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Electron-transfer Kinetics of Transition-metal Complexes in Lower Oxidation States. Part II.[1] The Electrochemical Electron-transfer Rate of the $Cr(bipy)_3^+/Cr(bipy)_3$ System as Measured by the Galvanostatic Double-pulse Method[2]

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The kinetic parameters of the electron-transfer reaction, $Cr(bipy)_3^+ + e \rightleftarrows Cr(bipy)_3$, were measured by the galvanostatic double-pulse method at a dropping mercury electrode in *N,N*-dimethylformamide. The apparent and the corrected standard rate constants were 1.0 ± 0.2 and 0.3 cm s^{-1} respectively, and the transfer coefficient was 0.6 ± 0.1 at 25 °C. These rate constants were discussed in comparison with the corresponding homogeneous rate constant on the basis of the theoretical equation of Marcus. They were quite inconsistent with the value, 10^3 cm s^{-1}, predicted from the corresponding homogeneous rate constant.

The polarograms of $Cr(bipy)_3^+$ and $Cr(bipy)_3$ exhibited three waves with half-wave potentials of -0.21, -0.65 and -1.19 V *vs.* a cationic glass electrode. The diffusion coefficients of these complexes, as determined polarographically, were identical: 3.2×10^{-6} cm^2 s^{-1} at 25 °C.

The theory of Marcus has been successfully applied to a number of electron-transfer reactions[3,4] in order to make the theoretical predictions of (1) the rate constants for the homogeneous and the electrochemical electron-transfer reactions, (2) the transfer coefficients for them, and (3) the correlation between the rate constants for the homogeneous electron-exchange reaction, $A^z + A^{z-n} \rightleftarrows A^{z-n} + A^z$, and the corresponding electrochemical electron-transfer reaction, $A^z + ne \rightleftarrows A^{z-n}$. Here, z is the number of the ionic charge, and n, the number of electrons transferred. This paper is concerned with the third aspect: the rate constants of these two types for the $Cr(bipy)_3^+/Cr(bipy)_3$ system are compared and discussed in the light of the theory of Marcus.

According to this theory, the homogeneous electron-exchange rate constant, k_{ex}, is related to the corresponding electrochemical electron-transfer rate constant, k_{el}, by the following simple relationship:[5]

$$(k_{ex}/Z_{hom})^{1/2} = k_{el}/Z_{el} \qquad (1)$$

where Z_{hom} is the hypothetical collision number of two uncharged species in a solution when they have a unit concentration, and where Z_{el} is the collision number of an uncharged species with a unit area of the electrode when it has a unit concentration. An electron-transfer reaction with which this relationship is to be tested must have such a large rate constant that the rates of other possible coupled processes, *e.g.*, the bond-rupture, bond-formation, and atom-transfer processes, can be neglected, as this theory is based on the assumption that the reaction proceeds through an outer-sphere mechanism. With the Z values of 10^{11} M^{-1} s^{-1} for Z_{hom} and 10^4 cm s^{-1} for Z_{el}, the (1) relation holds fairly well in the reactions with a rather small rate constant,[5–7] *e.g.*, V^{3+}/V^{2+}, Eu^{3+}/Eu^{2+}, Tl^{3+}/Tl^+, and $Co(phen)_3^{3+}/Co(phen)_3^{2+}$, but it is insufficient in those with a large rate constant,[5] *e.g.*, Fe^{3+}/Fe^{2+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, and MnO_4^{2-}/MnO_4^-. According to recent investigations, however, it is quite probable that the reactions of aquo-complexes proceed through a mechanism other than the outer-sphere mechanism.[8] The reaction of $Co(phen)_3^{3+}$-$(t_{2g}^6)/Co(phen)_3^{2+}(t_{2g}^5 e_g^2)$ is also inappropriate for the present purposes, because the two reactants are in different spin states.[8] Consequently, the excellent agreement between the theoretical prediction and experimental results found for these reactions cannot be a support for the validity of Eq. (1) Unfortunately, there are not many homogeneous electron-exchange reactions that have been confirmed to proceed through an outer-sphere mechanism, and even the concept of outer- and inner-sphere mechanisms has never been established in electrochemical electron-transfer reactions. Therefore, we recommend a system with a sufficiently large homogeneous electron-exchange rate constant for testing Eq. (1), for the same reasons as were discussed in a previous paper treating the potential dependence of the transfer coefficient.[9] Generally an electron-exchange reaction is very fast if it satisfies the following two conditions:[8] (1) the reactants have "conducting" unsaturated ligands, such as cyanide, phenanthroline, bipyridine, and cyclopentadienyl, that is, the reactants are characterized by a highly delocalized π-electron distribution, and (2) the reactants are a pair of complexes differing by one in the number of electrons in the lower orbitals not used in ligand bondings. The electron-exchange reaction between $Fe(phen)_3^{3+}(t_{2g}^5)$ and $Fe(phen)_3^{2+}$-(t_{2g}^6) is a reaction satisfying these conditions; its second-order rate constant[10] is larger than 3×10^7 M^{-1} s^{-1} and some 10^7 times as large as that of the $Co(phen)_3^{3+}/Co(phen)_3^{2+}$ system.[6,7]

It should be borne in mind that Eq. (1) has been derived by neglecting the contribution to the activation free energy from the free energy required to bring the reactant(s) and the product(s) to the positions where electron-transfer takes place. This contribution is referred to as a "work term" in the Marcus theory. The work term may reasonably be neglected in a homogeneous electron-exchange reaction where one of the reactants is uncharged. Our choice of the $Cr(bipy)_3^+(t_{2g}^5)/Cr(bipy)_2(t_{2g}^6)$ system is based partly on this reasoning and partly on its electronic configuration, which is analogous to that of the $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ system, thus promising a large electron-transfer rate constant. Recently we have measured the rate constant of the homogeneous electron-transfer reaction between $Cr(bipy)_3^+$ and $Cr(bipy)_3$ in *N,N*-dimethylformamide (DMF) by the electron spin resonance method using the line-broadening procedure.[1] The observed second-order rate constant was $1.5\times10^9\ M^{-1}\ s^{-1}$ at 25 °C. This was in good agreement with the rate constant calculated non-empirically according to the theory of Marcus, with the inner-sphere reorganization energy neglected. Furthermore, the oxidation-reduction potential of the $Cr(bipy)_3^+/Cr(bipy)_3$ system is negative *vs.* the oxidation potential of mercury, so the Frumkin correction can be applied, if necessary, to this system. According to Eq. (1), the predicted value for the standard rate constant of this system should be larger than $10^3\ cm\ s^{-1}$, beyond the upper limit accessible by existing techniques. In this experiment measurements are made by the galvanostatic double-pulse method; the standard rate constant obtainable by this method is $10\ cm\ s^{-1}$ at most.

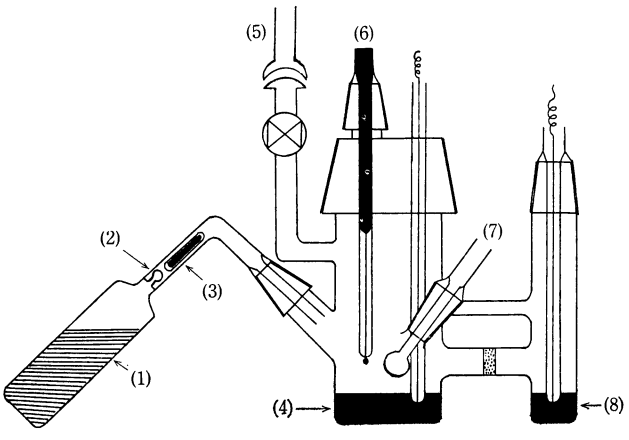

Fig. 1. Electrolysis cell: (1) electrolytic soln, (2) breakable seal, (3) hammer, (4) mercury pool A, (5) joint to vacuum line and inlet for nitrogen gas, (6) working electrode, (7) cationic glass electrode, (8) mercury pool B.

Experimental

Complexes. Both complexes, tris-(2,2′-bipyridine)-chromium(I) perchlorate and tris-(2,2′-bipyridine)-chromium (0), are very sensitive to oxygen. They were prepared and handled in a vacuum or in a nitrogen atmosphere. The preparation and analysis of these complexes were described in a previous paper.[1]

Reagents. Lithium perchlorate (Yoneyama Chemical Industries) and DMF(Wako Pure Chemical Industries) were used as the supporting electrolyte and the solvent, respectively. The former was recrystallized from an oxygen-free aqueous solution under a nitrogen atmosphere and then dried *in vacuo*. The latter was purified in a way described previously.[1]

Solutions. The $Cr(bipy)_3ClO_4$ and $Cr(bipy)_3$ solutions were prepared by dissolving the required amounts of lithium perchlorate and one of the complexes in DMF so that their concentrations might be 0.5 M and of the order of 10^{-3} M with respect to the supporting electrolyte and the complexes. The solutions were then stored in evacuated glass ampoules fitted with breakable-seals. The solution ampoule was connected with the cell *via* a tapered joint. Each aliquot was about 25 ml. All operations in preparing the solutions were performed *in vacuo*, with the subsidiary use of nitrogen. The electrolytic solution used in the double-pulse measurement must contain both the oxidant and the reductant.[11] It was prepared within the cell by the partial electrolytic reduction of a $Cr(bipy)_3ClO_4$ solution at a controlled potential. The concentrations of both species were determined polarographically.

Cell. The Pyrex-glass electrolysis cell shown in Fig. 1 was used. After the cell had been evacuated, nitrogen gas was introduced into it until an atmospheric pressure was reached. The electrolytic solution was then transferred into the cell through the broken breakable-seal by the appropriate rotation of the ampoule around the tapered joint. A cation-permiable glass electrode (CGE) served as a reference electrode in the polarographic measurements and controlled potential electrolyses. Its e.m.f. was −50 mV *vs.* SCE, as measured by the use of a conventional agar bridge; this was sufficiently reproducible within the limits of accuracy of this experiment, *i.e.*, 2 mV. The cell was evacuated easily and completely by the use of this reference electrode. Besides the CGE, a dropping mercury electrode (DME) and two mercury pool electrodes were fitted in the cell. The DME, the CGE, and the mercury pool electrode, A, were used in the polarographic measurements. The apparent area of the mercury pool A was about $10\ cm^2$. The two mercury electrodes, A and B, served as the working and the couter electrodes respectively in the controlled potential electrolyses. The compartment of the latter electrode was separated by a fritted glass from that of the former electrode. The progress of the controlled potential electrolysis was followed polarographically. A controlled current double-pulse was applied between the DME and the mercury pool electrode A.

Procedure and Devices. A controlled current double-pulse was applied to each drop of DME 3.0 s after the birth of the drop. The controlled current double-pulse generator equipped with an ohmic-drop compensating unit,[13] the synchronizing and timing circuit for DME,[14] and the potentiostat[15] which were used in this experiment have all been described elsewhere. Measurements were made at room temperature maintained at 25 °C.

Results and Discussion

A typical polarogram taken in a 0.3 mM solution of $Cr(bipy)_3$ is shown in Fig. 2. It exhibits three oxidation waves, with half-wave potentials of −0.21, −0.65, and −1.19 V *vs.* CGE respectively. The waves at −0.65 and −1.19 V are reversible, and their wave-heights are identical when corrected for the drop area. Two oxidation waves and a reduction wave with half-wave potentials of −0.20, −0.64, and −1.17 V *vs.* CGE appeared in a polarogram taken in a 0.5 mM solution of $Cr(bipy)_3^+$. After the $Cr(bipy)_3^+$ had been reduced completely to $Cr(bipy)_3$ by the controlled-potential electrolysis at −1.5 V, the polarogram was exactly the same as that of $Cr(bipy)_3$. On the basis of these experimental results and the proportionality between the wave-height and the concentration of $Cr(bipy)_3ClO_4$, the half-wave potential of −1.19 V *vs.* CGE can be assigned to the following redox system:

$$Cr(bipy)_3^+ + e \rightleftharpoons Cr(bipy)_3 \qquad (2)$$

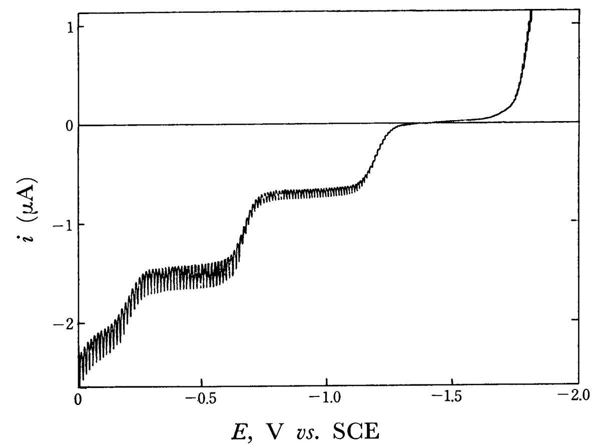

Fig. 2. Polarogram of 0.3 mM $Cr(Bipy)_3$ in a DMF soln containing 0.5 M $LiClO_4$.

There have been several polarograms of $Cr(bipy)_3{}^{3+}$ reported.[16] They were measured in solvents other than DMF, but in these polarograms one can find a wave corresponding to each wave in Fig. 2.

The diffusion coefficients of $Cr(bipy)_3{}^+$ and $Cr(bipy)_3$ were identical; they were determined to be 3.2×10^{-6} $cm^2\,s^{-1}$ at 25 °C.

The results obtained by the galvanostatic double-pulse measurement were analyzed according to the following equation:

$$\log (I_0/nFC_O) = \log k_s + \alpha \log(C_R/C_O) \tag{3}$$

where I_0 is the exchange current density; k_s, the standard rate constant; α, the transfer coefficient, and the C's, the concentrations of the oxidant, O, and the reductant, R. An experimental plot in accordance with Eq. (3) is shown in Fig. 3. The standard rate constant and the transfer coefficient were determined to be 1.0 ± 0.2 cm s^{-1} and 0.6 ± 0.1 respectively. Such a large apparent standard rate constant approaching 1 cm s^{-1} has rarely been reported for the electrochemical electron-transfer reactions of transition-metal complexes.

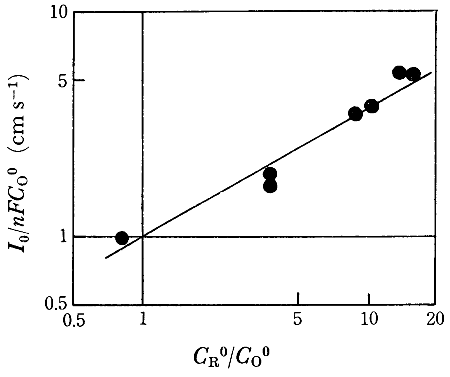

Fig. 3. Plot of log $(I_0/nFC_O{}^0)$ *vs.* log $(C_R{}^0/C_O{}^0)$.

Thus, we have found that the rate constants for the homogeneous and the electrochemical electron-transfer reactions of the $Cr(bipy)_3{}^+/Cr(bipy)_3$ system are both sufficiently large; this system is now considered to be appropriate for testing Eq. (1). Its electrochemical rate constant, however, is quite inconsistent with the value predicted by Eq. (1), *i.e.*, 10^3 cm s^{-1}.

TABLE 1. THE OBSERVED, THE CORRECTED AND THE CALCULATED RATE CONSTANTS FOR THE $Cr(bipy)_3{}^+/Cr(bipy)_3$ SYSTEM AT 25°C

k_{el} (cm s^{-1})		
Observed	Corrected	Calculated
1.0 ± 0.2	0.3	10^3

If the positions occupied by the reactant and the product in their respective activated complexes are located within the diffuse double-layer, the work term for $Cr(bipy)_3{}^+$ in the electrochemical reaction should not be neglected, whereas this term may reasonably be neglected in the homogeneous electron-transfer of this system. These positions are referred to as the sites of the pre-electrode. The electrical potential at the pre-electrode site must be known in order for the work term to be evaluated. However, this is rather a difficult task. Assuming that the double-layer structure is of the Gouy-Chapman type and that both pre-electrode sites are located on the outer Helmholtz plane, the work term correction can be made according to the Frumkin procedure. Although the validity of the latter assumption is not quite certain, a Frumkin correction is applied as a trial to the electrochemical rate constant obtained above.

The data of the ϕ_2-potential in a DMF solution of lithium perchlorate are not available, but the electrocapillary curves for several electrolytes in this solvent have been reported.[17] The extent of the specific adsorption of perchlorate ions may be seen to be the least of all the anions studied. The electrocapillary curves were analyzed on the assumption that neither the anions nor the cations were specifically adsorbed on the electrode. The ϕ_2-potential at −1.19 V *vs.* CGE was obtained as −76 mV. The corrected standard rate constant was 0.3 cm s^{-1}. The corrected rate constant does not agree with the predicted value better than the apparent rate constant.

The original theory of Marcus regarding the electrochemical reaction does not state anything explicitly about the location of pre-electrode sites. The experimental results show, though, that the corrected rate constant cannot be larger than the observed one, wherever the pre-electrode site is located. Consequently, it is evident that Eq. (1) cannot hold unless the apparent electrochemical rate constant is immeasurably large. The same situation can be expected for a system satisfying the following conditions: (1) the number of electrons transferred is one; (2) k_{ex} is larger than 10^8 $M^{-1}\,s^{-1}$; (3) either species of the system is positively (or negatively) charged, or both species are, and (4) the standard electrode potential is negative (positive) *vs.* the zero-charge potential. Equation (1) has been applied exclusively to systems these conditions are not satisfied.

References

1) Part I: T. Saji and S. Aoyagui, This Bulletin, **46**, 2101 (1973).

2) Presented at the 17th Symposium on Polarography and Electroanalytical Chemistry, Fukuoka, Oct., 1971.

3) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964) and papers cited therein.

4) M. E. Peover and J. S. Powell, *J. Electroanal. Chem.*, **20**, 427 (1969).

5) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

6) H. Bartelt, *Electrochim. Acta*, **16**, 629 (1971).

7) B. R. Baker, F. Basolo, and H. M. Neuman, *J. Phys. Chem.*, **63**, 371 (1959).

8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., John Wiley & Sons Inc., New York, N. Y. (1967), Chap. 6.

9) K. Suga, H. Mizota, Y. Kanzaki, and S. Aoyagui, *J. Electroanal. Chem.*, **41**, 313 (1973).

10) D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **43**, 3765 (1965).

11) After this investigation was made, a new galvanostatic double-pulse set-up has been proposed.[12] It requires only either the oxidant or the reductant to be contained in the bulk of solution.

12) H. Mizota, H. Matsuda, Y. Kanzaki, and S. Aoyagui, *J. Electroanal. Chem.*, **45**, 385 (1973).

13) M. Kogoma and S. Aoyagui, *ibid.*, **34**, 123 (1972).

14) T. Rohko, M. Kogoma, and S. Aoyagui, *ibid.*, **38**, 45 (1972).

15) Y. Kanzaki and S. Aoyagui, *ibid.*, **36**, 297 (1972).

16) A. A. Vlcek, *Nature*, **189**, 393 (1961). Y. Sato and N. Tanaka, This Bulletin, **42**, 1021 (1969).

17) V. D. Bezuglyi and L. A. Korshikov, *Elektrokhimiya*, **3**, 390 (1967).