(δF −107.25 (m, 1F), −111.75 (m, 2F), −129.4 (m, 3F)) and in its ^{1}H spectrum a singlet at 6.1 ppm. Its mass spectrum shows the following major fragments: 288 (M$^+$, 88%), 237 (40), 219 (26), 120 (26), 102 (100). If we now examine the differences in mass spectra of products **4d** and **5d**, we observe that the fragment *m/e* 102 (corresponding to phenylacetylene species) occurs as the major peak for **4d**, while on the other hand, the fragment *m/e* 120 (corresponding to the phenylfluoroacetylene species) is more intense in the case of **5d**. Chemical shifts for fluorine atoms for **5d** are also very similar to those observed for **5a** (formed by heating of **3a**), while $J_{\mathrm{F-H}}$ (24 Hz) for **5d** is characteristic of cis olefinic coupling constants.[6] On the basis of the above mentioned differences in mass fragments and NMR data, we have established that product **4d** is 1-phenyl-3,4,5,6,7,8-hexafluorocyclooctatetraene, formed in a cyclobutene ring opening reaction of the primarily formed product **3d** (which was not detected in the case of R = H), while product **5d** was found to be a bond shifted isomer of **3d**. The product **5a** is also a bond-shifted isomer of the primarily formed cyclooctatetraene **4a** (which was not detected by heating of **3a**). On heating (T = 150 °C), product **4d** was transformed into product **5d**.

The photoaddition of **1a** was completely quenched by piperylene and resulted in a complex mixture of piperylenehexafluorobenzene products. The reaction with diphenyl and diethoxycarbonylacetylene is very slow under the above mentioned conditions.

References and Notes

(1) W. Hartman, H. G. Heine, and L. Schrader, *Tetrahedron Lett.*, 3101 (1974); D. Bryce-Smith, R. R. Deshpande, and A. Gilbert, *ibid.*, 1627 (1975); J. Berridge, D. Bryce-Smith, and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, 964 (1974); H. G. Heine and W. Hartman, *Angew. Chem.*, **87**, 708 (1975); D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **32**, 1309 (1976).

(2) L. A. Paquette, *Tetrahedron*, **31**, 2855 (1975).

(3) B. Šket and M. Zupan, *J. Chem. Soc., Chem. Commun.*, 1053 (1976).

(4) I. Leban and L. Golič, unpublished observation.

(5) R. Fields, *Annu. Rep. NMR Spectrosc.*, **5A**, 99 (1972).

(6) R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).

Boris Šket, Marko Zupan*

Department of Chemistry and "J. Stefan" Institute
University of Ljubljana
61001 Ljubljana, Yugoslavia

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Theoretical Studies of the Oxidized and Reduced States of a Model for the Active Site of Rubredoxin

Sir:

Although non-heme iron–sulfur proteins are ubiquitous among living systems, their role in biological processes is understood in only a few systems and even in these cases the details of the electron transfer and chemical processes they promote have not been elucidated.[1-5] The physical propertes are best understood for rubredoxin (Rd, hereafter), plant ferredoxin (Fd, hereafter), bacterial ferredoxin, and high potential iron–sulfur protein containing one, two, four, and eight irons, respectively, with each iron tetrahedrally coordinated to four sulfurs, and contained in clusters of one, two, or four irons.[1-4] In this initial study we use ab initio quality theoretical methods to examine the electronic properties of the active site of oxidized and reduced Rd for several geometries.

To model the active site of Rd, we have replaced the four cysteine ligands of the Fe with (SH)$^-$ groups. The Fe–S bond length was set to the average distance of 2.21 Å from the crystal structure studies[6] (more recent results[7] do not confirm the large inequalities of the Fe–S bond lengths of the early structural work[6]) and the sulfur atoms placed tetrahedrally. The S–H bond distance was fixed at 1.33 Å (as in SH$_2$) and the H–S–Fe angle was chosen as the average value 107° of the C(β)–S–Fe angle from the crystal structure studies[6] (except for geometry A where the angle was taken as 92.2°). The spectrum of low excited states was examined for three different sets of S–Fe–S–H dihedral angles, as indicated in Figure 1. Geometry C most closely models the experimentally determined structure (oxidized Rd, we also find a lowest energy for this geometry).

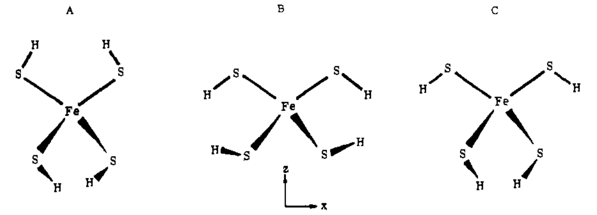

Figure 1. Geometries of Fe(SH)$_4$ model complexes.

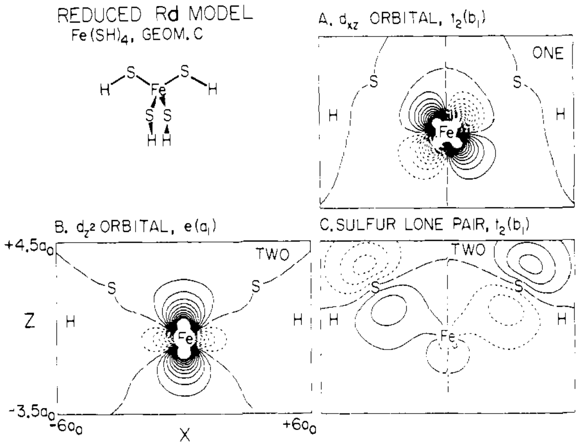

Figure 2. Amplitudes for the d orbitals for the quintet ground state of the reduced model, Fe(SH)$_4{}^{2-}$. Long dashes indicate zero amplitude, solid and dotted lines indicate positive and negative amplitude (separation of adjacent contours is 0.05 au). In this state four d orbitals are singly occupied while the d_{z^2} orbital is doubly occupied.

We carried out Hartree–Fock (HF)[8] calculations on a number of excited states as discussed below. The calculations are ab initio except that the argon core of the Fe atom[9] and the Ne core of each S atom[10] were replaced with ab initio effective potentials. This allows ab initio quality calculations using an extensive "double zeta" basis set.[11]

The oxidized complex may be considered as Fe$^{\mathrm{III}}$(SH$^-$)$_4$ or [Fe(SH)$_4$]$^-$ and the reduced state as Fe$^{\mathrm{II}}$(SH$^-$)$_4$ or [Fe(SH)$_4$]$^{2-}$. However, no restrictions were made on the shape or localization of the various orbitals; they were solved self-consistently for numerous states of both the oxidized and reduced forms.

In oxidized Rd, the Fe can be thought of as ferric d^5 and hence can lead to either high spin (S = $\frac{5}{2}$ or sextet), intermediate spin (S = $\frac{3}{2}$ or quartet), or low spin (S = $\frac{1}{2}$ or doublet). Magnetic susceptibility results[12] clearly indicate an S = $\frac{5}{2}$ ground state which is also consistent with ESR[13] and Mössbauer[14] experimental results. We considered the lower states of each spin and found (see Table I) that the ground state is clearly high spin with the lowest quartet state higher by over 1.5 eV and the lowest doublet state higher by over 3 eV. This result confirms experimental observation and indicates our methods are accurate enough to predict ground state spins.

A d^5 configuration leads to only one sextet state and consequently the lower excited states are found to result from spin-forbidden (sextet to quartet) d–d transitions, as indicated in Table I. In oxidized Rd, the charge transfer bands are found to start at ~2.2 eV;[15] however, there is a weak band observed at 1.66 eV[16] which, on the basis of these calculations, could be

Table I. Excited States of $Fe(SH)_4$ (energies in eV). A, B, and C Indicate the Geometries (See Figure 1 for coordinate system)

	Configuration[a]					Calculated						
	z^2	xy	x^2-y^2	xz	yz	A		B		C		Exptl[b]
Oxidized	1	1	1	1	1	$^6A_1$	0^c	$^6A_1$	0^c	$^6A_1$	0^c	0
	2	1	1	1	0	^4E	1.76	^4E	1.87^e	$^4B_2$	1.72	1.66
	2	1	0	1	1			$^4B_2$	1.61			
	1	2	1	1	0	^4E	2.06	^4E	2.21			
	1	1	2	1	0	^4E	2.25	^4E	2.48			
	2	2	1	0	0	$^2B_2$	3.06					
Reduced	2	1	1	1	1	$^5A_1$	0^d	$^5A_1$	0^d	$^5A_1$	0^d	0
	1	2	1	1	1	$^5B_1$	0.39	$^5B_1$	0.42	$^5A_2$	0.37	
	1	1	2	1	1	$^5B_2$	0.59	$^5B_2$	0.70	$^5A_1$	0.52	≤ 0.50
	1	1	1	2	1	^5E	0.72	^5E	0.75	$^5B_1$	0.72	0.68–0.87
	1	1	1	1	2	^5E	0.72	^5E	0.75	$^5B_2$	0.80	
	2	2	1	1	0	^3E	2.56					
	2	2	2	0	0	$^1A_1$	4.70					

[a] With our coordinate system, z^2 and xy are e_g-type d orbitals while x^2-y^2, xz, and yz are t_{2g} type. [b] Eaton et al., ref 16. [c] Total energies for the $^6A_1$ state are −65.2598, −65.2637, and −65.2706 h for geometries A, B, and C, respectively. [d] Total energies for the $^5A_1$ state are −65.2461, −65.2579, and −65.2554 h for geometries A, B, and C, respectively. [e] ORD and CD spectra suggest the presence of a band at 1.91 eV: D. J. Newman and J. R. Postgate, *Eur. J. Biochem.*, **7**, 45 (1968).

a spin-forbidden d–d transition (calculated at 1.72 eV, for geometry C). This band has been previously assigned as a $^4T_1 \leftarrow {}^6A_1$ d–d transition by Rawlings et al.[17]

In reduced Rd, the Fe can be thought of as ferrous d^6, and again magnetic susceptibility experiments clearly indicate a high spin ($S = 2$ or quintet) ground state, rather than intermediate spin ($S = 1$ or triplet) or low spin ($S = 0$ or singlet). We find that the ground state is high spin with the lowest triplet and singlet states over 2 and 4 eV higher, respectively. Again, this result is in agreement with experimental observation.

The self-consistent d orbitals of the quintet ground state (geometry C) are shown in Figure 2. Note here that for our coordinate system the tetrahedral e orbitals are d_{z^2} and d_{xy} (not d_{z^2} and $d_{x^2-y^2}$) while the t_2 orbitals are d_{xz}, d_{yz}, and $d_{x^2-y^2}$ (not d_{xz}, d_{yz}, and d_{xy}). On each $(SH)^-$ group there is a lone pair perpendicular to the H–S–Fe plane. There is a second lone pair and an S–H bond pair in this plane. These pairs have different effects upon the Fe orbitals, leading to a symmetry lower than T_d.

There are five low-lying quintet d^6 states. In T_d symmetry this would lead to ^5E and $^5T_2$ states. We find that even with four S in T_d symmetry the orientations of the four S–H bonds cause significant splitting, leading to ^5E-like states at 0.0 and 0.37 eV and $^5T_2$-like states at 0.52, 0.72, and 0.80 eV (geometry C). Thus we find dipole-allowed d–d transitions at 0.52, 0.72, and 0.80 eV, in excellent agreement with the spectroscopic studies of Eaton and co-workers[16] who find one electronic transition with a peak at <0.50 eV and another broad transition at 0.68–0.87 eV, both with circular dichroism consistent with d–d transitions. We find no other spin-allowed d–d transitions and no spin-forbidden transitions below the energy (2.2 eV) expected for charge transfer transitions; this is consistent with the experimental results.[14]

Averaging appropriate subcomponents leads to a ^5E–$^5T_2$ splitting of $10Dq = 0.50$ eV $= 4030$ cm^{-1}. This is a bit less than the value of 4400 cm^{-1} observed for tetrahedral aquo ferrous iron complexes,[18a] as would be expected for sulfur ligands.[18b]

The sulfur lone pairs interact sufficiently with the iron d_{xz} and d_{yz} orbitals to cause the states with two electrons in either of these d orbitals to be highest. A comparison of the reduced states of all three geometries shows that the energy separation of the d–d transitions is sensitive to the dihedral angle of the S–H bond. The position of the S–H bond pair strongly influences the orientation of the S lone pair pointing toward the Fe, which in turn directly influences the energies of the Fe d_{xz} and d_{yz} orbitals. This sensitivity may lead to a mechanism for protein conformation to provide control over redox potentials and related properties of the protein.[19]

Similar models of the active site of Rd have previously been calculated with the extended Hückel[20] and Xα methods.[21]

In summary, using ab initio calculations on a model of the active site of Rd, we find electronic and spectroscopic properties in excellent agreement with experiment. Thus we find unequivocally that the oxidized and reduced forms are high spin, and we obtain excellent agreement (~0.06 eV error) with experimental excitation energies.

These calculations, being ab initio, allow us to compare energies for various geometries and hence to solve for the local geometry of the oxidized and reduced active sites, even for excited states.

Similar studies should be particularly useful for the ferredoxins where one could determine the geometric distortions for various oxidized and reduced states and investigate models for the electron transfer mechanisms. Such studies are in progress.

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References and Notes

(1) G. Palmer, "The Enzymes", 3rd ed, Vol. 12, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1975, p 1.

(2) W. Lovenberg, Ed., "Iron-Sulfur Proteins", Vols. 1 and 2, Academic Press, New York, N.Y., 1973.

(3) W. H. Orme-Johnson, *Annu. Rev. Biochem.*, **42**, 159 (1973).

(4) M. Llinás, *Struct. Bonding (Berlin)*, **17**, 176 (1973).

(5) E. T. Lode and M. J. Coon, *J. Biol. Chem.*, **246**, 791 (1971).

(6) K. D. Watenpaugh, L. C. Sieker, J. R. Herriott, and L. H. Jensen, *Acta Crystallogr., Sect. B*, **29**, 943 (1973).

(7) (a) D. E. Sayers, E. A. Stern, and J. R. Herriott, *J. Chem. Phys.*, **64**, 427 (1976); R. G. Shulman, P. Eisenberger, W. E. Blumberg, and N. A. Stombaugh, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4003 (1975); (b) L. H. Jensen and K. D. Watenpaugh, private communication.

(8) Open-shell HF calculations used the method of W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., *Chem. Phys. Lett.*, **6**, 147 (1970). The calculation of molecular integrals, reprocessing for the GVB program, iteration to converged wave functions for the average high-spin reduced state, transformation to molecular integrals for the CI calculations, and the CI calculations themselves to obtain the five quintet states for the reduced model (C geometry) used 45 min of CPU time on a 360 model 91 computer. Far longer computer times were involved with the earlier geometries as we explored levels of basis, correlation, effectiveness of solving for averaged reduced states, etc.

(9) C. F. Melius, B. D. Olafson, and W. A. Goddard III, *Chem. Phys. Lett.*, **28**,

457 (1974); M. J. Sollenberger, M. S. Thesis, California Institute of Technology, 1975.
(10) R. A. Bair and W. A. Goddard III, unpublished results.
(11) A. J. Wachters, *J. Chem. Phys.*, **52**, 1033 (1970); S. Huzinaga, *ibid.*, **42**, 1293 (1965).
(12) W. D. Phillips, M. Poe, J. F. Weiher, C. C. McDonald, and W. Lovenberg, *Nature (London)*, **227**, 574 (1970).
(13) J. Peisach, W. E. Blumberg, E. T. Lode, and M. J. Coon, *J. Biol. Chem.*, **246**, 5877 (1971).
(14) K. K. Rao, M. C. W. Evans, R. Cammack, D. O. Hall, C. L. Thompson, P. J. Jackson, and C. E. Johnson, *Biochem. J.*, **129**, 1063 (1972).
(15) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970).
(16) W. A. Eaton, G. Palmer, J. A. Fee, T. Kimura, and W. Lovenberg, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 3015 (1971).
(17) J. Rawlings, O. Siiman, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 125 (1974).
(18) (a) T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory", Harper and Row, New York, N.Y., 1965, p 82; (b) C. K. Jørgensen, "Oxidation Numbers and Oxidation States", Springer, New York, N.Y., 1969, p 84.
(19) Professor J. L. Lehn has made similar suggestions, private communication.
(20) G. H. Loew and D. Y. Lo, *Theor. Chim. Acta*, **32**, 217 (1974); G. H. Loew, M. Chadwick, and D. A. Steinberg, *ibid.*, **33**, 125 (1974); G. H. Loew and D. Lo, *ibid.*, **33**, 137 (1974); G. H. Loew, M. Chadwick, and D. Lo, *ibid.*, **33**, 147 (1974).
(21) J. G. Norman, Jr., and S. C. Jackels, *J. Am. Chem. Soc.*, **97**, 3833 (1975).
(22) National Institutes of Health Trainee, 1976–1977.

Raymond A. Bair,[22] William A. Goddard III*
Contribution No. 5446, the Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

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Photochemically Induced Skeletal Rearrangement of Alkyl Substituted Indenes[1]

Sir:

Previous studies of the photochemistry of indene and alkyl substituted indenes have dealt with the sensitized dimerization of indene systems.[2] Indene itself is reported to "polymerize" upon direct irradiation, and direct irradiation of 1,1-dimethylindene gives no reported monomeric products.[2] This contrasts with 1,1-diphenylindenes which, upon irradiation, give rearrangement products resulting from phenyl migration to the indene 2 position.[2,3] We now wish to report the photorearrangement of certain alkyl substituted indenes.

A number of alkyl substituted indenes were photolyzed at 25 °C in dilute hydrocarbon (cyclohexane or *n*-hexane) solutions (ca. 10^{-2} M) in evacuated, sealed, quartz photolysis tubes. Photoproducts were isolated (preparative GLC) and identified by a comparison of spectral data (^{1}H NMR, IR) with authentic sample spectra. Quantum efficiencies of product formation (Φ_{pdl}) and loss of starting material (Φ_{dis}) were determined by analytical GLC analysis relative to the trans to cis photoisomerization of 1-phenyl-2-butene.[4] The indenes studied, their photoproducts, and measured quantum efficiencies are presented in Table I.[5]

The observed photorearrangement, as depicted with 2-ethyl-1-methylindene, is an exchange of the indene 1 and 2 carbons, with the formation of an approximately equimolar ratio of the possible indene olefin isomers. This photorearrangement is observed only for indenes substituted at the 1 and 2 positions. (The introduction of an alkyl group at the 3 position essentially quenches the rearrangement.) The presence of at least one alkyl substituent at the 1 or 2 position is required since McCullough reports that no deuterium scrambling is observed upon irradiation of 1,1,3-trideuterioindene.[2]

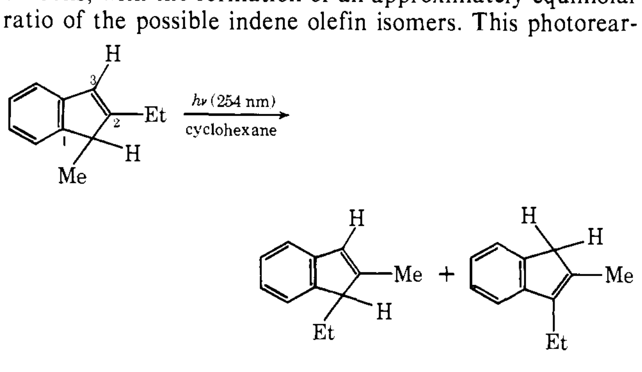
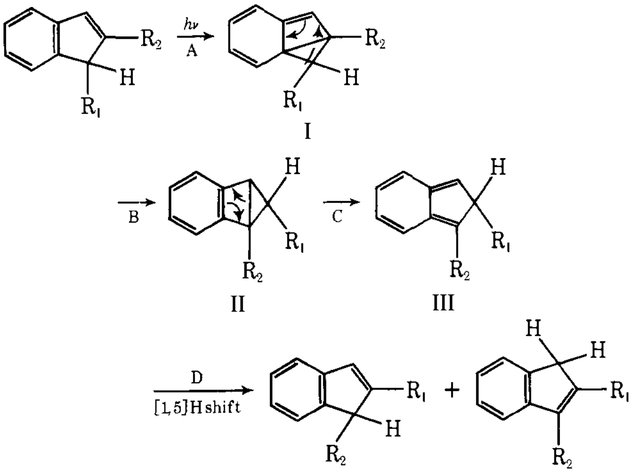


Table I. Substituted Indene Photoproducts and Quantum Efficiencies[a]

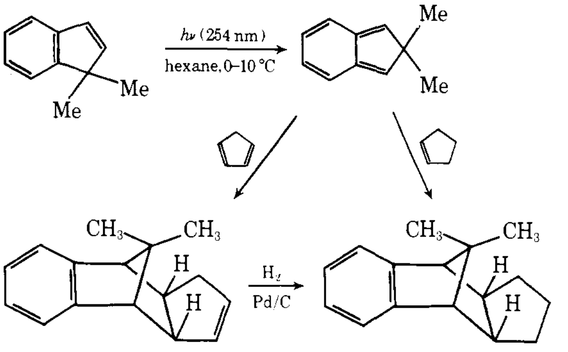
Starting material	Φ_{dis}	Photoproduct(s)	Φ_{pdt}
1-Methylindene	0.16	2-Methylindene	0.03
2-Methylindene	0.13	1-Methylindene	0.03
		3-Methylindene	0.02
3-Methylindene	0.12	None	—
1,3-Dimethylindene	—	None	—
2-Ethyl-1-methylindene	0.23	1-Ethyl-2-methylindene	0.12
		3-Ethyl-1-methylindene	0.10
1,1-Dimethylindene	—	2,2-Dimethylisoindene	—

[a] All photolyses in dilute hydrocarbon solutions, at 25 °C.

Scheme I. Proposed Rearrangement Mechanism



Irradiation of 1,1-dimethylindene gives 2,2-dimethylisoindene (2,2-dimethyl-2*H*-indene) as the sole product. Photolysis of a hexane solution (10^{-2} M) of 1,1-dimethylindene at 0–10 °C can be used to produce solutions of 2,2-dimethylisoindene, in 10–15% concentration relative to 1,1-dimethylindene.[6,7] These solutions are stable for several days at −20 °C and for 1–2 h at 25 °C.[8] UV and emission spectroscopy examinations of room temperature solutions of 2,2-dimethylisoindene show long wavelength absorption in the 330–430-nm region with maxima at 370, 398, and 423 nm, and an emission maximum at 456 nm.[9] (By comparison, *o*-xylylene has an absorption maximum (EPA, 77 K) at 373 nm and an emission maximum at 446 nm).[10] The presence of 2,2-dimethylisoindene was further confirmed by Diels–Alder trapping of the isoindene at 25 °C, with cyclopentadiene and cyclopentene.



A mechanism that explains the above rearrangements is presented in Scheme I. An initial [2 + 2] photocycloaddition