Determination of Reorganization Energy from the Temperature Dependence of Electron Transfer Rate Constant for Hydroquinone-tethered Self-assembled Monolayers (SAMs)

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The temperature dependence on the electron transfer rate constant (k_{app}) for hydroquinone redox center in H_2Q(CH_2)_nSH-SAMs (n = 1, 4, 6, 8, 10, and 12) on gold electrode was investigated to obtain reorganization energy (\lambda) using Laviron's formalism and Arrhenius plot of ln [k_{app}/T^{1/2}] vs. T^{-1} based on the Marcus density-of-states model. All the symmetry factors measured for the SAMs were relatively close to unity and rarely varied to temperature change as expected. The electron tunneling constant (\beta) determined from the dependence of the k_{app} on the distance between the redox center and the electrode surface gives almost the same \beta values which are quite insensitive to temperature change. Good linear relationship of Arrhenius plot for all H_2Q(CH_2)_nSH-SAMs on gold electrode was obtained in the temperature range from 273 to 328 K. The slopes in Arrhenius plot deduced that \lambda of hydroquinone moiety is ca. 1.3-1.4 eV irrespectively of alkyl chain length of the electroactive SAM.

Key Words: Hydroquinone-tethered SAM, Reorganization energy, Temperature dependence, Rate constant, Heterogeneous electron transfer

Introduction

The phenomenon of long-range electron transfer (ET) has been a crucial research topic not only for the vectorial electron flow in the biological macrostructure such as redox proteins, metalloenzymes, and photosynthetic reaction centers but also for the development of biomolecular electronics and nanometer-scale electronic materials. As model structures to study the long-range ET, many electroactive SAMs recently have drawn much interest because they provide an ideal two-dimensional molecular arrangement of a specific redox molecule containing alkanethiol tether attached on an electrode surface. With their controlled thickness and chemical functionality, the electroactive SAMs have been extensively investigated for the effects of distance, interfacial structure, and chemical environment on the electron transfer rate between the redox-active molecule and an electrode surface. However, there have been only a few studies on the temperature dependence of heterogeneous ET for the electroactive SAMs since Murray et al. have reported cyclic voltammetry from 115 to 180 K in butyronitrile/ethyl chloride solvent for monolayer films of ferrocene-terminated SAM on gold electrode. With an exception of Forster and Faulkner's report for the temperature dependence on the ET dynamics using Os(II) bipyridyl complexes monolayer, all these studies have been directed on SAMs containing ferrocene to estimate the reorganization energy (\lambda) from the slope of an Arrhenius plot using a Marcus formalism with potential steps and cyclic voltammetry. \lambda is a parameter of great interest in ET chemistry because it controls rate constant of ET reaction with the reaction free energy. \lambda is a measure of the free energy required to activate the motions of all the atoms of the initial state, including those in the solvent shell, from their equilibrium positions to those of the final state. One method to estimate \lambda in electrochemical redox reaction is to measure the temperature dependence of ET rate constant at different temperatures. Recently, we have reported the electrochemical characteristics such as distance-dependence of ET rate and kinetic parameters for H_2Q-terminated SAMs. In this note, for the first time, we report the reorganization energy of H_2Q-terminated SAMs on gold. It is interesting to estimate \lambda of H_2Q moeity because its ET mechanism is quite different from that of ferrocene in SAMs. For example, ferrocene as a typical outer-sphere redox couple undergoes simple one electron transfer reaction without structural change in nuclear configuration. However, H_2Q follows complex 2H^+, 2e^- coupled redox reaction accompanying severe molecular structural changes.

Experimental Section

Materials and Reagents. Gold wire (99.999%, 0.5 mm diameter) for electrode was obtained from Johnson Matthey. Ethanol (J.T. Baker) and perchloric acid (70% in water, reagent grade from JFS Chemicals) were used as received. The 2-(n-mercaptoalkyl)hydroquinone derivatives used in this work were synthesized and purified by a previously reported method. Their structures were confirmed by 'H NMR spectroscopy.

Electrode and Monolayer Preparation. The gold bead electrodes were prepared by annealing the tip of a gold wire...
in a gas-oxygen flame. This bead electrode was immersed for 10 min in a hot “pirhana” solution (3 : 1 mixture of concentrated H₂SO₄ and 30% H₂O₂). After copious rinsing with deionized water, the Au electrode was electrochemically cleaned by potential cycling in 0.5 M H₂SO₄ in the potential range of –0.30 V and 1.5 V vs. SCE until typical cyclic voltammogram of clean gold was obtained. Roughness factor for these Au electrodes was measured to be in the 1.1-1.2 range and actual areas were obtained from the slope of the linear plot of cathodic current versus (scan rate)⁸ for the reversible reduction of Ru(NH₃)₆³⁺. To do this, we have utilized a diffusion coefficient of 7.5 × 10⁻⁶ cm²s⁻¹ (at 25 °C in 0.1 M NaCl) as previously reported.¹³

After rinsing with deionized water, ethanol, and drying with nitrogen gas blowing, the gold electrode was immersed for 1 day in the ethanol solution containing 1 mM H₂Q(CH₂)₆SH (n = 1, 4, 6, 8, 10, and 12). The electrode was rinsed with copious amount of fresh ethanol and deionized water prior to use in electrochemical experiments.

Measurements. Electrochemical measurements were carried out in a dual jacketed-electrochemical cell (BAS) with home-made Au bead electrode as a working electrode, platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. Voltammetric experiments were performed with the use of a BAS 100B/W Potentiostat and a software package. A low temperature thermostat (Lauda Co., RE104) was used for temperature control of dual jacketed-electrochemical cell. Electrochemical measurements were performed in aqueous 0.1 M HClO₄ solutions. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ cm with a UHQ II system (Elga) and deaerated by purging with nitrogen gas.

Figure 1 shows typical cyclic voltammograms recorded from three different gold electrodes coated with H₂Q(CH₂)₆SH-SAM and measured in the 0.1 M HClO₄ solution at three different temperatures at a scan rate of 100 mV s⁻¹. In each voltammogram, a pair of redox peaks was observed to be symmetrical around its formal potential and due to the oxidation and reduction of hydroquinone which follows a 2e⁻, 2H⁺ transfer reaction mechanism. The surface density of hydroquinone estimated from the integration of the redox peak areas was in the range of (3.8-4.7) × 10⁻¹⁰ mole·cm⁻², which is close to a full monolayer coverage. When the temperature is increased, the peak-to-peak separation (ΔEₚ) in voltammogram is decreased. The peak splittings observed are 282 mV at 273 K, 191 mV at 298 K, and 110 mV at 328 K, respectively. This change in the peak splitting demonstrates that the electron-transfer rate increases as temperature rises as expected. The temperature dependence of ΔEₚ is generally observed for all the other hydroquinone-terminated SAMs with different alkyl chain length.

In order to investigate the temperature dependence on the ET rate constant for hydroquinone redox center in H₂Q(CH₂)₆SH-SAMs, we have measured a change in peak splitting as a function of log (scan rate) using well-known Laviron’s formalism.¹⁴ Figure 2 presents typical changes in ΔEₚ depending on log(scan rate) for H₂Q(CH₂)₆SH-SAMs on gold at three different temperatures. According to Laviron’s formalism, the apparent ET rate constant (kₐp) and symmetry factors (α or (1-α)υ) can be determined in a straightforward manner from the equation 1 and 2, i.e.

Eₚ – Eₚ'= - (RT/αυF) ln [αυF υ/RTkₐp]  \hspace{1cm} (1)

Eₚ – Eₚ'= - (RT/(1-α)υF) ln [(1-α)υF υ/RTkₐp]  \hspace{1cm} (2)
Table 1. Symmetry factors of H$_2$Q(CH$_2$)$_n$SH-SAMs ($n=1,4,6,8,10,12$) on Au electrode in aqueous 0.1 M HClO$_4$ at six different temperatures. The values of $cn$ and $(1-\alpha)n$ are symmetry factors due to reduction and oxidation of hydroquinone group, respectively.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>273</th>
<th>288</th>
<th>298</th>
<th>308</th>
<th>318</th>
<th>328</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sym. Factor</td>
<td>$n=1$</td>
<td>$n=4$</td>
<td>$n=6$</td>
<td>$n=8$</td>
<td>$n=10$</td>
<td>$n=12$</td>
</tr>
<tr>
<td>$(1-\alpha)n$</td>
<td>0.97</td>
<td>1.16</td>
<td>1.06</td>
<td>1.08</td>
<td>1.01</td>
<td>0.88</td>
</tr>
<tr>
<td>$cn$</td>
<td>0.96</td>
<td>0.71</td>
<td>0.69</td>
<td>0.65</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>$n$</td>
<td>1.09</td>
<td>1.12</td>
<td>1.13</td>
<td>0.98</td>
<td>1.13</td>
<td>0.93</td>
</tr>
<tr>
<td>$1-\alpha n$</td>
<td>0.89</td>
<td>1.20</td>
<td>1.14</td>
<td>1.03</td>
<td>0.94</td>
<td>1.00</td>
</tr>
<tr>
<td>$cn$</td>
<td>1.01</td>
<td>0.77</td>
<td>0.86</td>
<td>0.67</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>$n$</td>
<td>1.07</td>
<td>1.06</td>
<td>1.12</td>
<td>1.04</td>
<td>0.98</td>
<td>0.88</td>
</tr>
<tr>
<td>$1-\alpha n$</td>
<td>0.88</td>
<td>0.74</td>
<td>0.79</td>
<td>0.83</td>
<td>0.81</td>
<td>0.78</td>
</tr>
<tr>
<td>$cn$</td>
<td>0.99</td>
<td>1.12</td>
<td>1.12</td>
<td>1.06</td>
<td>1.02</td>
<td>0.94</td>
</tr>
<tr>
<td>$n$</td>
<td>1.01</td>
<td>0.72</td>
<td>0.76</td>
<td>0.79</td>
<td>0.81</td>
<td>0.75</td>
</tr>
<tr>
<td>$1-\alpha n$</td>
<td>0.92</td>
<td>1.22</td>
<td>1.20</td>
<td>0.99</td>
<td>0.75</td>
<td>1.04</td>
</tr>
</tbody>
</table>

where the peak potential separation is larger than 200 mV/$n$. $\upsilon_k$ and $\upsilon_b$ are the critical scan rates obtained by extrapolating the linear portion of the plot of peak potential ($E_p$) vs. $\ln(\upsilon)$ to the formal cathodic and anodic potentials, i.e. $E_a^o$ and $E_a^o$. The slope of the linear portion in the plot of $E_p$ vs. $\ln(\upsilon)$ curve is $RT/\alpha nF$ for the cathodic branch and $RT/(1-\alpha)nF$ for the anodic branch, respectively. The values of $cn$ and $(1-\alpha)n$ values obtained in each condition of temperature and alkyl chain number ($n$) are very close to 2, i.e. the total number of transferred electrons in the redox reaction of hydroquinone/quinone.

We have already reported the distance dependence of $k_{app}$ for the H$_2$Q(CH$_2$)$_n$SH-SAMs with different alkyl chain length on gold at room temperature only. In order to see the temperature dependence of $k_{app}$ in this work, we have extended the electrochemical kinetic measurement for the same SAMs over the temperatures range 273-328 K. Figure 3 shows the plot of the logarithmic heterogeneous ET rate constant with respect to the number ($n$) of methylene group of alkyl chain spacer at each temperature. The simplified equation 3 derived from the Marcus theory gives the electron tunneling constant ($\beta$) from the dependence of the $k_{app}$ on the distance ($d$) between the redox center and the electrode surface.

$$k_{app}(d_2) - k_{app}(d_1) \exp[-\beta(d_2-d_1)]$$

In the equation 3, $\beta$ is the slope of the plot of $\ln(k_{app})$ vs. $d$. Here, the distance $d$ can be simply displaced with the number of CH$_2$ group in alkyl chain length ($n$). The slopes of the plots shown in Figure 3 give almost the same $\beta$ value, which are ranging from 1.0 to 1.1 per CH$_2$ unit within alkyl chain spacer (shown in Table 2). This observation indicates that the $\beta$ value, as a measure of the activation energy barrier at electron-transfer elementary step, is quite insensitive to temperature change. The physical meaning of the temperature independence of $\beta$ value can be understood from that the structure of the monolayer does not change systematically.
whether this characteristics is maintained in view of reaction kinetics. On the other hand, it is interesting to note an Arrhenius plot producing an activation energy that temperature-independent, values are quite small compared to that (rate constant of H
\[\text{intercepts of the plot in Figure 3 present the heterogeneous Table 3. The deduced reorganization energy of H}_2\text{O moity}\]

<table>
<thead>
<tr>
<th>(n)</th>
<th>(-d\ln[k_{\text{app}}]/dT)</th>
<th>(\lambda) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((6.4 \pm 0.1) \times 10^3)</td>
<td>(1.3 \pm 0.1)</td>
</tr>
<tr>
<td>4</td>
<td>((7.2 \pm 0.2) \times 10^3)</td>
<td>(1.4 \pm 0.1)</td>
</tr>
<tr>
<td>6</td>
<td>((7.2 \pm 0.2) \times 10^3)</td>
<td>(1.4 \pm 0.1)</td>
</tr>
<tr>
<td>8</td>
<td>((7.2 \pm 0.2) \times 10^3)</td>
<td>(1.4 \pm 0.1)</td>
</tr>
<tr>
<td>10</td>
<td>((7.1 \pm 0.2) \times 10^3)</td>
<td>(1.4 \pm 0.1)</td>
</tr>
<tr>
<td>12</td>
<td>((6.9 \pm 0.2) \times 10^3)</td>
<td>(1.4 \pm 0.1)</td>
</tr>
</tbody>
</table>

d ln\[k_{\text{app}}T^{1/2}\]/dT [\text{K}^{-1}]\]

\[\lambda = -4.03 \times 10^{-8}\] (4)

where \(\lambda\) is the reorganization energy of H\(_2\)O, \(k_{\text{app}}\) is the apparent rate constant, \(T\) is the temperature, and \(R\) is the gas constant. The first term in the expression represents the reorganization energy associated with the electron transfer reaction, and the second term represents the activation energy for the thermal motion of the solvent molecules. The term \(k_{\text{app}}\) is the product of the pre-exponential factor and the exponential term, which accounts for the effect of temperature on the rate constant.

The reorganization energy \(\lambda\) can be determined from the slope of the Arrhenius plot using the equation:

\[
\ln \left[ k_{\text{app}}T^{1/2} \right] = -4.03 \ln(\lambda) \frac{d(T^{-1/2})}{dT} + C
\]

where \(C\) is a constant and the slope of the plot is \(-4.03\ln(\lambda)\). This equation shows that the slope of the Arrhenius plot is directly proportional to the reorganization energy, which is a measure of the energy required to change the electronic structure of the redox couple in the SAM.

The reorganization energy depends on various factors such as the electronic structure of the redox couple, the solvent properties, and the SAM surface. In the case of H\(_2\)O-SAMs, the reorganization energy is expected to be low due to the high dielectric constant of water, which facilitates the transfer of an electron between the redox couple and the solvent.

In conclusion, the Arrhenius plot provides a useful tool for determining the reorganization energy of H\(_2\)O-SAMs, which is an important parameter in understanding the electron transfer dynamics in such systems.
configurational change. However, H$_2$Q undergoes substantially large molecular structural changes in nuclear configuration during its proton-coupled redox process: e.g. dissociation of two O-H bonds and losing of resonance characteristic of a benzene ring. This configurational change might be responsible for the $\lambda_{\text{eq}}$ value of H$_2$Q moiety in the electroactive SAMs on gold.

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References