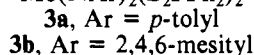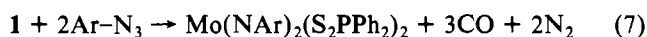the isolated monocarbonyl product. A variety of analogous species may be prepared via the interaction of **1** with various acetylenes.[20] The IR spectrum of Mo(CO)(PhC≡CH)(S₂PPh₂)₂ displays a strong ν(CO) absorption at 1931 cm⁻¹ but does not show a carbon–carbon stretch of the coordinated alkyne. In the room-temperature ¹H NMR spectrum, the resonance due to the acetylenic hydrogen atom appears at 12.54 ppm, approximately 9.5 ppm downfield from the corresponding resonance in free phenylacetylene (3.05 ppm). Likewise, in the ¹³C NMR of Mo(CO)(PhC≡CH)(S₂PPh₂)₂ the resonance of the ≡CH carbon atom is found at 209.5 ppm with $^1J_{C-H}$ = 218 Hz. As noted by Templeton and Ward,[21] the ¹³C NMR chemical shifts of coordinated alkynes provide a convenient qualitative assessment of the formal electron-donation number of these ligands. Applying this criterion and considering all of the above observations provide strong evidence that the alkyne ligand is acting as a formal 4-electron donor in Mo(CO)(PhC≡CH)(S₂PPh₂)₂, and thus an 18-electron configuration about the Mo atom is maintained.[22]

Equimolar amounts of **1** and MoO₂(S₂PPh₂)₂ react smoothly to produce 2 equiv of the oxo-transfer[23] product, MoO(S₂PPh₂)₂ (eq 6). Since the structures and reactivity patterns

$$1 + MoO_2(S_2PPh_2)_2 \rightarrow 2MoO(S_2PPh_2)_2 + 3CO \quad (6)$$
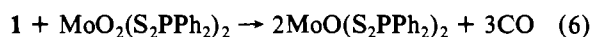
of transition-metal oxo and imido complexes are often similar,[24] it became of interest to investigate the possibility of synthesizing the species Mo(NAr)(S₂PPh₂)₂ via an analogous imido group transfer reaction. The requisite bis(imido) complexes Mo(NAr)₂(S₂PPh₂)₂ (**3**) were prepared by the treatment of **1** with aryl azides as shown in eq 7. However, when

$$1 + 2Ar-N_3 \rightarrow Mo(NAr)_2(S_2PPh_2)_2 + 3CO + 2N_2 \quad (7)$$
$$\textbf{3a, Ar} = p\text{-tolyl}$$
$$\textbf{3b, Ar} = 2,4,6\text{-mesityl}$$

solutions containing equimolar amounts of **1** and **3a** are warmed, **1** simply decomposes (vide supra) and **3a** remains unchanged, as determined by IR and NMR spectroscopy. Apparently, the imido ligands are so strongly bound in **3a** that they are rendered insufficiently nucleophilic to participate in the ligand-transfer reaction. Likewise, the reaction between equimolar amounts of **1** and *p*-tolyl azide at room temperature failed to give the desired Mo(Ntol)(S₂PPh₂)₂ product. Instead, the reaction produced equimolar quantities of the bis(imido) species, **3a**, and unreacted **1** as shown in eq 8. While Mo-

$$1.0\,\text{tol-N}_3 + 1.0\,\textbf{1} \rightarrow 0.5\,\textbf{3a} + 0.5\,\textbf{1} + N_2 + {}^3/_2CO \quad (8)$$
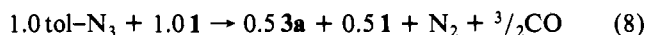
(Ntol)(S₂PPh₂)₂ is a likely intermediate in this sequence, its rate of reaction with tolyl azide must be much faster than that of tolyl azide with **1**.

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Franck–Condon Barriers to Outer-Sphere Reductive Cleavage

David M. Stanbury

Reductive cleavage as a fundamental mechanistic step permeates reaction chemistry. In organic chemistry, alkyl halides, for example, are cleaved by single-electron reducing agents.[1] In inorganic chemistry, reductive cleavage of peroxides and halogens may be cited. In many cases it is uncertain whether electron transfer and bond cleavage are concerted or sequential; the controversy in this regard is particularly prominent for reductive cleavage of alkyl halides, where it remains to be established whether the radical anions exist in solution.[2,3] Inorganic chemistry furnishes examples where the reduced products are clearly nonbonded, e.g., reduction of I₂⁻ to two iodide ions. The reverse process, oxidative bond formation, is less commonly observed, but it is, of course, of equivalent dynamic significance.

Both reductive cleavage and oxidative bond formation have been observed for reactions involving the I₂⁻/2I⁻ and (SCN)₂⁻/2SCN⁻ couples.[4,5] Oxidations of I⁻ and SCN⁻ by substitution-inert oxidants such as IrBr₆²⁻ and [Os(bpy)₃]³⁺ were found to have rate laws with terms first order in oxidant and second order in reducing agent. The following mechanism was proposed:

$$Ox + 2X^- \rightleftharpoons Red + X_2^- \qquad k_1, k_{-1}, K_{eq} \quad (1)$$

$$Ox + X_2^- \rightarrow Red + X_2 \qquad k_2 \quad (2)$$
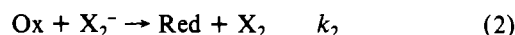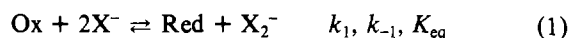
Under the experimental conditions k_1 was rate limiting.[5] In another series of experiments the reverse (k_{-1}) paths were observed by generating the species X₂⁻ pulse radiolytically in the presence of Red.[4] The validity of the proposed mechanism was confirmed by the fact that the ratio of the two rate constants, k_1/k_{-1}, was equal to the equilibrium constant, K_{eq}, which was calculated independently on the basis of the established reduction potentials.[4]

At the time of these studies it was considered that this interpretation posed a dilemma.[5] Electron transfer was viewed as occurring in concert with bond formation (in the k_1 direction). The bond length in I₂⁻ was estimated to be 3.10 Å by applying Badger's rule to the vibrational frequency (obtained from a matrix-isolation Raman spectrum), while the

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(21) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (b) Templeton, J. L.; Ward, B. C. *Ibid.* **1980**, *102*, 3288.
(22) For similar instances of 4-electron-donor alkyne ligands, see ref 3, 4, and the following: (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. (b) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349. (c) Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167. (d) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Ibid.* **1982**, *1*, 227. (e) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850.
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(2) Bigot, B.; Roux, D.; Salem, L. *J. Am. Chem. Soc.* **1981**, *103*, 5271.
(3) Bowman, W. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 25.
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nonbonded van der Waals separation of two iodide ions was estimated to be 4.08 Å on the basis of the ionic radius of I⁻. The Franck–Condon principle dictated that this 0.98 Å difference be divided between stretching of I_2^- and compression of two iodide ions. This was seen to impose a formidable energy barrier, and so we felt compelled to propose the existence of an intermediate charge-transfer complex as a means to circumvent this barrier. In this paper we wish to show that the Franck–Condon barrier for direct electron transfer is not inaccessibly high.

Adaption to the Cross Relationship

Several studies have noted that the cross relationship of Marcus–Hush theory gives an adequate correlation for a large number of reactions of both I⁻ and SCN⁻ of the above type.[5-8] The cross relationship is given as
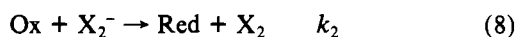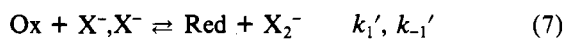
$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2}$$

$$\log f = \left[\frac{\log^2 K_{eq}}{4 \log\left(\dfrac{k_{11}k_{22}}{Z^2}\right)} \right] \quad (3)$$

where k_{12} is the rate constant for a "cross"-reaction such as k_1, K_{eq} is the equilibrium constant (i.e., k_1/k_{-1}), and Z is a frequency factor, which is often taken as 10^{11} M⁻¹ s⁻¹. k_{11} and k_{22} in the cross relationship are rate constants for the self-exchange reactions (4) and (5).

$$*X_2^- + 2X^- \rightarrow 2*X^- + X_2^- \qquad k_{11} \qquad (4)$$

$$Ox + *Red \rightarrow Red + *Ox \qquad k_{22} \qquad (5)$$
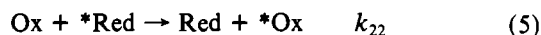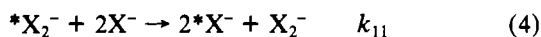
Values of k_{22} for complexes of the type under consideration are often available, but values of k_{11} have never been measured; however, it was found that a proper empirical choice of k_{11} would lead to a reasonably good correlation. It was noted that this definition of k_{11} as a third-order rate constant led to incompatible dimensions in the cross relationship.[5]

The problem of dimensional incompatibility can be avoided by expressing the mechanism as shown in eq 6–8. The notion

$$2X^- \rightleftarrows X^-,X^- \qquad K_{IP} \qquad (6)$$

$$Ox + X^-,X^- \rightleftarrows Red + X_2^- \qquad k_1', k_{-1}' \qquad (7)$$

$$Ox + X_2^- \rightarrow Red + X_2 \qquad k_2 \qquad (8)$$

of forming an ion pair of two like-charged ions has received some attention, and for I⁻ a value for K_{IP} of 0.02 M⁻¹ has been calculated from the Fuoss equation at zero ionic strength.[9] When corrected to 0.1 M ionic strength, K_{IP} becomes 0.035 M⁻¹. This mechanism yields the following identities: $k_1 = k_1'K_{IP}$ and $K_{eq} = K_{IP}k_1'/k_{-1}'$. Furthermore, the self-exchange reaction is now defined for the second-order reaction

$$*X_2^- + X^-,X^- \rightleftarrows *X^-,*X^- + X_2^- \qquad k_{11}' \qquad (9)$$
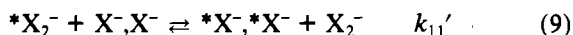
and the problem of dimensional incompatibility is resolved. With this modification a value of 3×10^4 M⁻¹ s⁻¹ is obtained for k_{11}' for the $I_2^-/2I^-$ couple.

Franck–Condon Factors

The remaining task is to determine whether the Franck–Condon barrier is intolerably high for a rate constant of 3×10^4 M⁻¹ s⁻¹. The "experimental" Franck–Condon barrier, ΔG^* = 37 kJ/mol, was obtained from

$$k_{11}' = Z \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad (10)$$

and it may be expressed as the sum of the solvent, ΔG_o^*, and molecular, ΔG_i^*, reorganizational barriers

$$\Delta G^* = \Delta G_o^* + \Delta G_i^* \qquad (11)$$

Solvent reorganizational barriers have been estimated for a number of self-exchange reactions of small molecules, and they are in the range 30–40 kJ/mol.[10,11] Thus we have tried several approaches to estimating ΔG_i^*. In the initial model it was assumed that the two iodide ions were hard spheres, and so ΔG_i^* was the energy required to stretch the bond in I_2^- from 3.10 to 4.08 Å, i.e., from its normal bond length to twice the ionic radius of I⁻. The energy was calculated by assuming that entropy effects could be neglected as usual, and so a Morse potential was appropriate:[12]

$$V_{I_2^-} = D_e[1 - \exp(-a(R - R_e))]^2 \qquad (12)$$

Here D_e is the well depth and R_e is the equilibrium bond length. a is given by

$$a = \pi \nu_e (2\mu/D_e)^{1/2} \qquad (13)$$

where ν_e is the vibrational frequency and μ is the reduced mass. A value of 0.91 eV was used for D_e, which was consistent both with gas-phase thermochemical estimates and with estimates based on vibrational anharmonicity.[13] ν_e was taken as the vibrational fundamental of 115 cm⁻¹.[14] With R held to 4.08 Å, a value of ΔG_i^* of 46 kJ/mol was obtained. This exceeds the experimental ΔG^*; after inclusion of ΔG_o^* the calculated barrier is implausibly large.

A refinement was introduced by recognizing that the dissociation of I_2^- is assisted by the solvent. This can be understood in terms of the Born model of solvation; i.e., the solvation energy of I_2^- is less than the solvation energy of I⁻ plus I· because of the difference in ionic radii.[15] The magnitude of this effect can be estimated in two ways. The dissociation rate constant for I_2^- is 9×10^5 s⁻¹ in aqueous solution;[16] from the Arrhenius expression and a reasonable estimate of 1×10^{14} s⁻¹ for the A factor, an activation energy for dissociation of 46 kJ/mol may be calculated. Alternatively, since $\Delta H° = -23$ kJ/mol for the association of I⁻ with I·[17] and since the association reaction is diffusion controlled[16] (with an estimated activation enthalpy of 19 kJ/mol),[18] the activation enthalpy for dissociation may be estimated to be 42 kJ/mol. The average of these two self-consistent estimates, 44 kJ/mol, is only 50% of the gas-phase dissociation energy.

When this solvent-assisted dissociation energy was used as D_e in the Morse potential, it was found that only 29 kJ/mol was required to stretch the I_2^- bond to twice the ionic radius of I⁻. Thus 8 kJ/mol remained for the solvent-reorganizational barrier. Although this was a substantial improvement, it was felt that a higher solvent-reorganizational barrier might be expected.

A further refinement was attempted by allowing the two iodide ions to be soft, rather than hard, spheres. Since most of the Coulombic repulsion had been accounted for in K_{IP}, the Lennard–Jones potential

$$V_{I^-,I^-} = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right] \qquad (14)$$

was tried as a helpful starting point, and the parameters ϵ and

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(11) Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847.
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(13) Howard, W. F., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 2956.
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Table I. Self-Exchange Parameters for Dihalide Radical Anions

	I_2^-	Br_2^-	Cl_2^-
$\nu,^a$ cm^{-1}	115	150	250
$R_e,^a$ Å	3.10	2.80	2.70
$k_{dis},^b$ s^{-1}	9.0×10^5	7.0×10^5	1.0×10^5
$D_e,^c$ kJ/mol	40.2	40.8	45.7
μ, g/mol	63.5	40.0	17.7
$\epsilon,^d$ J	3.9×10^{-21}	2.7×10^{-21}	2.0×10^{-21}
$\sigma,^d$ Å	3.9	3.6	3.4
$r_{ionic},^e$ Å	2.04	1.80	1.64
$\Delta G_i^*,^f$ kJ/mol	29.0	25.8	22.3
$\Delta G_i^*,^g$ kJ/mol	26.0	25.0	21.8
$R^{\ddagger},^h$ Å	3.73	3.36	3.07

^{a} Reference 14. ^{b} Aqueous dissociation rate constant for X_2^-; see ref 16, pp 33, 38, and 42. ^{c} Solvent-assisted-dissociation activation energy, calculated as described in the text. ^{d} Reference 19; Br$^-$ and Cl$^-$ parameters taken as those of Kr and Ar, respectively. ^{e} Reference 24. ^{f} Calculated by the solvent-assisted hard-sphere model. ^{g} Calculated by the solvent-assisted Lennard–Jones model. ^{h} Interatomic distance in the transition state calculated for the solvent-assisted Lennard–Jones model.

σ were appropriated from the known isoelectronic xenon system.[19] If the energy of the pair of reactants is taken to be the sum of V_{I^-,I^-} plus $V_{I_2^-}$, then the transition state has the energy of this sum under the condition that the interatomic separation be the same in both potentials. ΔG_i^* is this energy when minimized as a function of the interatomic distance. This problem has no analytical solution, and so the sum of the two potentials was evaluated at 0.02-Å intervals between 3 and 4 Å. In this way the minimum was located at 3.73 Å, with a value of 26 kJ/mol for ΔG^*. By going from a hard-sphere model to a Lennard–Jones potential only 3 kJ/mol was gained. A correct potential would probably include some residual Coulombic repulsion, and this would reduce the gain from 3 kJ/mol to a value approaching zero. Thus, despite an intuitive concern that our model, by neglecting Coulombic effects, is unrealistic, the introduced error is seen to be energetically negligible.

In summary, it can be seen that some simple ideas about molecular forces can result in a calculated inner-sphere Franck–Condon barrier that is substantially less than the "experimental" barrier. Inclusion of the solvent reorganization gives a barrier that is somewhat high. Perhaps our estimate of the solvent barrier is too high. In this regard, the diffusion-controlled reactivity of the $I^-/I\cdot$ couple also implies an anomalously low solvent-reorganizational barrier.[5] It is also possible that since bond formation in the transition state is significant, release of solvent molecules results in $\Delta S^* > 0$; this effect would lower ΔG^* and bring the model more in line with experiment. Another source of error is more fundamental; the cross relationship was derived in terms of parabolic energy surfaces, while we have used the Morse potential for X_2^-. At this point the magnitude of error thereby incurred is unknown,

although recent studies on certain Cu(I)/Cu(II) couples indicate that the error may be substantial.[20] What we wish to emphasize, though, is that the molecular reorganizational barrier is not absurdly high; thus it is probably not necessary to invoke a charge-transfer intermediate in reactions involving the $I_2^-/2I^-$ couple. Our earlier discussion failed to recognize that it is very easy to stretch the bond in I_2^-.[5]

Other Treatments

The model that has been described above shares many conceptual similarities with that described by Bigot et al. for reductive cleavage of $H_2C(NO_2)Cl$.[2] In that model, however, the potential surfaces were calculated by using CI–SCF methods, and the solvent-assisted bond cleavage was treated microscopically. The contribution from the solvent-reorganizational term was neglected, but since the results of these calculations were not compared with experimental data, the magnitude of this error is unknown.

Recently, theoretical arguments have been advanced that dissociative electron-transfer reactions should yield LFER's in accord with Marcus' theory.[21] A related approach was used to extract activation barriers for self-exchange reactions involving alkyl halides.[1] It should be possible to analyze these barriers in terms of a microscopic model as we have done for the $I_2^-/2I^-$ system.

It is difficult to extend our treatment to other inorganic reactions because of a lack of data. Outer-sphere reductive cleavage of Cl_2^- has been observed to proceed with a rate constant less than diffusion controlled only for the reaction with Fe^{2+}.[22] For Br_2^- the reaction with Fe^{2+} is inner sphere.[22] Br_2^- has been reduced by [Ru(bpy)$_3$]$^{2+}$ with a reported rate constant of 3.1×10^9 M^{-1} s^{-1}, but since there are no comparable data, and since the rate constant is approaching diffusion control, an estimate of k_{11}' would be very uncertain.[23]

Sufficient data are available to estimate ΔG_i^* for the Br_2^- and Cl_2^- systems by using the Morse potential as described above. The data, parameters, and results are presented in Table I. It can be seen that ΔG_i^* decreases smoothly as the halogens get smaller. Contrary to this trend ΔG_o^* would be expected to increase with the smaller halogens. At this stage we are reluctant to speculate on the net outcome of these factors.

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