of Li interaction energies in the first row of the periodic table ($NH_3 > H_2O > HF$). However, this picture leads one to expect strong H···NH_3, H···OH_2, and H···FH interactions as well, and Lathan et al.[14] found that these interactions did not lead to bound species (at the SCF level). The H···NH_3 is isoelectronic with the Li···NH_3 so one must surmise that the key difference is the much greater polarizability of Li. The electrostatic potential at 2 Å from the atom is significantly more positive for Li than H, so electrostatic effects may play an important role as well.[15]

If charge transfer were of dominant importance in stabilizing these complexes, one might expect the F atom, which has a greater electron affinity than the alkali metals, to have a larger interaction energy with NH_3 than does Li. As shown in Table I, the F···NH_3 complex (^{2}A) is weakly bound and the ^{2}E complex not bound at all. This is consistent with the directionality of the electrostatic potential in $^2\Sigma$ and $^2\Pi$ F atom, with a single electron in either the p_z (σ) or $p_{x,y}$ (π) orbitals. An interaction of the type H_3N: ·F: (^{2}A) is favorable, because the nitrogen is approaching an "electropositive side" of the fluorine. The interaction H_3N: :F: (^{2}E) is repulsive because the "negative end" of NH_3 is approaching the "negative side" of F.[16]

Further studies are in progress on these complexes, specifically Morokuma component analysis[17] and configuration interaction calculations. The latter are of considerable interest, since the dispersion energy, which depends on the polarizabilities of the atom and hydride, is likely to be much larger in this case than that for $(H_2O)_2$ (1 kcal/mol).[18]

We thus expect that our SCF calculated interaction energies may be somewhat less than the actual ΔE's of complex formation. On the basis of the calculated dipole moments and interaction energies in Table I, molecular beam studies of a radical atom···dipolar molecule interactions would be of considerable interest.

Acknowledgment. Supported by the National Science Foundation (Grants GP-39317, GP-41509X, and CHE-7681718), the University of California Committee on Research, and the National Institute of General Medical Sciences (GM-20564 and GM-70718).

References and Notes

(1) G. H. F. Diercksen and W. P. Kraemer, *Theor. Chim. Acta*, **23**, 387, 393 (1972); P. Schuster and H. Preuss, *Chem. Phys. Lett.*, **11**, 35 (1971); P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **94**, 9236 (1972).
(2) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **59**, 5842 (1973).
(3) G. H. F. Diercksen, W. P. Kraemer, and B. O. Roos, *Theor. Chim. Acta*, **36**, 249 (1975).
(4) P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **96**, 4766 (1974); H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **61**, 799 (1974).
(5) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1954.
(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(7) V. A. Nicely and J. L. Dye, *J. Chem. Phys.*, **52**, 4795 (1970).
(8) For H, we used a 4s Gaussian set contracted to 2 functions (4/2), for Li, we used 9s and 4p contracted to 4s and 2p (9s5p/4s2p); for Na we used (11s7p/7s4p), for O, N, and F, we used (9s5p/4s2p) with a single d function (exponent 0.8); for P, S, and Cl, we used (12s8p/6s4p) with a single d function (exponent 0.6). The total energies and geometries for the atoms and molecules considered here are Li (E_T = −7.431 22), Na (E_T = −161.838 28); F (E_T = −99.373 11), HF (E_T = −100.039 68, R(FH) = 0.905 Å); H_2O (E_T = −76.035 24, R(OH) = 0.957 Å, θ(HOH) = 106.2°); H_3N (E_T = −56.199 09, R(NH) = 1.004 Å, θ(HNH) = 107.5°); HCl (E_T = −459.548 75, R(ClH) = 1.275 Å); H_2S (E_T = −398.663 63, R(SH) = 1.328 Å, θ(HSH) = 92.2°); H_3P (E_T = −342.445 29, R (PH) = 1.421 Å, θ(HPH) = 93.3°). For HF, H_2O, and NH_3, the above are energy optimized geometries, whereas for HCl, H_2S, and H_3P, experimental geometries were used. For details about the basis set and method of contraction of the Gaussian functions, see T. H. Dunning and P. J. Hay in "Modern Theoretical Chemistry", Vol. 2, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., (1977). For Li···FH, Li···OH_2, and Li···NH_3, the internal hydride geometry was geometry reoptimized at the minimum energy Li···B distance. The internal distances were changed by less than 0.01 Å and the angle changes less than 2° upon complex formation. The dipole moments (in debyes) calculated for the monomers were, for H_3N, H_2O, HF, H_3P, H_2S, and HCl: 1.918, 2.241, 2.092, 0.755, 1.379, and 1.462, respectively.
(9) P. Kollman, J. McKelvey, S. Rothenberg, and A. Johansson, *J. Am. Chem. Soc.*, **97**, 955 (1975).
(10) P. Kollman, *J. Am. Chem. Soc.*, **94**, 1872 (1971).
(11) G. E. Chamberlain and Z. C. Zorn, *Phys. Rev.*, **129**, 677 (1963).
(12) P. Kollman, *J. Am. Chem. Soc.*, in press.
(13) See P. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 283 (1972), for a comparison of Mulliken population and exact charge density difference plots for studying intermolecular interactions.
(14) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
(15) By electrostatic effects for a neutral atom, we mean "penetration effects", since all the multipole moments of the change distribution vanish. We have pointed out[12] that the electrostatic pontential at 2 Å from Li is +0.034 au ("double zeta" basis); at 2 Å from H, the electrostatic potential is +0.005 au.
(16) The results are consistent with the potential surfaces reported by Noble and Kortzeborn for F atom interacting with HF. The $^2\Pi$ state of F···H–F was bound by ~2 kcal/mol; the $^2\Sigma$ state of F···H–F was repulsive. This is consistent with the fact that in this case F is acting as the electron donor and can do so effectively only if its "negative side" points toward the HF molecule.
(17) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).
(18) G. H. F. Diercksen, W. von Niessen, and B. Roos, *Theor. Chim. Acta*, **36**, 249 (1975), and O. Matsuoka, E. Clementi, and Y. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976).

Michael Trenary, Henry F. Schaefer III*
Department of Chemistry, University of California
Berkeley, California 94720

Peter Kollman*
Department of Pharmaceutical Chemistry
School of Pharmacy, University of California
San Francisco, California, 94143
Received December 13, 1976

A Direct Measurement of Dynamic Spin-Interconversion Rates in the Spin-Equilibrium Protein Ferric Myoglobin Hydroxide

Sir:

Various hemeproteins including cytochrome P-450,[1-8] catalase,[9] myoglobin, and hemoglobin,[10,11] have been reported to possess an electronic structure for Fe(III) in which two electronic states of differing spin multiplicity are in thermal equilibrium (a spin-equilibrium)[12] with one another. The question arises as to the existence and role of this unusual electronic structure for in vivo biological functions of these proteins and especially as to the nature of this involvement in electron transfer/storage activity. For an idealized Fe(III) heme center of O_h symmetry, the spin-equilibrium is between a low-spin ^{2}T(S = ½) state and a high-spin ^{6}A(S = 5/2) state,

$$^2\mathrm{T}(S = {}^1/_2) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^6\mathrm{A}(S = {}^5/_2) \qquad (1)$$

In this work we wish to report on the dynamics of this spin-equilibrium process in which the spin-interconversion rates, k_1 and k_{-1}, have been directly measured in solution for horse ferric myoglobin hydroxide using laser stimulated Raman temperature-jump kinetics.[13] The interpretation of the anomalous magnetic properties of ferric myoglobin hydroxide as arising from a thermal equilibrium between an S = ½ low-spin and S = 5/2 high-spin electronic state has been extensively documented in solution by the reversible temperature dependence of its electronic spectrum,[10,14] variable-temperature magnetic susceptibility data[11] (reproduced satisfactorily in our laboratory) and by its EPR spectrum[15] (see also ref 25). Beattie and West, using conventional capacitive discharge T-jump,[14] have previously established a *lower* limit of 2×10^5 s^{-1} for the sum of the forward (k_1) and reverse (k_{-1}) rate constants for the spin change of the protein, while EPR studies have been used to estimate an *upper* limit for k of 10^{10} s^{-1}.[15] Furthermore, Beattie and West's correlation of the visible

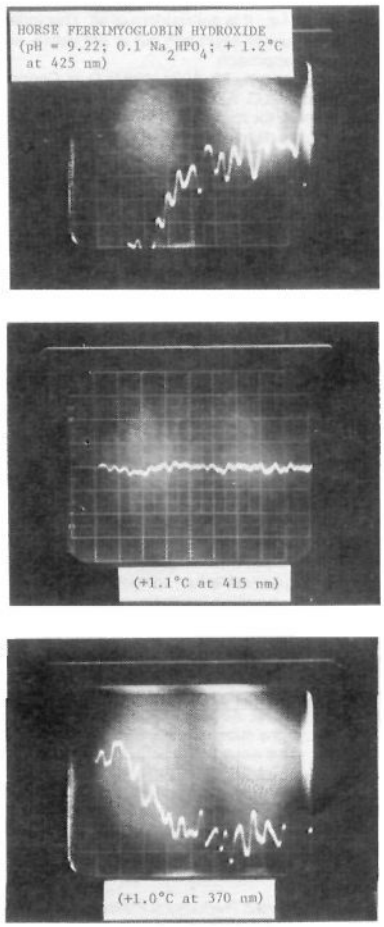

Figure 1. Intensity vs. time (ns) spin relaxation traces for horse ferric myoglobin hydroxide monitored at 425 nm (low-spin band), 415 nm (isosbestic point), and 370 nm (high-spin band); each horizontal scale division is 20 ns; [FeMb] $\sim 10^{-3}$ M.

difference spectrum (480–650 nm) with the relative amplitudes of wavelength-dependent relaxation experiments provides strong evidence that the "immeasurably" fast relaxation process observed in their T-jump experiment is indeed derived from a spin state population change; similar variable-temperature spectral behavior is also observed in the Soret band spectral region, with a characteristically high-spin band occurring at 370 nm and a low-spin band at 425 nm.

Horse ferric myoglobin was obtained from Sigma Chemical Co. and the phosphate buffer, NaH_2PO_4, was recrystallized from distilled water prior to use. The sample was prepared by dissolving the ferric myoglobin in triply distilled water to about 1.2×10^{-3} M and then immediately adding NaH_2PO_4 to 0.1 M with gentle agitation until all material was dissolved. The solution was degassed gently with bubbling argon and sufficient 1 M NaOH was added to bring the solution to pH 9.22 ± 0.01 (>55% hydroxide form). In order to prevent excessive "cavitation" by the intense laser pulse, the sample was gently degassed under vacuum and then cooled to 1 °C in the sample chamber to minimize both thermal decomposition and the overall solution density change caused by the estimated 2–3° temperature-jump.

The laser Raman temperature-jump apparatus used in the experiment has been previously described.[13] The 1.41 μ Nd-laser pulse is well defined and delivers about 2 J in about 25 ns to the sample. The relaxation of the sample transmittance signal in the Soret region (360–420 nm) was found to be stronger than that in the visible for our apparatus and sample concentration. Figure 1 shows the three relaxation spectra obtained at 370 nm (high-spin band), 415 nm (isosbestic point), and 425 nm (low-spin band) where it is easily seen that the nature of the observed relaxation is dependent upon the monitoring wavelength only in sign and amplitude. Furthermore, the 425 and 370 nm traces appear typical of a first-order exponential time dependent process, as expected for a simple low-spin $\rightleftarrows$ high-spin interconversion. Some wavelength-independent phenomena were, however, observed to begin about 2 μs after the laser pulse, or well after the spin-state related phenomena were completed. These delayed baseline fluctuations were reproduced almost exactly by a 1 °C sample of degassed 10^{-3} M phosphate buffer and increased steadily with increasing temperature, allowing its assignment to cavitation effects. After more than 25 laser pulses, the UV–VIS spectrum of the sample was unchanged, demonstrating a lack of sample decomposition under the conditions of the experiment.

The oscilloscope traces obtained in Figure 1 indicate an apparent relaxation time of the order of the laser pulse heating time of about 25 ns. However, in comparison with traces for the very fast relaxation process for the

$$4Na^+ + [Fe(CN)_6]^{4-} \rightleftarrows 3Na^+ + [Fe(CN)_6 \cdot Na]^{3-} \quad (2)$$

reaction for which the relaxation time is believed to be less than 1 ns at 0.34 M,[16] the myoglobin traces appeared to be longer than the response time of the apparatus. The "true" relaxation time was therefore determined by using a method of moments integral deconvolution procedure.[17] A similar approach is frequently employed in the deconvolution of luminescence lifetimes data for fast decay processes induced by relatively slow excitation sources.[18] Because the trigger-to-laser pulse time was not found to be constant, the "second" method was selected: $\tau = (\sigma_D^2 - \sigma_S^2)^{1/2}$. The function σ_D^2 of the relaxation trace derivatives is equal to

$$\frac{^2D}{^0D} - \left[\frac{^1D}{^0D}\right]^2 \quad (3)$$

where

$$^nD = \int_{-\infty}^{\infty} (\text{trace derivative}) \cdot t^n \, dt \quad (4)$$

a form analogous to the estimated variance of a continuous distribution from its mean. It is easily verified that σ_D^2 is independent of the absolute scale imposed on the transmittance values. The value of σ_S^2 includes all the contributions from the ferricyanide relaxation phenomenon, the laser pulse heating time, and the response time of the instrument.[18] The sum, σ_S^2, was calculated from the ferricyanide trace derivatives to be 29.3 ns^2. Thus, by subtracting these contributions from the σ_D^2 values calculated from the derivatives of the individual relaxation traces, values of the myoglobin hydroxide spin relaxation time were obtained for each trace. Of the 12 relaxation traces recorded at (1.0 ± 0.5) °C and at wavelengths of 370–425 nm, four were rejected by visual inspection prior to analysis as clearly indicating spurious, nonrandom noise over otherwise well-defined traces (these four traces yielded a mean calculated relaxation time of (26 ± 3) ns). The eight remaining traces yielded an average τ *of 14.9 ns* with the range of values for individual traces being 12–18 ns. From this relaxation time, k_1 and k_{-1} for the $^2T \rightleftarrows {}^6A$ process of the protein can be determined by solving the simultaneous equations

$$\tau^{-1} = k_1 + k_{-1} \quad (5)$$

$$K_{eq} = k_1/k_{-1} \quad (6)$$

where $K_{eq} = [^6A]/[^2T] = 1.42$ at 1 °C for ferric myoglobin hydroxide.[19] The values of k_1 and k_{-1} are thus 3.9×10^7 and 2.8×10^7 s^{-1}, respectively.

Spin-interconversion rate constants $>10^7$ s^{-1} for this Fe(III)

protein are among the fastest yet measured for any six-coordinate spin-equilibrium compound, the rest of which are all synthetic in nature with spin-interconversion rate constants ranging from $\sim 5 \times 10^5$ to 1.5×10^7 s^{-1}.[20-24] It is likely, however, that there are other systems such as the $[Fe^{III}(dtc)_3]$, $[Fe^{III}(benzac)_2trien]^+$, $[Fe^{III}(salmeen)_2]^+$, and $[Co^{II}(terpy)_2]^{2+}$ complexes[25] for which the spin-interconversion rates are as fast or perhaps faster than for the present ferric myoglobin hydroxide case. Thus, the low-spin $\rightleftarrows$ high-spin dynamics of this spin-equilibrium heme center in a protein environment does not seem particularly distinguished from those operative in simple inorganic compounds. It is clear, however, that with k's $> 10^7$ s^{-1} *intra*molecular spin multiplicity changes are not expected to be rate determining in *inter*molecular (second order) electron transfer reactions in which spin-equilibrium enzyme centers might participate.

Finally, it should be noted that ferric myoglobin hydroxide must undergo a stereochemical change upon a change in spin multiplicity. Assuming that the coordination number about Fe(III) remains six[26] (four porphyrin N's, the proximal histidine N and the OH^- oxygen) during the low-spin $\rightleftarrows$ high-spin-interconversion process, the high-spin form is expected to have the iron atom displaced out of the porphyrin plane (toward the histidine moiety) by $\lesssim 0.5$ Å relative to the in-plane low-spin form.[27] Thus, if the rate determining step in the spin conversion process is this geometry change, the rather large k_1 and k_{-1} rate constants reflect a facile (in-plane) $\leftrightarrow$ (out-of-plane) movement of the iron atom. Future studies will focus on obtaining k_1 and k_{-1} spin-interconversion rate constant data for synthetic spin-equilibrium porphyrin compounds to establish the influence (if any) of the protein environment on the spin-interconversion kinetics.

Acknowledgment. Support of this work by The Robert A. Welch Foundation and the Energy Research and Development Administration is gratefully acknowledged. E.V.D. wishes to especially thank ERDA for a summer fellowship and travel grant (Grant T-179) to the Brookhaven National Laboratory as administered under the auspices of the Associated Universities Program. We also thank Dr. Mitchell Hoselton for assistance with the laser T-jump apparatus and Professor John Olsen for the myoglobin sample.

References and Notes

(1) M. Sharrock, E. Munch, P. G. Debrunner, V. Marshall, J. D. Lipscomb, and I. C. Gunsalus, *Biochemistry*, **12**, 258 (1973).
(2) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 913 (1975).
(3) J. P. Collman and T. N. Sorrell, *J. Am. Chem. Soc.*, **97**, 4133 (1975).
(4) C. K. Chang and D. Dolphin, *J. Am. Chem. Soc.*, **97**, 5948 (1975).
(5) C. K. Chang and D. Dolphin, *J. Am. Chem. Soc.*, **98**, 1607 (1976).
(6) J. H. Dawson, R. H. Holm, J. R. Trudell, G. Barth, R. E. Linder, E. Bunnenberg, C. Djevassi, and S. C. Tang, *J. Am. Chem. Soc.*, **98**, 3707 (1976).
(7) J. H. Dawson, J. R. Trudel, G. Barth, R. E. Linder, E. Bunnenberg, C. Djevassi, R. Chiang, and L. P. Hager, *J. Am. Chem. Soc.*, **98**, 3709 (1976).
(8) S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **98**, 2412 (1976).
(9) C. D. Coryell, F. Stitt, and L. Pauling, *J. Am. Chem. Soc.*, **59**, 633 (1937).
(10) P. George, J. Beatlestone, and J. S. Griffith, "Haematin Enzymes", Vol. 19, Pergamon Press, New York, N.Y., I.U.B. Symposium Series, 1961, pp 105-141.
(11) I. Morishima and T. Iizuka, *J. Am. Chem. Soc.*, **96**, 5270 (1974).
(12) See for example: R. L. Martin and A. H. White, *Transition Met. Chem.*, **4**, 113 (1968); E. K. Barefield, D. H. Busch, and S. M. Nelson, *Q. Rev. (Chem. Soc.)*, **22**, 457 (1968).
(13) D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Am. Chem. Soc.*, **94**, 1554 (1972).
(14) J. K. Beattie and R. J. West, *J. Am. Chem. Soc.*, **96**, 1933 (1974).
(15) A. Ehrenberg, *Ark. Kemi*, **19**, 119 (1962).
(16) D. H. Turner, Ph.D. Thesis, Columbia University, New York, N.Y., 1972.
(17) While a deconvolution least-squares approach for obtaining τ is probably better in the general case, it has not been employed here for two reasons. First, although the least-squares approach has proven successful in our hands for long lifetime traces, the parameters obtained for the "shorter" MbOH traces here were disappointing in their instability while converging, and frequently could not be made to converge at all. Secondly, it is suspected that for the relatively small 2-ns intervals used in the MbOH calculations the "random" error in each reading is not independent from those of adjacent readings; i.e., it is not random at all. This independence is essential for a least-squares approach but is not nearly so crucial for the method of moments approach.
(18) S. S. Brody, *Rev. Sci. Instrm.*, **28**, 1021 (1957); D. H. Cooper, *ibid.*, **37**, 1407 (1966); J. N. Demas and G. A. Crosby, *Anal. Chem.*, **42**, 1010 (1970).
(19) The molar susceptibility for myoglobin in aqueous solution at pH 11.0 (88% hydroxide form) has been measured to be $\chi_M = 10\,780 \times 10^{-6}$ cgsu and that for a solution at pH 6.5 (7% hydroxide form) $\chi_M = 14\,180 \times 10^{-6}$ cgsu at 1.7 °C (J. Beetlestone and P. George, *Biochemistry*, **3**, 707 (1964)). Extrapolation to 100% hydroxide form yields $\chi_M = 10\,260 \times 10^{-6}$ cgsu, corresponding to $\mu = 4.75$ μ_B. Assuming low-spin and high-spin limits of 2.20 and 5.92 μ_B (as for myoglobin CN^- and myoglobin F^-, respectively), myoglobin hydroxide is calculated to possess an equilibrium constant ($K_{eq} = [hs]/[ls] = (\mu^2 - \mu_{ls}^2)/(\mu_{hs}^2 - \mu^2)$) of 1.42 at 1.7 °C.
(20) J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *J. Am. Chem. Soc.*, **95**, 2052 (1973).
(21) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).
(22) M. A. Hoselton, R. S. Drago, L. J. Wilson, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6967 (1976).
(23) E. V. Dose, K. M. M. Murphy, and L. J. Wilson, *Inorg. Chem.*, **15**, 2622 (1976).
(24) M. G. Simmons and L. J. Wilson, *Inorg. Chem.*, **16**, 126 (1977).
(25) And as discussed in ref 22 and 23.
(26) It has usually been assumed that Fe(III) porphyrin complexes must undergo a coordination number change of six $\rightarrow$ five upon low-spin $\rightarrow$ high-spin conversion (for example, see ref 14). This is *not* a necessary requirement in the present case, since the ferric myoglobin fluoride and cyanide compounds are apparently both six-coordinate, and yet, high-spin and low spin, respectively. It, therefore, seems reasonable that ferric myoglobin hydroxide is a $^2T \rightleftarrows {}^6A$ spin-equilibrium species which remains six-coordinate throughout the spin conversion processes. Furthermore, the azido derivative, which is also a spin-equilibrium case (P. George, J. Beetlestone, and J. S. Griffith, *Rev. Mod. Phys.*, 441 (1964); J. Beetlestone and P. George, *Biochemistry*, **3**, 707 (1964)), undergoes formation/dissociation of the sixth N_3^- ligand more slowly than the spin interconversion rates reported here (D. E. Goldsack, W. S. Eberlain, and R. A. Alberty, *J. Biol. Chem.*, **240**, 4312 (1965); **241**, 2653 (1966)). At present, however, there is insufficient evidence to show that, in the substrate-bound oxidized form of P_{450} enzymes, different spin states are associated with the same coordination number (Sharrock et al., *Biochim. Biophys. Acta*, **420**, 8 (1976)).
(27) Based on a comparison of x-ray structures for the low-spin six-coordinate species $[Fe(Im)_2(TPP)]^+$ (R. Countryman, D. M. Collins, and J. L. Hoard, *J. Am. Chem. Soc.*, **91**, 5166 (1969); **94**, 2066 (1972)), and the high-spin five-coordinate species, [Fe(Cl)(proto-IX)] (J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967)), where Δ(Fe-porphyrin plane) ~ 0.46 Å.
(28) Robert A. Welch Foundation Predoctoral Fellow and ERDA Research Fellow under the Associated Universities Program (summer 1976).
(29) Robert A. Welch Foundation Predoctoral Fellow.

Eric V. Dose,[28] Michael F. Tweedle,[29] Lon J. Wilson*
Department of Chemistry, William Marsh Rice University Houston, Texas 77001

Norman Sutin*
The Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York 11973
Received December 14, 1976

Organic Reactions of Oxide-Free Carbon Surfaces, an Electroactive Derivative[14]

Sir:

In the absence of the usual oxides, surfaces of graphite and related forms of carbon are quite reactive. For example, at room temperature a highly exothermic reaction occurs with molecular oxygen to regenerate surface oxides.[1,2] This chemistry is known to occur exclusively in prismatic regions, that is, surfaces other than the basal plane, {0001}.[3] Although the structure of the reactive centers is unknown, those represented by I, II, and III seemed to us more likely on thermodynamic grounds than the various alternative possibilities. By analogy with structurally similar molecules, these surface functions might be expected to undergo cycloaddition reactions with olefinic substrates. Preliminary evidence presented below tends to support this description.

Synthetic carbon fiber was freed of surface oxides by pyrolysis at 1020 °C in a vacuum system (10^{-5} Torr).[4] Samples were allowed to cool to room temperature and were then exposed to vapors of a variety of potential substrates. The total quantity of substrate adsorbed was determined manometrically