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Interaction between CO_2 and Electrochemically Reduced Species of N-propyl-4,4'-bipyridinium Cation

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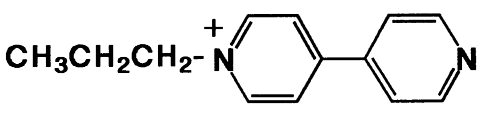
The one-electron reduced species of N-propyl-4,4'-bipyridinium cation (1^+) which is generated under electrolysis at -1.1 V *vs.* SCE was found to be able to react with CO_2 although it is even a neutral radical. The intermediate CO_2 adduct was furthermore reduced by one-electron at the same electrolysis potential to form a stable CO_2 adduct.

Electrochemically direct reduction of CO_2 giving CO_2 anion radical ($CO_2^{-\cdot}$) requires a more negative potential than -2 V *vs.* SCE with platinum or glassy carbon electrodes.[1] However, using electrode of other material or modified electrodes allow reduction at a more positive potential than -2 V *vs.* SCE to generate a variety of reduction products.[1] Many metal complexes *e.g.* nickel, ruthenium, rhenium used as mediators achieve the same result.[2] In the reduction processes proceeding at a more positive potential than -2 V *vs.* SCE, CO_2 is activated *via* adsorption on the electrode surfaces or coordination to the metal complexes. However, it remains unknown that such an activation of CO_2 is particular to transition metals. If organic radicals which can be generated under electrolysis at a more positive potential than -2 V *vs.* SCE and can interact with CO_2 are found, the organic compounds could be used as functional electrodes or catalytic mediators for electrochemical CO_2 reductions. There are many reports concerning electrochemically reductive production of carboxylic acids from CO_2 and organic compounds such as carbonyl compounds, alkenes, imines, or organic halides.[3] However, these electrolyses were in many cases performed at more negative potentials than -2 V *vs.* SCE, and $CO_2^{-\cdot}$ generated during the electrolyses reacted with the organic compounds. Therefore, there are few reports showing that an electrochemically generated radical reacts with CO_2 except for the reports about quinone derivatives anion radicals.[4] We will report here that the reduced species of N-propyl-4,4'-bipyridinium cation (1^+) which is generated at -1.1 V *vs.* SCE interacts with CO_2 and furthermore activates it.

1^+ was synthesized by refluxing the acetone solution (35 cm^3) of 4,4'-bipyridine (25.6 mmol) and an equimolar *n*-propyl bromide for 40 hours. After refluxing the white solid was collected, and then recrystallized in acetonitrile/ether.[5] The cyclic voltammograms (CVs) of 1^+ were measured in the presence of various concentrations of CO_2 (Fig. 1a). The CV of 1^+ exhibited two successive and reversible redox couples ($E_{p/2}$) at -0.98 V and -1.71 V *vs.* SCE under N_2 atmosphere in acetonitrile. The CV of 1^+ drastically changed under



1^+

atmospheric CO_2: the second redox wave at -1.71 V *vs.* SCE disappeared completely and a large reversible redox wave ($E_{p/2}$) at -1.00 V *vs.* SCE appeared. The CO_2 concentration dependent CVs show that at low concentration of CO_2 the second redox wave gradually disappeared, and that the new redox wave appeared around -1.1 V *vs.* SCE. As CO_2 concentration increased, the redox wave became larger and finally combined with the redox wave at -0.98 V *vs.* SCE to form a single large reversible redox wave. These results indicate that the one-electron reduced species of $\mathbf{1}^+$ interacted with CO_2 and then it was furthermore reduced by one electron at the same electrolysis potential to form the adduct of $\mathbf{1}^-$ and CO_2. Also, during the electrolysis of $\mathbf{1}^+$ at -1.1 V *vs.* SCE in acetonitrile, one and two Faradays of electricities for $\mathbf{1}^+$ flowed under N_2 and CO_2 atmospheres, respectively. We feel the CO_2 adduct is quite stable at least within the time scale of the CVs because the CVs exhibit clearly pronounced reversibility.[6)] When CO_2 is again replaced by N_2, the CV returned once more to the original characteristic cyclic voltammetric pattern under N_2.

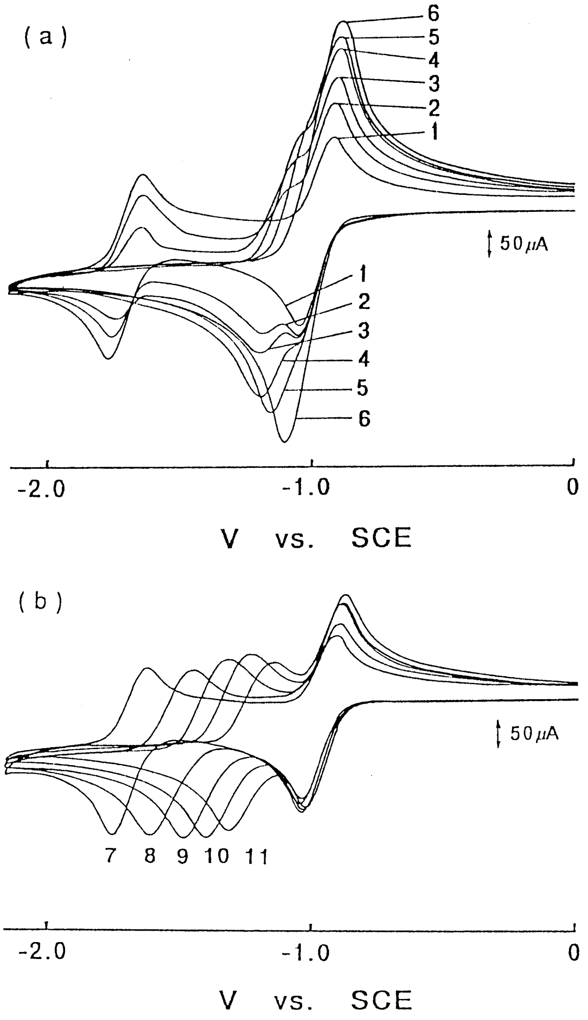


Fig. 1. Cyclic voltammograms of $\mathbf{1}^+$ (0.01 mol dm^{-3}) in N_2-saturated acetonitrile containing (n-Bu_4N)ClO_4 (0.10 mol dm^{-3}) as an electrolyte in the presence of (a) CO_2 and (b) CH_3OH; (a) concentrations of [CO_2] are (starting with CV 1) 0, 2.8, 4.3, 9.9, 38.9, 241 x 10^{-3} mol dm^{-3}, and (b) concentrations of [CH_3OH] are (starting with CV 7) 0, 0.24, 0.74, 1.50, 3.60 mol dm^{-3}. The electrode was a 0.30 cm diam glassy carbon disk. The scan rate was 0.10 V s^{-1}.

The interaction between the one-electron reduced species of $\mathbf{1}^+$ and CO_2 would be electrostatic. Namely, $\mathbf{1}^\bullet$ and CO_2 would act as a base and an acid, respectively. Therefore, in order to compare the reaction between the reduced species of $\mathbf{1}^+$ and CO_2 with protons, the CV of $\mathbf{1}^+$ was measured in the presence of CH_3OH (Fig. 1b). With increasing CH_3OH concentrations, the second wave drastically shifted to the positive potential whereas the first one hardly changed. These results indicate that the two-electron reduced species of $\mathbf{1}^+$ undergoes equilibrium reaction with a proton (CH_3OH), however the reaction with CO_2 forms a CO_2 adduct and is irreversible in the time scale of the CV. They also indicate that the one-electron reduced species of $\mathbf{1}^+$ can react with CO_2, however its reaction with CH_3OH hardly occurs.

In order to examine the electronic structure of the CO_2 adduct, the electronic spectra of 1^+ under electrolysis were measured and the molecular orbital (MO) calculations were also performed. As shown in Fig. 2, electronic spectra of 1^+ under N_2 atmosphere at -1.1 V *vs.* SCE showed that the absorption at 264 nm disappeared rapidly and the peak at 371 nm due to generation of one-electron reduced species $1^\bullet$ and the peak at 538 nm probably assignable to the dimer of $1^\bullet$ appeared. At -1.8 V *vs.* SCE at which the two-electron reduced species 1^- is generated, both absorbances at 371 and 538 nm disappeared. By contrast, the electronic spectra of 1^+ at -1.1 V *vs.* SCE under CO_2 atmosphere showed that the large peak at 397 nm appeared with the absorbance at 379 nm which was also observed under N_2 atmosphere although it was slightly red-shifted. The absorption at 538 nm initially appeared, however, then disappeared. From the results the new absorption at 397 nm is considered to be indebted to the CO_2 adduct.

The MO calculation of interaction between 1^- and CO_2 was performed with the PM3 method in the program package MOPAC *ver.* 6.[7] Since no change was observed in the reduction of N,N'-dipropyl-4,4'-

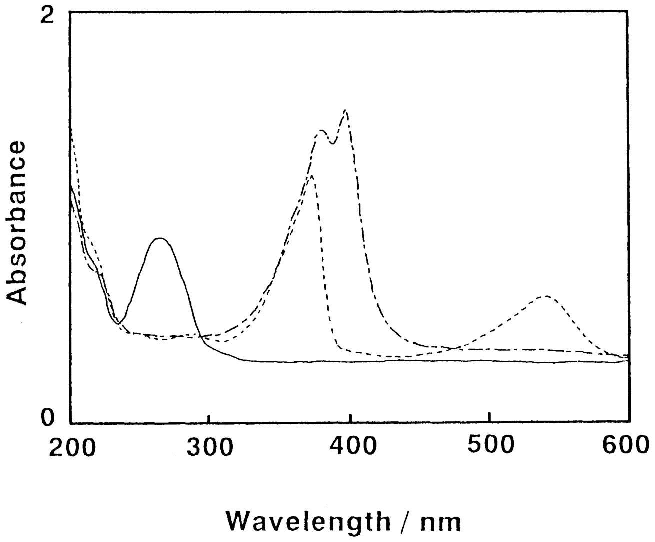


Fig. 2. UV-vis spectroelectrochemistry of 1^+ (5.0×10^{-4} mol dm^{-3}) in acetonitrile containing (n-Bu_4N)ClO_4 (0.10 mol dm^{-3}) with a Pt mesh electrode; ——— before electrolysis; ----- after electrolysis at -1.1 V *vs.* SCE under N_2 atmosphere; —·—·— after electrolysis at -1.1 V *vs.* SCE under CO_2 atmosphere. Path length of the cell was 0.050 cm.

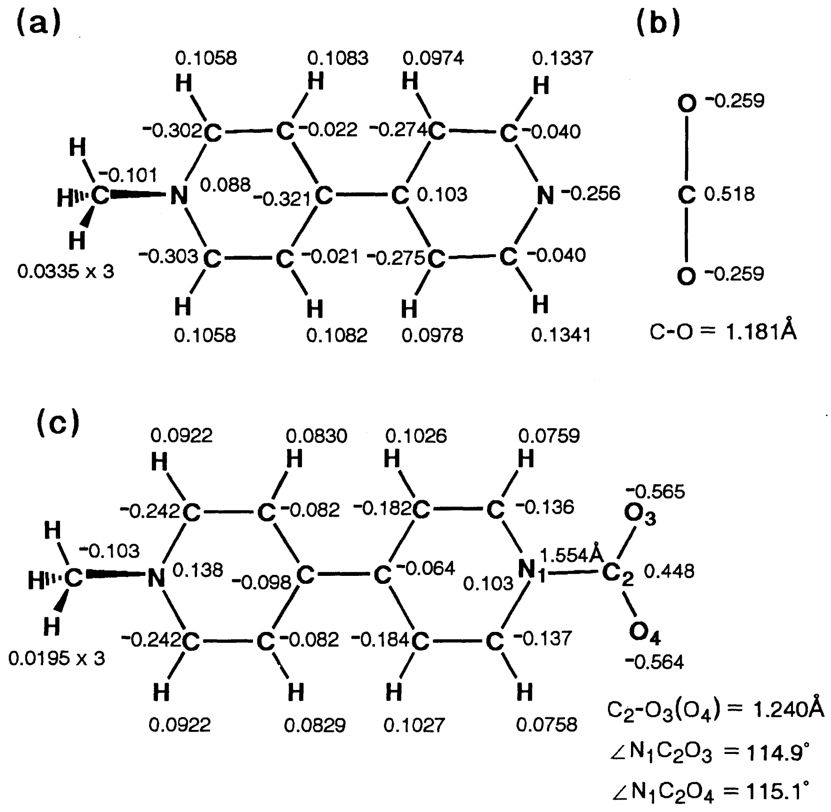


Fig. 3. Illustration of (a) 1^- (UHF), (b) CO_2 (RHF), and (c) the CO_2 adduct of 1^- (UHF) showing the PM3-calculated partial atomic charges and geometries of CO_2 parts.

bipyridinium dication under CO_2 atmosphere, it is proposed that CO_2 interacts with 1^- at the nitrogen atom which was not alkylated. In fact, when CO_2 approaches the nitrogen atom of 1^-, CO_2 is bent and C-O distance gradually lengthened. Fig. 3c depicts the stable structure and the charge distribution of the CO_2 adduct. The result indicates that the negative charge (-0.681) transferred from the bipyridine rings to the CO_2. The absorption observed in the electronic spectra under electrolyses of 1^+ can be qualitatively explained by the polarized structure of the CO_2 adduct. Namely, the absorption around 370 nm which was observed under both N_2 and CO_2 atmospheres can be assigned to π-π^* transition of one-electron reduced species of 1^+. The absorption at 397 nm which was observed only under CO_2 atmosphere can be assigned to charge transfer from the attached CO_2 anion to π^* of a pyridine ring. The MO calculation for interaction between the one-electron reduced species ($1^\bullet$) and CO_2 was also performed. However, in order to obtain the stable structure of the CO_2 adduct, a cation such as a proton was required. This suggests that the electrolyte, tetrabutylammonium cation, played an important role in the reaction between $1^\bullet$ and CO_2.

In summary, a compound like 1^+ which has both an electron-accepting part and a nucleophilic part can be reduced at a more positive potential than -2 V *vs.* SCE and can also interact with CO_2 even at more positive potentials though the one-electron reduced species is neutral. The compound 1^+ was found to be an electrochemically switchable carrier of CO_2. At the same time CO_2 bound to the reduced species of 1^+ was activated by transferring electrons from the bipyridine rings to CO_2. Further investigation of this phenomenon is expected to lead us to design better functional electrodes or mediators for electrochemical CO_2 reductions.

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References

1) I. Taniguchi, "Electrochemical and Photoelectrochemical Reduction of Carbon Dioxide," in "Modern Aspects of Electrochemistry," ed by J. O'M. Bockris, R. E. White, and B. E. Conway, Plenum Publishing Corporation (1989), No. 20, Chap. 5, pp. 327 - 400.
2) J. P. Collin and J. P. Sauvage, *Coord. Chem. Rev.*, **93**, 245 (1989).
3) E. Haruki, "Organic and Bioorganic Chemistry of Carbon Dioxide," ed by S. Inoue and N. Yamazaki, Kodansha Ltd., Tokyo (1982), Chap. 2, pp. 5 - 78.
4) H. Tanaka, H. Nagao, and K. Tanaka, *Chem. Lett.*, **1993**, 541; M. B. Mizen and M. S. Wrighton, *J. Electrochem. Soc.*, **136**, 941 (1989); L. O. S.Bulhoes and A. J. Zara, *J. Electroanal. Chem.*, **248**, 159 (1988).
5) ^1H nmr measurements were performed by JEOL JNM-GX400. 1^+ (D_2O): δ 0.99 (t, 3H, 3-CH_3), 2.09 (m, 2H, 2-CH_2), 4.63 (t, 2H, 1-CH_2), 7.92 (d, 2H, 3'-py), 8.41 (d, 2H, 2'-py), 8.78 (d, 2H, 3-py), 8.96 (d, 2H, 2-py). Anal. Found: C, 55.42; H, 5.38, N: 9.90%. Calcd for $C_{13}H_{15}N_2Br$: C, 55.93; H, 5.42; N, 10.03%.
6) Possibility of catalytic CO_2 reductions by 1^+ is being investigated.
7) MOPAC *ver.* 6 by J. J. P. Stewart, JCPE, P044; Revised by Yoshihisa Inoue for FACOM.

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