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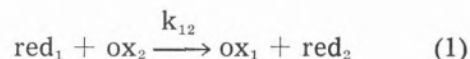


THE ROLE OF BOND ORDER AND ENTROPY OF TRANSITION STATES IN ELECTRON TRANSFER REACTIONS

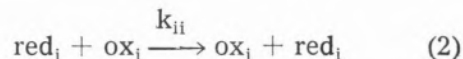
Part 3. — Cross-reaction Relationships.

Discrepancies between Marcus cross-relation rate constants for electron transfer reactions $\text{Co}^{3+}_{(aq)}$ ions and experimental values are examined through a general intersecting-state model. The observed rate constant discrepancies are well accounted for by an increase in the distance of the minimum of the potential energy curves with a decrease in the reaction energy.

Within the theory of Marcus [1] the rate constant of the reaction



can be estimated from the self-exchange reaction rates k_{ii} ,



and the equilibrium constant K_{12} , through the equation

$$k_{12} \cong (k_{11} k_{22} K_{12})^{1/2} \quad (3)$$

with all processes considered to be adiabatic. Although good agreement with experiment is generally found [2], the rates of a number of very exothermic electron transfer reactions are much slower than predicted by the cross-relations [1-6]. The disagreement between theory and experiment has lead several authors to suggest that the adiabatic approximation cannot be used in the inverted region and suggestions were also made that nuclear tunnelling could be important here [7, 8]. The most prominent disagreements from theory involve electron transfer reactions of $\text{Co}(\text{H}_2\text{O})_6^{3+}$ which is a very strong oxidant ($E^\circ = 1.8 \text{ V}$ [9]). For example, the calculated rates are 2×10^5 times higher than the experimental rate for $\text{Fe}(\text{phen})_3^{2+}/\text{Co}(\text{H}_2\text{O})_6^{3+}$ [4] and 3×10^5 for $\text{Co}(\text{terpy})_2^{2+}/\text{Co}^{3+}_{(aq)}$ [5]. In this paper we intend to examine such discrepancies, which give further support to the hypothesis that electron transfer reactions can be treated as any other ordinary chemical reaction [10].

ON THE VALIDITY OF MARCUS CROSS-REACTION RELATIONS

For the reaction [1] Marcus has shown that the rate constant can be estimated by eq (3),

neglecting the work terms of bringing the reactants together. This implies that

$$\Delta G_{12}^\ddagger = (\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger + \Delta G_{12}^0) / 2 \quad (4)$$

where ΔG_{11}^\ddagger are the activation free energies of the self-exchange reactions and ΔG_{12}^0 the free energy of reaction [1]. Since for electron transfer reactions

$$\Delta G^\ddagger = [\Delta G^0 + (1/2)fd^2]^2 / 2fd^2 \quad (5)$$

where f is the average metal-ligand stretching force constant and d is the sum of the bond distensions up to the transition state [10], then

$$\Delta G_{12}^\ddagger = (1/2) [(1/4)f_{12}d_{12}^2 + \Delta G_{12}^0 + (\Delta G_{12}^0)^2 / f_{12}d_{12}^2] \quad (6)$$

Under conditions where the square term can be neglected ($|\Delta G_{12}^0| \ll 2(\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger)$) eqs (4) and (6) imply

$$f_{11} d_{11}^2 + f_{22} d_{22}^2 = 2 f_{12} d_{12}^2 \quad (7)$$

As long as the relevant force constants for all reactions have similar values, which is a reasonable assumption if ions of identical charge are involved [11], then

$$d_{11}^2 + d_{22}^2 = 2 d_{12}^2 \quad (8)$$

The intersecting-state model (ISM) [10, 12] shows that eq (8) is satisfied when d and the reduced bond distension η are independent of the reaction free energy. Since

$$d = \eta l \quad (9)$$

where l is the sum of the equilibrium lengths of the metal-ligand bonds, $l = l_{ox} + l_{red}$, and

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2 \lambda^2} (\Delta G^0)^2 \quad (10)$$

this independence requires neglecting the effect of the configuration entropy parameter

λ , i.e., $|\Delta G^0| \ll \lambda$. Then eqs (9) and (10) show that

$$[(l_{11}/n_{11}^\ddagger)^2 + (l_{22}/n_{22}^\ddagger)^2] = 2 (l_{12}/n_{12}^\ddagger)^2 \quad (11)$$

If there is a constancy of the transition state bond orders, i.e., $n_{11}^\ddagger = n_{22}^\ddagger = n_{12}^\ddagger$, then the equation

$$l_{11}^2 + l_{22}^2 = 2 l_{12}^2 \quad (12)$$

is a reasonable estimate of the metal-ligand equilibrium bond lengths and eq (3) is valid. There are several approximations involved in the Marcus cross-reaction relationships, but the most restrictive ones appear to be the constancy of n^\ddagger and $|\Delta G_{12}^0| \ll \lambda_{12}$. Those are the conditions which are going to be examined for some electron transfer reactions of $\text{Co}_{(aq)}^{3+}$.

EFFECT OF THE REACTION ENERGY ON $\text{Co}_{(aq)}^{3+}$ ELECTRON TRANSFERS

Electron transfer reactions of Co(III) ions with Co(II) and Fe(II) complexes, with a ΔG^0 range of 200 kJ mol^{-1} , were studied within the ISM formalism. The bond distension parameter d was estimated from eq (5) in order to reproduce the experimental ΔG^\ddagger values, and through $d = \eta (l_{ox} + l_{red})$ the reduced bond distensions were calculated (see Table 1). According to eq (10) η should show a square dependence on ΔG^0 . This is observed in Figure 1 for the data of Table 1, with one slope ($\lambda = 315 \text{ kJ mol}^{-1}$) for the $\text{Co(III)}/\text{Co(II)}$ systems and a higher one ($\lambda = 160 \text{ kJ mol}^{-1}$) for data involving the Fe(III) and Fe(II) species. For metal aquo-ions and a few mixed complexes λ was found empirically to be linearly related with the activation entropy, $\lambda/\text{kJ mol}^{-1} = 360 + 4T\Delta S^\ddagger$ (standard state 1 mol dm^{-3}) [13]. The same relation may not be exactly valid for the complexes under study, but it can interpret the large change in λ for the reactions of $\text{Co(III)}/\text{Co(II)}$ and $\text{Co(III)}/\text{Fe(II)}$. For example, the activation entropy for the reaction $\text{Fe}_{(aq)}^{3+}/\text{Cr}_{(aq)}^{2+}$ is ca.

Table 1
Bond distensions and the effects of the configuration entropy, $k(\eta^0)/k(\eta)$,
for Electron Transfer Reactions of $\text{Co}^{3+}_{(\text{aq})}$ ions.

Reaction	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ (a)	$\Delta G^0/\text{kJ mol}^{-1}$	$f/10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ (e)	$l/\text{\AA}$ (f)	$d/\text{\AA}$	η	$k(\eta(0))/k(\eta)$ (g)
1 $\text{Co(terp)}_2^{2+}/\text{Co(bipy)}_3^{3+}$	58.8	— 62.5	3.5	4.02	0.446	0.111	7
2 $\text{Co(terp)}_2^{2+}/\text{Co(phen)}_3^{3+}$	55.0	— 68.5	3.5	4.02	0.443	0.110	4
3 $\text{Co(terp)}_2^{2+}/\text{Co}^{3+}_{(\text{aq})}$	42.9	— 203	3.0	4.12	0.574	0.139	2×10^6
4 $\text{Co(terp)}_2^{2+}/\text{Co(phen)}_2^{3+}$	45.4	— 95.0	3.2	4.02	0.465	0.116	60
5 $\text{Co}^{2+}_{(\text{aq})}/\text{Co}^{3+}_{(\text{aq})}$	69.0 (b)	0	2.8	4.11	0.449	0.109	—
6 $\text{Co(terpy)}_2^{2+}/\text{Co(phen)}_3^{3+}$	50.5	— 110.5	3.2	4.05	0.494	0.122	2×10^3
7 $\text{Fe}^{2+}_{(\text{aq})}/\text{Co}^{3+}_{(\text{aq})}$	66.6 (c)	— 104	2.7	4.13	0.575	0.139	2×10^7
8 $\text{Fe(phen)}_3^{2+}/\text{Co}^{3+}_{(\text{aq})}$	55.8 (d)	— 64	2.8	4.03	0.497	0.123	2×10^3

(a) Estimated from ref. 5 with a preexponential factor of $10^{13} \text{ M}^{-1} \text{ s}^{-1}$. (b) F. Basolo and R.G. Pearson. «Mechanisms of Inorganic Reactions», Wiley, 1968, 2^{ed}, p. 466. (c) Ref. 14. (d) Ref. 4. (e) $f = \sqrt{6} (f_{\text{ox}} + f_{\text{red}})/2$; from the ratio of stretching frequencies (11) of $\text{Co}(\text{NH}_3)_6^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$; for the aquo and mixed complexes the metal-oxygen force constants were taken into consideration with a coordination number of 6. (f) $l = r_{\text{Me}} + r_{\text{L}}$; crystal ionic radii (r_{Me}); $r_{\text{L}} = 1.38 \text{ \AA}$ for water and 1.40 \AA for nitrogen atoms (Y. Marcus, J. Solution Chem., 1983, 12, 271). (g) $k(\eta(0))/k(\eta)$ is the ratio of the calculated rate by the theory of Marcus, $\lambda \gg |\Delta G^0|$, and the experimental rate.

85 $\text{J mol}^{-1} \text{ K}^{-1}$ more negative than for $\text{Co}^{3+}_{(\text{aq})}/\text{Cr}^{2+}_{(\text{aq})}$ [14].

The intercept of the two reaction systems is the same, $\eta(0) = 0.108$, which corresponds to a transition state bond order of $n^\ddagger = 1$, typical of outer-sphere reactions [10, 13]. So, for

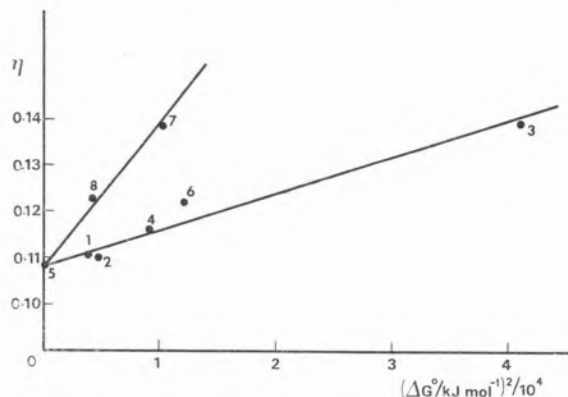


Fig. 1 — Variation of the reduced bond distension, η , with the free energy of reaction, ΔG^0 , for electron transfer reactions of $\text{Co}^{3+}_{(\text{aq})}$ ions. Legend for reactions in Table 1.

all the reactions under consideration n^\ddagger is constant. However the dependences of η on $(\Delta G^0)^2$ reveal that one cannot neglect the effect of the configuration entropy parameter λ and, consequently, Marcus cross-relations are not obeyed.

To assess if such an effect is responsible for the discrepancies reported earlier, ISM is employed to calculate the rates of electron transfer neglecting the variation of η with ΔG^0 . Table 1 presents the ratio of the calculated rate constants at constant $\eta(0) = 0.108$, $k(\eta(0))$, and the experimental rates, $k(\eta)$. Ratios as high as 10^6 - 10^7 were found for the reactions $\text{Co(terp)}_2^{2+}/\text{Co}^{3+}_{(\text{aq})}$ and $\text{Fe}^{2+}_{(\text{aq})}/\text{Co}^{3+}_{(\text{aq})}$ where the second term in eq (10) is a significant percentage (35 %) of the first term. This reveals that the quadratic dependence of d and η on ΔG^0 , not considered in the theory of Marcus, is mainly responsible for the failure of the cross-relations when $|\Delta G^0|$ is high and/or λ is low.

CONCLUDING REMARKS

The view of the ISM formalism that electron transfer reactions can be treated as any other ordinary chemical process has been helpful in interpreting several of the anomalous features observed with the theory of Marcus, where discrepancies between theoretical and experimental rate constants as high as 10^7 have been found [2-8]. This can be attributed mainly to the effect of the configuration entropy which is not considered in the theory of Marcus. However when such an effect is small, Marcus-equation coincides with the ISM-equations and agreement between both treatments exist, although the latter model provides further mechanistic insights. The concept of the transition state bond order accounts basically for the kinetic distinction between normal outer-sphere and inner-sphere reactions, but n^\ddagger can also contribute to cases where the Marcus cross-reaction relationships fail, namely systems where reactions of different natures are considered. For relatively slow reactions of $n^\ddagger = 1$, we have shown [13] that Marcus-equation is closely verified when $|\Delta G^\circ| \leq 4\lambda$, i.e. when the second term in the equation of η is ca. 5 % of the first term. However, when the transition state bond order is high, e.g. $n^\ddagger = 1.5$ the condition for the validity of the theory of Marcus is slightly more restrictive, $|\Delta G^\circ| \leq 5\lambda$.

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REFERENCES

- [1] R.A. MARCUS, J. Chem. Phys., **26**, 867 (1957); Faraday Discuss. Chem. Soc., **29**, 21 (1960).
- [2] R.A. MARCUS and N. SUTIN, Biochim. Biophys. Acta, **811**, 265 (1985).
- [3] E. KÖNIG and S. HERZOG, J. Inorg. Nucl. Chem., **32**, 585 (1970).
- [4] R.J. CAMPION, N. PURDIE and N. SUTIN, Inorg. Chem., **3**, 1091 (1964).
- [5] R. FARINA and R.G. WILKINS, Inorg. Chem., **7**, 514 (1968).
- [6] C. CREUTZ and N. SUTIN, J. Am. Chem. Soc., **99**, 241 (1977).
- [7] S. EFRINA and M. BIXON, Chem. Phys. Lett., **25**, 34 (1974).
- [8] R.A. MARCUS and N. SUTIN, Inorg. Chem., **14**, 213 (1975).
- [9] D.A. JOHNSON and A.G. SHARPE, J. Chem. Soc., 3490 (1964).
- [10] S.J. FORMOSINHO, Rev. Port. Quím., **28**, 38 (1986).
- [11] J.R. FERRARO, «Low Frequency Vibrations of Inorganic and Coordination Compounds», Wiley-Interscience, New York, 1970.
- [12] A.J.C. VARANDAS and S.J. FORMOSINHO, J. Chem. Commun., 163 (1986); J. Chem. Soc., Faraday Trans. 2, **82**, 953 (1986).
- [13] S.J. FORMOSINHO, Rev. Port. Quím., **28**, 48 (1986).
- [14] J. BURGESS, «Metal Ions in Solution», Wiley, London, 1978, chap. 13.

RESUMO

O papel da ordem de ligação e da entropia dos estados de transição nas reacções de transferência de electrões.

Parte 3 — «Relações-cruzadas» nas reacções de transferência de electrões.

O uso das «relações-cruzadas» da teoria de Marcus para estimar constantes de velocidades de reacções de transferência do electrão, em especial de $\text{Co}^{3+}_{(aq)}$; dá por vezes valores muito superiores ao experimental. Este desacordo é interpretado, pelo modelo de intersecção de estados, como devido a um aumento da separação das curvas de energia potencial quando ΔG° diminui.