

Cyclic and Normal Pulse Voltammetric Studies of 2,3,6,7,10,11-Hexaphenylhexazatriphenylene Using a Benzonitrile Thin Layer-Coated Glassy Carbon Electrode

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The method of interposing a thin layer of immiscible organic solvent (benzonitrile, BN) between a glassy carbon electrode surface and an aqueous solution has been successfully applied to study the electrode reaction of a highly hydrophobic organic molecule, 2,3,6,7,10,11-hexaphenylhexazatriphenylene (HAT). Four couples of well-defined redox peaks of HAT were observed at the BN thin layer-coated electrode in N₂-saturated 2 M HClO₄ aqueous solution. By cyclic voltammetry, square-wave voltammetry, and normal pulse voltammetry, the thermodynamic and kinetic parameters (i.e., the formal potential, standard rate constant, and cathodic transfer coefficient) for the multistep redox reaction of HAT and its diffusion coefficient were evaluated. The good agreement between the observed normal pulse voltammograms and the calculated one with use of the obtained kinetic and thermodynamic parameters demonstrated that the evaluated parameters are reasonable and that the present approach is useful in the kinetic study of the multistep redox reaction of hydrophobic reactants. A probable reaction mechanism for the whole redox reaction of HAT was also proposed.

Introduction

Previous reports from our group have shown that polyquinoxaline (PQL)-modified graphite electrodes possess an excellent catalytic activity for electrochemical reduction of oxygen to hydrogen peroxide in acidic solution.^{1–3} This excellent electrocatalytic activity was considered to be due to the high reactivity of reduced pyrazine rings in the polymer toward molecular oxygen. As 2,3,6,7,10,11-hexaphenylhexazatriphenylene (HAT, Figure 1) contains three equivalent pyrazine rings in its structure, a similar electrocatalytic activity of HAT for oxygen reduction in acidic media could be expected. HAT is also one of a series of planar bridged ligands which contain three sites for possible bidentate coordination to a metal ion. It is thought that delocalization of the π -electron system may provide facile electronic communication between coordinated metal centers leading to interesting chemical and physical properties.⁴ These kinds of nitrogen heterocyclic molecules and their metal complexes have been extensively studied in the context of supramolecular chemistry,^{5–8} photochemistry,^{9–12} and organometallic chemistry.^{13–16} Despite much attention to these interesting molecules, their chemical and electrochemical properties have not been widely explored, probably because they are insoluble or hardly soluble in most of the common solvents.¹⁷

Recently, Anson et al. have developed a new method for examining the electrochemistry of hydrophobic reactants by interposing a thin layer of immiscible organic solvent between the graphite electrode surface and aqueous solution¹⁸ and they

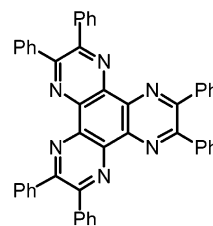


Figure 1. Structure of 2,3,6,7,10,11-hexaphenylhexazatriphenylene (HAT).

have studied the electrocatalytic reduction of oxygen by cobalt 5,10,15,20-tetraphenylporphyrin dissolved in the thin layer of benzonitrile on the graphite electrode.¹⁹ This approach allows well-defined cyclic voltammetric response to be readily obtained when an electroactive hydrophobic species is dissolved in the organic thin layer. In addition, this method is also very useful for the study of the electron transfer at the boundary of two immiscible solution phases^{20–24} and the ion transfer across the interfaces.^{25,26} In applying this method, several kinds of reactants and immiscible organic solvents have been utilized,²⁷ and recently, Park and Oyama have used a glassy carbon electrode as the working electrode instead of a graphite electrode.²⁸

The remarkable features of this method, especially its simplicity and requiring a limited amount of reactant, make it suitable for the study of the electrochemical properties of HAT, since HAT is a highly hydrophobic compound and is not commercially available. In the present study, we tried to apply this simple method to examine the electrochemical multistep redox reduction of HAT, which contains three equivalent pyrazine moieties, in the presence of proton. The experiments were carried out at glassy carbon electrodes covered with a thin

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layer of benzonitrile solution containing HAT in HClO_4 aqueous solution. The thermodynamic and kinetic parameters (i.e., the formal potential, standard rate constant, and cathodic transfer coefficient) of the individual redox steps of HAT and its diffusion coefficient were evaluated by using cyclic, normal pulse, and square-wave voltammetries. In addition, the reaction mechanism of the whole reduction of HAT was also proposed.

Experimental Section

Materials. 2,3,6,7,10,11-Hexaphenylhexazatriphenylene (HAT) was synthesized and purified according to the procedures described in our previous report.²⁹ Benzonitrile (BN), tetra-*n*-butylammonium perchlorate (TBAP), 60% perchloric acid (Kanto Chemical Co. Inc., Japan), and ferrocene and decamethylferrocene (DMFc, Wako Pure Chemical Industries, Ltd., Japan) were of analytical grade and were used as received. Aqueous solutions used in the electrochemical measurements were saturated with BN before use. A small rod of glassy carbon (GC) (GC-20s, Tokai Carbon Co; length 5.0 mm, diameter 3.0 mm) was used as the working electrode.²⁸ The rod was connected to a glass tube (diameter 3.0 mm) with a piece of heat-shrinkable tube (thickness 0.5 mm). The electrical connection was made to a copper wire at the inside of the glass tube by using a drop of mercury.

Apparatus and Procedures. Electrochemical studies were performed with use of a conventional two-compartment three-electrode cell with a glassy carbon working electrode, a Pt wire auxiliary electrode, and a NaCl-saturated Ag/AgCl reference electrode ($\text{Ag}/\text{AgCl}/\text{NaCl}_{(\text{sat.})}$). N_2 gas was directly bubbled into the cell solution for 20 min to remove oxygen in aqueous solution before electrochemical measurements, and flushed over the cell solution throughout the measurements. All the electrochemical measurements were performed at room temperature ($25 \pm 1^\circ\text{C}$).

Cyclic voltammetry, normal pulse voltammetry, and square-wave voltammetry were performed by using a computer-controlled electrochemical system (CHI 604A, CHI Instruments Inc., USA).

GC working electrodes were polished with fine emery paper and then with alumina powder (particle size: 1.0 and $0.06\ \mu\text{m}$, Marumoto Kogyo Co. Ltd.) on a polishing microcloth wetted with Milli-Q water before use. The surface of the GC electrode was then carefully sonicated in Milli-Q water for 10 min. After the electrode was dried in air, we followed the same procedure as described by Shi and Anson¹⁸ to spread $1\ \mu\text{L}$ of BN solution across the electrode surface and the shrinkable tube with a micropipet. Then the electrode was immediately inverted and immersed in the N_2 -saturated aqueous solution. To remove the residual oxygen in the thin layer and equilibrate the partition of supporting electrolyte between the two phases, the electrochemical measurements, unless otherwise noted, were started after the electrode was immersed in the aqueous solution for at least 10 min. The thickness of the BN layer could be estimated to be ca. $80\ \mu\text{m}$ from the volume of BN solution coated on the electrode. The thickness was also estimated to be $76\ \mu\text{m}$ from the cyclic voltammograms of decamethylferrocene obtained at the BN thin layer-coated GC electrode.¹⁸

Results and Discussion

Cyclic Voltammetry of HAT at the BN Thin Layer-Coated GC Electrode. Similar to cobalt tetraphenylporphyrin,¹⁹ HAT adsorbed on the GC electrode also yielded an indistinct cyclic voltammetric response in aqueous media. Therefore, the "BN

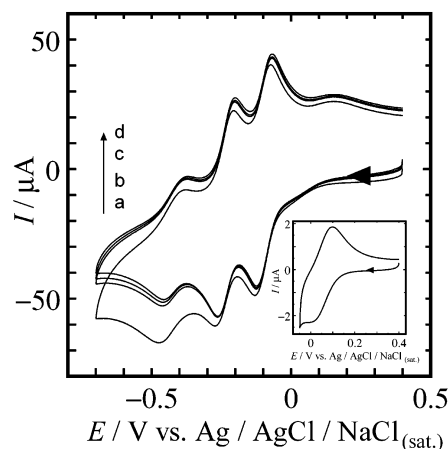


Figure 2. Cyclic voltammograms obtained at the GC electrode covered with a thin layer of 0.1 M TBAP benzonitrile solution containing 0.5 mM HAT in N_2 -saturated 2 M HClO_4 aqueous solution. The scan rate was $500\ \text{mV s}^{-1}$. Voltammograms a, b, c, and d were recorded after the GC electrode was immersed in the aqueous solution for 0, 10, 20, and 30 min, respectively. The inset shows the cyclic voltammogram obtained at the GC electrode covered with a thin layer of 0.1 M TBAP benzonitrile solution containing 0.5 mM HAT in N_2 -saturated 2 M HClO_4 aqueous solution. In this case, the scan rate was $10\ \text{mV s}^{-1}$ and the potential scanning range was limited between 0.4 and $-0.05\ \text{V}$ vs. $\text{Ag}/\text{AgCl}/\text{NaCl}_{(\text{sat.})}$.

thin layer-coated electrode method" was used to examine the electrochemical behavior of HAT.

Since oxygen dissolved in the BN thin layer was presumed to influence the electrochemical measurements of HAT even though the aqueous solution had been previously saturated with N_2 , we first examined the cyclic voltammetric behavior of HAT by considering this. The typical cyclic voltammograms (CVs) obtained by using four BN thin layer-coated GC electrodes in N_2 -saturated 2 M HClO_4 aqueous solution are shown in Figure 2, in which the BN thin layer contained 0.5 mM HAT and 0.1 M TBAP and the CVs were recorded at the individual electrodes after they were immersed in the aqueous solution for different periods of time. The CV (voltammogram a) measured immediately after immersed in the solution is greatly different from the other CVs. This difference is due to the reduction current of the residual oxygen in the thin layer, since oxygen in the BN thin layer shows the reduction peak at about $-0.45\ \text{V}$ vs. SCE.¹⁹ Immersion of the electrode in the N_2 -saturated aqueous solution for about 10 min seems to be enough to remove the influence of residual oxygen since the voltammograms (b, c, and d) are almost the same. In addition, as the electrodes used for obtaining CVs (b, c, and d in Figure 2) were prepared individually, these uniform CVs also suggest that the present thin layer approach possesses a good reproducibility and that the BN thin layer coated on the electrode is stable for at least 30 min.

The electrochemical behavior of HAT in the absence of proton was examined at the BN thin layer-coated GC electrode in N_2 -saturated 0.1 M NaClO_4 aqueous solution with cyclic voltammetry (data not shown). At the first scan, the CV of HAT obtained in the potential range from 0.4 to $-1.7\ \text{V}$ vs. $\text{Ag}/\text{AgCl}/\text{NaCl}_{(\text{sat.})}$ showed a large reduction peak at $-1.48\ \text{V}$ and two small oxidation peaks at -0.49 and $-0.08\ \text{V}$. Two new reduction peaks at -0.18 and $-0.35\ \text{V}$ were found at the second scan. When the potential scan was repeated continuously, the reduction peak current at $-1.48\ \text{V}$ decreased, while the other redox peak currents increased. All the redox peaks could still be found in the CVs obtained in the potential range from 0.4 to $-0.7\ \text{V}$ after the potential scan was repeated several times in

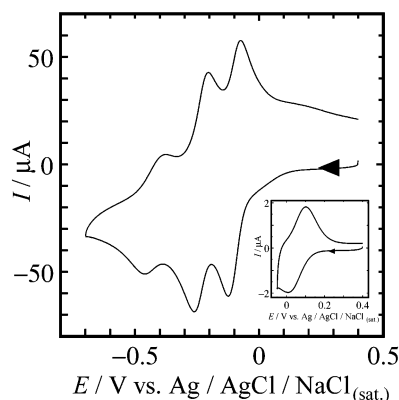


Figure 3. Cyclic voltammogram obtained at the BN thin layer-coated GC electrode in N_2 -saturated 2 M $HClO_4$ aqueous solution. The thin layer contained only 0.5 mM HAT. The scan rate was 500 mV s^{-1} . The inset shows the cyclic voltammogram obtained at the same electrode at 10 mV s^{-1} in a potential range of 0.4 to -0.05 V vs $Ag/AgCl/NaCl_{(sat.)}$.

TABLE 1: Peak Potentials, Formal Potentials, and Peak Potential Differences of Each Redox Step of HAT Obtained by CV at the Benzonitrile Thin Layer-Coated GC Electrode in 2 M $HClO_4$ Aqueous Solution^a

redox step of HAT	E_{pc}/V	E_{pa}/V	E^0/V	$\Delta E_p/mV$
1st step ^b	0.020	0.091	0.055	71
2nd step ^c	-0.071	-0.120	-0.096	49
3rd step ^c	-0.206	-0.260	-0.233	54
4th step ^c	-0.384	-0.455	-0.420	71

^a The benzonitrile thin layer contained 0.1 M TBAP and 0.5 mM HAT. ^b Scan rate was 10 mV s^{-1} . ^c Scan rate was 500 mV s^{-1} .

the potential range from 0.4 to -1.7 V . On the other hand, no redox peak was observed at the fresh electrode scanned in the potential range from 0.4 to -0.7 V . These facts may suggest that the reduction of HAT at -1.48 V produces the corresponding anion radical and then the produced anion radicals undergo some following chemical reactions to produce unknown products. The observed redox peaks, except for the peak at -1.48 V , are due to the redox reactions of the unknown products and the related reaction mechanism has not been clarified yet.

On the other hand, four couples of well-defined redox peaks of HAT were observed at the BN thin layer-coated electrode in N_2 -saturated 2 M $HClO_4$ aqueous solution, as shown in Figure 2, which indicates that the redox reaction of HAT undergoes a four-step redox reaction under the present conditions. The peak currents of the individual couples are different, but the anodic and cathodic peak currents for each couple can be considered to be almost the same. The anodic and cathodic peak potentials (E_{pa} and E_{pc}) and their separation ($\Delta E_p = |E_{pa} - E_{pc}|$) and formal potentials (E^0), estimated as $(E_{pa} + E_{pc})/2$, of each redox step are summarized in Table 1. The ΔE_p values of the 1st and 4th redox steps are 71 mV and those of the 2nd and 3rd redox steps are 49 and 54 mV, respectively. Thus, the 1st and 4th steps may be regarded as a one-electron process and the 2nd and 3rd steps as a two-electron process³⁰ in agreement with the normal pulse voltammetric data (vide infra).

The influence of supporting electrolyte contained in the BN layer on the electrochemical behavior of HAT was also examined. Figure 3 shows the typical CV of HAT obtained at the GC electrode covered with the BN thin layer containing no TBAP in 2 M $HClO_4$ aqueous solution. In this case, $HClO_4$ is equilibrated between H_2O and BN and the initial concentrations of H^+ , ClO_4^- , and $HClO_4$ in the BN layer are calculated to be 2.4, 2.4, and 20 mM, respectively.²⁵ From the comparison of

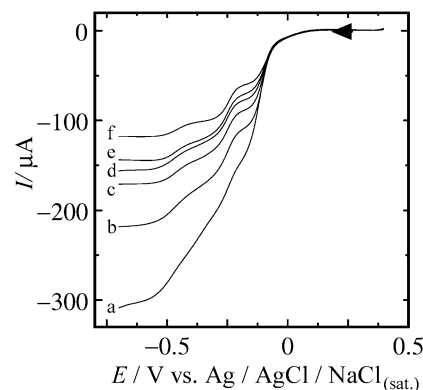


Figure 4. Normal pulse voltammograms obtained at the BN thin layer-coated GC electrode in N_2 -saturated 2 M $HClO_4$ aqueous solution. The thin layer contained only 0.5 mM HAT. Sampling time was (a) 16, (b) 25, (c) 36, (d) 49, (e) 64, and (f) 81 ms. The background correction was made for each voltammogram.

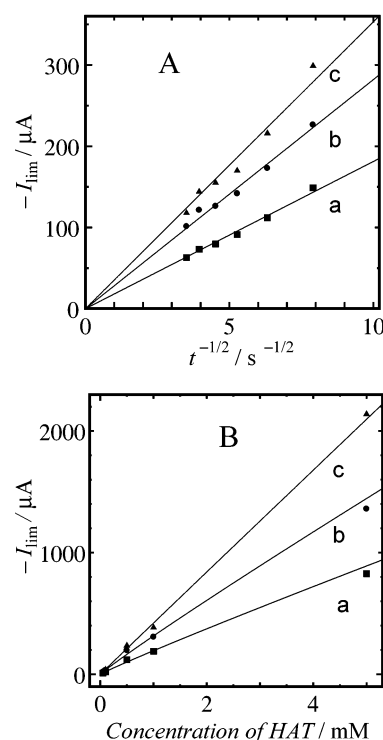


Figure 5. (A) Plots of $-I_{lim}$ vs $t_s^{-1/2}$ for (a) 2nd, (b) 3rd, and (c) 4th reduction steps of HAT, at -0.20 , -0.26 , and -0.65 V , respectively. Data were taken from Figure 4. (B) Plots of $-I_{lim}$ vs the concentration of HAT for (a) 2nd, (b) 3rd, and (c) 4th reduction steps.

Figures 2 and 3, we can see clearly that the redox behavior of HAT at the BN thin layer-coated electrode is actually independent of whether the BN thin layer contains TBAP as electrolyte or not. This fact demonstrates that the electrolyte concentration in the BN layer is enough for the electrode reaction of HAT to proceed and that the rate of proton transfer from the H_2O phase to the BN phase across the BN/ H_2O interface is adequate to sustain the proton-consuming redox reaction of HAT at the GC/BN interface. We have also measured the CV of HAT at the BN thin layer (containing no TBAP)-coated GC electrode in 0.5 M $HClO_4$ and found that the redox peaks shift, as expected, negatively compared with those (Figure 3) obtained in the aqueous solution containing 2 M $HClO_4$. However, the concentrations of ions (H^+ etc.) in the BN phase decrease, as the concentration of $HClO_4$ in the aqueous phase is decreased, and consequently the electrolyte concentrations in the BN layer

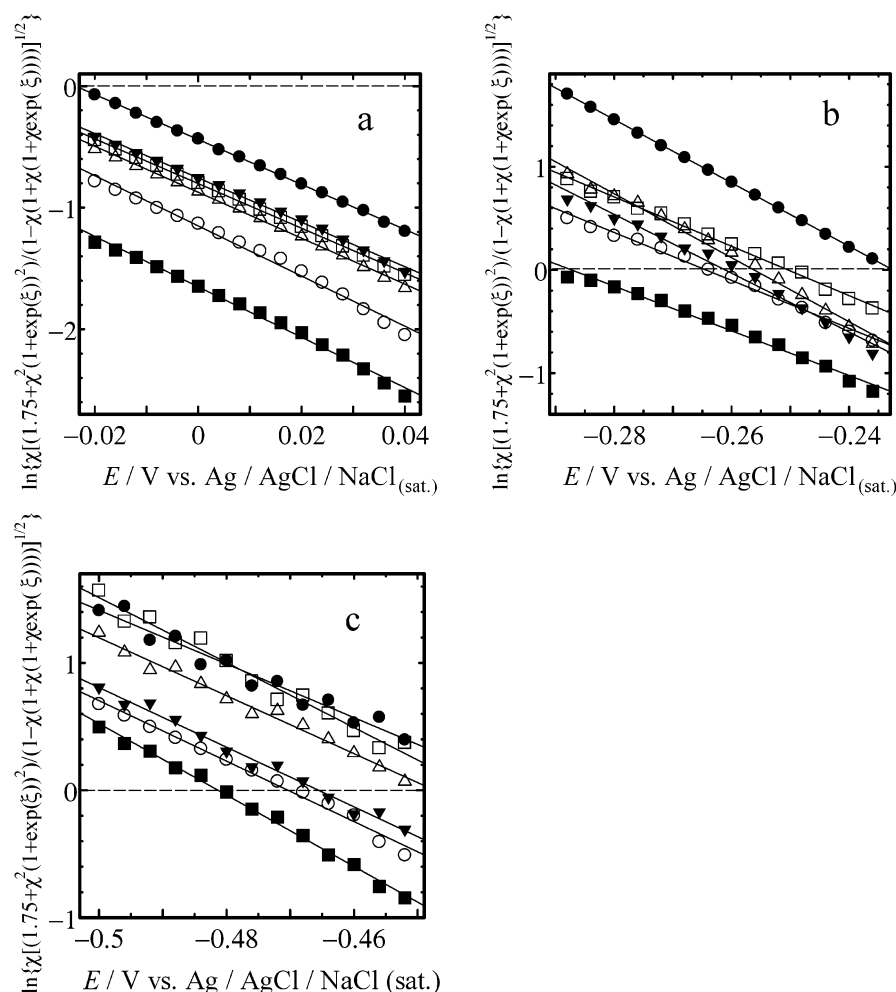


Figure 6. Modified log plot of normal pulse voltammograms for (a) 1st, (b) 3rd, and (c) 4th reduction steps of HAT. Sampling time was (■) 16, (○) 25, (△) 36, (▼) 49, (□) 64, and (●) 81 ms.

become insufficient for the electrode reaction of HAT to proceed. Therefore, the quantitative analysis of the electrode kinetics of HAT at the BN thin layer-coated electrode with use of normal pulse voltammetry will be carried out only in 2 M $HClO_4$ solution, as shown in the next section.

Normal Pulse Voltammetry of HAT at the BN Thin Layer-Coated GC Electrode. Figure 4 shows the normal pulse voltammograms (NPVs) obtained for the reduction of HAT at the BN thin layer-coated GC electrode in 2 M $HClO_4$ solution. The sampling time (τ_s) was changed between 16 and 81 ms. These NPVs were corrected with the respective background currents, which were obtained at the same condition except that the BN thin layer contained no HAT. Each NPV exhibits four waves corresponding to the four redox steps of HAT in accordance with the above-mentioned CV data. The ratio of the limiting currents of these steps is about 1:2:2:1. This also suggests that the number of electrons involved in the 1st, 2nd, 3rd, and 4th steps is 1, 2, 2, and 1, respectively. The fact that the Cottrell plots of the limiting current (i_{lim}) against $\tau_s^{-1/2}$ are nearly linear and pass through the origin, as shown in Figure 5A, indicates that the effect of finite diffusion of HAT in the BN thin layer, which may result from its limited thickness, on the voltammogram is negligible under the experimental conditions used here.³¹ As discussed above, it is reasonably assumed that six electrons are totally involved in the reduction of HAT. Thus, from the slope of the plot c (Figure 5A), using the normal pulse voltammetric Cottrell equation (eq 1), we estimated the diffusion coefficient of HAT in the BN layer to be 9.3×10^{-6}

$cm^2 s^{-1}$.

$$(i_d)_{Cott} = nFAC \left(\frac{D}{\pi \tau_s} \right)^{1/2} \quad (1)$$

Then, the diffusion layer thickness ($\sqrt{\pi D \tau_s^{32}}$) at the longest sampling time, 81 ms, was estimated to be ca. $15 \mu m$. It is much thinner than the thickness of the BN layer (ca. $80 \mu m$). Thus, the equations of normal pulse voltammetry for the conventional electrochemical system could also be used to analyze the data obtained at the present BN thin layer-coated electrode. In addition, the limiting currents of the 2nd, 3rd, and 4th steps were found to be proportional to the concentration of HAT in the BN layer in the examined range of its concentration from 0.05 to 5 mM (Figure 5B), indicating that most of the protons consumed during the electrode reaction are rapidly supplied from the 2 M $HClO_4$ aqueous solution across the BN/ H_2O interface.

The kinetic parameters for the 1st, 3rd, and 4th reduction steps of HAT can be evaluated from the analysis of the rising part of each current–potential curve shown in Figure 4 by using the following equations:^{33–38}

$$E = E^* - \frac{RT}{\alpha_c n F} \ln \left\{ x \left[\frac{1.75 + x^2(1 + \exp(+\xi))}{1 - x(1 + \exp(+\xi))} \right]^{1/2} \right\} \quad (2)$$

with

$$x = i/(i_d)_{Cott} \quad (4)$$

$$E^* = E_{1/2}^r + \frac{RT}{\alpha_c n F} \ln \left(\frac{4}{3^{1/2}} \frac{k^0 \tau_s^{1/2}}{D^{1/2}} \right) \quad (3)$$

$$\xi = \frac{nF}{RT} (E - E_{1/2}^r) \quad (5)$$

$$D = (D_{\text{ox}})^{\alpha_a} (D_{\text{red}})^{\alpha_c} \quad (6)$$

where E is the electrode potential, i is the normal pulse voltammetric current, $E_{1/2}^r$ is the reversible half-wave potential of the redox couple of each step, D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced states of HAT, respectively, k^0 is the standard rate constant, α_a and α_c are the anodic and cathodic transfer coefficients, respectively, and R and T have their usual meanings. By assuming that the diffusion coefficients of each redox state of HAT have the same value we can see that the limiting current for each step is directly proportional to the number of electrons involved in it. Therefore, we may reasonably take $1/6$ of the total limiting current as those for the 1st and 4th steps and $1/3$ of that as those for the 2nd and 3rd steps based on the electron number involved in each redox step of HAT.

The modified log plots of the second term on the right-hand side of eq 2 against E for the 1st, 3rd, and 4th reduction steps of HAT gave almost straight lines, the slopes of which were almost constant for each step within experimental errors, at different τ_s values, as shown in Figure 6. As can be seen from eq 2, the α_c values can be evaluated from the slope of each modified log plot, and the E^* values for each sampling time can be obtained from intersections of these lines with the zero line. The E^* shifted to the direction of negative potential from $E^{0'}$ with decreasing τ_s , as expected from eq 3. The plots of E^* against $\ln(\tau_s)$, shown in Figure 7, give straight lines. Their slopes also enable us to evaluate the α_c values, and the α_c values evaluated from Figures 6 and 7 were in agreement with each other. The α_c values are summarized in Table 3.

The standard rate constant, k^0 , can be evaluated from the intercept of the plots shown in Figure 7 by means of eq 3. With the assumption that all the redox states of HAT have the same diffusion coefficient, $E^{0'}$ may be considered to be equal to $E_{1/2}^r$. Here we can take the mean potential of redox peaks of the cyclic voltammogram (Figure 3) and the peak potential of the square-wave voltammogram (Figure 8) as $E^{0'}$. The $E^{0'}$ values obtained by cyclic voltammetry coincide well with those obtained by square-wave voltammetry (Table 2). The mean $E^{0'}$ values obtained by these two methods were used for evaluating k^0 . The values of k^0 are summarized in Table 3.

We could not analyze the 2nd step reaction of HAT by using the same approach to obtain its kinetic parameters because this step was reversible on the time scale of the present measurements. Therefore, we tried to use eq 7,

$$E = E_{1/2}^r - \frac{RT}{nF} \ln \left(\frac{(i_d)_{\text{Cott}} - i}{i} \right) \quad (7)$$

which is applied to a reversible reaction, to fit the experimental data. The plots of E against $\ln[(i_d)_{\text{Cott}} - i]/i$ gave straight lines at all the sampling times as expected. The value of n estimated from the slopes was ca. 2.

By substituting the kinetic parameters listed in Table 3 in eqs 1 to 6 for the 1st, 3rd, and 4th redox steps of HAT and in eq 7 for the 2nd redox step, we calculated the theoretical current–potential curves for each step (I_1 , I_2 , I_3 , and I_4) and took the sum of the current of each step (I_{1+2} , I_{1+2+3} , and

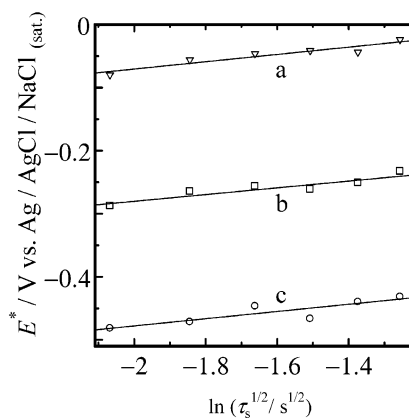


Figure 7. The plots of E^* vs $\ln(\tau_s^{1/2})$ for (a) 1st, (b) 3rd, and (c) 4th reduction steps of HAT.

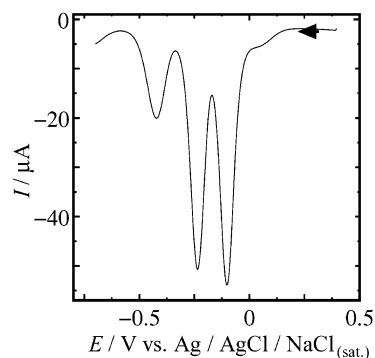


Figure 8. Square wave voltammogram obtained at the BN thin layer-coated GC electrode in N_2 -saturated 2 M HClO_4 aqueous solution. The thin layer contained only 0.5 mM HAT. Step potential: 4 mV. Amplitude: 25 mV. Frequency: 15 Hz.

TABLE 2: Formal Potentials of Each Redox Step of HAT Obtained by CV and SWV at the Benzonitrile Thin Layer-Coated GC Electrode in 2 M HClO_4 Aqueous Solution^a

redox step of HAT	$E^{0'}/\text{V}$	
	CV ^b	SWV ^c
1st step	0.055 ^d	
2nd step	−0.09 ^e	−0.102 ^c
3rd step	−0.232 ^e	−0.236 ^c
4th step	−0.42 ^e	−0.420 ^c

^a The benzonitrile thin layer contained only 0.5 mM HAT. ^b Formal potentials, taken as the average of the anodic and cathodic peak potentials of cyclic voltammograms. ^c Formal potentials, taken as the peak potentials of square-wave voltammograms. ^d Scan rate was 10 mV s^{-1} . ^e Scan rate was 500 mV s^{-1} .

TABLE 3: Values of k^0 and α_c of Each Redox Step of HAT

redox step of HAT	$10^3 k^0 / \text{cm s}^{-1}$	α_c
1st step	1.1	0.44
2nd step	reversible	reversible
3rd step	4.7	0.25
4th step	3.6	0.45

$I_{1+2+3+4}$) to compare the observed voltammograms and the calculated ones (see Figure 9). Figure 9 clearly demonstrated the good agreement between the observed and calculated voltammograms, confirming that the evaluated kinetic and thermodynamic parameters for each redox step of HAT as well as its diffusion coefficient are reasonable.

Mechanism of the Whole Redox Reaction of HAT. The study on the electrochemical reduction of substituted pyrazines in aqueous acidic media, reported by Swart and Anson, showed

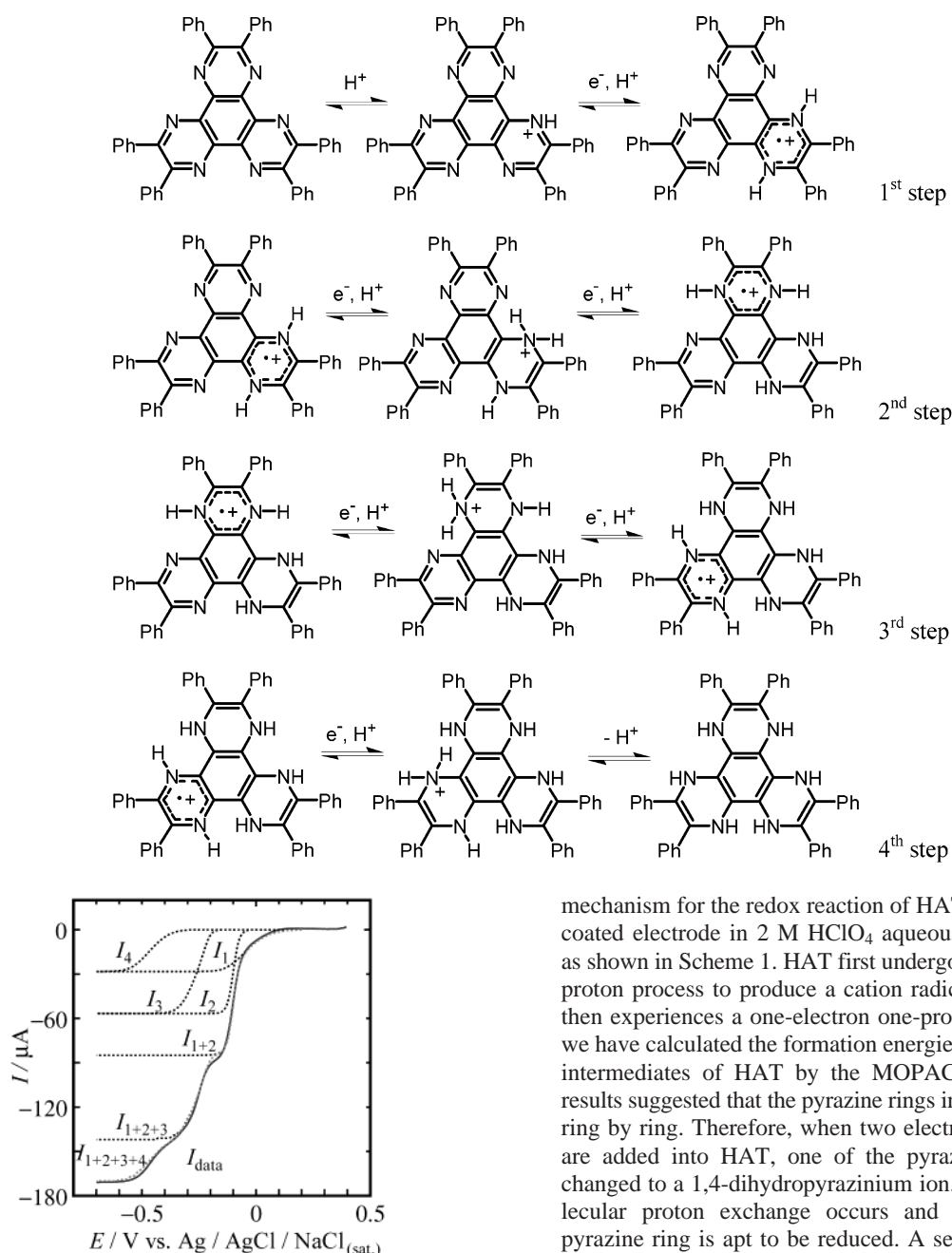
SCHEME 1: Reaction Mechanism of HAT at the BN Thin Layer-Coated Electrode in 2 M HClO₄ Aqueous Solution

Figure 9. Typical normal voltammogram (I_{data}) obtained for the reduction of HAT at the BN thin layer-coated GC electrode in N₂-saturated 2 M HClO₄ aqueous solution. The thin layer contained only 0.5 mM HAT. Sampling time was 36 ms. The dotted voltammograms were calculated based on the theoretical current–potential equation, using the obtained kinetic parameters. I_1 , I_2 , I_3 , and I_4 show the results calculated for each step. I_{1+2} , I_{1+2+3} , and $I_{1+2+3+4}$ are the sum of current of the 1st and 2nd steps, the 1st, 2nd, and 3rd steps, and the 1st, 2nd, 3rd, and 4th steps, respectively.

that pyrazine is reduced to 1,4-dihydropyrazinium ion via a 2-proton 1-electron process that is followed by a 1-proton 1-electron reduction process.³⁹ This reduction product has been reported to slowly decompose in an acid aqueous solution via hydrolysis. However, the reduction product with an electron-withdrawing substituent in the pyrazine ring is expected to be relatively stable. HAT contains three pyrazine rings in its molecular structure. According to the mechanism for the redox reaction of pyrazine and the electron numbers involved in each reduction step of HAT (mentioned above), a probable reaction

mechanism for the redox reaction of HAT at the BN thin layer-coated electrode in 2 M HClO₄ aqueous solution is proposed as shown in Scheme 1. HAT first undergoes a one-electron two-proton process to produce a cation radical. The cation radical then experiences a one-electron one-proton process. Recently, we have calculated the formation energies of possible reduction intermediates of HAT by the MOPAC PM3 method,⁴⁰ and results suggested that the pyrazine rings in HAT may be reduced ring by ring. Therefore, when two electrons and three protons are added into HAT, one of the pyrazine rings in HAT is changed to a 1,4-dihydropyrazinium ion. Probably an intramolecular proton exchange occurs and consequently another pyrazine ring is apt to be reduced. A series of such processes may result in a six-proton six-electron reduced form of HAT.

Conclusions

The BN thin layer-coated GC electrode was successfully applied to clarify the multistep redox reaction of hydrophobic HAT in 2 M HClO₄ aqueous solution with use of cyclic voltammetry, square-wave voltammetry, and normal pulse voltammetry. We evaluated the diffusion coefficient of HAT in the BN thin layer solution and both the thermodynamic and kinetic parameters (i.e., n , E^0 , α_c , and k^0) of its multistep redox reaction. Good agreement between the observed normal pulse voltammograms and the calculated ones based on the evaluated parameters was obtained. The results demonstrated strongly that the approach used is very useful for the present purpose.

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