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Title	DOMINANT INFLUENCE OF INNER SHELL BOND STRETCHING FOR THE ACTIVATION OF IONS IN SOLUTION
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 31(1), 35-38
Issue Date	1983-11
Doc URL	<a href="https://hdl.handle.net/2115/25144">https://hdl.handle.net/2115/25144</a>
Type	departmental bulletin paper
File Information	31(1)_P35-38.pdf



## DOMINANT INFLUENCE OF INNER SHELL BOND STRETCHING FOR THE ACTIVATION OF IONS IN SOLUTION

By

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(Received April 11, 1983)

### Abstract

Some recently published data on photoemission from solution has been used to compute the relative contributions of the inner to the outer solvation shell on the activation energy of electron transfer reactions. One finds that using the experimental values of force constants, the inner shell contribution is about 3.2 times the outer shell one, for the results of five redox systems.

Recently, the free energy of reorganization for the electron transfer reaction in solution has been determined using photoemission from solution experiment.<sup>1)</sup> In this article we analyze the experimental results<sup>1,2)</sup> of the free energy of reorganization with the object of determining the relative contribution of the inner to the outer shell activation.

From photoemission experiment<sup>1)</sup> the reorganization energy,  $R^{\text{photo}}(\text{expt})$  has been found by means of calculations via a Born-Haber cycle for the reactions of the type.



If one accepts that this energy is a combination of:

$$R^{\text{photo}}(\text{expt}) = R_{\text{out}}^{\text{photo}} + R_{\text{inner}}(\text{calc}) \quad (2)$$

one can obtain  $R_{\text{out}}^{\text{photo}}$  from the value of  $R^{\text{photo}}(\text{expt})$ , by substituting for  $R_{\text{inner}}(\text{calc})$  from the theoretical expression of free energy of activation  $\Delta G_{\text{inner}}^{\ddagger}(\text{calc})$  (for one reactant ion),<sup>3-5</sup>

$$\begin{aligned} \Delta G_{\text{inner}}^{\ddagger}(\text{calc}) &= \frac{1}{2} \left[ \frac{n}{2} \frac{f_0 f_r}{f_0 + f_r} (\Delta q)^2 \right], \\ &= \frac{1}{4} R_{\text{inner}}(\text{calc}) \end{aligned} \quad (3)$$

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where  $n$  is the number of water or ligand molecules oriented orthogonally to an ion in the first shell when the ion is in solution,  $f_0$  and  $f_r$  are respectively the force constant for the ion-solvent vibration in the oxidized and reduced ion, and  $\Delta q$  is the equilibrium ion-solvent bond length difference of the oxidized and reduced ion.

However, for the exchange reactions involving two reactant ions the corresponding inner sphere reorganization energy  $R_{\text{inner}}^{\text{exchange}}$  (calc) can be expressed using Eq (3) as

$$R_{\text{inner}}^{\text{exchange}} (\text{calc}) = 2R_{\text{inner}} (\text{calc}) \quad (4)$$

Also :

$$\Delta G_{\text{inner}}^{\ddagger, \text{exchange}} (\text{cals}) = 2\Delta G_{\text{inner}}^{\ddagger} (\text{calc}) \quad (5)$$

Now, the outer sphere reorganization energy can be expressed as<sup>4,5</sup>

$$R_{\text{out}}^{\text{exchange}} (\text{calc}) = \frac{e_0^2}{4\pi\epsilon_0} \left( \frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{a_1 + a_2} \right) \quad (6)$$

where  $a_1$  and  $a_2$  are the radii of two ions with first solvation shell. It can be easily shown\*<sup>9</sup> that  $R_{\text{out}} (\text{calc})$  for one ion for photoemission from solution is approximately equal to  $R_{\text{out}}^{\text{exchange}} (\text{calc})$  for two ions when it assumed that  $a_1 = a_2$ . Hence, using this analogy one can also express Eq (2) as

$$R_{\text{photo}} (\text{expt}) = R_{\text{out(photo)}}^{\text{exchange}} + R_{\text{inner}} (\text{calc}) \quad (7)$$

$R_{\text{out}}^{\text{exchange}} (\text{photo})$  can be obtained when  $R_{\text{inner}} (\text{calc})$  in Eq (7) is calculated from Eq (3). Using the experimental force constants,  $f$  was computed from  $f = 4\pi^2 \omega^2 c^2 \mu / N$  (with  $\mu/N$  equal to mass of a water molecule<sup>9</sup> in aqua complexes,  $c$  velocity of light and  $N$  Avogadro's number) by utilizing the experimental symmetric stretching frequency,  $\omega$  data.<sup>7,8</sup> The coordination member of  $n=6$  was used.  $\Delta q$  values are taken from available EXAFs<sup>9</sup> and X-ray data.<sup>10-13</sup>

A comparison between  $R_{\text{inner}}^{\text{exchange}} (\text{calc})$  and  $R_{\text{out}}^{\text{exchange}} (\text{photo})$  is made in Table 1. Using the experimental force constants the average value of  $R_{\text{inner}}^{\text{exchange}} (\text{calc}) / R_{\text{out}}^{\text{exchange}} (\text{photo}) = 3.2$  (from column 8 of Table 1). However, this ratio becomes 4.3 when the values of the reorganization energy  $R_{\text{inner}}^{\text{exchange}} (\text{calc})$  is calculated using the available  $\Delta q$  values from EXAFs data.<sup>9</sup>

\* ) Using  $a_1 = a_2 = a$  in Eq. (6)  $R_{\text{out}}^{\text{exchange}} (\text{calc})$  becomes :

$$\frac{e_0^2}{4\pi\epsilon_0} \left( \frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \left( \frac{1}{2a} \right) \quad (6a)$$

But this Eq (6a) represents the value of  $R_{\text{out}} (\text{calc})$  for a single reactant ion. It is noteworthy that although this value is for a single ion, it is *not* for one at an electrode where image forces intervene and cause the value to be (approximately) halved.

*Electron Transfer Reaction in Solution*

TABLE 1. Relative Contributions of Inner and Outer Shell Reorganization Energy.\*

(1) Reactants	(2)	(3)		(4)		(5)	(6)	(7)	(8)
	$R_{\text{photo}}^{\text{photo}}$ (eV) <sup>a</sup>	Frequency (cm <sup>-1</sup> ) <sup>b</sup>		Force Constants (m dyne/A <sup>o</sup> )		$\Delta q^c$ A <sup>o</sup>	$R_{\text{inner}}^{\text{exchange}}$ (calc) (eV) <sup>d</sup>	$R_{\text{out}}^{\text{exchange}}$ (photo) = col. 2 - $\frac{1}{2}$ col. 6 (eV) <sub>r</sub>	$R_{\text{inner}}^{\text{exchange}}$ (calc) $\frac{R_{\text{out}}^{\text{exchange}}}{R_{\text{out}}^{\text{photo}}}$ (photo)
V <sup>2+</sup> /V <sup>3+</sup>	2.13	389	490	1.6	2.6	.19	2.68	0.79	3.4
Cr <sup>2+</sup> /Cr <sup>3+</sup>	2.05	389	490	1.6	2.6	.18(.20) <sup>e</sup>	2.41(2.97)	0.85(0.57)	2.8(5.2)
Mn <sup>2+</sup> /Mn <sup>3+</sup>	2.02	395	490	1.7	2.6	.20	3.08	0.48	6.4
Fe <sup>2+</sup> /Fe <sup>3+</sup>	2.11	389	490	1.6	2.6	.16(.14) <sup>e</sup>	1.9(1.46)	1.16(1.38)	1.6(1.1)
Co <sup>2+</sup> /Co <sup>3+</sup>	2.26	389	490	1.6	2.6	.17(.21) <sup>e</sup>	2.15(3.28)	1.19(0.62)	1.8(5.3)

<sup>a</sup> From ref. 1 and 2.

<sup>b</sup> From ref. 7 and 8;  $\omega_r$  and  $\omega_0$  are ion-ligand stretching frequencies of reduced and oxidized ions, respectively. Some values were taken from ions of similar structure.

<sup>c</sup> From ref. 9-13.

<sup>d</sup> From Eq (3) and (4).

<sup>e</sup> From EXAFs data of ref. 9.

<sup>f</sup> Quantities in the bracket are obtained using  $\Delta q$  value from EXAFs data of ref. 9.

\* Fe(cN)<sub>6</sub><sup>4-3-</sup> has not been included because the optical experimental process<sup>1)</sup> has become complicated by autoionization in this case.<sup>17)</sup>

The present calculations are of significance in the continued evaluation of the principal source of activation in electrode reactions. It has been in the past difficult to find clear and unambiguous fact with which to judge the relative weight of the source of activation in electron transfer reactions. The photoemission from solution experiments<sup>1)</sup> are unique in that they provide information of the reorganization energy of single ions. The reorganization energies from the kinetic data are not as clear as that of photoemission experiment<sup>1)</sup> since the former is obtained by assuming that such reactions are adiabatic in nature.<sup>14)</sup>

A different conclusion to that presented here was reached by Delahay,<sup>2)</sup> who used the Urey-Bradley method<sup>16)</sup> for the evolution of the stretching force constants of the ion-ligand bond in the inner shell. This method is in error since it uses only the diagonal elements of a force constant matrix instead of using a normal mode one.<sup>4,5)</sup> This force constant was the one used in an earlier paper by Hale<sup>16)</sup> and re-used by Delahay.<sup>2)</sup> In fact, the force constant for the ion-ligand bond in the inner shell is better calculated from the spectroscopic data of symmetric stretching frequency.<sup>4,5)</sup>

Earlier<sup>2)</sup> a comparison was made between  $R_{\text{out}}^{\text{exchange}}(\text{photo}) (= R_{\text{out}}^{\text{photo}})$  with  $R_{\text{inner}}^{\text{electrode}}(\text{calc}) (= R_{\text{inner}}(\text{calc}))$ . This is, however, an incorrect comparison

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since for an electrode reaction the outer sphere reorganization energy,  $R_{\text{out}}^{\text{electrode}}$  becomes about half of  $R_{\text{out}}^{\text{exchange}}$  due to presence of image forces near the electrode,<sup>5)</sup> One should, in fact, compare  $R_{\text{out}}^{\text{exchange}}$  (photo) with  $R_{\text{inner}}^{\text{exchange}}$  (calc) which is double the value of  $R_{\text{inner}}^{\text{electrode}}$  (calc) because, former case two ions are involved, and in the latter one.

### Acknowledgment

We gratefully acknowledge the financial support by the Robert Welch Foundation.

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