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Electron-transfer Kinetics of Transition-metal Complexes in Lower Oxidation States. Part III.[1] Electrochemical Rate Constants for the Fe(II)/Fe(I) Redox Systems

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Synopsis. The standard rate constants for the redox systems Fe(II)/Fe(I) are measured. They are about one tenth of those for the systems Fe(III)/Fe(II) and Cr(I)/Cr(0). The difference in the kind of molecular orbital occupied by the excess electron of the reductant species can account for the difference in the rate constant.

Transition-metal complexes in lower oxidation states have been widely studied from the structural chemical, magnetochemical, spectroscopic and kinetic points of view. Although electrochemical studies have also been made, they have been almost limited to polarographic ones. Eelctrode kinetic parameters have been measured so far only on two redox systems in lower oxidation states: one is the $Co(bipy)_3^{2+}/Co(bipy)_3^+$ system[2] and the other the $Cr(bipy)_3^+/Cr(bipy)_3$ system.[1] The standard rate constant of the latter system was discussed in comparison with the second order rate constant of the corresponding homogeneous homonuclear electron-transfer reaction.[3] It was pointed out that each of the electrochemical and the homogeneous electron-transfer reactions of this system fell into a class of the fastest reaction. Its electronic configuration differing by one in the number of electrons in metal t_{2g}-orbitals was considered to account for the high reaction rate.

This note treats the measurements of the standard rate constants of the redox systems $Fe(bipy)_3^{2+}/Fe(bipy)_3^+$ and $Fe(bipy)_2(CN)_2/Fe(bipy)_2(CN)_2^-$. According to our recent polarographic investigations,[4,5] the excess electron of a reductant complex of these systems occupies a ligand π^*-orbital.

Experimental

Each electrolytic solution contained a 2 mM electroactive species, *i.e.*, $Fe(bipy)_3^{2+}$, $Fe(bipy)_2(CN)_2$ or 2,2′-bipyridine in *N*,*N*-dimethylformamide (DMF). Supporting electrolyte was 0.2 M tetra-*n*-butylammonium perchlorate (TBAP). Either a platinum spherical electrode or a dropping mercury electrode (DME) was used as the working electrode. The standard rate constant (k°) was assumed to be identical with the rate constant at the half-wave potential ($E_{1/2}$). It was measured with the aid of the galvanostatic double-pulse method with the *in situ* generation of a reductant complex at the half-wave potential of the redox system. Measurements were made at 25±2 °C. Details of the experiments were described in a separate paper.[6]

Results and Discussion

Results obtained are listed in Table 1. They are summarized as follows: (1) a partial subtitution of a ligand bipy with a CN^- does not affect the rate constant, (2) the rate constant does not depend much on the material of the working electrode, platinum or mercury, (3) the rate constants are smaller about one order of magnitude than the rate constant for the $Cr(bipy)_3^+/Cr(bipy)_3$ system,[1] 1.0 cm s^{-1}, and (4) the rate constants for the Fe(II)/Fe(I) systems are nearly equal to the rate constant for the $bipy/bipy^-$ system. Feature (1) forms a striking contrast to findings obtained for Fe(III)/Fe(II) systems:[6] the apparent standard rate constants for $Fe(bipy)_3^{3+}/Fe(bipy)_3^{2+}$, $Fe(bipy)_2(CN)_2^+/Fe(bipy)_2(CN)_2$, $Fe(bipy)(CN)_4^-/Fe(bipy)(CN)_4^{2-}$ and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ become smaller in this order from about 1 cm s^{-1} to 0.2 cm s^{-1}. Features (3) and (4) may be consistent with the previous conclusion that the electron transferred in the course of electrochemical oxidation of Fe(I) complexes occupies a ligand π^*-orbital[4] and that of Fe(II) complexes a metal t_{2g}-orbital.[7] These facts may suggest that the electronic configuration of a redox species can be a predominant factor determining the electrochemical electron-transfer rate. It is known that the rate constant of a homogeneous electron-transfer reaction depends on the electronic configuration of the reactants. Such a dependence has been discussed on electrode reactions by Vlček[8] and later by Marcus[9] who has pointed out that when a reductant species loses a metal e_g-electron on oxidation, the rate is slower than when it loses a t_{2g}-electron. This has been interpreted on the basis of his theory[10] as follows: a t_{2g}-electron transfer, compared with an e_g-electron transfer, requires a lesser change in bond lengths or bond geometry and in its turn smaller energy of reorganization of the inner coordination shell.

Table 1. Standard rate constants at 25 °C for the redox systems Fe(II)/Fe(I) as compared with those for the Fe(III)/Fe(II) and $BIPY/BIPY^-$ systems

Redox system	Electrode	$E_{2/1}$(V SCE)	k°(cm s^{-1})
$Fe(bipy)_3^{3+}/Fe(bipy)_3^{2+}$	Pt	1.03[a]	1.1[a]
$Fe(bipy)_3^{2+}/Fe(bipy)_3^+$	Pt	−1.26	0.16
$Fe(bipy)_2(CN)_2^+/Fe(bipy)_2CN)_2$	Pt	0.47[a]	0.41[a]
$Fe(bipy)_2(CN)_2/Fe(bipy)_2(CN)_2^-$	Pt	−1.60	0.11
$bipy/bipy^-$	Pt	−2.09	0.21
$Fe(bipy)_3^{2+}/Fe(bipy)_3^+$	DME	−1.26	0.14
$Fe(bipy)_2(CN)_2/Fe(bipy)_2(CN)_2^-$	DME	−1.59	0.13
$bipy/bipy^-$	DME	−2.10	0.13

a) Ref. 6

Further support for the conclusion of this note will be furnished in a separate paper[11] by the same kind of experiments on more than twenty redox systems of tris-

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(2,2′-bipyridine) complexes of titanium, vanadium, chromium, molybdenum, iron, ruthenium, and osmium.

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