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Effect of adsorbed anions on the outer-sphere electron-transfer reactions of cobalt complexes at platinum single-crystal electrodes

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Abstract

The redox-electrode reaction of $[Co(phen)_3]^{2+/3+}$ (phen = 1,10-phenanthroline) in 0.1 M potassium halide solutions was studied kinetically at a platinum (111) single-crystal electrode (M = mol dm^{-3}). The formal rate constants were found to be dependent on the electrolyte anions and to decrease in the order $F^- > Cl^- > Br^-$. Furthermore, formal rate constants for this reaction in 0.1 M KF solution were obtained at platinum (111), (100), and (110) single-crystal electrodes and those modified with I^-, SCN^-, and CN^- adlayers. It was found that Miller indices had little effect on the heterogeneous electron-transfer rate. The iodide monolayer retarded the electron-transfer reaction, whereas the reaction was accelerated by the modification with cyanide and thiocyanate. Similar results were obtained for the redox-electrode reaction of $[Co(bpy)_3]^{2+/3+}$ (bpy = 2,2′-bipyridine) at the Pt(111) electrode and that modified with iodide and thiocyanate. These findings are discussed based on the electrical double layer effect and the theory of heterogeneous outer-sphere electron-transfer reactions reviewed by Weaver [M.J. Weaver, in: R.G. Compton, Comprehensive Chemical Kinetics, vol. 27, Elsevier, Amsterdam, 1987, Ch. 1]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous electron-transfer rate; Platinum single-crystal electrodes; Tris(1,10-phenanthlorine)cobalt complex; Tris(2,2′-bipyridine)cobalt complex

1. Introduction

Measurements of kinetic parameters of electrochemical reactions, such as formal rate constants $k°'$ and transfer coefficients α, have been a subject of experimental studies for more than half a century, and a large number of kinetic parameters, especially for electrode reactions of inorganic metal complexes, have been reported and compiled in the literature [1,2]. Such kinetic parameters have often been interpreted or discussed based on theories of outer-sphere electron-transfer reactions developed by Marcus [3], Hush [4], Levich [5], Dogonadze et al. [6], and their followers. Although the characteristic properties of the electrode | solution interface have often been ignored or given only little attention in these treatments, there is much experimental evidence that electrode materials and adsorbed species affect even the outer-sphere electron-transfer reactions kinetically. Dependence of the reaction rate on the electrode materials has often been explained by the electrical double layer effect [7,8]. Some workers made reference to the influence of the electronic structure of the electrodes on the electron-transfer rate besides the electrical double layer effect [9–14]. Adsorbed molecules often retard the electron-transfer reactions by increasing the electrode-reactant distance. Miller et al. [15] systematically investigated the dependence of the electrode-reactant distance on the reaction rate by varying the length of the hydrocarbon chain of ω-hydroxy thiol self assembled monolayers at a gold electrode. Adsorbed anions often accelerate the reaction by changing a reaction pathway from the outer-sphere to the inner-sphere, i.e. ligand-bridge type reaction [16–20].

Although these investigations demonstrated a significant role of the electrode | solution interface for the

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outer-sphere electron-transfer reactions, electrodes with structurally ill-defined surfaces such as polycrystalline electrodes have been used. Recent developments in techniques for preparing and handling of single-crystal electrodes [21,22] enabled us to investigate the kinetics of electrode processes at well-defined electrode surfaces, and in situ spectroscopic and microscopic techniques afford structural information about the various single-crystal electrode | solution interfaces [23,24]. However, there are few kinetic studies for the outer-sphere electron-transfer reactions at single-crystal electrodes [14,25–29]. In our previous paper [25], we reported that the observed $k^{\circ\prime}$ values for $[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$ in 0.1 M $KClO_4$ solution on platinum single-crystal electrodes showed clear dependence on the Miller indices of the surfaces and became larger in the order $(110) < (100) \ll (111)$. The single-crystal electrodes are useful to inspect the structural effect of the electrode | solution interfaces on the electrode processes, and accumulation of kinetic data on such well-defined surfaces would be expected to contribute to further developments in the theories of the heterogeneous electron-transfer reactions.

This paper describes the kinetics of the redox-electrode reactions of the tris(1,10-phenanthroline)cobalt complex:

$$- [Co(phen)_3]^{3+} + e^- \rightleftarrows [Co(phen)_3]^{2+} \qquad (1)$$

(phen = 1,10-phenanthroline) and of the tris(2,2′-bipyridine)cobalt complex:

$$[Co(bpy)_3]^{3+} + e^- \rightleftarrows [Co(bpy)_3]^{2+} \qquad (2)$$
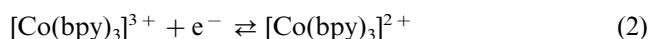
(bpy = 2,2′-bipyridine) at the three low index platinum single-crystal electrodes and those covered with thiocyanate, cyanide, or iodide monolayers. Clear influence of the adsorbed anions on the rate of electrode processes (1) and (2) was observed.

2. Experimental

$HClO_4$, KI, KCl (Merck), KF, KBr (Fluka), CoF_2 (Fluka), $KClO_4$, 1,10-phenanthroline monohydrate, 2,2′-bipyridine, $CoCl_2 \cdot 6H_2O$, NaCN, and KSCN (Kanto Chemicals) were used without further purification. $[Co(phen)_3]F_2 \cdot 6H_2O$ was prepared by crystallizing from the mixture of CoF_2 and threefold equivalent 1,10-phenanthroline aqueous solutions. $[Co(bpy)_3]Cl_2 \cdot 6H_2O$ was prepared by filtering its crystals which were deposited from a solution containing $CoCl_2$ and three molar equivalents of 2,2′-bipyridine. The stoichiometric number of water molecules for the prepared complexes were determined by elemental analysis.

Pt(111), Pt(100), and Pt(110) disks (ca. 8 mm in diameter and ca. 3 mm in thickness, or ca. 4 mm in diameter and ca. 3 mm in thickness) purchased from Firma MaTech (Germany) were used as the working electrode. The single-crystal electrodes were annealed in a hydrogen flame and quenched in ultra-pure water, and then transferred to 0.1 M $HClO_4$ solution in order to record the hydrogen adsorption–desorption waves to check the surface ordering. A platinum wire and Ag | AgCl | KCl$_{sat}$ were used as the auxiliary and the reference electrodes, respectively. The iodide- and thiocyanate-modified electrodes were prepared by immersing the electrodes in 10 mM KI solution and 10 mM KSCN solution for 15 min at open circuit, respectively. The cyanide-modified electrodes were prepared by immersing the electrodes in 0.1 mM NaCN solution for 1 min at open circuit.

All solutions were prepared with distilled water which had been purified with a Milli-Q system (Japan Millipore Ltd.). The test solution was deaerated with Ar gas (99.999%) for at least 15 min before each measurement. All electrochemical measurements were carried out with the dipping-technique [21] in which only the desired surface of the electrode established contact with the solution. A computer-controlled electrochemical system (CS-1090, Cypress System) was used for cyclic voltammetry. Ac impedance measurements were carried out using computer-controlled systems (HECS-311B potentiostat and HECS-332B two-phase lock-in amplifier, Huso Electrochemical System, and SI 1287 electrochemical interface and SI 1260 impedance/gain-phase analyzer, Solatron). The formal rate constant $k^{\circ\prime}$ was obtained by ac impedance measurements. Randles' equivalent circuit was assumed to analyze ac impedance data. The dc bias was set at the formal potential. The ac modulation amplitude was 5 mV and a frequency range from 10 to 4700 Hz was used.

3. Results and discussion

3.1. Effect of halide ions of electrolytes on the formal rate constants

Fig. 1 shows cyclic voltammograms for reaction (1) obtained in a series of 0.1 M potassium halide solutions at the Pt(111) electrode. Potassium iodide was not used as the electrolyte because the formal potential of the I_2/I^- couple is very close to that of reaction (1) and the solubility of the complex is poor in the solution. Fig. 2 shows complex-plane faradaic impedance plots for reaction (1) obtained at $E^{\circ\prime}$ (here we determined $E^{\circ\prime}$ as the midpoint of the anodic and cathodic peak potentials of cyclic voltammograms in Fig. 1 on the assumption that the redox couples have a common diffusion coefficient). Each line has a slope of 45°, which indicates that the process is in the semi-infinite linear

diffusion-controlled regime and the absence of complexity due to homogeneous chemical reactions. The
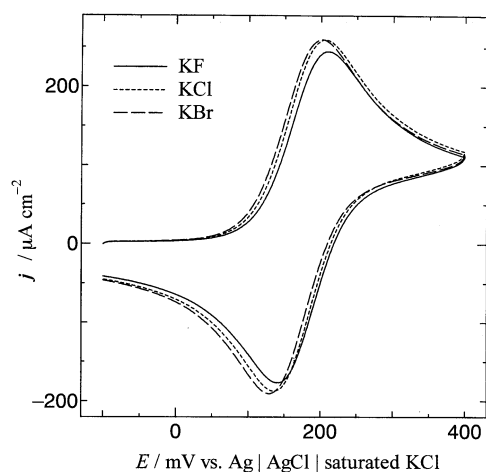

Fig. 1. Cyclic voltammograms for reaction (1) obtained in 0.1 M potassium halide solutions containing 1 mM [Co(phen)$_3$]F$_2$ at the Pt(111) electrode. Scan rate was 200 mV s^{-1}.
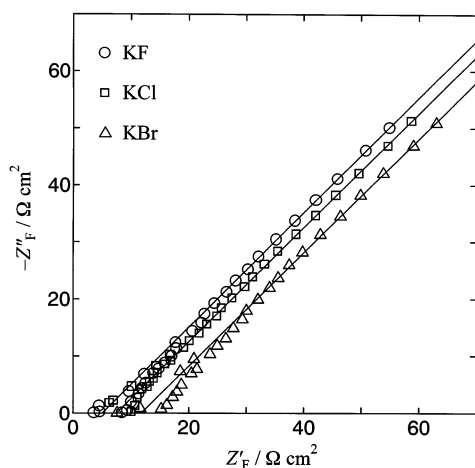

Fig. 2. Complex-plane plots of the faradaic impedance for reaction (1) at the formal potentials. The plots were obtained in 0.1 M potassium halide solutions containing 1 mM [Co(phen)$_3$]F$_2$ at the Pt(111) electrode.

Table 1
Formal potentials $E^{\circ\prime}$ versus Ag | AgCl | KCl$_{sat}$ and formal rate constants $k^{\circ\prime}$ for reaction (1) in 0.1 M potassium halide solutions

Electrode	Electrolyte	$E^{\circ\prime}$/mV	$10^2 k^{\circ\prime}$/cm s^{-1}
Pt(111)	KF	175 ± 2	9.2 ± 0.4
Pt(111)	KCl	171 ± 2	7.3 ± 0.3
Pt(111)	KBr	166 ± 2	4.3 ± 0.1
I–Pt(111)	KF	181 ± 3	0.88 ± 0.03
I–Pt(111)	KCl	175 ± 3	1.1 ± 0.2
I–Pt(111)	KBr	168 ± 2	1.3 ± 0.3
SCN–Pt(111)	KF	175 ± 1	15 ± 2
SCN–Pt(111)	KCl	172 ± 1	16 ± 1
SCN–Pt(111)	KBr	167 ± 1	2.0 ± 3

apparent formal rate constants $k^{\circ\prime}$ evaluated from the intercept of each line are summarized in Table 1 together with $E^{\circ\prime}$ values. The rate constants were found to be appreciably dependent on the electrolyte anions and they decreased in the order F$^-$ > Cl$^-$ > Br$^-$. So far, the following values of $k^{\circ\prime}$ for reaction (1) have been reported in the literature: 4.8×10^{-2} cm s^{-1} (1 M KCl, polycrystalline platinum rotating disk electrode) [30], 8×10^{-2} cm s^{-1} (1 M KCl, laser activated glassy carbon electrode) [31], 2×10^{-5} cm s^{-1} (1 M KCl, basal plane of highly oriented pyrolytic graphite) [31], 8.1×10^{-4} cm s^{-1} (0.5 M H$_2$SO$_4$, polycrystalline platinum electrode) [32]. The value of 7.3×10^{-2} cm s^{-1} which we obtained in 0.1 M KCl solution is comparable with the largest of those reported.

Adsorption of halides on the Pt(111) electrode surface have been characterized; fluorides do not specifically adsorb to the surface, and coverage of chlorides in the low potential region is considerably lower in neutral solutions [33], whereas bromides highly cover the platinum surface [34,35]. Accordingly the decrease in $k^{\circ\prime}$ values for the series of F$^-$, Cl$^-$ and Br$^-$ could be related to their surface coverage. Another possibility responsible for the kinetic effect may come from the ion-pair formation between [Co(phen)$_3$]$^{2+/3+}$ and halide ions in the solution; Baker et al. [36] suggested the formation of ion-pairs between [Co(phen)$_3$]$^{3+}$ and Cl$^-$ from the kinetic effect of Cl$^-$ on the homogeneous electron-exchange reaction between [Co(phen)$_3$]$^{2+}$ and [Co(phen)$_3$]$^{3+}$. The ion-pair formation was also experimentally supported by Mironov et al. [37] and Karmanova et al. [38]. [Co(phen)$_3$]$^{3+}$ forms a slightly more stable ion-pair than [Co(phen)$_3$]$^{2+}$ due to its higher positive charge, and the stability of the ion-pair increases in the order F$^-$ < Cl$^-$ < Br$^-$. According to the association constants in Ref. [38], 20% and 30% of [Co(phen)$_3$]$^{3+}$ are supposed to be associated with one anion in the KCl and KBr solutions under our experimental condition, respectively. Thus the trend of heterogeneous electron-transfer rate constants observed in a series of halide solutions might also be explained by the degree of stability of ion-pairs in the solution. In order to clarify the point, we compared the heterogeneous electron-transfer rates in a series of halide solutions using iodide-covered Pt(111) electrodes in order to avoid the coverage effect of anions. The results are listed in Table 1. All the $k^{\circ\prime}$ values drastically decreased compared with those obtained at the unmodified electrodes. In addition, one can see that the trend of the rate constants is opposite to that obtained at the unmodified electrodes, although the differences are rather small. In any case, ion-pairing cannot solely explain the observed large difference in rate constants at the unmodified electrodes.

As mentioned above, the presence of the iodide adlayer considerably reduces the rates in all the electrolyte
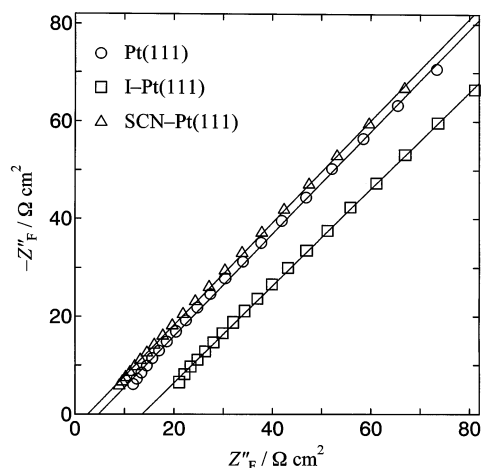
Fig. 3. Complex-plane plots of the faradaic impedance for reaction (2) at the formal potentials. The plots were obtained in 0.1 M KF solution containing 1 mM [Co(bpy)$_3$]Cl$_2$ at the Pt(111) electrode and one covered with iodide or thiocyanate.

Table 2
Influence of the adlayers on $E^{\circ\prime}$ versus Ag | AgCl | KCl$_{sat}$ and $k^{\circ\prime}$ for reaction (2)

Electrode	$E^{\circ\prime}$/mV	$10^2 k^{\circ\prime}$/cm s^{-1}
Pt(111)	107 ± 1	22 ± 0.2
I–Pt(111)	109 ± 1	4.8 ± 0.2
SCN–Pt(111)	110 ± 1	34 ± 0.3

solutions employed, indicating that the adsorption of halides to the electrode surface is more likely to be responsible for the sluggish electron-transfer kinetics. We found, however, that the thiocyanate adlayer facilitates rather than retards the reaction rates. It has been reported that thiocyanates form a stable and almost uniform monolayer on the Pt(111) surface [35,39]. The $k^{\circ\prime}$ values obtained on the thiocyanate-modified surface are comparable to or even higher than those at the unmodified surface in all the electrolyte solutions (see Table 1). The slow reaction on the iodide adlayer and the fast one on the thiocyanate adlayer were also observed for reaction (2) in 0.1 M KF solution using the Pt(111) electrode (see Fig. 3 and Table 2). Such a drastic change in rate constants should be ascribable to the different role of adsorbed molecules in the electron-transfer reaction. We will return to this point later.

3.2. Characterization of the electrode surface and decomposition of the complexes

During the measurements of cyclic voltammograms shown in Fig. 1, we noticed that some unknown species adsorbed on the platinum surface. Indeed, this was apparent from cyclic voltammograms shown in Fig. 4. The voltammogram recorded at clean Pt(111) elec-

trodes shows the characteristic hydrogen adsorption–desorption wave in 0.1 M HClO$_4$ solution as indicated by curve A. After recording a voltammogram as shown in Fig. 1 in 0.1 M KF solution containing 1 mM [Co(phen)$_3$]F$_2$, the electrode was transferred again to 0.1 M HClO$_4$ solution and cyclic voltammetry was performed. The voltammogram (curve B) shows that the wave originally appearing between 300 and 600 mV disappeared completely and no additional waves ascribable to the surface redox reaction of the complex were observed in the potential region. Similarly, cyclic voltammetry was also carried out in 0.1 M KF solution instead of 0.1 M HClO$_4$ solution; curve C shows that no redox wave was observed between -100 and 400 mV and indicates that the adsorbate is electro-inactive. A possible adsorbate may be 1,10-phenanthroline which is formed by the decomposition of the complex. Curve D in Fig. 4 was obtained independently for the clean Pt(111) electrode after immersion in 5 mM 1,10-phenanthroline solution for 10 min. The hydrogen adsorption–desorption wave was further depressed compared to curve B. We also performed kinetic measurements in the presence of 5 mM 1,10-phenanthroline in the solution in order to examine the effect and the possibility of the decomposition. The results are summarized in Table 3 and compared with those obtained in the solution without 1,10-phenanthroline. The addi-
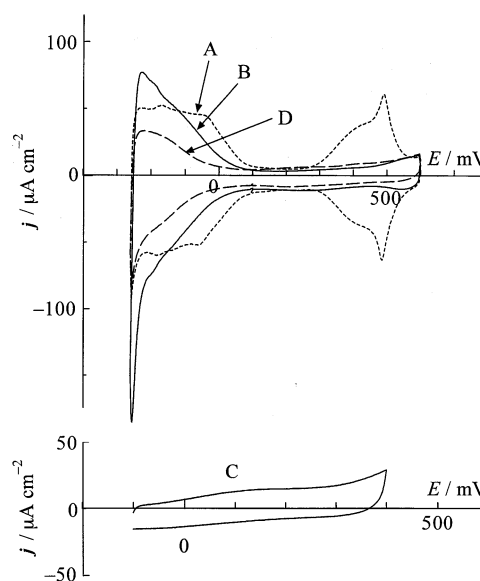

Fig. 4. Cyclic voltammograms for the Pt(111) electrode in 0.1 M HClO$_4$ (A, B, D) and in 0.1 M KF (C). Scan rates were 50 mV s^{-1} (A, B, D) and 200 mV s^{-1} (C). Potential is referred to Ag | AgCl | KCl$_{sat}$. Curve A is the characteristic hydrogen adsorption–desorption waves of the clean Pt(111) electrode in HClO$_4$ solution. Curves B and C were recorded in HClO$_4$ solution and KF solution, respectively, with the electrode used for the cyclic voltammetry in 0.1 M KF containing 1 mM [Co(phen)$_3$]F$_2$. Curve D was recorded using the electrode preliminarily immersed in 0.1 M KF containing 5 mM 1,10-phenanthroline.

Table 3
Influence of the presence of 1,10-phenanthroline in the solution on $E^{\circ\prime}$ versus Ag $\mid$ AgCl $\mid$ KCl$_{sat}$ and $k^{\circ\prime}$ for reaction (1)

Electrode	1 mM [Co(phen)$_3$]F$_2$+0.1 M KF		1 mM [Co(phen)$_3$]F$_2$, 0.1 M KF+5 mM 1,10-phenanthroline	
	$E^{\circ\prime}$/mV	$10^2 k^{\circ\prime}$/cm s^{-1}	E°/mV	$10^2 k^{\circ}$/cm s^{-1}
Pt(111)	175 ± 2	9.2 ± 0.4	177 ± 2	8.5 ± 0.3
I–Pt(111)	181 ± 3	0.88 ± 0.03	180 ± 3	1.2 ± 0.2
SCN–Pt(111)	175 ± 1	15 ± 2	180 ± 2	15 ± 4

tion of 1,10-phenantroline did not affect the rate constant. Since the stability constant for the formation of [Co(phen)$_3$]$^{2+}$ is large ($K_1 \cong K_2 \cong 10^7$ and $K_3 \cong 10^6$ [40,41]), the mole fraction of mono- or bis(1,10-phenanthroline)complexes would be, if any, very small. The fact that the presence of 1,10-phenanthroline did not give any appreciable change in the rate constant indicates that the adsorbed 1,10-phenanthroline or the decomposed species has little effect on the kinetics. A hydrogen adsorption wave similar to curve B (not shown) was observed for the clean Pt(111) electrode after the immersion in 0.1 M KF solution. Although the adsorbate may be due to some impurities in the KF, which was used as received, the influence of adsorbed species was not so significant because the integration of the charge under the voltammetric wave (curve B) of the hydrogen adsorption–desorption region (-260–100 mV) was almost equal to 80% of that in curve A, indicating that the contamination of the surface is not very significant as far as the electrode kinetics of reaction (1) are concerned.

3.3. The influence of crystallographic orientation and adlayers

The rate constants for reaction (1) were also measured at the unmodified platinum single-crystal electrodes of three different indices, i.e. Pt(111), Pt(100), and Pt(110), and those covered with iodide, thiocyanate, and cyanide in KF solution. The values of $E^{\circ\prime}$ and $k^{\circ\prime}$ are summarized in Table 4. The presence of the iodide layer at each single-crystal electrode decreased $k^{\circ\prime}$ down to ca. 10% of that obtained at each unmodified electrode. Values of $k^{\circ\prime}$ obtained at the thiocyanate-modified electrodes were comparable with or larger than those obtained at the unmodified electrodes. Acceleration of the electron-transfer rate was also observed for the reaction at cyanide-modified electrodes. We could not find any dependence of the electron-transfer rate on Miller indices at the unmodified or the modified electrodes.

Adsorbed anions often oblige electrochemical reactions to proceed through facile inner-sphere pathways instead of much slower outer-sphere routes [16–20]. However, [Co(phen)$_3$]$^{3+}$ is, at least, kinetically stable

[36]. Therefore, we may rule out the possibility of the inner-sphere pathway for the higher rate constant at CN- and SCN-modified electrodes.

Hromadova and Fawcett [28] linked the kinetics of the reduction of [Co(NH$_3$)$_6$]$^{3+}$, which depend on the crystallographic orientation of the gold single-crystal electrode, with the differences in the potential of zero charge. Although the potential of zero charges of platinum single-crystal $\mid$ electrolyte interfaces are summarized in Ref. [42], the data could not be directly applied for interpreting our experimental findings, because the potentials of zero charge in the literature are obtained under different conditions. Unfortunately, our attempt to measure the differential capacitance in order to determine the potential of zero charge under our experimental conditions failed because the capacitance minimum did not appear in the double layer region. The independence of the observed rate constants on the crystallographic orientation may indicate that the difference in the electrical double layer structure is small. On the other hand, the dependence of the observed rate constants on the adlayers may be attributed to the electronic double layer effect, since the adsorption of anions would shift the potential of zero charge, resulting in a change in the surface charge. To our knowledge, there has been no report for the potential of zero charge of CN-, SCN- and I-covered Pt(111) surfaces, and the potentials of zero charge for the unmodified

Table 4
Influence of surface modifications on $E^{\circ\prime}$ versus Ag $\mid$ AgCl $\mid$ KCl$_{sat}$ and $k^{\circ\prime}$ for reaction (1)

Electrode	$E^{\circ\prime}$/mV	$10^2 k^{\circ\prime}$/cm s^{-1}
Pt(111)	175 ± 2	9.2 ± 0.4
Pt(100)	174 ± 2	7.7 ± 0.2
Pt(110)	175 ± 1	8.2 ± 0.1
I–Pt(111)	181 ± 3	0.88 ± 0.03
I–Pt(100)	181 ± 2	0.86 ± 0.01
I–Pt(110)	176 ± 2	1.4 ± 0.2
SCN–Pt(111)	175 ± 1	15 ± 2
SCN–Pt(100)	174 ± 2	9.1 ± 0.5
SCN–Pt(110)	175 ± 2	11 ± 4
CN–Pt(111)	175 ± 2	21 ± 3
CN–Pt(100)	173 ± 1	23 ± 3
CN–Pt(110)	175 ± 2	21 ± 1

electrodes could not be determined due to the same reason as the case of unmodified electrodes. The reactants would be subject to charges on the adsorbed molecules, because they locate closer to the reactants than the charges on the substrate metal. According to Auger spectroscopic studies [35,43,44], the cyanide and thiocyanate layers on the Pt(111) surface retain counter cations, while the adsorbed iodide is almost neutral due to its partial charge-transfer, and the absence of the cations on the I–Pt(111) surface is expected under our experimental conditions. The presence of the counter cation on the cyanide and the thiocyanate layers indicates that these layers are negatively charged. The negative charge on the cyanide and the thiocyanate layers would not be completely compensated with the counter cations, since the surface coverages of the counter cations are three to fivefold smaller than those of the cyanide or the thiocyanate. Therefore, the electrical double layer effect due to the adsorbed species may be responsible for the different rate constants at each modified electrode, but we cannot further discuss this quantitatively at this stage.

We will consider other possibilities of the role of the adlayers based on a theoretical model for simple heterogeneous electron-transfer reactions reviewed by Weaver [45]. A rate constant without the influence of the work term, i.e. the electrical double layer, can be expressed as the electrostatic work-corrected rate constant

$$k_{corr} = \delta_r \nu_n \Gamma_n \kappa_{el} \exp(-\Delta G^*_{corr}/kT) \tag{3}$$

where δ_r is the effective thickness of the reaction zone, ν_n is the nuclear frequency factor, Γ_n is the nuclear tunneling factor, κ_{el} is the electronic transmission coefficient, ΔG^*_{corr} is the work-corrected Gibbs energy of activation, k is the Boltzmann constant, and T is the absolute temperature. Since we are concerned with the rate constant at the formal potential, ΔG^*_{corr} is equal to ΔG^*_{int} which is termed the intrinsic barrier. Moreover, ΔG^*_{int} is divided into additive contributions arising from the distortion of the reactant, ΔG^*_{in}, and the reorientation of the surrounding solvents, ΔG^*_{out}.

The presence of the iodide-layer will shift the plane of closest approach toward the solution side because of its size which is larger than that of an water molecule. The thickness of the iodide-layer is estimated to be ca. 0.4 nm from the van der Waals radius of iodide (0.215 nm estimated by Pauling [46] and 0.198 nm by Bondi [47]). The thickness of the primary water layer is estimated to be ca. 0.3 nm from the effective diameter of a water molecule. Although these values are somewhat uncertain, we tentatively assume the shift of the reaction plane by the iodide layer to be ca. 0.1 nm. On the other hand, the molecular axes of the adsorbed thiocyanate and cyanide are almost perpendicular to the Pt(111) surface [35,39,48–50], and thus the thickness of the thiocyanate layer and the cyanide layer are estimated to be ca. 0.606 and 0.415 nm from the molecular sizes, respectively [46].

The inner-shell reorganization is independent of the reactant-electrode distance, whereas, according to Marcus theory [3], the outer-shell reorganization is dependent on the distance as

$$\Delta G^*_{out} = m^2 \lambda_{out} = \frac{m^2 \Delta e^2}{2} \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{a} - \frac{1}{R} \right) \tag{4}$$

where m is the dimensionless parameter introduced by Marcus, Δe is the difference of charge between the oxidized and reduced forms, a is the radius of the reactant and of the product, R is the distance from the center of the reactant to its image charge (i.e. twice the distance from the center of the reactant to the electrode surface), ε_{op} is the optical dielectric constant of a medium (equal to the square of refractive index), and ε_s is the static dielectric constant. Eq. (4), which is usually employed, is an approximate one under the condition $R \gg a$, and Kharkats [51] derived a rigorous one for the outer-shell reorganization energy for homogeneous electron-transfer reactions based on Marcus' model:

$$\lambda_{out}^{hom} = \Delta e^2 \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$
$$\left[\frac{1}{2a} + \frac{1}{2b} - \frac{1}{R} - \frac{1}{4}(\psi(R,a) + \psi(R,b)) \right] \tag{5}$$

where

$$\psi(\alpha,\beta) = \frac{\beta}{\alpha^2 - \beta^2} + \frac{1}{2\alpha} \ln \frac{\alpha - \beta}{\alpha + \beta} \tag{6}$$

Setting $a = b$ in Eq. (5) and multiplying it by the factor of 1/2, we can obtain the rigorous expression of ΔG^*_{out} for electrochemical reactions:

$$\Delta G^*_{out} = m^2 \lambda_{out} = \frac{m^2 \Delta e^2}{2} \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{a} - \frac{1}{R} - \frac{\psi(R,a)}{2} \right) \tag{7}$$

Although the increase in the outer-sphere reorganization energy with the increase in the reactant-electrode distance estimated from Eq. (7) is somewhat larger than that from Eq. (4), the decrease in the rate constants of about one order of magnitude due to the presence of the iodide layer is not expected from the slight increase in the reactant-electrode distance of 0.1 nm, moreover the faster reaction observed at the CN- and SCN-modified electrodes than at the unmodified electrode contradicts the theoretical prediction from their molecular sizes.

The nuclear frequency factor, ν_n, is approximately given by [45]

$$\nu_n = \left(\frac{\nu_{out}^2 \Delta G^*_{out} + \nu_{in}^2 \Delta G^*_{in}}{\Delta G^*_{out} + \Delta G^*_{in}} \right)^{1/2} \tag{8}$$

where v_{out} is the characteristic frequency of the outer-shell reorganization, and v_{in} is the average vibrational frequency associated with the redox couple. The influence of the reactant-electrode distance on this factor is negligible because of the independence of the inner-shell reorganization energy on the distance and the weak dependence of the outer-shell reorganization energy on it.

The nuclear tunneling factor, Γ_n, is the correction for the contribution of the reaction without fully surmounting the Gibbs energy barrier. The magnitude of the nuclear tunneling correction at room temperature is commonly small [52]. Therefore, we can ignore the influence of the nuclear tunneling factor.

Estimation of κ_{el} is very difficult. Dependence of κ_{el} on the distance, r, between a donor and an acceptor site, is often found to exhibit, to a first approximation, an exponential behavior [45]:

$$\kappa_{el} = \kappa_{el}^{\circ} \exp[-\beta(r - r_0)] \tag{9}$$

where r_0 is the distance of closest approach and κ_{el}° is the electronic transmission coefficient at r_0. Usually the electronic coupling between the reactant and the electrode decays steeply with increase of the tunneling distance. Since the iodide layer increases r_0, κ_{el}° is considered to be smaller for the iodide-modified electrode than for the unmodified electrode. Moreover, the effective thickness of the reaction zone, δ_r, is smaller in non-adiabatic reactions than adiabatic reactions. Therefore, the iodide layer may significantly decrease the effective electron-tunneling distance, $\delta_r \kappa_{el}^{\circ}$. At first glance, the distance dependence of the electronic tunneling contradicts our experimental findings at the CN- and SCN-modified electrodes. However, the adiabaticity of reactions is affected by the electronic nature of the interlayer as well as the reactant-electrode distance. Schmickler [53,54] and Dogonadze et al. [55,56] developed a theory of resonance tunneling or the accelerated electron-transfer through energy levels in the interlayer, which can serve as a virtual intermediate state in an electrode process. If adsorbed thiocyanate and cyanide possess appropriate electronic energy levels, i.e. ones close to the donor–acceptor levels, electron-transfer via intermediate states would be possible. Larsson [57] applied the extended Hückel method to the problem of intramolecular electron-transfer, i.e. between the donor and the acceptor sites contained within a single molecule such as a binuclear complex. In his calculation, the electron-tunneling probability is predicted to be enhanced substantially by the electron-transfer via some π orbitals of cyanogen:

$$M_1 \cdots N \equiv C - C \equiv N \cdots M_2$$
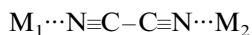
Therefore, we cannot rule out the possibility of the accelerated electron-transfer via π orbitals of adsorbed thiocyanate or cyanide.

4. Conclusions

We have investigated the influence of electrolyte anions, adsorbed anions, and crystallographic orientation on the kinetics of the outer-sphere electron-transfer reactions of cobalt complexes at platinum (111), (100), and (110) single-crystal electrodes. The rate constants were dependent on the electrolyte anions and decreased in the order $F^- > Cl^- > Br^-$. The effect of electrolyte anions may be ascribable to adsorption of the anions and their surface coverage. The electron-transfer rate was found to be affected by the adsorbed anions, whereas no clear influence of the crystallographic orientation was observed. The electrical double layer effect is considered to be responsible for the acceleration or the retardation of the electron-transfer by the adlayers. The retardation due to decrease of the effective electronic tunneling distance and the acceleration due to the electron-transfer via intermediate states are also considered as other possible factors. We could not determine whether the electrical double layer or the electronic tunneling is responsible for the influence of the adlayers on the rate constants due to our limited knowledge. Although we could not get information about the surface charge, kinetic studies on the redox couple of opposite charge may be necessary to check the electrical double layer effect. Knowledge of energy levels of adsorbed species would be needed to support the electron-transfer via intermediate states.

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