

Figure 1. Effect of pH on cyclic voltammograms of 1.0 mM 1-methyl-4,4'-bipyridinium chloride in aqueous 0.1 M NaCl solutions at 25 °C. The CV's of 1.0 mM dimethylviologen (MV^{2+}) and 1-benzylnicotinamide chloride (BNAC1) recorded at pH 7 are given for comparison. Scan rates are 90 mV/s.

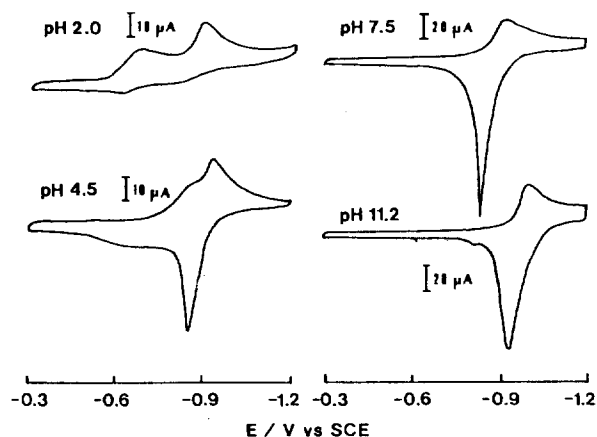


Figure 2. Effect of pH on cyclic voltammograms of 1.0 mM 1-benzyl-4,4'-bipyridinium chloride in aqueous 0.1 M NaCl solutions at 25 °C. Scan rates are 120 mV/s.

Results and Discussion

Cyclic voltammetric behavior of $RBPY^-$ depends highly on pH of media. In Figure 1, we illustrated CV of C_1RBPY^+ recorded at various pH. The CV response of C_1RBPY^+ at pH 2.7, which exhibits two redox waves, is quite similar to that of dimethylviologen (MV^{2+}), except that the anodic peak corresponding to the second reduction is virtually disappeared and that corresponding to the first reduction is much less pronounced in C_1RBPY^+ than in MV^{2+} . With increase of pH, the first redox wave moves to the negative direction and the first and second redox waves are merged into a broad wave near pH 7.5. Further increase of pH shifts the redox peak to more negative potential. At pH of 11.7, a single redox wave is observed with $E_{pc} = -1.12$ V and $\Delta E_p \approx 40$ mV. The cathodic wave observed at the high pH is similar to that of a NAD^+ analogue, 1-benzylnicotinamide (BNA^+) ion: anodic peak of BNA^+ is not observed presumably due to rapid dimerization of the reduction product,¹⁷ and the rate of the

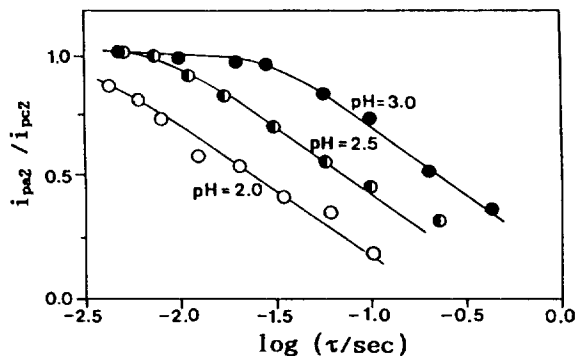


Figure 3. Ratio of anodic to cathodic peak currents at the second step of the redox reaction as a function of τ and pH (2.0–3.0). τ is the time(s) between $E_{1/2}$ and the switching potential. Scan rate changes from 0.5 to 50 V/s.

following reaction (if any) appears to be much slower for the reduction product of C_1RBPY^+ at the high pH.

The pH-dependent CV responses of other *N*-substituted-4,4'-bipyridinium salts are similar to that of C_1RBPY^+ (see Figure 2 for the results of $BBPY^+$): at highly acidic pH, two well-separated reduction peaks are observed and the anodic currents are much less than those of cathodic currents; two reduction waves are merged together at high pH. In contrast to the observations with C_1RBPY^+ , the second cathodic and anodic peaks are sharper than the peak expected for a reversible redox process. This indicates adsorption of the reduced species at electrode surface as the 1-substituent groups have more hydrophobic character.¹² Because of the complication arising from the electrode adsorption of the electroactive species in quantitative analysis of the CV, we confine further analysis to C_1RBPY^+ which is the least complicated one among $RBPY^+$ investigated in the present work.

The pK_a of HC_1RBPY^{2+} is reported to be 3.42.¹⁸ At $pH < 3.42$, the predominant species of C_1RBPY^+ is HC_1RBPY^{2+} and the species appears to exhibit similar reduction behavior to MV^{2+} . The measured first cathodic peak potential, E_{pc1} , is -0.73 V vs SCE and the difference between the cathodic and anodic peak potentials, ΔE_{p1} , is 60 mV. When the potential scan range is adjusted between -0.3 and -0.9 V, the ratio of anodic and cathodic peak currents, i_{pa1}/i_{pc1} , is near unity. This indicates that the first step of the redox reaction is nernstian with one-electron transfer as in Eq. (1).



The CV responses of C_1RBPY^+ under acidic condition also depend on the scan rate. At $pH < 3$, the CV of C_1RBPY^+ was similar to that of MV^{2+} showing two consecutive reversible redox waves when the scan rate was fast. The anodic peak corresponding to the second reduction decreases as the scan rate is slower and disappears virtually at very low scan rate. Similarly, the i_{pa1}/i_{pc1} ratio becomes less as the scan rate is lowered and the potential scan range is extended to -1.2 V. Also, the second cathodic peak potential (E_{pc2}) is shifted to less negative direction as the scan rate is slower: at pH 2.5, E_{pc2} values were ca. -1.03 V when the scan rate was > 10 V/s and ca. -0.95 V when the scan rate was 50 mV/s. These results clearly suggest that the product of the second step

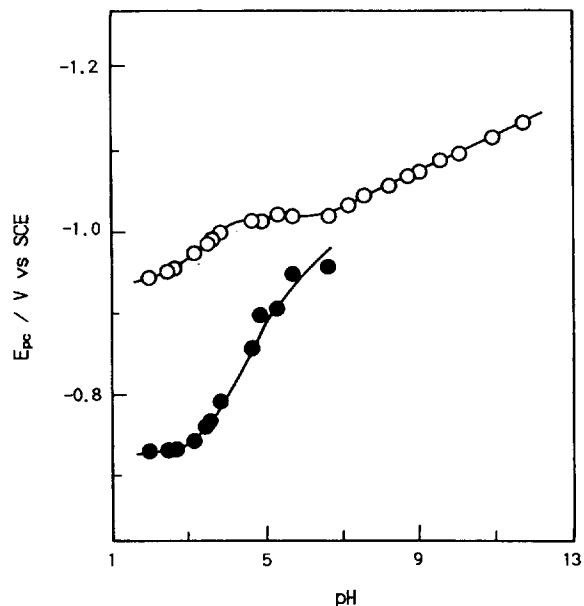


Figure 4. Effect of pH on the first (●) and the second (○) cathodic peak potentials of 1.0 mM C₁BPYCl in aqueous 0.1 M NaCl solutions at 25 °C.

electrode reaction, HC₁BPY₂⁻, reacts within this experimental time scale to produce a species that is not electroactive at potentials where the reduction of HC₁BPY⁺ is occurring.

Figure 3 shows a plot of i_{pa2}/i_{pc2} vs $\log \tau$ for the second redox waves under acidic conditions (pH 2.0-3.0), where τ is the time between the second $E_{1/2}$ (we assumed as $E_{pc2} + 30$ mV) and the switching potential. The range of scan rate was from 0.5 to 50 V/s. At large scan rates, the peak current ratio, i_{pa2}/i_{pc2} , is near unity because it is not enough time for HC₁BPY₂⁻ to be removed from the vicinity of the electrode surface by a following chemical reaction. The i_{pa2}/i_{pc2} value is over 0.95 at the scan rates greater than 7 V/s at pH 3.0. As the scan rate decreases, the peak currents ratio decreases (e.g., $i_{pa2}/i_{pc2} = 0.52$ at 1 V/s). As pH of the medium is lowered, the i_{pa2}/i_{pc2} vs $\log \tau$ curve is shifted to shorter τ , i.e., fast scan rate side, by the same magnitude as the pH changes. This indicates that the rate of chemical reaction is proportional to the concentration of H⁺ ion. From the Nicholson and Shain treatment of EC₁ processes,¹⁹ we estimated the pseudo-first-order rate constant (k_f) of the homogeneous chemical process and then the second-order rate constant (k_H) from the relationship of $k_f = k_H[H^+]$. The k_H value is $(3.7 \pm 0.3) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ for HC₁BPY₂⁻. Hence, the second reduction step of C₁BPY⁺ at low pH can be written as Eq. (2).



Characterization of the reaction product *P* is beyond the scope of this work. However, we believe that the reaction would be similar to the acid-catalyzed hydration reaction of dihydropyridines, NADH analogues.^{14,15} The k_H value for HC₁BPY₂⁻ is greater than the corresponding values observed with 1,3-disubstituted-1,4-dihydro-pyridines which depend largely on the nature of the substituent.^{14,15} The result of this work seems to reflect sensitivity of k_H on the position as well as the nature

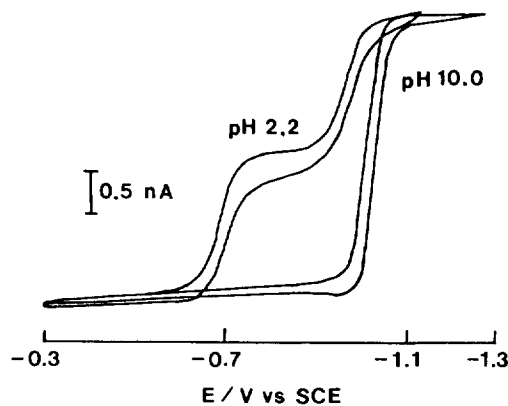


Figure 5. Effect of pH on cyclic voltammograms of 1.0 mM C₁BPYCl with a carbon microdisk electrode in aqueous 0.1 M NaCl solutions at 25 °C. Scan rates are 50 mV/s.

of substituents.

The first and second cathodic peak potentials (E_{pc}) taken at the scan rate of 90 mV/s are shown in Figure 4 as functions of pH. As pH of the medium is raised from pH 2, E_{pc2} is shifted to negative direction until pH becomes 4, while the E_{pc1} is virtually independent of pH below pH 3. The dependence of E_{pc2} on pH under acidic condition is parallel to the dependence of E_{pc2} on the scan rate and reflects the reaction of HC₁BPY₂⁻, in which H⁺ is involved. At pH range 4-7, E_{pc1} depends on pH with a slope of $\Delta E/\Delta \text{pH} \cong -60$ mV/pH, while the E_{pc2} is almost constant. For the electrode reactions with a preceding chemical reaction (Eq. (3)), E_{pc} varies linearly with $(RT/nF)\ln[K/(1+K)]$ where K is the equilibrium constant for the preceding reaction,¹⁹



If we assume that HC₁BPY₂⁻ is electroactive and C₁BPY⁻ is not electroactive in the working potential range, K can be substituted by $K_a[H^+]$, where K_a is the acid dissociation constant of HC₁BPY₂⁻, 4.0×10^{-4} . The dependence of the E_{pc1} on pH (Figure 4) agrees well with this prediction. The pH independence of E_{pc2} of HC₁BPY⁺ in the pH range of 4-7 is indicative that the $\text{p}K_a$ of HC₁BPY⁺ is much larger than 7. Thus, the electrode processes in the intermediate pH range can be written as Eq. (4).



As pH is raised, the pH-dependent reduction potential of Eq. (4-2) with a preceding reaction of Eq. (4-1) becomes more negative than the reduction potential of C₁BPY⁺ itself. Under this condition, a single wave characteristic of 2e⁻ reduction is observed because the second step reduction becomes easier than the first one.²⁰ This seems the case at pH > 7.5, where a single reduction wave is observed. The measured value of ΔE_p was 40 mV (Figure 1) at pH 11.7 is also suggestive of 2e⁻ process. This is quite contrary to the conclusion

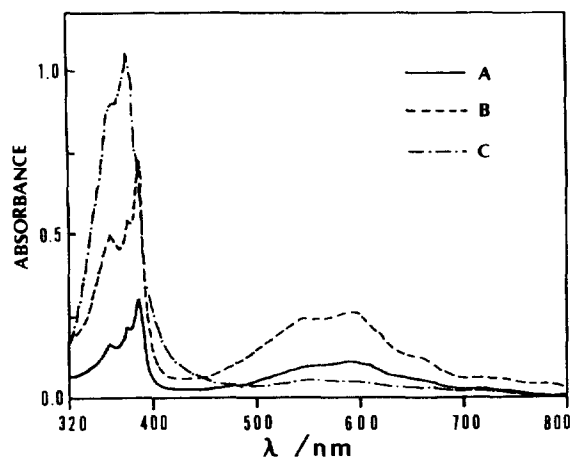


Figure 6. Absorption spectra at electrolysis time of 1 min; solution of aqueous 1.0 mM C₁BPYC1 and 0.1 M NaCl: (A: —) pH 3.8 and E_{app} of -0.85 V; (B: ---) pH 3.8 and E_{app} of -1.1 V; (C: -·-) pH 10.0 and E_{app} of -1.2 V. The solution prior to electrolysis is used as a blank.

drawn by Ishida *et al.*¹¹ who claimed that C₃BPY⁺ undergoes $1e^-$ reduction at -1.0 V in acetonitrile media. To ascertain the $2e^-$ nature of the reduction of C₁BPY⁺ at pH > 7.5, we obtained cyclic voltammograms with a microdisk electrode (Figure 5). The steady-state current i at the microdisk electrode is given by Eq. (5),²¹

$$i = 4nFDc\tau \quad (5)$$

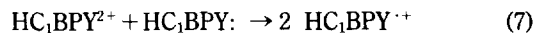
where n is the number of electrons in the electrode reaction, F is the Faraday's constant, D and C are the diffusion coefficient and concentration of the redox species, respectively, and τ is the radius of microdisk electrode. The steady-state current 3.2 nA at pH 10.0 is twice of that of the first reduction step 1.6 nA at pH 2.2. The two-fold difference in i values is too large to be attributed to the difference in D values between HC₁BPY²⁺ and C₁BPY⁺. Also, the rising portion of the current at pH 10.0 is steeper compared with pH 2.2 case. It is apparent that a single reduction step at high pH involves a direct $2e^-$ reduction.

The reduction potential of a direct $2e^-$ process at high pH shows a continuous shift to the negative direction as pH is further raised. But the slope of $\Delta E/\Delta pH$ is about 30 mV/pH (Figure 4). Combining this result with the $2e^-$ nature of the reduction, we are safe to conclude that the electrode process above pH 7.5 is mainly a single $2e^- + H^+$ reduction as in Eq. (6).



Absorption spectra of the reduced species of C₁BPY⁺ obtained by spectroelectrochemical techniques are shown in Figure 6. The spectrum at pH 3.8 with the electrode potential (E_{app}) of -0.85 V (Figure 6a) is very similar to that of dimethylviologen cation radical (MV^{•+}).⁹ This supports that the reduction is *via* Eqs. (4-1) and (4-2) and suggests similarity in electronic structures between MV^{•+} and HC₁BPY^{•+}. The spectrum at the same pH (pH 3.8) with E_{app} of -1.1 V (Figure 6b) resembles Figure 6a with small amount of dimer

of cation radical, probably (HC₁BPY^{•+})₂: the dimer absorbs light more strongly near 520 nm than near 600 nm, and exhibits an absorption band at 360 nm.^{13b} This can be explained by comproportionation reaction between electrogenerated HC₁BPY: and HC₁BPY²⁺ in bulk as Eq. (7): the rate of the comproportionation reaction seems to be not fast enough to remove HC₁BPY: from the electrode surface and to result disappearance of the oxidation peak of HC₁BPY: during CV measurements.¹²



The spectrum at pH 10.0 with E_{app} of -1.2 V is very similar to that of MV: with small amount of MV^{•+}.²² Equilibrium constant for Eq. (7), K_{comp} , can be written as Eq. (8):²³

$$K_{comp} = \exp[-F/RT(E_2^{\bullet+} - E_1^{\bullet+})] \quad (8)$$

At pH 10.0, $E_2^{\bullet+}$ is more positive than $E_1^{\bullet+}$ and thus comproportionation reaction is thermodynamically unfavorable. This seems the reason why we observe so little HC₁BPY^{•+} at high pH.

So far, we have presented the pH-dependent electrochemical behavior of RBPY⁺ and discussed the results in terms of electrode reactions of RBPY⁺ involving preceding and following reactions. We focused the presentation on C₁BPY⁺. The changes of peak potentials and currents by electrode adsorption of RBPY⁺ as well as their reduction products bearing more hydrophobic substituents¹² did not allow us similar quantitative analysis of the CV data of the other RBPY⁺. However, the similarity in pH dependence of the patterns of CV responses of all RBPY⁺ investigated in the present study clearly suggests that the chemistry outlined for C₁BPY⁺ can also be applied to other N-monosubstituted-4,4'-bipyridinium ions.

In conclusion, we have shown that N-monosubstituted-4,4'-bipyridinium (RBPY⁺) ions are reduced *via* two consecutive $1e^-$ reduction processes with preceding protonation reaction in acidic solution. The $2e^-$ reduction product undergoes H⁺-catalyzed chemical reaction. The second-order rate constant (k_H) of the reaction is $(3.7 \pm 0.3) \times 10^3 M^{-1}s^{-1}$ for C₁BPY⁺. The $2e^-$ reduction product also reacts with HC₁BPY²⁺ to produce $1e^-$ reduction product. At basic condition, RBPY⁺ is reduced by one-step $2e^- + H^+$ process.

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