For **2** the seven skeletal pairs are appropriate for a capped closo 6-vertex polyhedron. Thus the geometries of both **2** and **3** are consistent with the n-bond pair, capped $n - 1$ vertex principle of SEC theory.[5] Very few examples of 7-pair, capped octahedral clusters are known. They include $Os_7(CO)_{21}$,[10] $[Rh_7(CO)_{16}]^{3-}$,[11] $[Rh_7(CO)_{16}I]^{2-}$,[12] and the cobaltaborane $[1,3-\{Co(\eta^5-C_5H_5)\}_3-(B_4H_4)]$.[13] The capped-pentagonal-bipyramidal polyhedron of **3** appears to be the first documented example of this geometry for an 8-vertex, 8-skeletal pair system and is particularly notable since it has been shown[14] that the dodecahedral structure, exemplified by $(\eta^5-C_5H_5)_4Co_4B_4H_4$,[15] may also accommodate this electron count. Finally we note the isolobal relationships[16] Ph–P $\longleftarrow\sigma\longrightarrow$ CH⁻ and $M(CO)_2$ (M = Fe, Ru, Os) $\longleftarrow\sigma\longrightarrow$ CH³⁺. Thus entire series of closo-$M_x(CO)_{2x+1}(PPh)_x$, nido-$M_x(CO)_{2x+2}(PPh)_x$, or capped $n - 1$ vertex ($n = 2x$) $M_x(CO)_{2x}(PPh)_x$ metallophosphorus clusters should exist. We are currently exploring these possibilities.

(10) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Mason, R.; Hitchcock, P. B.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1977**, 385. The anion Os₈(CO)₂₂²⁻ with 7 skeletal pairs has a bicapped octahedral structure. See: Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 60.
(11) Albano, V. G.; Bellon, P. L.; Ciani, G. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1024.
(12) Albano, V. G.; Ciani, G.; Martinengo, S.; Chini, P.; Giordano, G. *J. Organomet. Chem.* **1975**, 88, 381.
(13) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, 16, 3255.
(14) O'Neill, M. E.; Wade, K. *Inorg. Chem.* **1982**, 21, 461.
(15) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, 18, 257.
(16) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 711.

Electron Exchange in Models for Heme Proteins

Dabney White Dixon,* Michael Barbush, and Ataollah Shirazi

Department of Chemistry, Washington University St. Louis, Missouri 63130

Electron transfer between two cytochromes is generally postulated to take place only through the exposed heme edge.[1] If this is the case, the protein serves as an insulator. The rate of transfer then depends upon the rate constant for diffusion of the protein, k_D, the percentage of the surface area of the protein that is occupied by the heme, ϕ, and the probability that the hemes, once in contact, will transfer an electron, $P = k_r/k_d$, where k_r is the rate constant for electron exchange between two free hemes

(1) (a) Dickerson, R. E.; Timkovich, R. In "The Enzymes"; Boyer, P. D., Ed.; Academic Press: New York, 1975; Vol. 11, pp 397–547. (b) Salemme, F. R. *Annu. Rev. Biochem.* **1977**, 46, 299–329. (c) Ferguson-Miller, S.; Brautigan, D. L.; Margoliash, E. In "The Porphyrins"; Dolphin D., Ed.; Academic Press: New York, 1979; Vol. 7, pp 149–240. (d) Timkovich, R. in ref 1c, pp 241–294. (e) Cusanovich, M. A. In "Bioorganic Chemistry"; van Tamelen, E. E., Ed.; Academic Press: New York, 1978; Vol. 4, pp 117–145. (f) Kraut, J. *Biochem. Soc. Trans.* **1981**, 9, 197–202. (g) Capaldi, R. A.; Darley-Usmar, V.; Fuller, S.; Millett, F. *FEBS Lett.* **1982**, 138, 1–7. (h) Meyer, T. E.; Kamen, M. D. *Adv. Protein Chem.* **1982**, 35, 105–212.

Table I. Electron Self-Exchange Rate Constants in Model Hemes[a]

| complex	$10^{-7}k$, M⁻¹ s⁻¹
FeTPP(1-MeIm)₂	8.1 ± 0.7
Fe(3-MeTPP)(1-MeIm)₂	5.3 ± 0.6
Fe(4-MeTPP)(1-MeIm)₂	9.7 ± 0.8
Fe(4-OMeTPP)(1-MeIm)₂	6.8 ± 0.6

[a] Measured in CD₂Cl₂ at –21 °C.

and k_d is the rate constant for diffusion of the free heme.[2] Since $k_D \simeq k_d$

$$k = (k_r/k_d)k_D\phi^n = k_r\phi^n \qquad (1)$$

In the simplest model $n = 2$, but Sommer et al. have presented arguments that $1.5 \leq n \leq 2$.[3] In view of the fact that the heme exposure is ~1%,[4] one would expect a self-exchange rate 10^{-3} to 10^{-4} that of free heme.

Rate constants for electron self-exchange have been calculated for a few hemes from experiments involving stopped-flow cross reactions with other inorganic reagents. There is a wide spread of values:[5] FeTPPS(H₂O)³⁻/⁴⁻, ~1 × 10³;[6] FePPIX(H₂O)¹⁻/⁰, ~7 × 10⁵;[7] FeTMPyP(H₂O)⁵⁺/⁴⁺, 1.2 × 10⁶; FeTMPyP-(Im)₂⁵⁺/⁴⁺, >1 × 10⁷; FeTMPyP(H₂O)(OH)⁴⁺/³⁺, >1 × 10⁹;[8] and FePPIX(CN)₂³⁻/⁴⁻, 8 × 10¹⁰ M⁻¹ s⁻¹.[7a] The charge and spin-state effects and problems in calculating self-exchange rate constants from cross reactions with SO₂⁻· make it difficult to compare these rate constants for the models with those found for heme proteins.

We have therefore determined the rate constants for electron self-exchange in free hemes from NMR line-broadening measurements[9] on mixtures of the Fe(II) and Fe(III) species. This
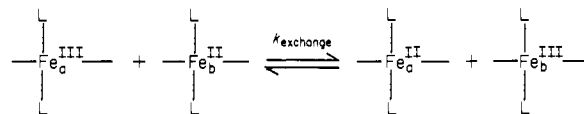
technique allows us to measure a direct self-exchange rate (no driving force for the reaction) and to use nonaqueous solvents (and therefore neutral, rather than highly charged, hemes). The Fe-(II)/Fe(III) mixtures are in the fast-exchange limit. Tetraphenylporphyrin derivatives have been used because they have less tendency to aggregate and fewer resonances than the natural hemes.[10]

The electron self-exchange rates of bis-1-MeIm hemes were measured in CD₂Cl₂. It was necessary to cool the solutions to –21 °C to prevent broadening of the peaks due to ligand exchange. Under these conditions the lifetime of the six-coordinate species is ~9 s for Fe(III)TPP(1-MeIm)₂⁺Cl⁻ (ref 11) and >20 s for Fe(II)TPP(1-MeIm)₂.[12] The Fe(III) hemes were reduced to Fe(II)/Fe(III) mixtures with aqueous Na₂S₂O₄. The rate constants were independent of concentration in the range experimentally accessible (3–12 mM), and also independent of the extent of reduction (2–40%). Steric and electronic changes on the porphyrin periphery (3-Me, 4-Me, 4-OMe) made little difference in the rate constant (Table I).

Electron self-exchange rate constants in proteins span a wide range, from ~10² to ~10⁷ M⁻¹ s⁻¹.[13-17] In general long cyto-

(2) Sutin, N. *Adv. Chem. Ser.* **1977**, 162, 156–172.
(3) Sommer, J.; Jonah, C.; Fukuda, R.; Bersohn, R. *J. Mol. Biol.* **1982**, 159, 721–744.
(4) Stellwagen, E. *Nature (London)* **1978**, 275, 73–74.
(5) Abbreviations: PPIX, protoporphyrin IX; TMPyP, tetrakis(4-N-methylpyridyl)porphyrin; TPPS, porphinetetrakis(4-benzenesulfonate).
(6) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, 104, 1575–1582.
(7) (a) Worthington, P.; Hambright, P. *J. Inorg. Nucl. Chem.* **1980**, 42, 1651–1654. (b) Cassatt, J. C.; Kukuruzinska, M.; Bender, J. W. *Inorg. Chem.* **1977**, 16, 3371–3372.
(8) Pasternack, R. F.; Spiro, E. G. *J. Am. Chem. Soc.* **1978**, 100, 968–972.
(9) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, 82, 2542–2549.
(10) A study of electron self-exchange in biscyano hemes has shown that the synthetic and the natural iron porphyrins have similar rate constants. Dixon, D. W.; Shirazi, A.; Barbush, M., unpublished results.
(11) Satterlee, J. D.; La Mar, G. N.; Bold, T. J. *J. Am. Chem. Soc.* **1977**, 99, 1088–1093.
(12) Dixon, D. W.; Barbush, M., unpublished results.

chromes (100–115 amino acids) exchange electrons slowly (10^2–10^4 M^{-1} s^{-1}) while short cytochromes (80–90 amino acids) do so quickly (10^6–10^7 M^{-1} s^{-1}).[18] As seen in Table I, the model compounds have rate constants only approximately 10-fold larger than those of the short cytochromes. This indicates that other factors serve either to decrease the rate of electron transfer in models or increase the rate in the small proteins. Differences in inner-sphere reorganization energies are presumably small, because neither the bond lengths nor the force constants change appreciably in going from the models to the proteins. Outer-sphere reorganization is important for the models (a contribution of ~2 kcal to $\Delta G^{\ddagger}$); in the proteins it would depend on the amino acid sequence. Electrostatic interactions are not important for the models (the Fe(II) species is uncharged) but may be very important for the proteins. Other contributing factors in the proteins might include differences in complex formation and sequence-specific effects.

We have shown that model hemes transfer electrons only approximately 10 times faster than the small cytochromes. The steric effect found experimentally is substantially smaller than that calculated, arguing that other factors play an important role in determining the rate of electron transfer in cytochromes.

(13) Senn, H.; Wüthrich, K. *Biochim. Biophys. Acta* **1983**, *746*, 48–60.
(14) Gupta, R. K. *Biochim. Biophys. Acta* **1973**, *292*, 291–295.
(15) (a) Gupta, R. K.; Koenig, S. H.; Redfield, A. G. *J. Magn. Reson.* **1972**, *7*, 66–73. (b) Oldfield, E.; Allerhand, A. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 3531–3535. (c) Kowalsky, A. *Biochemistry* **1965**, *4*, 2382–2388.
(16) Keller, R. M.; Wüthrich, K.; Schejter, A. *Biochim. Biophys. Acta* **1977**, *491*, 409–415.
(17) Keller, R. M. Wüthrich, K.; Pecht, I. *FEBS Lett.* **1976**, *70*, 180–184.
(18) (a) Heme exposure alone does not account for this wide range. For example, horse heart cytochrome *c*, with 0.6% heme exposure,[4] has an electron self-exchange rate constant of 10^3–10^4 M^{-1} s^{-1} (ref 14 and 15) while *Ps. aeruginosa* cytochrome *c*-551, with 3% heme exposure,[18b] has a rate constant of ~10^7 M^{-1} s^{-1} (ref 17). (b) Stellwagen, E., personal communication.

Neutral Products from Fluoride Abstraction in Gas-Phase Cation–Molecule Reactions[1]

Eric W. Redman, Kamalesh K. Johri, Robert W. K. Lee, and Thomas Hellman Morton*

Department of Chemistry, University of California Riverside, California 92521

Ion–molecule reactions corresponding to fluoride abstraction from a neutral molecule by an alkyl cation, reaction 1, have been widely observed.[2] Here we report the first experimental detection of electrically uncharged products of such a reaction. We have
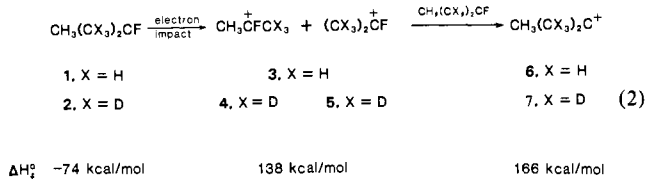
$$R^+ + R'F \longrightarrow R'^+ + RF \qquad (1)$$

used a specially designed electron bombardment flow (EBFlow) reactor[3] to collect neutral molecules that are formed by reactions of 2-fluoroisopropyl cation **3** in the gas phase, and we describe the use of NMR for identification and quantitation.

(1) Portions of this work were presented at the Western Regional Conference on Ion Chemistry, Lake Arrowhead, CA, January 1984.
(2) (a) McAskill, N. A. *Aust. J. Chem.* **1970**, *23*, 893–903. (b) Blint, R. J.; MacMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269–1278. (c) Dawson, J. H.; Henderson, W. A.; O'Malley, R. M.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 61–71. (d) Briscese, S. M. J.; Blair, L. K.; Riveros, J. M. *An. Acad. Bras. Cienc.* **1973**, *45*, 359–363. (e) Lias, S. G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 273–292. (f) Park, J. Y.; Beauchamp, J. L. *J. Phys. Chem.* **1976**, *80*, 575–584.
(3) (a) Burns, F. B.; Morton, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 7308–7313. (b) Marinelli, W. J.; Morton, T. H. *Ibid.* **1978**, *100*, 3536–3539; **1979**, *101*, 1908. (c) Morton, T. H. *Radiat. Phys. Chem.* **1982**, *20*, 29–40. (d) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243.

In previously reported examples, fluoride abstraction has been the only thermochemically accessible pathway for the experimentally observed production of R'^+ from the reactants shown in reaction 1. In these cases, mass spectrometric experiments have provided sufficient evidence for inferring the identity of the neutral product as RF. In closely related cases, however, studying the ionic products alone cannot prove that fluoride abstraction takes place. For example, the experimental observation of reaction 2 admits of two interpretations. From the heats of formation of

$$CH_3(CX_3)_2CF \xrightarrow[\text{impact}]{\text{electron}} CH_3\overset{+}{C}FCX_3 + (CX_3)_2\overset{+}{C}F \xrightarrow{CH_3(CX_3)_2CF} CH_3(CX_3)_2C^+$$

| 1. X = H | 3. X = H | 6. X = H |
| 2. X = D | 4. X = D   5. X = D | 7. X = D   (2) |

ΔH_f° −74 kcal/mol   138 kcal/mol   166 kcal/mol

the reactants and the ionic product,[4–6] thermochemical estimates predict that there are two possible exothermic pathways, fluoride abstraction or proton transfer. The first alternative would yield 2,2-difluoropropane ($\Delta H_f^{\circ} = -130$ kcal/mol[6]). The second alternative would produce hydrogen fluoride ($\Delta H_f^{\circ} = -65$ kcal/mol[7]) plus 2-fluoropropene ($\Delta H_f^{\circ} \approx -40$ kcal/mol[8]).

Electron impact on *tert*-butyl fluoride (**1**) forms ion **3** as the predominant ionization fragment (more than half of the total ionization at 70 eV).[9] The ion–molecule reaction of **3** with its parent neutral produce *tert*-butyl cation **6** with a rate constant of 4.4×10^{-10} cm^3 molecule^{-1} s^{-1}.[10] The ion chemistry gives no clue as to whether **3** abstracts fluoride ($\Delta H^{\circ} = -28$ kcal/mol) or undergoes proton transfer as represented by reaction 3 ($\Delta H^{\circ} \approx -3$ kcal/mol). Examination of the deuterium-substituted

$$(CH_3)_3C{-}F \quad H{-}CH_2\overset{|}{\underset{CH_3}{C}}{=}F^+ \longrightarrow (CH_3)_3C^+ + HF + CH_2{=}CFCH_3 \qquad (3)$$
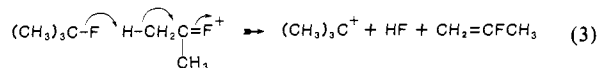
compound **2** using Fourier transform mass spectrometry (FTMS)[11] shows that only ion **7** is formed by the ion–molecule reaction,[12] but this result is consistent with either pathway.

The only way to distinguish which pathway is operating is to analyze the neutral products. We have collected these using our EBFlow reactor and have examined the major products using NMR. General operating characteristics of the EBFlow reactor have been presented elsewhere.[3] Variation of sample pressure in the EBFlow reaction vessel allows us to ascertain which products arise from homogeneous gas-phase ion–molecule reactions, as distinct from non-ionic or heterogeneous reactions. At low pressures, ion–molecule reaction products ought to be recovered

(4) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, in press.
(5) Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5714–5718.
(6) Williamson, A. D.; LeBreton, P. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 2705–2709. An independent estimate of the heat of formation of **3**, using the equivalent cores approximation (Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 536–539) and ESCA data, gives $\Delta H_f^{\circ} = 139$ kcal/mol, based on the proton affinity of fluoroethylene (Ridge, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 5670–5674) and the O_{1s} ionization energies of acetaldehyde and acetone (Mills, B. E.; Martin, R. L.; Shirley, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 2380–2385).
(7) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976.
(8) Based on Whangbo et al.: Whangbo, W.-H.; Mitchell, D. J.; Wolfe, S. *J. Am. Chem. Soc.* **1978**, *100*, 3698–3706 and ref 7.
(9) Heller, S. R.; Milne, G. W. A. "EPA/NIH Mass Spectral Data Base"; National Bureau of Standards: Washington, 1978; Vol. I., NSRDS-NBS 63, p 26.
(10) Park, J. Y.; Beauchamp, J. L., unpublished results.
(11) (a) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A. (b) Johlman, C. L.; White, R. L.; Wilkins, C. L. *Mass Spectrom. Rev.* **1983**, *2*, 389–415.
(12) Compound **2** was prepared from reaction of (diethylamino)sulfur trifluoride (DAST) with the corresponding alcohol, which was prepared by reaction of acetone-d_6 with methylmagnesium iodide. A sulfur dioxide impurity from workup of the DAST reaction could be easily resolved by FTMS or high-resolution mass spectrometry. In the 282-MHz ^{19}F NMR of neutral products from EBFlow radiolysis of **2**, compounds **8** and **9** appear as a broadened quartet and a broadened singlet separated by 0.4 ppm.