EPR spectra of frozen solutions containing electrochemically generated C_{60}^-, C_{60}^{2-}, C_{70}^-, and C_{70}^{2-} are displayed in Figure 2.[13] The 120 K EPR spectrum of C_{60}^- shows only slight anisotropy with $g = 2.001$ and a peak to peak separation of 5.5 G. In contrast, the low-temperature spectrum of C_{70}^- is quite anisotropic and three g values are readily discerned at $g = 2.007$, 2.003, and $\sim$2.000. The greater anisotropy for C_{70}^- seems reasonable in view of the fact that the symmetry of C_{70} is only D_{5h} compared to I_h for C_{60}. The C_{70}^{2-} resonance also displays greater anisotropy than the C_{60}^{2-} resonance. The spectrum of C_{60}^{2-} is a "quintet" centered at $g = 2.003$. The first set of satellites are 6.3 G (left) and 6.2 G (right) away from the main resonance. A second pair of satellites, of much lower intensity, lies further out at 13.9 G (left) and 14.0 G (right) from the center signal. Assuming that C_{60}^{2-} is an $S = 1$ diradical, its EPR spectrum shows more complexity than the triplet that should arise from simple dipolar coupling. This complexity probably arises from exchange coupling, and spectral simulation studies will be needed for a full interpretation of the spectrum.

C_{60} exhibits two prominent UV–visible bands at 257 and 330 nm in CH_2Cl_2 (0.05 M $[(n\text{-}Bu)_4N](BF_4)$) similar to the spectra reported in hexane.[3,4] Both major bands of C_{60} are replaced by bands of somewhat lower intensity at 262 and 339 nm after electrolysis is completed to produce C_{60}^-. Figure 3 displays the time-dependent spectrum obtained between 240 and 420 nm during electrolysis of C_{60} to produce C_{60}^-; the clean isosbestic points indicate the presence of only two spectrally detectable species in solution. A second reduction to C_{60}^{2-} gives a spectrum with broad bands at 263 and 340 nm. The conversion of C_{60}^- to C_{60}^{2-} also displays well-defined isosbestic points. The original C_{60} spectrum could be regenerated by reoxidation of C_{60}^- or C_{60}^{2-} at 0.00 V, thus demonstrating a high degree of reversibility for both processes. Similar behavior is observed upon reduction of C_{70}.[14]

In conclusion, this work reports the UV–vis and EPR spectra of the C_{60}^{n-} and C_{70}^{n-} ($n = 1, 2$) anions by spectroelectrochemical techniques. The EPR spectra suggest that the anions exist as radicals with $S = {}^1/_2$ ($n = 1$) and $S = 1$ ($n = 2$) ground states. In addition, a third reduction of C_{60}^{3-} and C_{70}^{3-} has been verified and a fourth reduction to C_{60}^{4-} and C_{70}^{4-} is reported for the first time.

Acknowledgment. We thank the Robert A. Welch Foundation (C-627, L.J.W.; E-680, K.M.K.) for support of this work. S.F. also thanks the U.S. National Institutes of Health for a NIGMS Training Grant (GM-08362) at Rice University. We also thank Professor Graham Palmer for helpful discussions concerning the EPR spectra.

---

(13) Samples for the EPR experiments were immediately collected from the freshly electrolyzed solutions, transferred into EPR tubes in the glovebox, promptly taken out of the box, and frozen in liquid nitrogen (and subsequently kept as such).

(14) UV–visible bands in CH_2Cl_2: C_{70} (333, 362, 381, and 466 nm); C_{70}^- (340, 386, and 483 nm; broadened). The C_{70}^{2-} spectrum is almost featureless except for a few ill-defined shoulders and two weak bands (609 and ca. 636 nm).

Agreement of Proton Transfer Cross Reaction Rates between Transition Metals with Those Predicted by Marcus Theory

S. Sôley Kristjánsdóttir and Jack R. Norton*

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Received December 27, 1990

Marcus noted in 1968[1] that a cross relation like the one he had derived for electron transfer should also apply to proton transfer.[2] If the intrinsic barrier ΔG_0^* for proton transfer from A to B (eq 1) is the average[3] of ΔG_{AA}^* and ΔG_{BB}^*, the barriers to proton self-exchange for A and B, respectively, the basic Marcus relation[4] gives eq 2 for ΔG_{AB}^*.[5-7] Restatement of eq 2 in terms of the corresponding rate and equilibrium constants gives eq 3, a cross relation like that familiar for electron transfer.

$$\text{A–H} + \text{B}^- \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} \text{A}^- + \text{B–H} \qquad K_{AB} = k_{AB}/k_{BA} \tag{1}$$

$$\Delta G_{AB}^* = {}^1/_2[\Delta G_{AA}^* + \Delta G_{BB}^* + \Delta G^\circ] \tag{2}$$

$$k_{AB} = \sqrt{k_{AA}k_{BB}K_{AB}} \tag{3}$$

Rate data are available for many proton transfer reactions where only one partner has a large intrinsic barrier: for example, the deprotonation of carbon acids by oxygen and nitrogen bases[5] and the deprotonation of transition-metal hydrides by nitrogen bases.[8] However, the validity of eqs 2 and 3 for systems *where both* ΔG_{AA}^* *and* ΔG_{BB}^* *are significant* has not been demonstrated experimentally. The slow H^+ exchange between 9-alkylfluorene and (9-alkylfluorenyl)lithium in ether does not obey eqs 2 and 3, perhaps because of the degree to which the (9-alkylfluorenyl)lithium is ion paired.[9] However, because carbonylmetalate anions do not form contact ion pairs in CH_3CN,[10] and because the conjugate transition-metal acids do not hydrogen bond to bases,[11] the apparent rate constants measured for the proton-transfer reactions of these acids should be those of the H^+ transfer steps themselves, and the rate constants for their cross reactions

---

(1) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(2) Later theoretical work has successfully treated H^+ transfer with a weak interaction model: (a) Dogonadze, R. R.; Kuznetsov, A. M.; Levich, G. *Electrochim. Acta* **1968**, *13*, 1025. (b) German, E. D.; Kuznetsov, A. M.; Dogonadze, R. R. *J. Chem. Soc., Faraday Trans. 2* **1980**, 1128. (c) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 2418. (d) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4083.

(3) Such an assumption is plausible during *electron* transfer because "the force field from one reactant does not influence the other",[4a] but it is less clear a priori that is true during *proton* transfer (which obliges the reactants to come into relatively close contact). Marcus remarked while discussing proton transfers in 1968 that "additivity might be expected to hold best if neither [intrinsic barrier] is near zero"[5a] and later used a simple BEBO model to show that it is not seriously in error even when one intrinsic barrier is substantially larger than the other.[5c]

(4) (a) Marcus, R. A. *J. Chem. Phys.* **1968**, *43*, 679. (b) Newton, T. W. *J. Chem. Educ.* **1968**, *45*, 571.

(5) Detailed discussions of the application of Marcus theory to proton-transfer reactions can be found in the following: (a) Cohen, A. O.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249. (b) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7225. (c) Marcus, R. A. *Faraday Symp. Chem. Soc.* **1975**, *10*, 60. (d) Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475. (e) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973. (f) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227. (g) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic: New York, 1985.

(6) Substitution of $\Delta G_0^* = (1/2)[\Delta G_{AA}^* + \Delta G_{BB}^*]$ into the basic Marcus relation[4] $\Delta G^* = (1 + \Delta G^\circ/4\Delta G_0^*)^2\Delta G_0^*$ and acceptance of the restriction that $\Delta G^\circ < 4\Delta G_0^*$ lead to eq 2. For slow proton transfers with large intrinsic barriers and relatively modest thermodynamic driving forces, the quadratic term can, as with methyl transfers,[7] be neglected. Marcus originally noted[1] that the application of cross relations like eqs 2 and 3 to proton transfers was probably limited to $|\Delta G^\circ/4\Delta G_0^*| < 1$.

(7) Lewis, E. S. *J. Phys. Chem.* **1986**, *90*, 3756. (Lewis does state that proton transfers are a case where a contribution from the quadratic term is possible.)

(8) (a) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945. (b) Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105.

(9) Murdoch, J. R.; Bryson, J. A.; McMillen, D. F.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 600.

(10) No contact ion pair formation between any organometallic anion and Na^+, K^+, or PPN^+ has ever been observed in CH_3CN.[8a,b,10a-g] There is weak interaction between Tl^+ and $[Co(CO)_4]^-$ in CH_3CN.[10b] (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (b) Schramm, C.; Zink, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 4554. (c) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669. (d) Edgell, W. F.; Barbetta, A. *J. Am. Chem. Soc.* **1974**, *96*, 415. (e) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (f) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *198*, 403. (g) Darensbourg, M. Y.; Jimenez, P.; Sacket, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521. For a review, see: Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, in press.

0002-7863/91/1513-4366$02.50/0

should conform to eqs 2 and 3.[12] We have therefore measured the cross reaction rate constants between the group 6 hydrides $HM(CO)_3Cp$ and $K[M(CO)_3Cp]$ (M = Cr, Mo, W) in CH_3CN and have compared the measured rate constants to the values calculated from eq 3.

The rates of these cross reactions were measured between −30 and +25 °C in an anaerobic stopped-flow apparatus we have described in detail elsewhere.[13] The measurement of these rates was complicated by the fact that none of the species involved have distinct absorption maxima but all have finite absorbance in the UV region. As the metal hydrides absorb less strongly than the corresponding anions, the reactions were run under pseudo-first-order conditions with the hydride reactant in excess. The progress of the reactions was monitored at those wavelengths where $\Delta A/A$ was maximal: 350 nm for k_{CrW}, 345 nm for k_{CrMo}, and 340 nm for k_{MoW}.[14] Even under these conditions $\Delta A/A$ was small enough that S/N ratios were poor for individual runs, but good pseudo-first-order rate constants k_{obsd} were obtained by averaging 16–32 runs. The same value of k_{obsd} was obtained for $PPN[W(CO)_3Cp]/HCr(CO)_3Cp$ as for $K[W(CO)_3Cp]/HCr(CO)_3Cp$. For the Cr,Mo couple K_{eq} (eq 1) was only 3.98, but with $HCr(CO)_3Cp$ in large excess, the change in $Mo(CO)_3Cp^-$ concentration was still effectively first-order, and eq 4 was used to obtain $k_{MM'}$.

$$-\frac{d(\Delta[Mo(CO)_3Cp^-])}{dt} = k_{obsd}(\Delta[Mo(CO)_3Cp^-])$$

$$k_{obsd} = k_{MM'}\left([HCr(CO)_3Cp] + \frac{2[Mo(CO)_3Cp^-]_0}{K_{eq}}\right) \quad (4)$$

For a given $[HM(CO)_3Cp]$ the k_{obsd} values were extrapolated to 25 °C, and k_{obsd} was then shown to be linear in $[HM(CO)_3Cp]$.

Table I. Observed and Calculated Rate Constants for Group 6 $HM(CO)_3Cp/K[M'(CO)_3Cp]$ Proton-Exchange Reactions in CH_3CN at 25 °C

	$k_{MM'}$, M^{-1} s^{-1}		$k_{M'M}$, M^{-1} s^{-1}		calcd/
M, M'	measd	calcd	measd	calcd	measd
Cr, Mo	1.66×10^4	2.6×10^4	4.17×10^3	6.53×10^3	1.6
Cr, W	3.12×10^4	1.5×10^5	4.94×10^1	2.38×10^2	4.8
Mo, W	8.5×10^3	1.4×10^4	5.4×10^1	8.9×10^1	1.7

The resulting values of the second-order rate constants $k_{MM'}$ at 25 °C are given in Table I. The activation parameters were $\Delta H^* = 6.77$ kcal/mol and $\Delta S^* = -16.6$ eu for Cr,Mo; $\Delta H^* = 6.04$ kcal/mol and $\Delta S^* = -17.6$ eu for Cr,W; and $\Delta H^* = 5.2$ kcal/mol and $\Delta S^* = -23.1$ eu for Mo,W.

The equilibrium constants K_{AB} for these cross reactions were calculated from our previous measurements of their CH_3CN pK_a values: 13.3 for $HCpCr(CO)_3$, 13.9 for $HCpMo(CO)_3$, and 16.1 for $HCpW(CO)_3$.[10e] The rate constants for self-exchange in CH_3CN at 25 °C were known from NMR measurements in our previous work: 18 000 M^{-1} s^{-1} for k_{CrCr}, 2500 M^{-1} s^{-1} for k_{MoMo}, and 650 M^{-1} s^{-1} for k_{WW}.[8a] The values thus calculated from eq 3 for the cross reaction rate constants are given in Table I.

The observed values of $k_{MM'}$ in Table I agree well with those calculated from eq 3, so Marcus theory passes the *first real test* of its applicability to *proton*-transfer reactions. The particularly good agreement for the Mo/W cross reaction may be due to the fact that the difference in geometry between $HMo(CO)_3Cp$ and $HW(CO)_3Cp$ is minimal.[15-17]

Acknowledgment. This research was supported by NSF Grant CHE-8819760. We thank Carol Creutz and Norman Sutin for helpful comments.

---

(11) Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics*, in press.

(12) Proton transfer between oxygen, nitrogen, and even carbon acids proceeds through hydrogen-bonded intermediates: Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(13) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.*, in press.

(14) At lower wavelengths $\Delta A/A$ became higher but the increased A_{tot} decreased the S/N.

(15) These metals have essentially equal covalent radii, as calculated from the M–Cl distances in $CpM(CO)_3Cl$ (1.50 Å and 1.51 Å for W and Mo, respectively),[16] so their M–H distances should be about equal. The covalent radius of Cr is considerably shorter (1.30 Å[17] as calculated from $[CpCr(CO)_3]_2SnCl_2$) so the Cr–H bond should be shorter.

(16) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197.

(17) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1975**, 230.