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## pH-Dependent Electrochemical Behavior of N-Monosubstituted-4,4'-Bipyridinium Ions

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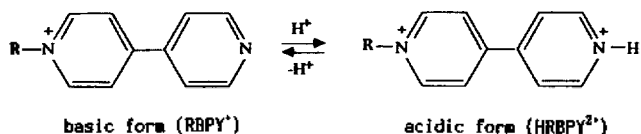
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The pH-dependent reduction behavior of N-monosubstituted-4,4'-bipyridinium ions (RBPY<sup>+</sup>; R=methyl(C<sub>1</sub>); benzyl; n-octyl; n-dodecyl) has been investigated by electrochemical and spectroelectrochemical techniques. At acidic condition, RBPY<sup>+</sup> is protonated and the protonated species are reduced by two consecutive one-electron processes. The 2e<sup>-</sup> reduced species undergoes a chemical reaction with H<sup>+</sup>. The second-order rate constant (*k<sub>H</sub>*) of the homogeneous chemical process is  $(3.7 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for the two electron reduction product of C<sub>1</sub>BPY<sup>+</sup>. At high pH, the electrode reduction of RBPY<sup>+</sup> is one-step 2e<sup>-</sup> transfer process with concomitant addition of H<sup>+</sup>, which is confirmed by cyclic voltammetric study using a microdisk electrode.

### Introduction

N-monosubstituted-4,4'-bipyridinium ions (RBPY<sup>+</sup>) are closely related with N,N'-disubstituted-4,4'-bipyridinium ions (viologens) via the following acid-base equilibrium.



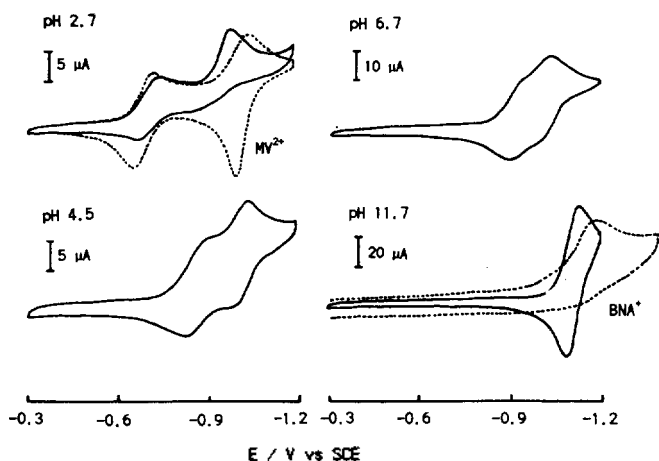
The acidic form has structural similarity to viologens which are very attractive materials as electron-transfer reagent in chemical<sup>1</sup> and photochemical<sup>2</sup> reductions of substrates, solar energy conversion,<sup>3</sup> and electrochromic display.<sup>4</sup> The basic form is a substituted pyridinium and can be considered as a coenzyme NAD<sup>+</sup> analogue. Because of these interesting characters, the pH-dependent electrochemical<sup>5,6</sup> and spectroscopic<sup>7,8</sup> behaviors of the RBPY<sup>+</sup> compounds as well as their ability as electron carriers<sup>9-11</sup> in redox reactions have been investigated. Recently, Ishida *et al.*<sup>11</sup> reported that the interaction between CO<sub>2</sub> and electrochemically reduced species of N-propyl-4,4'-bipyridinium cation (C<sub>3</sub>BPY<sup>+</sup>) activates the electron transfer from the bipyridine ring to CO<sub>2</sub>. They also claimed that C<sub>3</sub>BPY<sup>+</sup> is reduced by 1e<sup>-</sup> process at -1.0 V (*vs* SCE) in acetonitrile media. We have been interested in electrochemical behavior of viologens<sup>12,13</sup> and the reactions of the reduced NAD<sup>+</sup>, NADH, and their analogues.<sup>14,15</sup> In this paper, we present the pH-dependent reduction behavior of RBPY utilizing electrochemical and spectroelectrochemical techniques. Cyclic voltammetry (CV) with a microdisk electrode is used to determine the number of elec-

trons transferred in the reduction reactions. Also, the reaction rate of the electrogenerated 2e<sup>-</sup> reduction product of C<sub>1</sub>BPY<sup>+</sup> in acidic medium is determined.

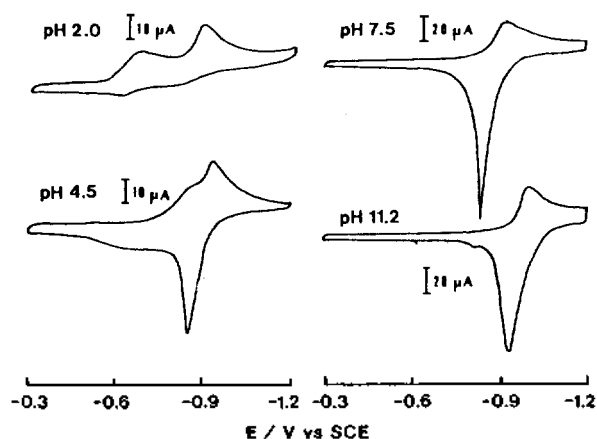
### Experimental

**Materials.** N-monosubstituted-4,4'-bipyridinium (RBPY<sup>+</sup>; R= methyl (C<sub>1</sub>); benzyl (B); n-octyl (C<sub>8</sub>); n-dodecyl (C<sub>12</sub>)) salts were prepared by reacting 4,4'-bipyridine with corresponding alkyl or benzyl halides according to known procedure.<sup>9</sup> Solutions of desired pH were prepared by appropriate mixing of 0.10 M HCl, 0.01 M NaOH+0.09 M NaCl, or 0.01 M Na<sub>2</sub>HPO<sub>4</sub>+0.07 M NaCl solutions. Reverse osmosed water which was further purified by passage through a purification train (Millipore Corp) was used.

**Apparatus and procedures.** Cyclic voltammetry (CV) was carried out with a BAS 100B electrochemical analyzer or a Tacussel PRG 5 potentiostat coupled with a GSTP3 function generator. Glassy carbon electrodes (Metrohm and BAS, area of 0.06-0.07 cm<sup>2</sup>) were polished using 0.1 μm alumina followed by sonication in pure water. A carbon microdisk electrode having a nominal diameter of 11 μm was prepared<sup>16</sup> and used. All potentials are reported against a saturated calomel electrode (SCE) unless otherwise specified. Solutions were purged with nitrogen to remove oxygen. Current was calculated by subtracting the background CV data taken without RBPY<sup>+</sup> from CV data recorded with RBPY<sup>+</sup>. A Hewlett-Packard 8452A diode array spectrophotometer was used to obtain absorption spectra where the potential of the working electrode (ITO coated glass, Delta Technologies) was controlled potentiostatically.



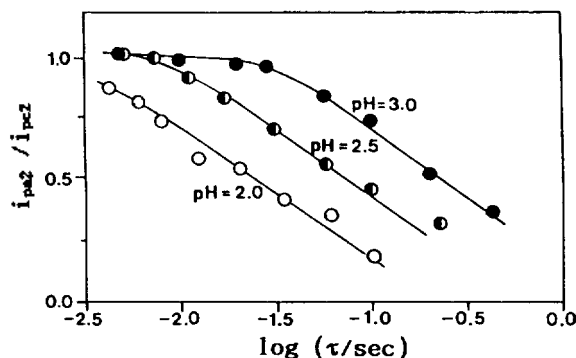
**Figure 1.** Effect of pH on cyclic voltammograms of 1.0 mM 1-methyl-4,4'-bipyridinium chloride in aqueous 0.1 M NaCl solutions at 25 °C. The CV's of 1.0 mM dimethylviologen ( $MV^{2+}$ ) and 1-benzyl-4,4'-bipyridinium chloride (BNA<sup>+</sup>) recorded at pH 7 are given for comparison. Scan rates 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  $C_1BPY^+$  recorded at various pH. The CV response of  $C_1BPY^+$  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  $C_1BPY^+$  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<sup>+</sup> analogue, 1-benzyl-4,4'-bipyridinium (BNA<sup>+</sup>) ion: anodic peak of BNA<sup>+</sup> is not observed presumably due to rapid dimerization of the reduction product,<sup>17</sup> 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  $\tau$  and pH (2.0–3.0).  $\tau$  is the time (s) between  $E_{1/2}$  and the switching potential. Scan rate changes from 0.5 to 50 V/s.

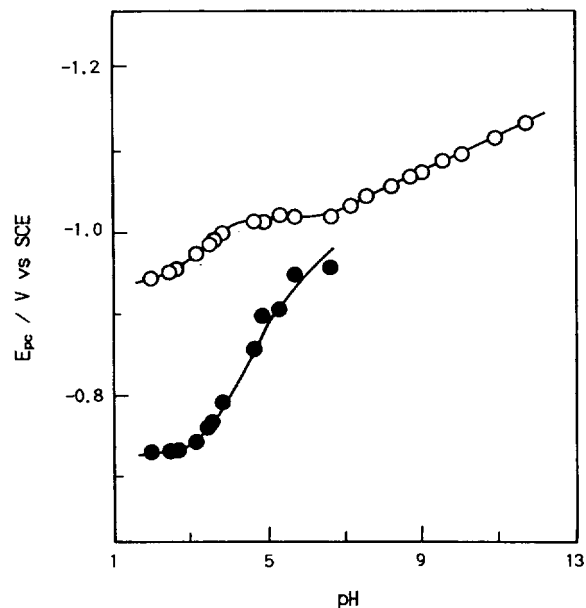
following reaction (if any) appears to be much slower for the reduction product of  $C_1BPY^+$  at the high pH.

The pH-dependent CV responses of other *N*-substituted-4,4'-bipyridinium salts are similar to that of  $C_1BPY^+$  (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  $C_1BPY^+$ , 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.<sup>12</sup> Because of the complication arising from the electrode adsorption of the electroactive species in quantitative analysis of the CV, we confine further analysis to  $C_1BPY^+$  which is the least complicated one among  $RBPY^+$  investigated in the present work.

The  $pK_a$  of  $HC_1BPY^{2+}$  is reported to be 3.42.<sup>18</sup> At  $pH < 3.42$ , the predominant species of  $C_1BPY^+$  is  $HC_1BPY^{2+}$  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,  $\Delta E_p$ , 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  $C_1BPY^+$  under acidic condition also depend on the scan rate. At  $pH < 3$ , the CV of  $C_1BPY^+$  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



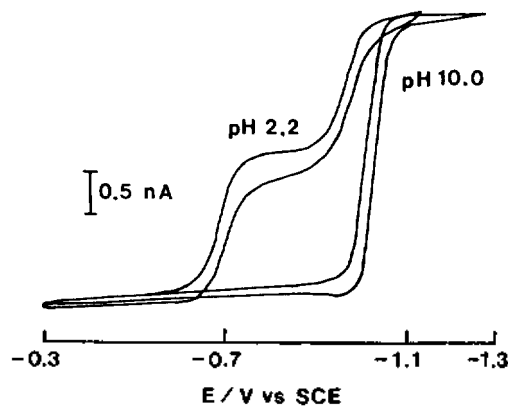
**Figure 4.** Effect of pH on the first (●) and the second (○) cathodic peak potentials of 1.0 mM C<sub>1</sub>BPYCl in aqueous 0.1 M NaCl solutions at 25 °C.

electrode reaction, HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup>, reacts within this experimental time scale to produce a species that is not electroactive at potentials where the reduction of HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup> 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  $\tau$  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 HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup> 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  $\tau$ , 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<sup>+</sup> ion. From the Nicholson and Shain treatment of EC<sub>2</sub> processes,<sup>19</sup> 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 HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup>. Hence, the second reduction step of C<sub>1</sub>BPY<sup>+</sup> 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.<sup>14,15</sup> The  $k_H$  value for HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup> is greater than the corresponding values observed with 1,3-disubstituted-1,4-dihydro-pyridines which depend largely on the nature of the substituent.<sup>14,15</sup> The result of this work seems to reflect sensitivity of  $k_H$  on the position as well as the nature



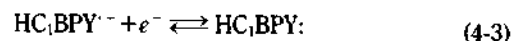
**Figure 5.** Effect of pH on cyclic voltammograms of 1.0 mM C<sub>1</sub>BPYCl with a carbon microdisk electrode in aqueous 0.1 M NaCl solutions at 25 °C. Scan rates are 50 mV/s.

of substituents.

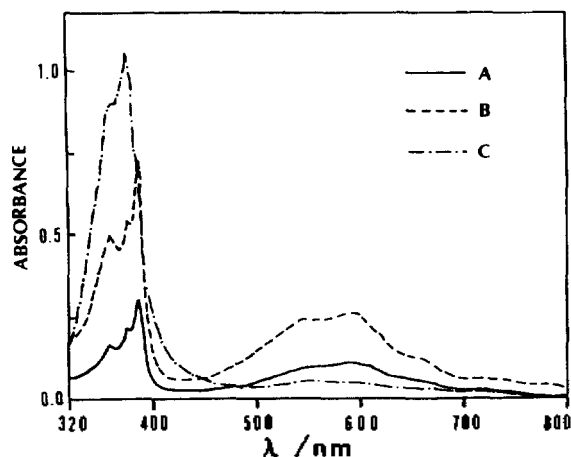
The first and second cathodic peak potentials ( $E_{pc}$ ) taken at the scan rate of 90 mV/s are shown in Figure 4 as functions of pH. As pH of the medium is raised from pH 2,  $E_{pc2}$  is shifted to negative direction until pH becomes 4, while the  $E_{pc1}$  is virtually independent of pH below pH 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 HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup>, in which H<sup>+</sup> 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,<sup>19</sup>



If we assume that HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup> is electroactive and C<sub>1</sub>BPY<sup>-</sup> 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 HC<sub>1</sub>BPY<sub>2</sub><sup>+</sup>,  $4.0 \times 10^{-4}$ . The dependence of the  $E_{pc1}$  on pH (Figure 4) agrees well with this prediction. The pH independence of  $E_{pc2}$  of HC<sub>1</sub>BPY<sub>2</sub><sup>-</sup> in the pH range of 4-7 is indicative that the  $\text{p}K_a$  of HC<sub>1</sub>BPY<sub>2</sub><sup>+</sup> 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 C<sub>1</sub>BPY<sup>+</sup> itself. Under this condition, a single wave characteristic of 2e<sup>-</sup> reduction is observed because the second step reduction becomes easier than the first one.<sup>20</sup> This seems the case at pH > 7.5, where a single reduction wave is observed. The measured value of  $\Delta E_p$  was 40 mV (Figure 1) at pH 11.7 is also suggestive of 2e<sup>-</sup> process. This is quite contrary to the conclusion



**Figure 6.** Absorption spectra at electrolysis time of 1 min; solution of aqueous 1.0 mM C<sub>1</sub>BPYCl 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.*<sup>11</sup> who claimed that C<sub>3</sub>BPY<sup>+</sup> undergoes  $1e^-$  reduction at  $-1.0$  V in acetonitrile media. To ascertain the  $2e^-$  nature of the reduction of C<sub>1</sub>BPY<sup>+</sup> 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),<sup>21</sup>

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

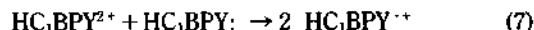
where  $n$  is the number of electrons in the electrode reaction,  $F$  is the Faraday's constant,  $D$  and  $C$  are the diffusion coefficient and concentration of the redox species, respectively, and  $\tau$  is the radius of microdisk electrode. The steady-state current 3.2 nA at pH 10.0 is twice 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 HC<sub>1</sub>BPY<sup>2+</sup> and C<sub>1</sub>BPY<sup>+</sup>. 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 C<sub>1</sub>BPY<sup>+</sup> 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<sup>•+</sup>).<sup>9</sup> This supports that the reduction is *via* Eqs. (4-1) and (4-2) and suggests similarity in electronic structures between MV<sup>•+</sup> and HC<sub>1</sub>BPY<sup>•+</sup>. 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 (HC<sub>1</sub>BPY<sup>•+</sup>)<sub>2</sub>; the dimer absorbs light more strongly near 520 nm than near 600 nm, and exhibits an absorption band at 360 nm.<sup>13b</sup> This can be explained by conproportionation reaction between electrogenerated HC<sub>1</sub>BPY<sup>•+</sup> and HC<sub>1</sub>BPY<sup>2+</sup> in bulk as Eq. (7): the rate of the conproportionation reaction seems to be not fast enough to remove HC<sub>1</sub>BPY<sup>•+</sup> from the electrode surface and to result disappearance of the oxidation peak of HC<sub>1</sub>BPY<sup>•+</sup> during CV measurements.<sup>12</sup>



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

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

At pH 10.0,  $E_2^{\bullet+}$  is more positive than  $E_1^{\bullet+}$  and thus conproportionation reaction is thermodynamically unfavorable. This seems the reason why we observe so little HC<sub>1</sub>BPY<sup>•+</sup> at high pH.

So far, we have presented the pH-dependent electrochemical behavior of RBPY<sup>+</sup> and discussed the results in terms of electrode reactions of RBPY<sup>+</sup> involving preceding and following reactions. We focused the presentation on C<sub>1</sub>BPY<sup>+</sup>. The changes of peak potentials and currents by electrode adsorption of RBPY<sup>+</sup> as well as their reduction products bearing more hydrophobic substituents<sup>12</sup> did not allow us similar quantitative analysis of the CV data of the other RBPY<sup>+</sup>. However, the similarity in pH dependence of the patterns of CV responses of all RBPY<sup>+</sup> investigated in the present study clearly suggests that the chemistry outlined for C<sub>1</sub>BPY<sup>+</sup> can also be applied to other N-monosubstituted-4,4'-bipyridinium ions.

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

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