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Carbon Dioxide Fixation Competed with Proton Addition to Methyl Acrylate

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The controlled potential electrolysis of CO_2-saturated CH_3CN containing $(Bu_4N)_3[Mo_2Fe_6S_8(SEt)_9]$, methyl acrylate, Bu_4NBF_4, and molecular sieves 4A at -1.60 - -1.70 V *vs.* SCE gave $^-OOCCH_2CH(C(O)OCH_3)COO^-$, $^-OOCCH_2CH_2C(O)OCH_3$, $CH_3CH(C(O)OCH_3)COO^-$, and $CH_3CH_2C(O)OCH_3$. The formation of those products may be explained in terms of a nucleophilic attack of either activated CO_2 or H^+ on the two-electron reduced cluster, followed by an electrophilic attack of free CO_2 or H^+ to olefinic carbons.

Utilization of CO_2 has been attracted a great deal of attention from the viewpoint of a C_1 source. From a practical aspect, CO_2 fixation to organic molecules with carbon-carbon bond formation may be more important than the reduction of CO_2 affording C_1 compounds such as CO and/or HCOOH,1-3) CH_3OH,4) and CH_4.5,6) As a model of biological CO_2 fixation, α- and β-keto acids have been synthesized catalytically by introduction of CO_2 to carbonyl carbon of thioesters7,8) and methyl carbon of ketones.9) Here we report 1,2-addition of CO_2 to methyl acrylate caused by not only electrophilic attack but also nucleophilic attack of CO_2 to olefinic carbons as a new type of CO_2 fixation.

The cyclic voltammogram (CV) of $(Bu_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ 8) in DMF (1.75 mmol dm^{-3}) using a glassy carbon disk electrode shows two one-electron (3-/4- and 4-/5-) redox couples at $E_{1/2}$ = -1.24 and -1.43 V *vs.* SCE at a sweep rate 10 mV/s (Fig. 1a). There was found no change in the CV of the MoFeS cluster in the presence of methyl acrylate (Fig. 1b). On the other hand, introduction of CO_2 by bubbling into the DMF solution of the cluster brings about an increase in the cathodic current of the second reduction wave of the MoFeS cluster (Fig. 1c). The cathodic current further increases in the coexistence of CO_2 and methyl acrylate (Fig. 1d). These observations indicate that the two-electron reduced cluster, $[Mo_2Fe_6S_8(SEt)_9]^{5-}$, first has a reciprocal action with CO_2, and then the activated CO_2 reacts with methyl acrylate. The interaction of CO_2 with the two-electron reduced MoFeS cluster was also evidenced by solution FT-IR spectra; $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]$, prepared by the reaction of $(Et_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ with an anion radical of acenaphtylene in the presence of excess of Et_4NCl,10) showed a strong band at 1645 cm^{-1} assignable to coordinated CO_2 in CO_2-saturated CD_3CN, since the band was not observed at all in an Ar-saturated CD_3CN solution of the reduced cluster.

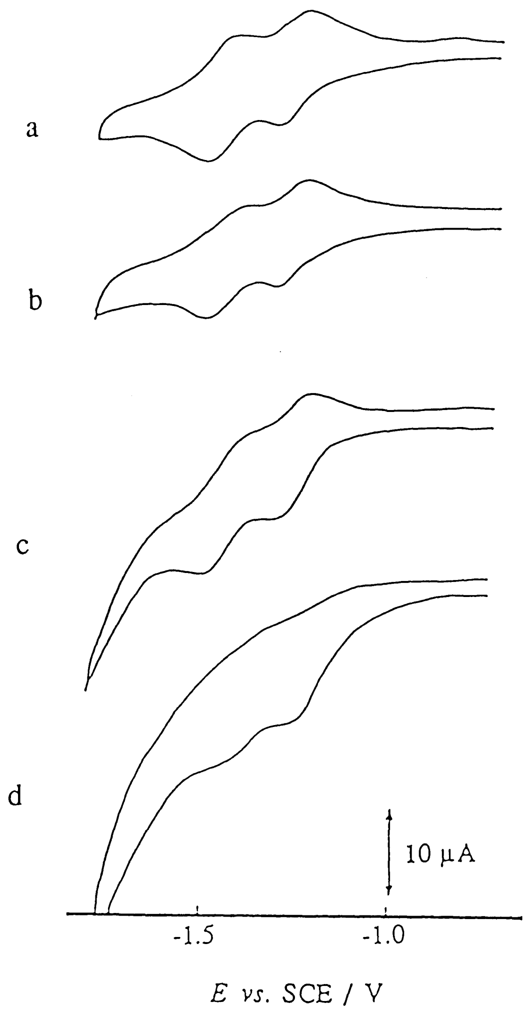
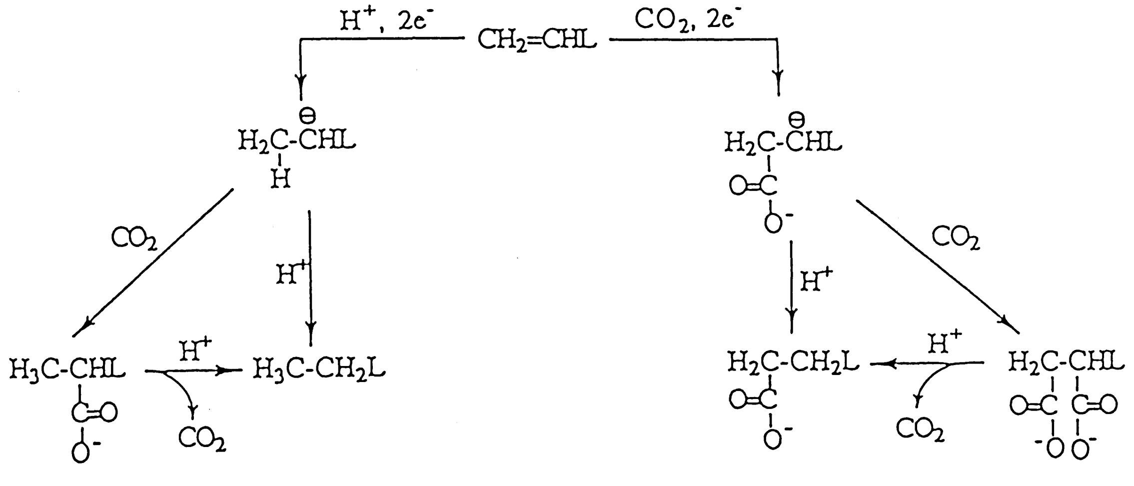


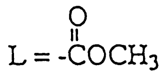
Fig. 1. Cyclic voltammogram of $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ in DMF (a), in the presence of methyl acrylate (b) or CO_2 (c), and the presence of methyl acrylate and CO_2 (d).

After 170 coulomb was passed in the controlled potential electrolysis of CO_2-saturated CH_3CN containing $(Bu_4N)_3[Mo_2Fe_6S_8(SEt)_9]$ (20 - 30 μmol), methyl acrylate (2 - 10 mmol), Bu_4NBF_4 (4.0 - 4.5 mmol), and molecular sieves 4A as a dehydration agent at -1.60 - -1.70 V *vs.* SCE, the solvent was removed under reduced pressure. The MoFeS cluster in the reaction mixture was decomposed by addition of 1 mol dm^{-3} HCl (10 cm^3), and the product was extracted with diethyl ether (10 cm^3). The resulting diethyl ether layer was dried over $MgSO_4$ and then treated with CH_2N_2 at room temperature. From the comparison of authentic samples of GC-Mass spectra, the formation of 1,1,2-trimethoxycarbonylethane ($CH_3OC(O)CH_2CH[C(O)OCH_3]_2$), dimethyl succinate ($CH_3OC(O)CH_2CH_2C(O)OCH_3$), dimethyl methylmalonate ($CH_3CH[C(O)OCH_3]_2$), and methyl propionate ($CH_3CH_2C(O)OCH_3$) were confirmed with the current efficiencies η = 4.3, 8.2, 12.8, and ca. 60%, respectively.

Although carbon dioxide can be fixed to RCH=CHR' (R = H, MeOCO; R' = COMe, CN, COOMe) by an electrochemical one-electron reduction of either CO_2 or those olefins under electrolysis at *ca.* -2.1 to -2.2 *vs.* SCE,[11) an anion radical of neither CO_2 nor methyl acrylate is formed under the present electrolysis conditions. In fact, cathodic current essentially did not flow in the electrolysis in the absence of the MoFeS cluster under the electrolysis conditions -1.6 - -1.7 V since methyl acrylate is not reduced at potentials more positive than -1.90 V *vs.* SCE in dry CH_3CN. On the basis of the facts that the two-electron reduced MoFeS cluster interacts with CO_2[12) and H^+,[13) but not with methyl acrylate, four reaction products in the present study may be formed by a competitive addition of CO_2 or H^+ to methyl acrylate, as depicted in Scheme 1; an electrophilic attack of a positively polarized terminal olefinic carbon of methyl acrylate to CO_2 activated by the two-electron reduced cluster will produce $^{-}OC(O)CH_2\overset{\ominus}{C}HL$ (L = $C(O)OCH_3$), which then undergoes an electrophilic attack of either free CO_2 or H^+ (involved in a solution) to produce $^{-}OC(O)CH_2CH(C(O)O^{-})L$ or $^{-}OC(O)CH_2$-CH_2L. Similarly, an initial electrophilic attack of methyl acrylate to H^+ activated by the cluster should generate $CH_3CH(C(O)O^{-})L$ and CH_3CH_2L *via* CH_3CHL as a reaction intermediate. In addition to those reaction paths, decarboxylation of $HOC(O)CH_2CH$-$(C(O)OH)L$ and $CH_3CH(C(O)OH)L$ affording $HOC(O)CH_2CH_2L$ and CH_3CH_2L, respectively took place during esterfication of crude products in acidic conditions.[14) Thus, present CO_2 fixation may be reasonably explained by a nucleophilic attack of activated CO_2, followed by an electrophilic attack of free CO_2 to olefinic carbons.



Scheme 1.


$L = -\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$

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12) Although the electronic absorption spectra of the MoFeS cluster after and before the electrolysis at -1.6 V was not consistent with each other, the reoxidation of the reaction mixture at -0.5 V in the presence of ethanethiolate recovered the original electronic absorption spectra of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ in CD_3CN.

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14) Neither 1,1,2-trimethoxycarbonylethane and dimethyl succinate was obtained by treatment of the electrolyzed solution with HCl-MeOH in a sealed tube at 100 °C.

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