

## Relationship between the Energy of Activation and the Overall Free Energy of Bridge-assisted Electron Transfer Reactions in Polar Media

JENS ULSTRUP

*Chemistry Department A, Building 207, The Technical University of Denmark, DK-2800 Lyngby, Denmark*

Experimental kinetic data for the bridge-catalyzed oxidation of  $[\text{Cr}(\text{bipy})_3]^{2+}$  by some closely related  $\text{Co}(\text{III})$  complexes have been analyzed on the basis of a newly developed quantum mechanical theory for coupled electron transfer reactions in polar media. The relation between the energy of activation and the overall Gibbs free energy of the reaction is found to agree with that predicted by the theory, and conclusions can be drawn as to the mechanism of the reaction and the relative positions of the electronic terms of the initial, intermediate, and final states.

Several cases of homogeneous catalysis of outer sphere electron transfer reactions have been reported.<sup>1-4</sup> In a systematic study of such reactions the influence of  $\gamma, \gamma'$ -bipyridyl on the kinetics of the electron transfer reaction between  $[\text{Cr}(\text{bipy})_3]^{2+}$  and some closely related  $\text{Co}(\text{III})$  complexes was investigated recently.<sup>5,6</sup> The observed strong catalysis was interpreted in terms of the formation of a  $\gamma, \gamma'$ -bipyridyl complex of chromium(II), in which an electron was first transferred from  $\text{Cr}^{2+}$  to coordinated  $\gamma, \gamma'$ -bipyridyl (bridge), and then by a second transfer from this ligand to  $\text{Co}(\text{III})$ . In such a series of electron transfer reactions between a common reducing ion and a series of closely related oxidizing ions the energy of reorganization of ligand and solvent spheres as well as electrostatic interactions between the reacting ions can be considered approximately constant, so that variation in the energy of activation  $E_a$  may be attributed solely to variation in the Gibbs free energy of the overall reaction,  $\Delta G^\circ$ .

The theory for a mechanism consisting of two coupled electron transfer reactions applicable to homogeneous as well as electrode reactions in polar media was developed recently.<sup>7-10</sup> The probability per unit time of an overall electron transfer from one ionic species to another or to an electrode, *via* a third species (a "bridge") was calculated under the assumption that the electronic state corresponding to the localization of the electron on the bridge is

a (quantum mechanical) virtual state. This corresponds to the "double" exchange mechanism suggested previously for inner sphere electron transfer reactions as opposed to a "chemical" mechanism which consists of two consecutive one-electron transfer steps involving a temporary oxidation or reduction of the electron-mediating species.<sup>11</sup> The theoretical results showed that for suitable relative positions of the electronic terms of the various states, a decrease in  $E_a$  (a catalysis) could be expected for the bridge-assisted path as compared with the direct electron transfer from the initial to the final state. The overall probability of electron transfer *via* the intermediate state was calculated from second order quantum mechanical perturbation theory,<sup>12</sup> under the assumption of a weak interaction between the reacting ions and the bridge. This assumption appears justified for the Co(III)- $\gamma,\gamma'$ -bipyridyl outer sphere interaction.  $\text{Cr}^{2+}$  is bound to  $\gamma,\gamma'$ -bipyridyl by a covalent chemical bond which, however, from thermodynamic data is found to be weak.<sup>5</sup> The perturbation treatment for the interaction between  $\text{Cr}^{2+}$  and coordinated  $\gamma,\gamma'$ -bipyridyl is therefore a first approximation, but it is emphasized that the arguments presented below concerning the distinction between direct and bridge-assisted electron transfer are also valid for stronger interactions between the reacting ions and the bridge.

The present work is an analysis of the kinetic data obtained previously in the light of the newly developed theory of bridge electron transfer reactions. In order to extend the  $\Delta G^\circ$  range they have been supplemented by new data for the reactions between  $[\text{Co}(\text{bn})_3]^{3+}$ , where bn stands for optically active (-)<sub>D</sub>-2,3-butanediamine, and the two chromium(II) complexes.

## EXPERIMENTAL

The materials were purified, and the two chromium(II) complexes synthesized as described previously.<sup>5,6</sup>  $[\text{Co}(\text{bn})_3]\text{Cl}_3$  was prepared as described in Ref. 13. All kinetic measurements were carried out in a nitrogen atmosphere and in an ionic medium 0.1 M in NaCl under pseudofirst order conditions in chromium(II);<sup>6</sup> the reactions between  $[\text{Co}(\text{bn})_3]^{3+}$  and both chromium(II) complexes were found to proceed by the same mechanisms as described earlier.

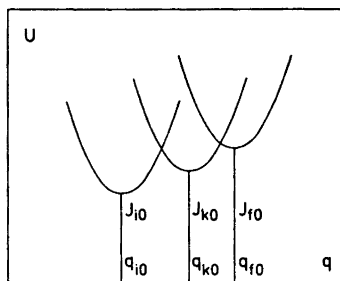
## RESULTS AND DISCUSSION

The determined rate constants and activation parameters for the direct (1) and bridge-assisted path (2) are given in Table 1. Here only the bridge-assisted path is considered (the reaction of the  $\gamma,\gamma'$ -bipyridyl complex of chromium(II)). Provided that the energy of reorganization of the ligand sphere and the interaction between the ions and the bridge can be neglected or

Table 1. Kinetic data for the reactions between the two chromium(II) complexes and  $[\text{Co}(\text{bn})_3]^{3+}$

$k_1$ l/mol sec	$k_2$ l/mol sec	$\Delta H_1^\ddagger$ kcal/mol	$\Delta H_2^\ddagger$ kcal/mol	$\Delta S_1^\ddagger$ cal/K mol	$\Delta S_2^\ddagger$ cal/K mol
9.8	206	12.8	7.8	-11.3	-36

Fig. 1. Electronic terms of the various states. The  $q_0$ 's are the equilibrium values of the solvent coordinate, and the  $J_0$ 's the equilibrium energies of the various states.  $U$  is the total potential energy of the system.



considered constant, the electronic terms of the initial (i), intermediate (k) and final state (f) can be plotted as in Fig. 1.  $q$  is a generalized solvent coordinate, and the harmonic approximation is adopted for the solvent librations in all the states.<sup>14</sup> It was shown previously,<sup>7</sup> that the overall energy of activation is then determined by the highest intersections point between the intermediate and either the initial or final term, whereas the energy of activation for the direct electron transfer corresponds to the intersection point between the initial and final term. As observed,<sup>6</sup> the energy of activation is always smaller for the bridge-assisted reaction, and  $q_{k0}$  must therefore be situated between  $q_{i0}$  and  $q_{f0}$ .

In the harmonic approximation for the solvent coordinate<sup>14-16</sup> the energy of activation for an elementary electron transfer, *e.g.* from the electron donating ion to the bridge, is given by the expression

$$E_a = \frac{[E_s^{ki} + \Delta J^{ki}]^2}{4E_s^{ki}} = \frac{[E_s^{ki} + \Delta J^{fi} - \Delta J^{fk}]^2}{4E_s^{ki}} \quad (1)$$

where  $E_s$  is the energy of reorganization of the solvent (*e.g.*  $E_s^{ki} = \frac{1}{2}\hbar\omega(q_{k0} - q_{i0})^2$ ;  $\omega$  is the characteristic solvent frequency), and  $\Delta J$  the heat of reaction. In the theory of Levich and Dogonadze,<sup>14</sup> whose symbols we shall use here,  $\Delta J$  is strictly speaking the internal energy of the reaction ( $\Delta U$ ). For reactions in solution this quantity can, however, with sufficient accuracy be put equal to the heat of reaction ( $\Delta H$ ). If the left hand intersection point is the higher, the overall energy of activation is thus given by an expression of the form of eqn. (1), whereas if the right hand intersection point is the higher, the energy of activation is given by

$$E_a = \frac{[E_s^{fk} + \Delta J^{fk}]^2}{4E_s^{fk}} + \Delta J^{ki} = \frac{[E_s^{fk} + \Delta J^{fi} - \Delta J^{ki}]^2}{4E_s^{fk}} + \Delta J^{ki} \quad (2)$$

where the superscripts refer to the states between which the transitions occur.

The variation of  $E_a$  for the different Co(III) complexes is mainly due to the change in the overall free energy of reaction  $\Delta G^\circ$ , other contributions to  $E_a$  being approximately constant. Provided that the entropy part of  $\Delta G^\circ$  is constant, which seems to be a reasonable assumption, considering that the same charge is found on all the ions except the acetatopentammine,  $\Delta J^{fi}$  in eqns. (1) and (2) can be replaced by  $\Delta G^\circ$  (including formally the entropy part of  $\Delta G^\circ$  in the constant  $E_s$ ). The dependence of  $E_a$  on  $\Delta G^\circ$  thus adopts the same form as the dependence on  $\Delta J^{fi}$ .

*A priori* it is necessary to consider the push-pull as well as the pull-push double exchange mechanism as defined in Ref. 8. Superexchange mechanisms<sup>11,17</sup> involving higher vacant and lower occupied orbitals of  $\gamma,\gamma'$ -bipyridyl might be considered, but as the difference between the energies of these orbitals is high (several electron volts<sup>5</sup>) such mechanisms would involve very high energies of activation. We therefore only consider the lowest empty bridge orbital in the push-pull mechanism and the highest filled bridge orbital in the pull-push mechanism.

Values of the overall  $\Delta G^\circ$  were calculated from the standard oxidation potentials of the Co(III)/Co(II) complexes,<sup>13,18-22</sup> the formation constant of the  $\gamma,\gamma'$ -bipyridyl complex,<sup>5</sup> and from the half-wave potential of the Cr(III)/Cr(II) couple,<sup>23</sup> since the equilibrium potential of the latter is not available. The possible error thus introduced is small and does not interfere with the trend of the results observed.

*The push-pull mechanism.* For this mechanism, within a series of related electron receiving Co(III) complexes, the final state electronic term is shifted vertically with respect to the initial and intermediate term, while the relative position of the latter two terms remains fixed.<sup>8</sup> Thus when  $\Delta J^{\text{fi}}$  ( $\Delta G^\circ$ ) increases, the final term is shifted upwards with respect to the initial and intermediate terms. If at a given  $\Delta J^{\text{fi}}$  the left hand intersection point is the higher,  $E_a$  is determined by this point *i.e.* by the energy of activation of the electron transfer from the donating ion to the bridge. Thus  $E_a$  should not depend upon the nature of the electron receiving ion ( $\Delta J^{\text{ki}}$  is a constant). When the right hand intersection point becomes the higher,  $E_a$  suddenly (*i.e.* within a few multiples of  $kT$ ) begins to increase with increasing  $\Delta J^{\text{fi}}$ , and the slope  $\alpha$  of the plot of  $E_a$  against  $\Delta J^{\text{fi}}$  will be  $0 < \alpha \lesssim 1$ , corresponding to a "normal" ( $\alpha \approx 0.5$ ) and/or a "barrierless" region,<sup>24</sup> whereas an "activationless" region ( $\alpha \approx 0$ ) does not exist.

*The pull-push mechanism.* In this case, when the electron receiving ion changes, the initial term changes with respect to the intermediate and final term, while the relative position of the latter terms does not change. If the left hand intersection point is the higher, a "normal" and an "activationless" range should be observed, corresponding to  $\alpha \approx 0.5$  and  $\alpha \approx 0$ , respectively, and with smooth transitions (*i.e.* within about  $E_a \approx 30$  kcal/mol) between the regions. If the right hand intersection point is the higher,  $E_a$  is given by eqn. (2), where  $\Delta J^{\text{fk}}$  is now a constant (*i.e.* the heat of reaction for the electron transfer from  $\text{Cr}^{2+}$  to  $\gamma,\gamma'$ -bipyridyl).

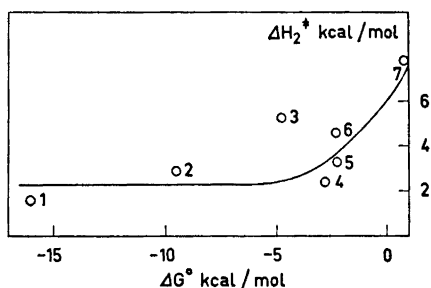


Fig. 2.  $\Delta H_2^\ddagger$  (kcal/mol) plotted against  $\Delta G^\circ$  for the bridge-assisted reaction. The numbers refer to the following Co(III) complexes: 1, acetatopentaammine; 2, hexammine; 3, tris-meso-butanediammine; 4, bis-diethylenetriammine; 5, tris-ethylenediammine; 6, tris-(racemic)-propanediammine; 7, tris-( $-$ )-butanediammine.

The experimental values of  $\Delta H_2^+$  are plotted against the overall  $\Delta G^\circ$  ( $\Delta J^{\text{fi}}$ ) in Fig. 2. The dependence changes rather suddenly (*i.e.* within a few multiples of  $kT$ ) from a region of very weak dependence to a region where  $\alpha$  is somewhere between 0.5 and 1. The Co(III) complex of *meso*-butanediammine does not fit the otherwise smooth correlation, and possible reasons for this were discussed previously.<sup>6</sup>

The experimental plot can be interpreted on the basis of the push-pull mechanism, as changing from a region where the left hand intersection point is the higher to a region, where the right hand one is the higher, for increasing  $\Delta G^\circ$  ( $\Delta J^{\text{fi}}$ ). The experimental points indicate that  $\alpha > 0.5$ , when the right hand point becomes the higher, corresponding to a "normal" and a "barrierless" region, and therefore  $|\Delta J^{\text{fk}}| \lesssim E_s^{\text{fk}}$ .

An alternative interpretation could be made on the basis of the pull-push mechanism. The horizontal part of the curve in Fig. 2 would then correspond to an "activationless" region, where either intersection point may be the higher. When  $\Delta G^\circ$  increases, the initial term is shifted downwards with respect to the other two terms. If the left hand intersection point is the higher, a smooth change of  $\alpha$  (*i.e.* within a change in  $\Delta G^\circ$  of the order  $E_s^{\text{ki}} \approx 30$  kcal/mol) from 0 to 1 is observed, while if the right hand intersection point during this shift becomes the higher, an abrupt (*i.e.* within a few multiples of  $kT$ ) change to unity is observed. Although this second interpretation cannot be rejected, it seems less probable, because of the large "activationless" range and because of the apparent shift from  $\alpha = 0$  to  $\alpha > 0.5$  within an extremely narrow range of  $\Delta G^\circ$ .

The experimental results show that meaningful correlations between  $E_a$  and  $\Delta G^\circ$  can be made for bridge-assisted electron transfer reactions, in analogy with what has been reported for direct electron transfer reactions. In principle the correlations allow a distinction between the push-pull and the pull-push mechanism, and they justify conclusions as to the relative positions of the terms of the various states.

The  $[\text{Cr}(\text{bipy})_3]^{2+}$ - $\gamma, \gamma'$ -bipyridyl-Co(III) system is not the one best suited for an experimental test of the correlations predicted by the theory, since it is not of strictly outer sphere nature; but it seems to be the only one, where a systematic study has been made on the relation between kinetic and thermodynamic parameters for a bridge electron transfer reaction. However, the arguments presented above are also qualitatively valid, when there is a somewhat stronger interaction between the bridge and the reacting ions than in general for outer sphere electron transfer reactions.

*Acknowledgement.* The author expresses his thanks to Dr. Yu. I. Kharkats, the Institute of Electrochemistry of the Academy of Sciences of the USSR, for helpful discussions.

#### REFERENCES

1. Gjertsen, L. and Wahl, A. C. *J. Am. Chem. Soc.* **81** (1959) 1572.
2. Campion, R. J., Deck, C. F., King, Jr., P. and Wahl, A. C. *Inorg. Chem.* **6** (1967) 672.
3. Ulstrup, J. *Acta Chem. Scand.* **23** (1969) 3091.
4. Jansen, P. H. and Ulstrup, J. *Acta Chem. Scand.* **23** (1969) 1822.
5. Ulstrup, J. *Acta Chem. Scand.* **25** (1971) 3397.

6. Ulstrup, J. *Trans. Faraday Soc.* **67** (1971) 2645.
7. Volkenstein, M. V., Dogonadze, R. R., Madumarov, A. K. and Kharkats, Yu. I. *Dokl. Akad. Nauk SSSR, Ser. Phys. Chem.* **199** (1971) 124.
8. Dogonadze, R. R., Ulstrup, J. and Kharkats, Yu. I. *J. Theoret. Biol.* *In press.*
9. Dogonadze, R. R., Ulstrup, J. and Kharkats, Yu. I. *J. Electroanal. Chem. Interfacial Electrochem.* **39** (1972) 47.
10. Dogonadze, R. R., Ulstrup, J. and Kharkats, Yu. I. *J. Electroanal. Chem. Interfacial Electrochem.* *In press.*
11. George, P. and Griffith, J. S. *Enzymes* **1** (1959) 347.
12. Landau, L. D. and Lifshitz, E. M. *Quantum Mechanics*, Pergamon, Oxford 1965.
13. Woldbye, F. *Studier over Optisk Aktivitet*, Polyteknisk Forlag, København 1968.
14. Levich, V. G. and Dogonadze, R. R. *Collect. Czech. Chem. Commun.* **26** (1961) 193.
15. Marcus, R. A. *J. Chem. Phys.* **24** (1965) 966.
16. Marcus, R. A. *J. Chem. Phys.* **43** (1965) 679.
17. Gould, E. S. and Taube, H. *Accounts Chem. Res.* **2** (1969) 321.
18. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, 2nd Ed., P. Haase and Son, Copenhagen 1957.
19. Bartelt, H. and Skilandat, H. *J. Electroanal. Chem.* **23** (1969) 407.
20. Bartelt, H. and Skilandat, H. *J. Electroanal. Chem.* **24** (1970) 207.
21. Bartelt, H. and Prügel, M. *Electrochim. Acta* **16** (1971) 1815.
22. Basolo, F. and Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd Ed., Wiley, New York, London and Sidney 1967.
23. Vlcek, A. A. *Nature* **189** (1961) 393.
24. Dogonadze, R. R. and Kuznetsov, A. M. *Itogi Nauki Elektrokhim.* 1967, Akademiya Nauk, SSSR 1969.

Received October 3, 1972.