

Notes

Re-Calculated Self-Exchange Rate Constants of Some Copper(I, II)-Polythiaether Complexes in Aqueous Media

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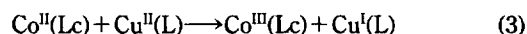
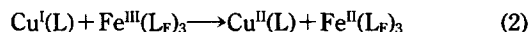
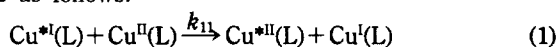
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Recently, Rorabacher *et al.* carefully measured the cross-reaction rate constants for the oxidation of copper(I)-polythiaether complexes by $\text{Fe}^{3+}(\text{L}_F)_3$ (L_F =4,7-dimethyl-1,10-phenanthroline) and for the oxidation of copper(II)-polythiaether complex by $\text{Co}^{2+}(\text{Lc})$ (Lc =diaquo-(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)) in aqueous solutions and confirmed that two widely discrepant self-exchange rate constants were acquired when they applied the classical Marcus cross-relation to their kinetic data¹. Similar results had been obtained earlier with simple copper(I, II)-polypyridyl complexes^{2,3} and Anson had pointed out how the classical Marcus formulation could be successfully modified to obtain consistent self-exchange rate constants from cross-reaction data⁴.

Since the electron transfer reactions exhibited by this class of simple copper(I, II) complexes involve the common features of bond breaking and/or bond formation it is appropriate to employ the Anson's method⁴ to analyze the data. The authors of reference 1 attempted to do so but their results differed from those to be expected on the basis of the procedure of reference 4. They mistakenly identified that the geometric mean method was the method of reference 4. In this Note we wish to show that the correct application of procedure of reference 4 leads to a new set of self-exchange rate constants for the copper(I, II)-polythiaether systems, some of which agree with the values reported in reference 1. The important purpose of the present work is to clearly present the method in reference 4, about which exists some lack of understanding^{1,5,8}.

For the copper(I, II)-polythiaether complex systems studied in reference 1, the self-exchange reaction and cross-reactions are as follows:



When the iron (III, II) and cobalt (II, III) complexes are assumed to be here) the redox couples which adhere to the Marcus cross relation, the method of the following postulates can be applied to calculate the self-exchange rate constants, k_{11} .

$$\lambda_{(1)}^{\text{I}} = \lambda_{(-1)}^{\text{II}} = 1/2[\lambda_{(2)}^{\text{I}} + \lambda_{(3)}^{\text{II}}] = 1/2[\lambda_{(-2)}^{\text{II}} + \lambda_{(-3)}^{\text{I}}] \quad (4)$$

where the superscripts refer to the oxidation state of copper and the subscripts refer to the forward and reverse directions of the three reactions. This procedure also involves the following assumptions:

$$\lambda_{(2)}^{\text{I}} = \lambda_{(-2)}^{\text{II}}; \lambda_{(3)}^{\text{II}} = \lambda_{(-3)}^{\text{I}} \quad (5)$$

$$\lambda_{(1)}^{\text{I}} \neq \lambda_{(2)}^{\text{I}} \neq \lambda_{(-3)}^{\text{I}} \quad (6)$$

$$\lambda_{(-1)}^{\text{II}} \neq \lambda_{(-2)}^{\text{II}} \neq \lambda_{(3)}^{\text{II}} \quad (7)$$

The combination of assumptions is self-consistent and conforms to the principle of microscopic reversibility. The assumption of unequal reorganization energies for the copper(I) and copper(II) complexes (Eq. (6) and (7)) implies that the reaction mechanism should vary depending on reaction conditions, *i.e.*, cross-reactions of strongly oxidizing or reducing condition may follow different microscopic pathways from cross-reactions with little or no driving force. The recent experimental data conclude that the microscopic pathways change upon variation of the reaction driving force⁷. Although likely mechanistic consequences were not described in the original paper⁴, a recent rationalization by Rorabacher could be certainly a possibility⁶. The results calculated on the basis of Eq. (4) are shown in Table 1.

Although some of the calculated self-exchange rate constants in Table 1 (ligands B, C, E, F, G) are reasonably in accord with the rate constants by the geometric mean method (5th column of Table 9 of reference 1) and some (ligand C, E, G, H) by the combination method (6th column of Table 9 of reference 1) in reference 1, the agreements are accidental because the three methods are based on different models¹⁴. The two methods in reference 1 are based on the classical Marcus theory or Marcus cross relationship, which assumes that two halves of the couple make the same contribution to the reorganization energy of both self-exchange and cross-reactions ($1/2 \lambda_{\text{self}} = \lambda_{\text{e} \rightarrow \text{o}} = \lambda_{\text{o} \rightarrow \text{e}}$). The classical Marcus theory was, however, designed for simple electron transfer reactions involving no breaking of chemical bonds, no formation of new chemical bonds but only fluctuations of bond lengths and bond angles and fluctuations of molecular orientations of the solvent in such a way to facilitate electron transfer. The classical Marcus theory was modified to extract the self-exchange rate constants for the redox couple involving bond-breaking and/or bond-formation ($\text{Cu}^{\text{II}}(\text{L})$ in this example) from the cross reaction studies with redox couples ($\text{Fe}^{\text{III/II}}(\text{L}_F)$ and $\text{Co}^{\text{III/II}}(\text{Lc})$ in this example) assumed to adhere to the Marcus cross relationship. The method assumes that two halves of the couple make the different contribution for electron transfer reactions involving bond-breaking and/or bond formation. The calculated results (columns 8, 9, 10) support the postulates for the copper(I, II) complexes.

The experimental values (measured by NMR line broadening method to be $10^{5.3}$, $10^{4.4}$ and $10^{5.1} \text{ M}^{-1}\text{s}^{-1}$ for the $[\text{14}] \text{aneS}_4$, $[\text{15}] \text{aneS}_5$ and $[\text{15}] \text{aneNS}_4$ ligands, respectively⁸) are different from the calculated values in the present work or those

Table 1. Rate Constants and Activation Parameters^a

Row	Redox pairs ^a	ΔG^b (eV)	E_f^c (V)	ΔG^{ad} (eV)	$10^2 W^e$ (eV)	σ^f (A)	λ^g (eV)	$\lambda_{o \rightarrow r}^h$ (eV)	$\lambda_{r \rightarrow o}^i$ (eV)	$k(MS)^{-1}$
1	Fe(L _F) ^{3+/2+}	0	0.939	0.186	3.5	13.2	0.60	0.30	0.30	3.3×10^8
2	Co(L _C) ^{3+/2+}	0	0.562	0.820	5.9	9.4	3.04	1.52	1.52	5.0×10^{-3}
3	Cu(A)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.079		0.542	4.2	9.1	2.02	0.50	1.52	2.1×10^2
4	Fe(L _F) ³⁺ / Cu(A)(OH ₂) ⁺	-0.298		0.327	2.3	11.0	1.74	0.30	1.44	1.2×10^6
5	Cu(A)(OH ₂) ^{2+/+}	0	0.641	0.507	2.2	8.8	1.94	0.97	0.97	8.0×10^{2a}
6	Cu(B)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.033		0.579	4.2	9.1	2.24	0.72	1.52	5.0×10
7	Fe(L _F) ³⁺ / Cu(B)(OH ₂) ⁺	-0.344		0.316	2.3	11.0	1.78	0.30	1.48	1.8×10^6
8	Cu(B)(OH ₂) ^{2+/+}	0	0.595	0.572	2.2	8.8	2.20	1.10	1.10	6.3×10^4
9	Cu(C)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.038		0.630	4.2	9.1	2.45	0.93	1.52	7.0
10	Fe(L _F) ³⁺ / Cu(C)(OH ₂) ⁺	-0.339		0.271	2.3	11.0	1.58	0.30	1.28	9.9×10^6
11	Cu(C)(OH ₂) ^{2+/+} / Cu(C)(OH ₂) ⁺		0.600	0.575	2.2	8.8	2.21	1.11	1.11	$5.5 \times 10^4(10^{5.3})$
12	Cu(D)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.068		0.541	4.2	9.1	2.15	0.63	1.52	2.2×10^2
13	Fe(L _F) ³⁺ / Cu(D) ⁺	-0.309		0.260	2.3	11.0	1.49	0.30	1.19	1.5×10^7
14	Cu(D)(OH ₂) ^{2+/+} / Cu(D) ⁺	0	0.630	0.477	2.2	8.8	1.82	0.91	0.91	2.4×10^{3a}
15	Cu(E)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.123		0.577	4.2	9.1	2.40	0.88	1.52	5.3×10
16	Fe(L _F) ³⁺ / Cu(E) ⁺	-0.254		0.307	2.3	11.0	1.59	0.30	1.29	2.5×10^6
17	Cu(E)(OH ₂) ^{2+/+} / Cu(E) ⁺	0	0.685	0.565	2.2	8.8	2.17	1.09	1.09	8.0×10^4
18	Cu(F)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.256		0.461	4.2	9.1	2.18	0.66	1.52	4.9×10^3
19	Fe(L _F) ³⁺ / Cu(F) ⁺	-0.121		0.410	2.3	11.0	1.77	0.30	1.47	4.7×10^4
20	Cu(F)(OH ₂) ^{2+/+} / Cu(F) ⁺	0	0.818	0.555	2.2	8.8	2.13	1.07	1.07	1.2×10^{2a}
21	Cu(G)(OH ₂) ^{2+/+} / Co(L _C) ²⁺	-0.256		0.478	4.2	9.1	2.25	0.73	1.52	2.6×10^3
22	Fe(L _F) ³⁺ / Cu(G) ⁺	-0.121		0.420	2.3	11.0	1.81	0.30	1.51	3.2×10^4
23	Cu(G)(OH ₂) ^{2+/+} / Cu(G) ⁺	0	0.818	0.582	2.2	8.8	2.24	1.12	1.12	4.2×10^4
24	Cu(H) ^{2+/+} / Co(L _C) ²⁺	-0.190		0.516	4.2	9.1	2.28	0.76	1.52	5.9×10^2
25	Fe(L _F) ³⁺ / Cu(H) ⁺	-0.187		0.232	2.3	11.0	1.16	0.30	0.86	4.6×10^7
26	Cu(H) ^{2+/+}	0	0.752	0.430	2.2	8.8	1.63	0.82	0.82	$1.5 \times 10^{4a}(10^{4.4})$

^aExperimental data from ref. 1.

^aA=1,4,7,10-tetrathiacyclododecane([12]aneS₄), B=1,4,7,10-tetrathiacyclotridecane([13]aneS₄), C=1,4,8,11-tetrathiacyclotetradecane([14]aneS₄), D=1,4,8,12-tetrathiacyclopentadecane([15]aneS₄), E=1,5,9,13-tetrathiacyclohexadecane([16]aneS₄), F=2,5,9,12-tetrathiatetradecane(Me₂-2,3,2-S₄), G=3,6,10,13-tetrathiapentadecane(Et₂-2,3,2-S₄) and H=1,4,7,10-pentathiacyclopentadecane([15]aneS₅). ^bStandard free energy change of the reaction between the redox pair. ^cFormal potential of the redox couple vs NHE. ^dActivation free energy for the same reaction. ^eWork expended in bringing the reactant redox pair together. ^fSum of the radii of the redox pair. ^gTotal reorganization energy for reaction. ^hReorganization energy contribution by the oxidized reactant in the redox pair. ⁱReorganization energy contribution by the reduced reactant in the redox pair. ^jRate constants for the reaction between the redox pair. Experimental values are in the brackets (entries 11 and 26). ^kValues calculated from the sum of $\lambda_{o \rightarrow r}$ and $\lambda_{r \rightarrow o}$ for two corresponding cross reactions.

in reference 1. The redox couple Co^{III/II}(L_C) were not shown to adhere to the classical Marcus cross relationship⁹. Use of redox couples adhering to the classical Marcus cross relation for cross reaction experiments with the Anson's method may lead to the calculated self-exchange rate constants in accord with the experimentally observed ones for bond breaking and/or bond forming electron transfer reactions.

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