# Electron-Transfer Kinetics of Quinones at Solid Electrodes in Aprotic Solvents at Low Temperatures

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Activation parameters for the electrochemical one-electron reduction of quinones were evaluated at glassy carbon, Au, and Pt electrodes from 170 to 298 K in aprotic solvents (N,N-dimethylformamide and propionitrile) by cyclic voltammetry. Systematic differences in the activation parameters among electrode materials were observed. The average of the activation enthalpy was  $13 \pm 2 \text{ kJ mol}^{-1}$  for the glassy carbon electrode,  $21 \pm 3 \text{ kJ mol}^{-1}$  for the Au electrode, and  $14 \pm 4 \text{ kJ mol}^{-1}$  for the Pt electrode in N,N-dimethylformamide, showing that the extent of the interaction between the electrode surface and the reactant is different for each electrode material. The Arrhenius plots for 1,4-benzoquinone curved down only at the glassy carbon electrode in both N, N-dimethylformamide and propionitrile, indicating that it was reduced by a different mechanism at low temperatures (<250 K) at the glassy carbon electrode. The experimental techniques and a simple cooling system for low-temperature electrochemistry are also described.

#### Introduction

Low-temperature electrochemistry is considered to be one of the most important techniques in the investigation of the kinetics, thermodynamics, and structure of electrogenerated species. Several authors have used this technique for the structural or kinetic aspects of electrolysis products.<sup>1-6</sup> However, there are few works on the kinetics of the electron-transfer process between electrodes and redox species at low temperatures, although this process is the most fundamental and common one in electrochemistry. In this paper we will present the electron-transfer kinetics of quinones at low temperatures (>170 K) in both N,Ndimethylformamide (DMF) and propionitrile (PN) and discuss the differences in activation parameters among electrode materials.

Concerning the activation parameters for electrode reactions, several authors have studied the electron-transfer kinetics of metal complex ions in aqueous and nonaqueous solutions. Randles and Somerton studied the electron-transfer reaction of metal complex ions at Hg, Pt, Au, and Ag electrodes and reported the values of 23-40 and 10-40 kJ mol<sup>-1</sup> as the enthalpy of activation of Hg and solid electrodes,<sup>7,8</sup> respectively. However, in their experiments no common complex ion was employed to each electrode, so that the effect of electrode materials on the activation parameters is not clear. Biegler, Gonzalez, and Parsons studied the electrontransfer reactions of  $Cd/Cd^{2+}$  and  $V^{2+}/V^{3+}$  couples at the Hg electrode in several aqueous and nonaqueous solvents<sup>9</sup> and discussed the solvent effect on the electron-transfer rate constant. They also measured the enthalpy of activation for the above ions in some mixed and pure solvent systems. Rüssel and Jaenicke evaluated the activation parameters for 1,4-diazines at the Au electrode in DMF and reported that the activation entropy obtained for pyrazine was very close to the value calculated on the basis of the Marcus theory.<sup>10</sup> The physical significance of the interpretation of the activation parameters has been recognized,11 but their systematic measurements have remained extremely rare. Recently, Weaver discussed the interpretation of the activation parameters<sup>12</sup> and measured the activation parameters for the reduction of several transition-metal complex ions, which transfer the electron via outer- or inner-sphere pathways, in aqueous solution at the Hg electrode.<sup>13</sup> However, he detected no clear systematic difference in the activation entropies between similar inner- and outer-sphere electrode processes.

The main thesis of these studies was turned to problems of the solution phase, such as the reorganization of solvent molecules. Although it has been known that the electrochemical electrontransfer rate depends on the electrode materials,<sup>14-16</sup> the effect of electrode material on the activation parameters has not been closely examined. To make this effect clear, we measured the activation parameters of quinone/semiquinone anion couples for several electrode materials. These systems will provide the simplest situation for the electrochemical investigation of non-bondbreaking electron-transfer reactions, because the electrical double layer effect is probably small for these systems, and because the semiquinone anions are fairly stable in aprotic media. At room temperature, the rate constants of the guinone/semiguinone anion couples were relatively large even at solid electrodes (0.1-0.2 cm  $s^{-1}$  in DMF, <sup>14</sup> 0.3–1.8 cm  $s^{-1}$  in acetonitrile<sup>14,17,18</sup>), so that lowtemperature electrochemistry offers an easier method for the determination of the activation parameters.

#### **Experimental Section**

A cooling system was constructed from a double-walled cooling cryostat made of Pyrex glass (o.d. 15 cm × 30 cm in length), a liquid nitrogen heat exchanger, and a simple temperature regulating system (Figure 1). A data acquisition system for lowtemperature cyclic voltammetry was constructed from a DEC PDP-11/V03 computer system, a Toho Giken Model 2020 potentiostat, a Toho Giken Model 2230 potential scanner, 12-bit A/D and D/A converters, digital I/O ports, and a programmable timer unit. The heat exchanger was constructed from a 5-dm<sup>3</sup> Dewar flask, and a small heater was immersed in the Dewar.<sup>19</sup> The flow rate of cooling gas was regulated by adjusting the period for which the heater was turned on. A copper-constantan thermocouple was inserted in the cryostat, and the thermocouple voltage was amplified with a temperature-controlled amplifier,  $\mu$ A727 (Fairchild Co.). The amplified voltage was fed to the A/D

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Figure 1. Schematic representation of the cooling system: POT, potentiostat; C.C., thermocouple; Cell, electrolysis cell; cry, cryostat; LD, liquid nitrogen Dewar; H, heater (5  $\Omega$ ); A, 100-fold preamplifier; A/D, A/D converter; D.O., digital output port; CPU, DEC LSI-11/2 microcomputer, S.S.R., solid state relay; T, transformer.

converter. Another thermocouple was inserted in the electrolysis cell in order to obtain the exact temperature of the sample solution. The software of the data acquisition system was written with Basic and assembly language. If the temperature in the cryostat was higher than the temperature at which experiments should be carried out, then a solid-state relay was turned on, and an ac voltage was applied to the heater in the heat exchanger. Switching noise generated from the relay was made negligibly small with a zero-crossing detector incorporated in the relay. The above routine concerning the temperature regulation was called every 0.5 s with a timer request routine, .MRKT, one of the system subroutines provided by DEC. During data sampling of cyclic voltammograms, the timer request was disabled in order to avoid latency resulting from the interruption of the temperature-regulating routine. The sampled data was stored in the computer memory, and then smoothing of the data by the least-squares procedure described by Savitzky and Golay<sup>20</sup> was carried out. After smoothing, the peak potentials were estimated and a heterogeneous electron-transfer rate constant was calculated from these values.

The solution resistance was compensated for with a Toho Giken Model 2022 IR compensation unit. This IR compensation unit consisted of a positive feedback circuit, a potential pulse generator, and an oscillation detector. If the voltage equivalent to the IR drop is fed back to the potentiostat, it begins to oscillate. Current responses for potential steps were monitored with an oscilloscope at each temperature, and an optimum amount of the feedback was determined so that the responses barely showed any ringing. The optimum amount was also determined by using the oscillation detector incorporated in the IR compensation unit. Synchronizing with a potential step, this unit starts counting a number of sign changes for dI/dt, where I is cell current. If the number of the sign changes exceeded a certain limit due to ringing, the unit detected overcompensation. This method could compensate 96–98% solution resistance in the range 0.05–100 k $\Omega$ , and the optimum amount estimated by this method agreed well with that for the former method.

TABLE I: Diffusion Coefficients at 298 K in 0.1 M TBAP

	<i>N</i> , <i>N</i> -dimethylformamide $10^6 D_0$ , cm <sup>2</sup> s <sup>-1</sup>	propionitrile $10^5 D_{\rm O}$ , cm <sup>2</sup> s <sup>-1</sup>		
1,4-benzoquinone	$9.65 \pm 0.08$	$2.18 \pm 0.01$		
1,4-naphthoquinone	$9.86 \pm 0.30$	$1.94 \pm 0.02$		
9,10-anthraquinone	$8.89 \pm 0.18$			
9-fluorenone	$10.30 \pm 0.30$			
5,8-dihydroxy-1,4-naphth-	$9.76 \pm 0.15$			

The density of the sample solution was measured with a pycnometer at various temperatures. Least-squares expressions for the densities of the 0.1 M tetrabutylammonium perchlorate (TBAP) solutions of DMF and PN were

$$d_{\rm DMF} =$$

 $0.9742 + 0.1010 \times 10^{-2}(T - 273.15)$  (213 < T < 298)  $d_{\rm PN} =$ 

 $0.8157 + 0.1017 \times 10^{-2}(T - 273.15)$  (173 < T < 298)

where T denotes the temperature (K) and  $d_{\rm DMF}$ , and  $d_{\rm PN}$  denote the density (g cm<sup>-3</sup>) of the DMF solution and the PN solution, respectively.

The surfaces of the planar glassy carbon (Tokai carbon, 0.013 cm<sup>2</sup>), Au (0.008 cm<sup>2</sup>), and Pt (0.008 cm<sup>2</sup>) electrodes were buffed with an aqueous suspension of fine alumina on a Millipore filter (type HA) for about 1 min before each measurement. In order to avoid leakage of the sample solution into the inner part of the electrode holder (Pyrex, o.d. 3 mm, i.d. 1.5 mm), the electrodes were sealed with a silicone tube (o.d. 2 mm, i.d. 1 mm, length 3 mm). The diffusion coefficients of the quinones at 298 K were determined by polarography on the basis of the equation derived by Lingane and Loveridge<sup>21</sup> (see Table I), and from these values the area of each electrode was determined. The diffusion coefficients at low temperatures were evaluated from the measurement of the peak height in the cyclic voltammograms at low potential scanning rates. The concentration of the quinones was 2.0 mM at 298 K, and no influence of the quinone concentration was found on the  $k_s$  value in the concentration range 0.5-2.0 mM.

The reference electrode used was  $Ag/10 \text{ mM } Ag^+(\text{solvent}) + 0.1 \text{ M } \text{TBAP}$ , where "solvent" denotes the solvent employed in the experiments. The rate constants were determined with an isothermal cell arrangement, whereas the half-wave potentials were measured with a nonisothermal cell arrangement in which the reference electrode was located outside the cryostat and kept at 298 K. In the latter cell arrangement, the reference electrode was connected to the electrolysis cell with a 0.1 M TBAP-solvent salt bridge.

Propionitrile was distilled twice over  $P_2O_5$  after pretreatment with calcium hydride. DMF was distilled twice under reduced pressure, after being dried with Type 4A molecular sieves. Other chemicals used were of analytical reagent grade.

## **Results and Discussion**

(i) Temperature Dependence of Half-Wave Potentials. The relationship between the half-wave potential shift of the first reduction step and the temperature is shown in figure 2. The shift was most pronounced in the case of 1,4-benzoquinone and decreased with an increase in the molecular size of the quinone. The positive shift should be attributed to the solvation of the semiquinone anion being stronger than that of the parent quinone; this solvent effect was more pronounced as the temperature decreased. The positive shift was very small for 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin). This can be explained in terms of the stronger hydrogen-bond formation for the semiquinone that shields the carbonyl oxygens of the semiquinone from the proximity of other solvent molecules when the quinone is reduced. Comparison of the shifts of 1,4-naphthoquinone with those of naphthazarin suggested that most of the solvation took place at the carbonyl oxygens and that the ring moiety was of only minor importance.

<sup>(20)</sup> Savitzky, A.; Golay, M. J. E. Anal. Chem. 1964, 36, 1627.



Figure 2. Relationship between the half-wave potential shift  $(\Delta E_{1/2})$  and the temperature (T): O, benzoquinone;  $\bullet$ , naphthoquinone;  $\blacksquare$ , fluorenone;  $\blacktriangle$ , anthraquinone;  $\blacklozenge$ , naphthazarin. The potential was measured with a nonisothermal cell arrangement in which the temperature of the reference electrode was kept at 298 K.  $\Delta E_{1/2} \equiv E_{1/2}(T) - E_{1/2}(298)$ , where  $E_{1/2}(T)$  denotes the half-wave potential of the first reduction step at the cell temperature, T. The half-wave potential was obtained from the relation  $E_{1/2} = (E_{p,c} + E_{p,a})/2$ , where  $E_{p,c}$  and  $E_{p,a}$  represent the potentials of the cathodic and anodic peaks in the cyclic voltammogram.



Figure 3. Relationship between the peak potential of the cyclic voltammogram and the reversibility parameter,  $\psi$ . The peak potentials are plotted in the normalized potential scale given by  $nF(E_p - E^\circ)/RT$ , where  $E_p$  and  $E^\circ$  denote the peak potential and the standard potential. The values of  $\alpha$  used in the simulation were (---) 0.3, (--) 0.5, (---) 0.7. The peak potentials of 2.0 mM naphthazarin in 0.1 M TBAP-DMF solution are given in the figure. Potential scanning rates in V s<sup>-1</sup>: ( $\bullet$ ) 30, (O) 20, ( $\blacksquare$ ) 10, ( $\square$ ) 7, ( $\blacktriangle$ ) 5, ( $\triangle$ ) 0.1 T = 218 K; electrode: glassy carbon.

The half-wave potential shift can be related to the standard reaction entropy,  $\Delta S_{rc}^{\circ}$ , given by<sup>22</sup>

$$\Delta S_{\rm rc}^{\circ} = F({\rm d}E_{\rm f}/{\rm d}T) \tag{1}$$

where  $E_{\rm f}$  is the formal potential. The temperature coefficient of the Galvani potential difference across the thermal liquid junction within an aqueous KCl salt bridge is considered to be very small  $(\sim 5 \times 10^{-5} \text{ V deg}^{-1})$ ,<sup>22</sup> and we also neglected this coefficient, although we measured  $E_{\rm f}$  using the 0.1 M TBAP-solvent salt brdige.<sup>23</sup> The standard deviation of  $\Delta S_{\rm rc}^{\circ}$  was found to be relatively large ( $\sim 10 \text{ J mol}^{-1} \text{ deg}^{-1}$ ), which was confirmed by repeated experiments. Therefore, the  $\Delta S_{\rm rc}^{\circ}$  values listed in Table

TABLE II: Standard Heterogeneous Electron-Transfer Rate Constants,  ${}^{a}k_{e}$ , at 298 K in 0.1 M TBAP

compd	solvent	electrode	$(k_{\rm s}/D_{\rm O}^{1/2}),$ s <sup>-1/2</sup>	$k_{\rm s},$ cm s <sup>-1</sup>
5,8-dihydroxy-1,4- naphthoquinone	DMF	GC <sup>ø</sup>	32.6	0.10
1,4-benzoquinone	DMF	Pt	33.4	0.12 <sup>c</sup>
-		Au	51.2	0.18°
		Pt	18.2	0.057
		Au	20.6	0.064
		GC	44.8	0.14
	PN	Au	12.9	0.062
		GC	39.3	0.18
1,4-naphthoquinone	DMF	Pt	21.0	0.063
		Au	43.1	0.13
		GC	31.9	0.10
	PN	Au	25.0	0.11
		GC	38.5	0.17
9,10-anthraquinone	DMF	Pt	17.1	0.051
		Au	39.1	0.12
		GC	63.2	0.19
9-fluorenone	DMF	Pt	13.2	0.042
		Au	36.7	0.12
		GC	36.2	0.12

<sup>a</sup>Concentration of quinones, 2.0 mM. <sup>b</sup>Glassy carbon. <sup>c</sup>Results of Rosanske and Evans;<sup>14</sup> experimental conditions: 0.5 mM quinone; 0.3 M tetrabutylammonium perchlorate as the base electrolyte; 294.6-295.0 K.

III are the averages of the results obtained from the glassy carbon, Pt, and Au electrodes.

(ii) Determination of Standard Electron-Transfer Rate Constants. The standard heterogeneous electron-transfer rate constant,  $k_{s}$ , was evaluated from the measurement of the peak separation in the cyclic voltammogram by using working curves calculated with the finite difference method.<sup>24</sup> The peak potentials in the cyclic voltammograms are known to depend on the values of both the transfer coefficient,  $\alpha$ , and  $k_s$ , which is shown in Figure 3. In this figure, the reversibility parameter,  $\psi$ , is given by<sup>25</sup>

$$\psi = \gamma^{\alpha} k_{\rm s} / (\pi a D_{\rm O})^{1/2} \tag{2}$$

In the above equation,  $\gamma$  and a represent  $(D_{\rm O}/D_{\rm R})^{1/2}$  and nFv/RT, respectively, where  $D_0$  and  $D_R$  are the diffusion coefficients of a reactant and product, v is the potential scanning rate, and the other symbols have their usual meanings. As can be seen from the figure, the effect of  $\alpha$  on the peak separation is relatively small because both the cathodic and anodic peaks shift in the same direction as  $\alpha$  changes. A variation of  $\alpha$  from 0.5 ± 0.2 leads to a maximum  $k_s$  error of  $\pm 10\%$  in the  $\psi$  range larger than 0.1. For  $\psi > 0.5$ , this error decreases to  $\pm 5\%$ . In Figure 3, the peak potentials of naphthazarin are also plotted against  $\psi$ , whose value was determined from the peak separation by using the working curve corresponding to  $\alpha = 0.5$ . This procedure gave a method for evaluating the approximate value of  $\alpha$  from the peak potential of the cyclic voltammogram, and, in this case, it is clear that  $\alpha$ is close to 0.5. However, the evaluated value of  $\alpha$  was found reproducible only to about  $\pm 30\%$  on repeated runs, suggesting that it was difficult to determine an accurate value for  $\alpha$  from the cyclic voltammogram, especially at solid electrodes. Since we determined  $k_s$  in the  $\psi > 0.5$  range, the evaluated values of  $k_{\rm s}$  are considered accurate enough for the purpose of this paper. Although it is very important to determine an accurate value for  $\alpha$  in the study of electrode kinetics, it would not greatly deviate from 0.5 in the case of simple redox reactions in nonaqueous media. Therefore, we assumed  $\alpha$  to equal 0.5 in the following discussion.

The  $k_s$  values of the quinones obtained with several solid electrodes at 298 K are summarized in Table II. The  $k_s$  values for the Pt electrode were slightly smaller than those reported by Rosanske and Evans,<sup>14</sup> whose results were based on somewhat

<sup>(22)</sup> Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. J. Am. Chem. Soc. 1979, 101, 1131.

<sup>(23)</sup> As long as TBAP is used as the base electrolyte, this neglect will cause only a small error in the estimation of  $\Delta S_{rc}^{\circ}$ ; experimental error will be far larger. Even if the error is large,  $\Delta S_{rc}^{\circ}$  can always be discussed comparatively.

<sup>(24)</sup> Feldberg, S. W. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; p 199.

<sup>(25)</sup> Nicholson, R. S. Anal. Chem. 1965, 37, 1351.

TABLE III: Kinetic Parameters for the Reaction Q +  $e \rightarrow Q^{-}$  in 0.1 M TBAP

				glassy carbon		Au		Pt	
compd	$-E_{1/2},^{a}$ V	$\Delta H^*_{D,O}$ , b kJ mol <sup>-1</sup>	$\Delta S_{\rm rc}^{\circ}$ , J mol <sup>-1</sup> deg <sup>-1</sup>	$\frac{\Delta H^*}{\text{kJ mol}^{-1}}$	$\Delta S^*, \\ J \text{ mol}^{-1} \text{ deg}^{-1}$	$\frac{\Delta H^*}{\text{kJ mol}^{-1}}$	$\Delta S^*$ , J mol <sup>-1</sup> deg <sup>-1</sup>	$\frac{\Delta H^*}{\text{kJ mol}^{-1}}$	$\Delta S^*$ , J mol <sup>-1</sup> deg <sup>-1</sup>
N,N-Dimethylformamide									
5,8-dihydroxy-1,4-naphth- oquinone	0.784	11.5	-8	12.8	-45.3				
1,4-benzoquinone	0.896	15.3	-64	11.6 33.1°	-38.5 32.4 <sup>c</sup>	23.7	-13.2	13.4	-50.7
1,4-naphthoguinone	1.066	11.0	-36	11.9	-49.1	20.8	-18.3	14.4	-45.6
9,10-anthraquinone	1.301	13.4	-38	16.2	-30.3	16.8	-32.2	9.5	-62.8
9-fluorenone	1.711	11.5	-48	12.7	-45.6	22.1	-11.7	19.7	-30.9
Propionitrile									
1,4-benzoquinone	0.853	9.41	-68	15.1 31.7°	-36.1 29.8°	19.9	-30.3		
1,4-naphthoquinone	1.030	11.0	-48	15.5	-32.6	20.7	-21.6		

<sup>a</sup> Measured at 298 K, where the potential was referred to Ag/10 mM Ag<sup>+</sup>(solvent). <sup>b</sup> Activation enthalpy for the diffusion of the quinone. This value is defined by  $D_0 = A_{D,O} \exp(\Delta S^*_{D,O}/R) \exp(-\Delta H^*_{D,O}/RT)$ , where  $A_{D,O}$  and  $\Delta S^*_{D,O}$  denote the frequency factor and activation entropy for the diffusion. <sup>c</sup>Observed in the temperature range of less than 250 K.



Figure 4. Relationship between the half-wave potential and the apparent heterogeneous standard rate constant at the glassy carbon electrode. The potential dependence of the apparent rate constant,  $k_{a}^{app}$ , was estimated from the capacitance-potential data and from a given value of the corrected rate constant,  $k_s^{cor}$ , and is given with solid lines. The  $k_s^{cor}$  values are also shown in the figure. The relationship between  $k_s^{\text{cor}}$  and  $k_s^{\text{app}}$  is given by the following equation:  $k_s^{\text{app}} = K_s^{\text{cor}} \exp(\alpha nF\phi_2/RT)$ . In the figure, the  $k_s$  values obtained from the experiments are also shown as  $(\Box)$ naphthazarin, (O) benzoquinone, (•) naphthoquinone, (•) anthraquinone,  $(\Delta)$  fluorenone.

different experimental conditions (see footnote c in Table II). As can be seen from Tables II and III, an effect of the half-wave potential on  $k_s$  was not detected, suggesting that the double layer effect would not be important in this system. In the capacitance-potential curves obtained at the glassy carbon electrode, a dip was observed at -0.17 V vs. Ag/Ag<sup>+</sup> (10 mM) at 298 K and this still appeared even at 220 K. If one assumes that this dip corresponds to the potential of zero charge,  $E_{\rm pzc}$ ,<sup>26</sup> and that the rate constants corrected for the ionic double layer effect,  $k_s^{cor}$ , take a specific value for a series of the quinones, then the apparent rate constant,  $k_s^{app}$ , should decrease with a negative increase in the potential. This is shown in Figure 4, in which  $k_s^{app}$  was calculated from the capacitance-potential data and a given value of  $k_s^{cor}$ . As shown in this figure, no clear tendency was detected between the  $k_s$  value and the potential, suggesting that the actual  $d\phi_2/dE$  is smaller than that predicted by the simple theory of the double layer,<sup>27</sup> where  $\phi_2$  denotes the potential at the outer



Figure 5. ln  $(k_s/D_0^{1/2})$  vs. 1/T plots for anthraquinone (A) and fluorenone (B) in DMF. Electrode: (•) glassy carbon, (•) Au. The standard deviation of the  $k_s$  value is shown in the figure as an error bar.

Helmholtz plane. Very recently, Grzeszczuk and Smith reported the electron-transfer rate constants of several biphenyls at Pt and Hg electrodes in DMF and acetonitrile.<sup>28</sup> The biphenyls were reduced in the potential range of -0.62 V vs. Ag/AgI to -2.15 V in DMF at the Hg electrode ( $E_{pzc} = 0.08$  V) and also showed no clear tendency between the observed  $k_s$  value and the potential. Capon and Parsons pointed out that the double layer effect was small in the case of the reduction of a neutral substance like quinone in nonaqueous solvents.29

(iii) Evaluation and Interpretation of Activation Parameters. The temperature dependence of  $k_s$  can be expressed by

$$k_{\rm s} = \rho A \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$
(3)

where  $\rho$  is the transmission coefficient,  $\Delta S^*$  and  $\Delta H^*$  are the so-called real entropy and enthalpy of activation,  $1^2$  and A is the frequency factor. The frequency factor has conventionally been assumed to be the collision number for gas-phase heterogeneous collisions given by<sup>30</sup>

$$Z_{\rm e} = (k_{\rm B}T/2\pi m)^{1/2} \tag{4}$$

where m is the mass of the reactant and  $k_{\rm B}$  is the Boltzmann constant. Since there is much controversy about equating  $Z_e$  with the frequency factor,<sup>31</sup> we simply calculated the activation entropy by assuming that  $\rho = 1$  and  $A = (298k_B/2\pi m)^{1/2}$ . Figure 5 shows ln  $(k_s/D_0^{1/2})$  vs. 1/T plots for 9,10-anthraquinone and 9-

(30) Marcus, R. A. J. Chem. Phys. 1965, 43, 679.
 (31) Hupp, J. T.; Weaver, M. J. J. Electroanal. Chem. 1983, 152, 1.

<sup>(26)</sup> Unfortunately, a concentration dependence of this dip was observed; the dip potentials were 0.25 V for 0.01 M TBAP, and 0.5 V for 0.001 M TBAP. At present, we cannot determine whether this dip really corresponds to  $E_{pzc}$ . In spite of this, we consider that the double layer effect of  $\Delta H^*$  would not be significant for the following reasons: (i) if real  $E_{pzc}$  is more negative than that estimated here, a more pronounced double layer effect should be observed; (ii) if real  $E_{pzc}$  is more positive, the potential dependence of  $k_s^{app}$ becomes smaller. The influence of the double layer on  $\Delta H^*$  was reported to be small even in this case.33

<sup>(27)</sup> Delahay, P. "Double Layer and Electrode Kinetics"; Wiley: New York, 1965.

<sup>(28)</sup> Grzeszczuk, M.; Smith, D. E. J. Electroanal. Chem. 1983, 157, 205.

<sup>(29)</sup> Capon, A.; Parsons, R. J. Electroanal. Chem. 1973, 46, 215.



Figure 6. ln  $(k_s/D_0^{1/2})$  vs. 1/T plots for benzoquinone in PN. Symbols are as in Figure 5.

fluorenone.<sup>32</sup> Interestingly, similar plots for benzoquinone displayed downward curvature in both DMF and PN, and this appeared only at the glassy carbon electrode (Figure 6). Table III summarizes the activation parameters of the quinones together with some thermodynamic parameters. From the table, it is suggested that  $\Delta H^*$  and  $\Delta S^*$  remain fairly constant for a series of the quinones investigated, including the values of benzoquinones at temperatures higher than 250 K.

It is also found from the table that these values strongly depend on the electrode material. Since the difference in the activation parameters among the electrode materials cannot be explained in terms of the double layer effect,<sup>33</sup> as described above, the difference should be explained in terms of parameters describing the nature of the electrode materials. Vojnović and Šepa<sup>15</sup> proposed a relationship between the exchange current,  $i_0$ , and the density of electron states at the Fermi level,  $p_f$ , as  $\ln i_0 = \ln p_f$ + constant on the basis of the Levich and Dogonadze-Chizmadzhev theory.<sup>34</sup> However, this relation predicts the larger magnitude of  $k_s$  at the Pt electrode than the Au one by a factor of 10 due to the proportionality between  $p_f$  and  $i_0 [p_f(Au) = 1.14 \times 10^{34} \text{ erg}^{-1} \text{ cm}^{-3}, p_f(\text{Pt}) = 1.17 \times 10^{35} \text{ erg}^{-1} \text{ cm}^{-3}]$ .<sup>35</sup> Neither such a large difference nor even the order  $k_s(Au) < k_s(\text{Pt})$  was observed in our experiment.

It is clear that there are systematic differences in the activation parameters among the electrode materials. The average values of the enthalpies of activation at the glassy carbon, Au, and Pt electrodes were respectively  $13 \pm 2$ ,  $21 \pm 3$ , and  $14 \pm 4$  kJ/mol in DMF for the quinones listed in Table III. However, the activation parameters for anthraquinone differ greatly from those of the average values. This quinone seems to take specific values concerning the activation parameters irrespective of the nature of the electrode materials. Accordingly, one may conclude that there exist at least two limiting cases in the electrode-reactant system. One of these is the system where the activation strongly depends on the nature of the electrode material and another is the system where the activation mainly depends on the structure of the reactant system, including solvent molecules surrounding

the reactant. The effect of the solvent on the activation parameters is not significant, as can be seen from Table III. This is likely if one can accept the idea that the activation more strongly depends on the electrode material than the reactant system. Recently, Rüssel and Jaenicke evaluated the value of  $\Delta S^*$  in the case of the reduction of pyrazine at the Au electrode in DMF on the basis of the Marcus theory, and reported that a reasonable agreement was obtained between the theoretical value  $(-9.1 \text{ J deg}^{-1} \text{ mol}^{-1})$ and the experimental value (-12.4 J deg<sup>-1</sup> mol<sup>-1</sup>).<sup>10</sup> The theoretical  $\Delta S^*$  value is close to our values for the Au electrode, but very different from the values obtained at the glassy carbon and Pt ones. In the above evaluation, the temperature coefficient of the reactant radius, dr/dT, was neglected, but this should not be neglected in order to explain the effect of the electrode materials in terms of the Marcus theory.<sup>36,37</sup> From the  $\Delta S^*$  values in Table III, the coefficients for benzoquinone were evaluated as  $-3.5 \times$  $10^{-13}$  (T > 250 K) and 5.0 ×  $10^{-13}$  m deg<sup>-1</sup> (T < 250 K) for the glassy carbon,  $-4.7 \times 10^{-14}$  m deg<sup>-1</sup> for Au, and  $-4.9 \times 10^{-13}$  m deg<sup>-1</sup> for Pt. Changes in the reactant radius will correspond to those in the electrode-reactant distance in the activated state. However, it is not clear whether the Marcus theory can really be applied to such a discussion. Electrostatic treatments are not always successful in explaining ion-solvent interactions even in

an equilibrium state. It is interesting to discuss the electron-transfer process of benzoquinone occurring in the lower temperature range (<250 K). At the lower temperature, the larger  $\Delta H^*$  values were observed only at the glassy carbon electrode. The model responsible for the activation must explain why benzoquinone was unique in exhibiting such large activation enthalpies. Such a model can be given if one assumes that the activation of the electron transfer for benzoquinone proceeds at the glassy carbon electrode via a surface-adsorbed state. It was reported that the carbonyl oxygen of benzoquinone was more sensitive toward cationic perturbation than the larger quinones,<sup>38</sup> and this indicates that the electron density of the carbonyl oxygen of benzoquinone increases more than that of the larger quinones as the cationic field increases. If there are enough electropositive sites at the glassy carbon surface, the carbonyl oxygen of benzoquinone can approach them. If such sites are available as -OH, then the carbonyl oxygen could form a hydrogen bond. Therefore, the strongest interaction between the carbonyl oxygen and the surface positive site is expected for benzoquinone in this model. Enough such sites will not be available with the metal electrodes, so that this can explain the difference in the activation parameters between the glassy carbon and metal electrodes in the lower temperature range. In this model, desolvation should accompany from both the carbonyl oxygen and the electrode surface when the interaction occurs. In this case, if the extent of the desolvation is great before the electron transfer, a positive  $\Delta S^*$  would be expected. In addition to this effect, it should be noted that the activation entropies estimated here include the contribution of  $\rho$ , because in the evaluation of  $\Delta S^*$  we assumed that  $\rho = 1$ . If this contribution is significant, a decrease in  $\Delta S^*$  would lead to a decrease in  $\rho$  (i.e., nonadiabaticity at high temperatures).

**Registry No.** DMF, 68-12-2; TBAP, 1923-70-2; PN, 107-12-0; C, 7440-44-0; Au, 7440-57-5; Pt, 7440-06-4; naphthazarin, 475-38-7; 1,4-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4; 9,10-anthraquinone, 84-65-1; 9-fluorenone, 486-25-9.

<sup>(32)</sup> Since  $\ln D_0$  vs. 1/T plots should give straight lines, these plots also correspond to the Arrhenius plots. See footnote b in Table III.

<sup>(33)</sup> Even if the double layer effect is not negligible, it was reported that there was only a small difference between the (ideal) activation enthalpy corrected for the double layer effect and that not corrected.<sup>11</sup>

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