

Method for the Evaluation of the Reorganization Energy of Electron Transfer Reactions Produced under Restricted Geometry Conditions

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The kinetics of the electron transfer reactions between $\text{S}_2\text{O}_8^{2-}$ and the complexes $(\text{Ru}(\text{NH}_3)_5\text{L})^{2+}$ (L = pyridine, pyrazine, and 4-cyanopyridine) have been studied in micellar (SDS) solutions. A method for the evaluation of the reorganization energy of these reactions, based on the comparison of their rate constants, is proposed. From the results obtained, we concluded that the observed rate constants go through a minimum for the surfactant concentration in which the reorganization energy goes through a maximum. The method can be applied to any kind of restricted geometry conditions.

Introduction

The study of bimolecular reactions under restricted geometry conditions (or in restricted reaction spaces) is an area of growing interest.¹ Restricted geometry conditions are produced when one or both reactants are forced to remain totally or partially confined in a restricted reaction space. According to this, the study of reactivity in this circumstance encompasses phenomena such as heterogeneous catalysis,^{2a} enzymatic catalysis,^{2b} reactivity in micellar systems³ and microemulsions⁴ in the presence of polyelectrolytes,⁵ and others.

The interest in this type of study arises from the enormous changes in the reactivity frequently observed when a reaction changes from a conventional reaction medium to reaction conditions of the kind previously mentioned, in such a way that changes of several orders of magnitude in the rate constants are not rare. This is generally true for any kind of reaction and, in particular, for electron transfer reactions.⁶ In fact, electron transfer reactions under restricted geometry conditions are involved in many natural or artificial processes, such as solar energy conversion and storage,⁷ photodynamic tumor therapy,⁸ molecular electronics,⁹ molecular machines,¹⁰ and so forth. Obviously, to quantify the effects of the restricted geometry conditions on electron transfer reactions, it is necessary to know how these conditions influence the factors controlling the kinetics of the electron transfer processes. One of these factors, according to the Marcus–Hush¹¹ theory, is the so-called reorganization free energy, λ . This free energy, and the reaction free energy, ΔG° , determine the activation free energy of the electron transfer and, thus, the rate constant of the process:

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \quad (1)$$

In conventional reaction media, such as “normal” solutions, it is a simple matter to obtain the changes in λ when the solvent is changed.¹² However, the procedures employed in these conventional reaction media cannot be employed in the conditions of the reactions considered in this paper (see Discussion

section). We are currently interested in the study of electron transfer reactions in micellar solutions and other reaction media producing restricted geometry conditions.¹³ For this reason, we considered the development of an approach to obtain the changes in the reorganization energy when the electron transfer reactions proceed under restricted geometry conditions. This method is presented here and applied to the case of the reactions between peroxodisulfate, $\text{S}_2\text{O}_8^{2-}$, and the ruthenium complexes $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$, when L = pyridine (py), pyrazine (pz), and 4-cyanopyridine (4-CNpy).

Experimental Section

Materials. $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ complexes as perchlorate salts (L = pz and 4-CNpy) were prepared and purified according to published procedures.¹⁴ Sodium peroxodisulfate was from Fluka and SDS from Merck. Both were used without further purification. All the solutions were prepared with deionized water from a Millipore Milli-Q system, having a conductivity of $<10^{-6} \text{ S m}^{-1}$.

Kinetics Measurements. Kinetic runs corresponding to the complexes with pz and 4-CNpy as ligands were carried out as described in ref 15 for L = py. The concentration of the reactants in the reaction mixture were the same as in ref 15: $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+} = 2 \times 10^{-5} \text{ mol dm}^{-3}$ and $[\text{S}_2\text{O}_8]^{2-} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$. Pseudo-first-order rate constants were obtained from the slopes of the linear plots of $\ln(A_t - A_\infty)$ versus time, where A_t and A_∞ are the absorbances at time t and when the reaction is finished, respectively. The uncertainty in the rate constant was less than 5%. All the measurements were performed at 298.2 K.

Electrochemistry. The redox potential of the $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ was obtained by the differential pulse voltammetry technique (DPV). The equipment, procedure, and electrodes have been previously described.¹⁶ Under our working conditions, the relationship between the peak and half-wave potentials is given by the following expression:¹⁷

$$E_{\text{peak}} = E_{1/2} + \frac{\Delta E}{2} \quad (2)$$

where ΔE is the voltage amplitude of the pulse (5 mV in our

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TABLE 1: Observed Rate Constants^a for the Reactions [Ru(NH₃)₅py]²⁺ + S₂O₈²⁻ (*k_{py}*), [Ru(NH₃)₅pz]²⁺ + S₂O₈²⁻ (*k_{pz}*), and [Ru(NH₃)₅(4-CNpy)]²⁺ + S₂O₈²⁻ (*k_{4-CNpy}*) in SDS Micellar Solutions

10 ² [SDS]/mol dm ⁻³	10 ² <i>k_{py}</i> /s ⁻¹ ^b	10 ² <i>k_{pz}</i> /s ⁻¹	10 ² <i>k_{4-CNpy}</i> /s ⁻¹
0.80	17.3	5.3	0.45
0.82	13.6	4.2	0.38
0.84	11.3	3.2	0.30
0.86	9.7	2.8	0.27
0.88	8.5	2.4	0.24
0.90	7.6	2.2	0.18
1.0	5.1	1.4	0.15
1.2	3.2	0.93	0.092
1.4	2.5	0.74	0.068
2.0	1.7	0.45	0.051
3.0	1.4	0.38	0.047
4.0	1.4	0.46	0.045
6.0	1.5	0.55	0.050
8.0	1.7	0.65	0.059
10	2.0	0.76	0.069
12	2.4	0.80	0.071
14	2.7	0.89	0.079
16	3.2	1.0	0.098
18	3.6	1.1	0.10
20	4.0	1.3	0.11
22	4.4	1.4	0.12
25	4.9	1.6	0.13

^a Rate constants in aqueous solutions are as follows: *k_{py}* = 90 s⁻¹, *k_{pz}* = 7.46 s⁻¹, and *k_{4-CNpy}* = 1.56 s⁻¹. ^b Data taken from ref 15.

TABLE 2: Redox Potentials (*E*^o) vs NHE at 298.2 K for the Couple [Ru(NH₃)₅py]^{3+/2+} in SDS Micellar Solutions

10 ² [SDS]/mol dm ⁻³	<i>E</i> ^o /V	10 ² [SDS]/mol dm ⁻³	<i>E</i> ^o /V
0.80	0.125	6.0	0.232 ^a
0.82	0.126 ^a	7.5	0.246
0.84	0.127	8.0	0.248 ^a
0.86	0.127 ^a	10	0.254
0.88	0.128 ^a	12	0.261 ^a
0.90	0.129 ^a	14	0.262 ^a
1.0	0.132 ^a	15	0.262
1.2	0.140	16	0.260 ^a
1.4	0.145 ^a	18	0.253 ^a
2.0	0.162	20	0.240
3.0	0.181	22	0.216 ^a
4.0	0.205 ^a	25	0.147 ^a
5.0	0.224		

^a Values obtained from fit of experimental data.

experiments). As ΔE is small, E_{peak} can be identified with $E_{1/2}$ which for a reversible system represents the standard formal redox potential of the couple, that is, $E_{1/2} = E^{\circ'}$, where

$$E^{\circ'} = E^{\circ} + RT \ln \frac{\gamma_{\text{ox}}}{\gamma_{\text{red}}} \quad (3)$$

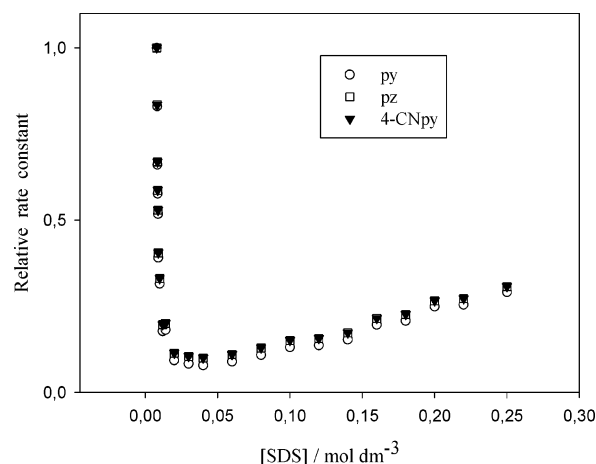
In eq 3, E° is the standard potential of the [Ru(NH₃)₅py]^{3+/2+} couple, and γ_{ox} and γ_{red} are the activity coefficients of the oxidized and reduced components of this couple.

Results

Table 1 contains the kinetic data corresponding to the three electron transfer reactions. The data corresponding to [Ru(NH₃)₅py]²⁺ in Table 1 were taken from ref 15.

Table 2 contains the data corresponding to the standard formal potentials of the [Ru(NH₃)₅py]^{3+/2+} couple. Some of these data were obtained through an interpolation procedure (see the table).

The variations of the redox potentials of the ruthenium complex when the surfactant concentration increases deserve some comments. Thus, under electrostatic grounds only, a

**Figure 1.** Plot of the relative rate constants (see text) vs [SDS]/mol dm⁻³.

decrease in the standard formal potential would be expected according to eq 3. This is so because in the presence of a negatively charged micelle a greater stabilization would be expected for the oxidized form of the couple than for the reduced form. That is, γ_{ox} should be expected to decrease more than γ_{red} in eq 3. This would produce a decrease in $E^{\circ'}$, which is opposite to the observed increase, for the lower surfactant concentrations, in Table 2. However, this behavior has been observed previously: *The redox potentials of couples of opposite-sign charge from the charge in the micelles can vary in a different sense from that expected under electrostatic grounds only.*^{18,19} These results can be explained by considering that the ions of opposite-sign charge to the micellar charge are placed at the Stern layer of the micelles.¹⁹ In this layer, the strong micellar field causes a strong decrease in the local dielectric constant, as a consequence of dielectric saturation effects.²⁰ This decrease in the local dielectric constant will produce an increase in both γ_{ox} and γ_{red} in eq 3, but more marked in γ_{ox} , because this corresponds to a species with a higher charge. *So, the observed increase in the standard formal redox potentials is not so much due to the direct effect of the field on the ruthenium complex (oxidized and reduced forms) as to the effect of the field on the solvent, which produces a more dielectrically saturated state of the medium (solvent).*⁶

It is worth pointing out that at [SDS] > 0.01 mol dm⁻³ the standard formal redox potential of the ruthenium couple decreases. This point will be considered in the Discussion section.

Discussion

General Overview of the Results. Figure 1 gives a plot of the relative rate constants for the three redox processes considered here. The relative rate constants are defined as the ratio between k_{obs} at a given SDS concentration and k_{obs} at the lower surfactant concentration, that is, [SDS] = 8×10^{-3} mol dm⁻³. As can be seen from the figure, variations of these rate constants are the same when the concentration of the surfactant is changed. This is an essential point in relation to the method to be developed later. According to this, the kinetic data can be explained by following the same line as in ref 15, which corresponds to the data of the Ru(NH₃)₅py²⁺ + S₂O₈²⁻ reaction. That is, the data correspond to the expectations of the pseudophase model by considering that the ruthenium complexes are distributed between the micellar and aqueous phases, and the oxidant (S₂O₈²⁻) remains in the aqueous phase. It can be

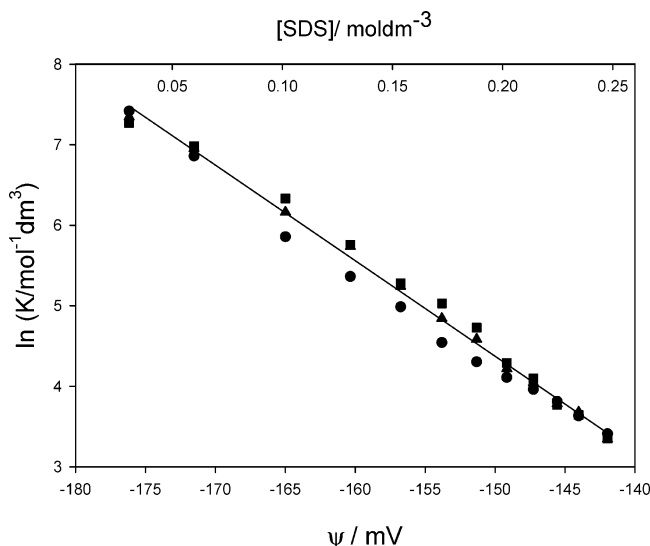


Figure 2. Plot of $\ln K$ vs surface potential of the SDS micellar solutions for the processes $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+} + \text{S}_2\text{O}_8^{2-}$ (●), $[\text{Ru}(\text{NH}_3)_5\text{pz}]^{2+} + \text{S}_2\text{O}_8^{2-}$ (▲), and $[\text{Ru}(\text{NH}_3)_5(4\text{-CNpy})]^{2+} + \text{S}_2\text{O}_8^{2-}$ (■).

shown²¹ that, in this case, the equation of Menger and Portnoy for unimolecular processes²²

$$k = \frac{k_w + k_m K[T]}{1 + K[T]} \quad (4)$$

would still be valid. In this equation, k_w and k_m are the rate constants of the processes taking place at the aqueous and micellar phases, respectively, and K is the equilibrium constant for the binding of the ruthenium complexes to the micelles

$$K = \frac{[S]_m}{[S]_w [T]} \quad (5)$$

with $[S]_m$ being the concentration of the ruthenium complexes bound to the micelles and $[S]_w$ the concentration of the complexes in the aqueous phase. Finally, $[T]$ is the concentration of the micellized surfactant.²³

Obviously, eq 4 cannot fit the data in Figure 1, because this equation, for high enough concentrations of the surfactant, predicts a constant value of k ($=k_m$). Thus, the rising part of the curve in the figure cannot be accounted for by eq 4 unless a variation of the parameters in the model is allowed. In fact, the experimental points can be fitted to eq 4 by allowing a variation of K when the surfactant concentration changes. This variation, as shown in ref 15, is due to a change in the surface potential of the micelles as a consequence of counterion condensation.^{24,25} In fact, as expected, a plot of $\ln K$ versus the potential of the micelles is linear (see Figure 2 and ref 15).

Now, an explanation for the decrease of the redox potentials of the ruthenium couple for $[\text{SDS}] > 0.01 \text{ mol dm}^{-3}$ can be given. This decrease is simply a consequence of the desorption of the ruthenium from the micellar surface caused by the decrease of the binding constant of the complex (that, as mentioned already, is a consequence of the diminution of the absolute value of the micellar surface potential).

Interpretation of the Results Based on the Marcus–Hush Treatment. The classical Marcus–Hush treatment of the electron transfer reaction is based on the transition state theory. According to this, the second-order rate constant, $k =$

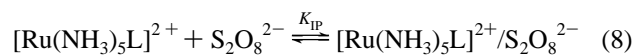
$k_{\text{obs}}/[\text{S}_2\text{O}_8^{2-}]$, for an intermolecular electron transfer process is written as

$$k = A \exp(-\Delta G^\ddagger/RT) \quad (6)$$

with ΔG^\ddagger given by eq 1. The preexponential term, A , is given by²⁶

$$A = K_{\text{IP}} \kappa_{\text{el}} \nu_n \quad (7)$$

where K_{IP} is the equilibrium constant for the formation of the encounter, or precursor, complex from the separate reactants, that is, for the process



On the other hand, κ_{el} is the electronic transmission coefficient, and ν_n is the nuclear frequency factor.²³

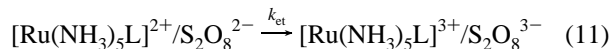
From eqs 6 and 7, it follows that

$$k = K_{\text{IP}} \kappa_{\text{el}} \nu_n \exp(-\Delta G^\ddagger/RT) \quad (9)$$

or

$$k = K_{\text{IP}} k_{\text{et}} \quad (10)$$

where k_{et} is the first-order electron transfer rate constant corresponding to the process precursor complex \rightarrow successor complex, which in the present case is



It is important to realize that the free energies, λ and $\Delta G^{\circ'}$, appearing in eq 1, correspond to this process. In particular, this implies that $\Delta G^{\circ'}$ is not the reaction free energy corresponding to the process reactant \rightarrow product, ΔG_r . These reaction free energies are related by

$$\Delta G^{\circ'} = \Delta G_r + w_p - w_r \quad (12)$$

where w_p and w_r are respectively the works of formation of the successor complex from the separate products and the work of formation of the precursor complex from the separate reactants (eq 8).

It is clear from eq 10 that to have the variations of λ when the reaction medium changes it is necessary, first of all, to separate K_{IP} and k_{et} . In conventional reaction media, there are several procedures to accomplish this separation.³ In fact, in favorable cases, K_{IP} can be calculated through an Eigen–Fuoss approach²⁷ or an MSA calculation.²⁸ However, these procedures are hard to apply to microheterogeneous systems, due to the asymmetry introduced by the micellar electric field. This asymmetry precludes a simple calculation of the potential of mean force corresponding to the interaction between the reactant constituents of the precursor complex.

Our approach, to obtain the variations of λ in microheterogeneous systems, is based on the study of the kinetics of three closely related reactions: in the present case, the oxidation of the three ruthenium complexes, $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ ($\text{L} = \text{py}$, pz , and 4-CNpy) by $\text{S}_2\text{O}_8^{2-}$. This approach relies on the assumption that the interaction of these complexes with the oxidant and the micelles will be the same. In fact, Figures 1 and 2 give support to the idea of similar interactions with the micelles. On the other hand, the idea of the same interactions with the oxidant receives support from the fact that, in the oxidation of the ruthenium complexes with anionic oxidant, the union of the

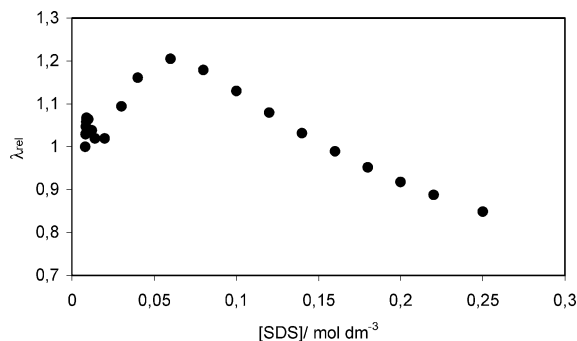


Figure 3. Plot of the values of the relative reorganization free energy (see text) vs [SDS]/mol dm⁻³.

reactants happens by the ammonia side of the complexes because this is favorable for the formation of hydrogen bonds, which reinforces the electrostatic interactions between the oxidant and the ruthenium complexes.^{7,29} According to this, it seems reasonable to suppose that the preexponential term in eq 6 is the same in the case of the three reactions. Under these circumstance, it is easy to show (see Appendix) that the reorganization energy is given by

$$\lambda = \frac{(E_2 D_3 - E_3 D_2) F^2}{D_3 K_2 - D_2 K_3} \quad (13)$$

where F is the Faraday constant and

$$\begin{aligned} D_i &= (E^{\circ'})_{\text{Ru}_i} - (E^{\circ'})_{\text{Ru}_1} \\ E_i &= (E^{\circ'})_{\text{Ru}_i}^2 - (E^{\circ'})_{\text{Ru}_1}^2 \\ K_i &= 4RT \ln k_i/k_i \end{aligned} \quad (14)$$

1 (py); $i = 2$ (pz) and 3 (4-CNpy)

Parameters appearing in eq 13 can be calculated from the experimental data appearing in Tables 1 and 2. To calculate the potential terms (D_i , E_i), we considered that the differences in the redox potentials of the complexes are a constant, independent of the reaction media, which is consistent with the fact that all the complexes seem to have the same interaction with the micelles (see ref 30). Thus, we take $E^{\circ'}[\text{Ru}(\text{NH}_3)_5\text{-pz}]^{2+} - E[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+} = 0.175$ V and $E^{\circ'}[\text{Ru}(\text{NH}_3)_5(4\text{-CNpy})]^{2+} - E[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+} = 0.224$ V.³¹

It is worth pointing out that the values of λ calculated from eq 13 are very sensitive to small changes in the values of the redox potentials used in the calculation. However, the variations in λ are not particularly sensitive to these small changes of the redox potentials. Thus, we preferred to calculate relative values of the reorganization energy, λ_{rel} . The relative reorganization free energies are defined as the ratios between the reorganization energy at a given surfactant concentration and the reorganization energy at the lowest concentration of SDS, that is, $[\text{SDS}] = 8 \times 10^{-3}$ mol dm⁻³. These relative values are given in Figure 3. It is interesting to note that λ_{rel} goes through a maximum corresponding to a minimum value of the rate constant. These variations are similar to the variations for the reorganization energies obtained for intramolecular electron transfer reactions in micellar media.^{6,32,33}

Now, it is clear that variations in relative k values, as observed in Figure 1, are caused by the fact that as a consequence of the interaction of the ruthenium complexes with the micelles the reaction becomes less favorable from a thermodynamic point

of view, because the ruthenium complexes become less reductive (Table 2). Indeed, the interaction with the micelles produces a greater reorganization energy, reminiscent of the ionic strength effects observed on this energy in conventional electrolyte solutions.³⁴ Notice that, according to data in Table 1 and Figure 1, the rate constants increase after the minimum value at intermediate surfactant concentrations. This increase corresponds to a decrease of λ and $\Delta G^{\circ'}$ (see Figure 3 and Table 2). Of course, this merely reflects a lower interaction of the ruthenium complexes with the micelles, as a consequence of the counterion condensation.

In conclusion, we have developed a procedure to obtain variations of the reorganization energies corresponding to bimolecular electron transfer reactions in micellar media. The procedure, of course, can be employed in other systems corresponding to restricted geometry conditions.

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Appendix: Derivation of Equation 13

Bearing in mind eqs 1 and 6 in the text, one can write

$$k = A \exp[-(\lambda + \Delta G^{\circ'})^2 / 4\lambda RT] \quad (A.1)$$

or

$$\ln k = \ln A - \frac{(\lambda + \Delta G^{\circ'})^2}{4\lambda RT} \quad (A.2)$$

The free energy of the process precursor complex \rightarrow successor complex is given by

$$\Delta G^{\circ'} = -F[(E^{\circ'})_{\text{S}_2\text{O}_8^{2-}} - (E^{\circ'})_{\text{Ru}}] + w_p - w_r \quad (A.3)$$

with F being the Faraday constant, $(E^{\circ'})_{\text{S}_2\text{O}_8^{2-}}$ the redox potential of the $\text{S}_2\text{O}_8^{2-/3-}$ couple, and $(E^{\circ'})_{\text{Ru}}$ the redox potential of the $\text{Ru}(\text{NH}_3)_5\text{L}^{3+/2+}$ couple ($\text{L} = \text{py}$, pz , and 4-CNpy). w_p is the work of forming the successor complex from the separate products, and w_r the work needed to form the precursor complex from the separate reactants.

Using eqs A.2 and A.3, one can write

$$\ln k = \ln A - \frac{\{\lambda - F[(E^{\circ'})_{\text{S}_2\text{O}_8^{2-}} - (E^{\circ'})_{\text{Ru}}] + w_p - w_r\}^2}{4\lambda RT} \quad (A.4)$$

and also

$$\ln k = \ln A - \frac{[\lambda + F(E^{\circ'})_{\text{Ru}} + \alpha]^2}{4\lambda RT} \quad (A.5)$$

where

$$\alpha = -F(E^{\circ'})_{\text{S}_2\text{O}_8^{2-}} + w_p - w_r \quad (A.6)$$

Now, one can apply eq A.5 to each one of the reactions studied in the present work in order to establish a relationship between them (see Discussion section). This relationship can be given by

$$4\lambda RT \ln \frac{k_1}{k_2} = 2F(\lambda + \alpha)D_2 + F^2E_2 \quad (A.7)$$

where k_1 and k_2 correspond to the rate constants of the processes $\text{Ru}(\text{NH}_3)_5\text{py}^{2+} + \text{S}_2\text{O}_8^{2-}$ and $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+} + \text{S}_2\text{O}_8^{2-}$, respectively. D_2 and E_2 are given by

$$D_2 = (E^\circ)_{\text{Ru}_2} - (E^\circ)_{\text{Ru}_1} \quad (\text{A.8})$$

$$E_2 = (E^\circ)_{\text{Ru}_2}^2 - (E^\circ)_{\text{Ru}_1}^2 \quad (\text{A.9})$$

Ru_2 and Ru_1 are referred to $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$, respectively.

In the same way, one can write

$$4\lambda RT \ln \frac{k_1}{k_3} = 2F(\lambda + \alpha)D_3 + F^2E_3 \quad (\text{A.10})$$

$$D_3 = (E^\circ)_{\text{Ru}_3} - (E^\circ)_{\text{Ru}_1} \quad (\text{A.11})$$

$$E_3 = (E^\circ)_{\text{Ru}_3}^2 - (E^\circ)_{\text{Ru}_1}^2 \quad (\text{A.12})$$

with k_3 being the rate constant of the process $\text{Ru}(\text{NH}_3)_5(4\text{-CNpy})^{2+} + \text{S}_2\text{O}_8^{2-}$ and $(E^\circ)_{\text{Ru}_3}$ the redox potential of the $\text{Ru}(\text{NH}_3)_5(4\text{-CNpy})^{3+/2+}$ couple.

The use of eqs A.7 and A.10 results in

$$\lambda = \frac{(E_2D_3 - E_3D_2)F^2}{D_3K_2 - D_2K_3} \quad (\text{13})$$

where $K_2 = 4RT \ln k_1/k_2$ and $K_3 = 4RT \ln k_1/k_3$.

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