photochemical reaction was immediately converted to RFH$^+$ by DQ (Eq. 3). The high RFH$^+$ concentration in steady-state during the electrolysis should maximize the efficiency of photochemical reaction between $C_6H_5CH_2OH$ and (RFH$^+$)* in Eq. 1.

On the basis of above results, the reaction mechanisms may be summarized as Scheme 1. In the absence of DQ the comproportionation which decreases the RFH$^+$ concentration occurs, and RFH$^+$ is regenerated by the oxidation of RFH$_2^{+\bullet}$ on the GC electrode.[11] On the other hand, in the presence of DQ the quick recovery of FlH$^+$ by the reaction between FlH$_3^+$ and DQ can maximize the rate of the photochemical reaction. On the GC electrode DQ is regenerated by the oxidation of DQH$_2$.[11] This double mediatory system involving DQ as well as RF is regarded as excellent because it can maximize the rate of the photochemical reaction, maintaining the high selectivity and efficiency.

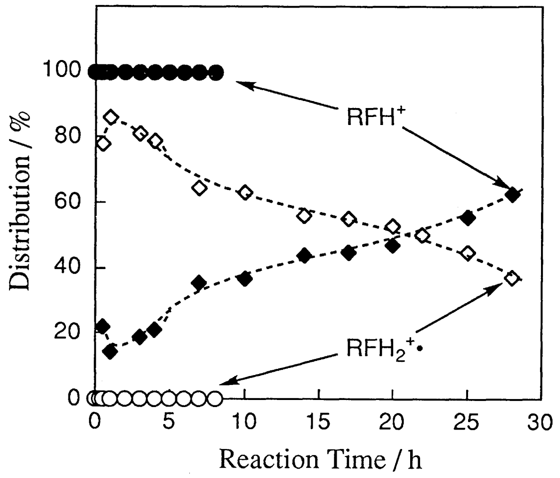
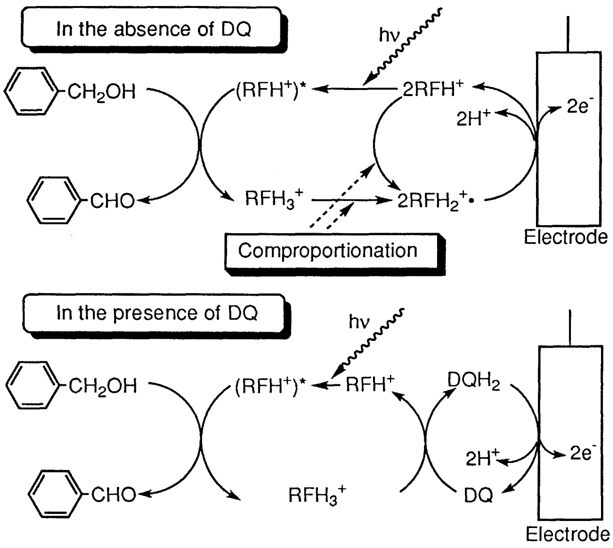


Figure 2. Distribution of the RFH$^+$ and RFH$_2^{+\bullet}$ concentrations per the initial RF concentration (3.3 x 10^{-3} M) during the electrochemical oxidation of $C_6H_5CH_2OH$, the electrolysis conditions are identical to those in Figure 1, ◆◇: in the absence of DQ, ●○: in the presence of DQ (5 x 10^{-3} M).



Scheme 1. Comparison of the oxidation mechanisms of RF-mediated electrochemical oxidation of $C_6H_5CH_2OH$ in the absence and presence of DQ.

This work was financially supported by Grant-in-Aids for Scientific Research (Nos. 07215260 and 07750917) from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

Present address: Department of Applied Chemistry, Faculty of Engineering, Kansai University, 3-3-35 Yamate-Cho, Suita 564.

1 O. S. Ksenzhek and S. A. Petrova, *Bioelectrochem. and Bioenerg.*, **11**, 105 (1983).

2 V. I. Birss, H. Elzanowska, and R. A. Turner, *Can. J. Chem.*, **66**, 86 (1988).

3 H. Durliat, M. B. Barrau, and M. Comtat, *Bioelectrochem. and Bioenerg.*, **19**, 413 (1988).

4 M. Ishikawa, Y. Takahashi, M. Morita, and Y. Matsuda, *Denki Kagaku*, **62**, 1227 (1994).

5 S. Fukuzumi, K. Tanii, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 2*, **1989**, 2103.

6 S. Fukuzumi, K. Tanii, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1989**, 816.

7 M. Ishikawa, K. Yamamoto, and S. Fukuzumi, *J. Chem. Soc., Chem. Commun.*, **1992**, 1008.

8 M. Ishikawa, Y. Matsuda, K. Yamamoto, and S. Fukuzumi, *Chem. Lett.*, **1992**, 2269.

9 Y. Kyogoku and B. S. Yu, *Bull. Chem. Soc. Jpn.*, **42**, 1387 (1969).

10 A 500 W xenon lamp with a filter transmitting light of $\lambda >$ 310 nm was used as a light source.

11 The applied potentials of the GC electrode in the absence and the presence of DQ correspond to the oxidation potentials of RFH$_2^{+\bullet}$ (0.5 V vs. Ag/AgCl) and DQH$_2$ (0.75 V vs. Ag/AgCl), respectively. Even if the GC electrode was polarized at 0.75 V (vs. Ag/AgCl) in the absence of DQ, only ca. 15% acceleration of the formation rate of C_6H_5CHO was observed.