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Evaluation of Acidity of CO_2 in Protic Media. Carboxylation of Reduced Quinone

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In order to evaluate the acidity of CO_2 in protic media, interaction of CO_2 with reduced 2,3,5,6-tetramethylquinone (TMQ) was investigated by means of cyclic voltammetry in CH_3CN, CH_3OH, and CH_3CN / H_2O. Predominant carboxylation of TMQ in CH_3OH and CH_3CN / H_2O (9:1 v/v) indicates that the acidity of CO_2 is almost equivalent or stronger than that of proton in those media.

Much attention has been paid to utilization of CO_2, and a variety of transition metal complexes as homogeneous catalysts have proven to be active for electro- and photochemical CO_2 reduction under protic conditions.[1] There is, however, a controversy about the mechanism of generation of CO and HCOOH; which of proton or CO_2 attacks low valent coordinatively unsaturated metal centers at the initial stage of the reduction ?[2] In the former, formato complexes (M-OC(O)H) are produced by insertion of CO_2 to the resulting M-H bond (Eq. 1),[2] while metal carboxylates (M-C(O)OH) would be generated by protonation of metal-(η^1-CO_2) complexes in the latter (Eq. 2)[3] The formation of HCOOH is reasonably explained by the irreversible

$$[M]^{n+} \xrightarrow{H^+} [M\text{-}H]^{(n+1)+} \xrightarrow{CO_2} [M\text{-}OC(O)H]^{(n+1)+} \qquad (1)$$

$$[M]^{n+} \xrightarrow{CO_2} [M\text{-}CO_2]^{n+} \xrightarrow{H^+} [M\text{-}C(O)OH]^{(n+1)+} \qquad (2)$$

reduction of both M-OC(O)H and M-C(O)OH, while the CO evolution has been ascribed to (i) irreversible reduction of metal-CO complexes resulting from dehydroxylation of M-C(O)OH,[3] (ii) decarbonylation of M-OC(O)H affording M-OH,[4] and (iii) degradation of products during an electrolysis.[2] Thus, it is very hard to determine which of M-OC(O)H or M-C(O)OH operates in the catalytic cycles of the CO_2 reduction. If Eqs. 1 and 2 are assumed to be primarily governed by the relative acidity of CO_2 and proton in solutions, the evaluation of the acidity of CO_2 in protic media is much of interest in connection with the reaction mechanism of the reduction of CO_2 catalyzed by transition metal complexes. This letter describes a competitive electrophilic addition of CO_2 and proton to reduced 2,3,5,6-tetramethylquinone (TMQ) in CH_3CN / H_2O and CH_3OH, which are widely used in electro- and photochemical CO_2 reduction.

The cyclic voltammogram (CV) of TMQ shows two $[TMQ]^{0/-}$ and $[TMQ]^{-/2-}$ redox couples at $E_{1/2}$ = -0.75 and -1.31 V *vs*. Ag / AgCl ($E_{1/2} = (E_{pc} + E_{pa}) / 2$) in dry CH_3CN under N_2 (a solid line in Fig. 1(a)). Introduction of CO_2 to the solution (0.24M) results in the increase in an irreversible cathodic peak current at -0.83 V and an anodic wave appears at +0.05 V (a dotted line in Fig. 1(a)). The original $[TMQ]^{0/-}$ and $[TMQ]^{-/2-}$ redox couples in CH_3CN were completely regenerated with the same peak current intensities upon removing CO_2 by bubbling N_2 into the solution for 20 min. These results clearly indicate that $[TMQ]^{2-}$ forms a CO_2 adduct (Eq. 3) in CH_3CN, similarly to a 1:2 CO_2 adduct of 9,10-phenanthrenequinone.5)

$$TMQ + 2e^- + 2CO_2 \rightleftharpoons [TMQ{\cdot}2CO_2]^{2-} \qquad (3)$$

To evaluate the acidity of CO_2 in protic media, the redox behavior of TMQ in CH_3CN / H_2O and CH_3OH was investigated under N_2 and CO_2 atmospheres. The $E_{1/2}$ value of the $[TMQ]^{-/2-}$ couple in CH_3CN underwent pronounced anodic shifts compared with that of the $[TMQ]^{0/-}$ one with increasing amount of H_2O in the solution,6) and two pairs of the cathodic and anodic waves of the $[TMQ]^{-/2-}$ and $[TMQ]^{0/-}$ couples coalesce at E_{pc} = -0.65 and E_{pa} = -0.53 V in CH_3CN / H_2O (9:1 v/v, a solid line in Fig. 1(b)), as described elsewhere.6) Similarly, the CV of TMQ also shows only one pair of cathodic and anodic waves at -0.56 and -0.06 V in CH_3OH under N_2 (a solid line in Fig. 1(c)). On the basis of the fact that the anodic peak potential of 2,3,5,6-tetramethylhydroquinone (TMQ·2H) was observed at +0.59 and +0.60 V in CH_3CN / H_2O (9:1 v/v) and CH_3OH, respectively, TMQ dianion mainly exists as a mono-protonated anionic form, $[TMQ{\cdot}H]^-$ rather than the neutral $[TMQ{\cdot}2H]^0$ in those media (Eqs. 4 and 5).7) On the other hand, the CV of TMQ in CO_2-saturated CH_3CN / H_2O (9:1 v/v) and CH_3OH

$$TMQ + 2e^- + H^+ \rightleftharpoons [TMQ{\cdot}H]^- \qquad (4)$$

$$TMQ + 2e^- + 2H^+ \rightleftharpoons [TMQ{\cdot}2H]^0 \qquad (5)$$

displays the cathodic and anodic waves at -0.64 and +0.29 V, and -0.52 and +0.33 V, respectively (dotted lines in Fig. 1(b) and (c)), suggesting the formation of the CO_2 adducts. There are four possible compositions of the CO_2 adducts such as $[TMQ{\cdot}H{\cdot}CO_2]^-$, $[TMQ{\cdot}H{\cdot}CO_2H]^0$, $[TMQ{\cdot}CO_2{\cdot}CO_2H]^-$, and $[TMQ{\cdot}(CO_2H)_2]^0$, except for $[TMQ{\cdot}2CO_2]^{2-}$ existing in CO_2-saturated dry CH_3CN. Concerning the formation of $[TMQ{\cdot}H{\cdot}CO_2]^-$ and $[TMQ{\cdot}H{\cdot}CO_2H]^0$, it is not clear whether H^+ or CO_2 initially attacks $[TMQ]^{2-}$. However, $[TMQ{\cdot}H{\cdot}CO_2H]^0$ may be ruled out from the view that $[TMQ{\cdot}H]^-$ is the

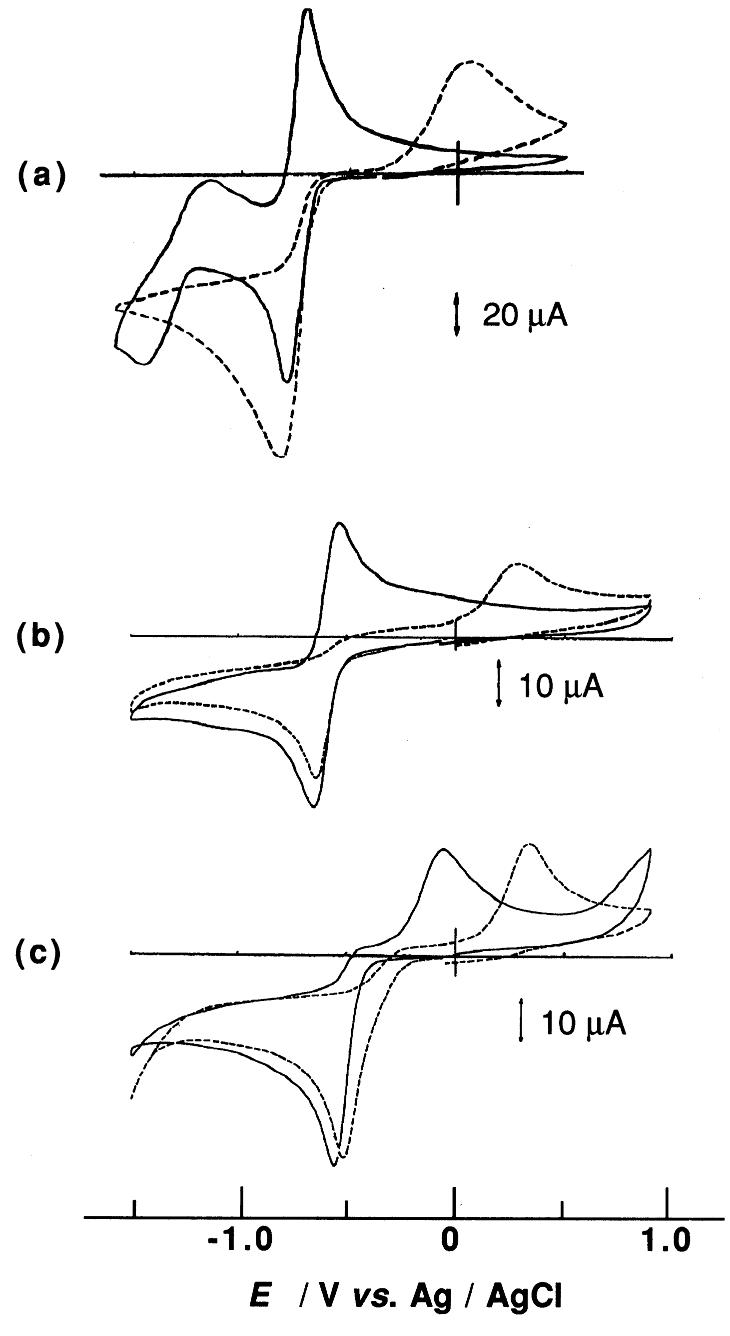

Fig. 1. CVs of TMQ (3.40 mM, (a); 0.96 mM, (b); 1.22 mM, (c)) under N_2 (solid lines) and CO_2 (dotted lines) in CH_3CN (a), CH_3CN / H_2O (9:1 v/v, (b)) and CH_3OH (c), containing Bu_4NBF_4 (0.1 M) at 100 mV/s; working electrode: glassy carbon.

main species in CH_3CN / H_2O (9:1 v/v) and CH_3OH under N_2, as described above. The remaining two, $[TMQ{\cdot}CO_2{\cdot}CO_2H]^-$ and $[TMQ{\cdot}(CO_2H)_2]^0$, formally generated by protonation of $[TMQ{\cdot}2CO_2]^{2-}$ apparently result from an initial electrophilic attack of CO_2 to $[TMQ]^{2-}$ in CH_3CN / H_2O (9:1 v/v) and CH_3OH. It is, therefore, concluded that the acidity of CO_2 is almost equivalent or stronger than that of proton of those media under CO_2.

The generation of CO and HCOOH in the reduction of CO_2 catalyzed by homogeneous catalysts has often been explained by both Eqs. 1 and 2 without a direct evidence presumably due to the lack of the knowledge concerning the acidity of CO_2 in protic media.[2,3] The present study reveals that the reaction of Eq. 2 is favored over Eq. 1 from the standpoint of the electrophilicity of CO_2 in CH_3CN / H_2O (9:1 v/v) and CH_3OH.

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7) $[TMQ{\cdot}H]^-$ may exist as an equilibrium mixture with $[TMQ]^{2-}$ in CH_3OH and CH_3CN / H_2O (9:1 v/v). Taking into the account of the agreement of the anodic peak potential of TMQ in CH_3OH with the reported value of $[TMQ{\cdot}H]^-$ (Ref. 6), the equilibrium in CH_3CN / H_2O (9:1 v/v) may be shifted to $[TMQ]^{2-}$ compared with that in CH_3OH.

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