

the energy of the highest occupied molecular orbital, is significantly higher than E_A , the acceptor level of the metal.¹⁵ In previous work we have related molecular energy levels to structure through the use of substituent constants;¹⁻⁴ in particular it has been shown that the gas phase ionization potentials of mono- and disubstituted benzenes are well correlated in this way.¹ This seems to be general.¹⁶ Therefore, for compounds **1** the ionization potentials would increase with the Hammett substituent constant, σ_x , and in fact their electrochemical oxidation potentials in solution indicate that this is true.³ Therefore, under the assumption that this relationship also holds in the solid state, substitution of $E_{\text{HOMO}} = -m_1\sigma_x + b_1$ (m_1, b_1 are positive constants) into the equation above for positive charging of the organic compounds yields $\ln(Q/M) \propto -m_1\sigma_x - E_A + b_1$. Thus, for a given metallic bead acceptor¹⁷ and constant experimental variables $\ln(Q/M) \propto -\sigma_x$. Similarly for negative charging of the organic solid $\ln(Q/M) \propto E_D - E_{\text{LUMO}}$, when E_D , the donor level of the metal, is significantly greater than E_{LUMO} , the energy of the lowest unoccupied molecular orbital.¹⁵ Since the electron affinities, which are direct measures of E_{LUMO} , can be shown to be linear functions of the Hammett substituent constant in aromatics generally,¹⁸ one can substitute $E_{\text{LUMO}} = -m_2\sigma_x + b_2$ (m_2, b_2 are positive constants). Using a given metallic donor¹⁷ then $\ln(Q/M) \propto +\sigma_x$. This treatment therefore predicts a linear dependence of $\ln(Q/M)$ on substituent constant, but having negative slope for positive charging of the organic and positive slope for negative charging. Thus, the relationships derived not only correctly rationalize the linear nature of the dependence of $\ln(Q/M)$ on substituent, but also the sign of the slope relative to the sign of charging.

Significantly, the present results demonstrate that triboelectric charging of solids is directly related to the *molecular* structure of the *bulk* and moreover apparently to the molecular orbital energy levels of the isolated molecules (in gas phase or solution).¹⁹ In this regard the results for the polystyrenes **2** are especially noteworthy. While the relationship of triboelectrification and triboluminescence²⁰ is obscure, both clearly relate to molecular properties. A recent report from these laboratories describes similar correlations for injection of charge from amorphous solids in a less explicit but analogous manner.²¹ The application of linear free energy relationships (and other chemical principles) to the correlation and elucidation of these and related physiochemical interactions of solids makes the processes amenable to study at the molecular level and allows molecular structural control of the phenomena.

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- (14) Metallic beads are used since they can easily be made electrically neutral. Against a film of the same metal, the charge acquired by the bead is negligible.
- (15) The restriction that E_{HOMO} be significantly greater than E_A or that E_D be significantly greater than E_{LUMO} avoids intermediate cases where the electrochemical analogy is not as straightforward. In these other cases, very low and irreproducible charging levels result.
- (16) For example we find that the first four ionization potentials of substituted pyridine *N*-oxides (data of J. P. Maier and J. F. Muller, *Tetrahedron Lett.*, 2987 (1974)) are linearly correlated (correlation coefficients $r = 0.994, 0.995, 0.945, 0.935$, respectively) by the sums of the σ_{para} substituent constants.
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Theoretical Models for Oxidized Rubredoxin. SCF-X α -SW Calculations on FeS₄⁵⁻, Fe(SH)₄⁻, and Fe(SCH₃)₄⁻

Sir:

Determination of the X-ray structure of oxidized rubredoxin to nearly small-structure accuracy¹ has stimulated interest in correlation of measurable properties of this iron-sulfur protein with the structural results.² Especially intriguing is the question of the reasons for and the effects of one of the four approximately tetrahedral Fe-S bonds being significantly shorter (2.05 (3) Å) than the other three (2.24 (3), 2.32 (3), and 2.34 (2) Å). Rubredoxin is also an important model for understanding the more complex ferredoxins, which contain iron-sulfur clusters with significant Fe-Fe as well as Fe-S bonding.^{3,4} Common to rubredoxin and most ferredoxins are Fe^{III} \rightarrow Fe^{II} reduction potentials which are low compared to an aqueous environment,² and there is much interest^{3,4} in how the proteins create this particular degree of stability for Fe^{III} relative to Fe^{II}.

We have begun a comprehensive theoretical study of models for the Fe(SR)₄ core in rubredoxin using the SCF-X α scattered wave method,⁵ which, in the overlapping sphere modification,^{6,7} yields quite accurate electronic structures at moderate cost.^{8,9} The only previous calculations on rubredoxin¹⁰ used the iterative extended-Hückel LCAO technique. Direct comparison of extended-Hückel and X α -SW methods have shown them to be comparable in speed, despite the much more approximate nature of the former.¹¹ Here we report preliminary results for FeS₄⁵⁻, Fe(SH)₄⁻, and Fe(SCH₃)₄⁻ as models for oxidized rubredoxin. The first was calculated in T_d and the last two in D_{2d} symmetry, using Fe-S = 2.29 Å, S-H = 1.34 Å, S-C =

1.82 Å, and $(\text{Fe-S-R}) = 107.2^\circ$. Since oxidized rubredoxin has five unpaired electrons,¹² each calculation was done in both spin-restricted and -polarized form; i.e., using the same and separate potentials, respectively, for electrons of different spin. Figure 1 shows the resulting spin-restricted SCF energy levels¹³ and spin-polarized levels for $\text{Fe}(\text{SCH}_3)_4^-$. "Watson spheres"¹⁴ were used to simulate the crystal stabilization of these negative ions; hence the zero point of each energy scale is arbitrary. Important aspects of these results are summarized below.

The spin-restricted diagrams divide at -0.30 hartree into lower energy levels, essentially unperturbed from the free ligands (S^{2-} , SH^- , and SCH_3^-), and upper levels, FeS_4 -localized and in order of increasing energy of Fe-S bonding, S nonbonding, and Fe-S antibonding type; the last are always half-filled. The upper levels of $\text{Fe}(\text{SH})_4^-$ and $\text{Fe}(\text{SCH}_3)_4^-$ are *nearly identical* in ordering and Fe vs. S character, and may be simply related to corresponding FeS_4^{5-} levels using the $T_d \rightarrow D_{2d}$ correlations $a_1 \rightarrow a_1$, $e \rightarrow a_1 + b_1$, $t_2 \rightarrow b_2 + e$, and $t_1 \rightarrow a_2 + e$. Exceptions are the S(3p) nonbonding $2a_1$ and $3t_2$ orbitals of FeS_4^{5-} , which correlate with the lower energy $2a_1$, $2b_2$, and $2e$ S(3p)-H(1s) bonding orbitals of $\text{Fe}(\text{SH})_4^-$. The spin-restricted Fe-S bonding and antibonding orbitals are, respectively, 64–76% ligand and 70–85% iron for FeS_4^{5-} , 50–79% ligand and 65–95% iron for $\text{Fe}(\text{SH})_4^-$, and 55–79% ligand and 63–92% iron for $\text{Fe}(\text{SCH}_3)_4^-$.

The spin-polarized energy orderings are *all* consistent with the observed five unpaired electrons of oxidized rubredoxin. Using $\text{Fe}(\text{SCH}_3)_4^-$ as an example, occupation of orbitals in order of increasing energy makes $8e^\uparrow$ the highest occupied level, leaving unpaired spins in the Fe-S antibonding levels $6a_1^\uparrow$, $3b_1^\uparrow$, $6b_2^\uparrow$, and $8e^\uparrow$.

Spin polarization produces marked changes in the Fe vs. ligand character of the Fe-S levels. For all three models, the spin-up and -down Fe-S *antibonding* orbitals become mainly ligand and metal, respectively; since only the spin-up levels are occupied, the HOMO's of the models thus switch from mainly iron to mainly sulfur in character. For FeS_4^{5-} and $\text{Fe}(\text{SH})_4^-$, the up and down Fe-S *bonding* orbitals become mainly metal and ligand, respectively; since both are occupied, the averaged result is a slight increase in iron character. In $\text{Fe}(\text{SCH}_3)_4^-$, the situation is more complex for the spin-up Fe-S *bonding* levels, since as their energies decrease from the spin-restricted values they begin to overlap, and thus interact with, the slower-moving S-C bonding levels; one merged group of spin-up Fe-S-C bonding levels, all with considerable iron character, results. The spin-down Fe-S bonding orbitals increase in energy faster than the spin-down S-C levels, and the two groups thus remain distinct in character. The averaged result strongly reflects the spin-up Fe-S/S-C level interaction.

Our main conclusions from these results follow. Firstly, properties of oxidized rubredoxin dependent on the HOMO's and LUMO's—the Fe-S antibonding orbitals—should be calculable nearly as accurately using the $\text{Fe}(\text{SH})_4^-$ as the $\text{Fe}(\text{SCH}_3)_4^-$ model. By far the *largest* difference in character of these orbitals between the two models is for the b_1^\downarrow level, which is 82% iron in $\text{Fe}(\text{SH})_4^-$ and 72% iron in $\text{Fe}(\text{SCH}_3)_4^-$. In contrast, SCF- $X\alpha$ -SW calculations on $\text{Fe}_4\text{S}_4(\text{SR})_4^{2-}$ models for oxidized ferredoxins show that the character of even the highest energy levels is markedly affected by the substitution of $\text{R} = \text{CH}_3$ for $\text{R} = \text{H}$.¹⁵ This difference is reasonable since Fe-S antibonding levels in the 4-Fe cluster are lowered in energy by involvement in Fe-Fe bonding, and therefore interact more strongly with lower-lying, mainly ligand levels.

Secondly, $\text{Fe}(\text{SCH}_3)_4^-$ is a distinctly superior model to $\text{Fe}(\text{SH})_4^-$ for properties dependent on the Fe-S bonding

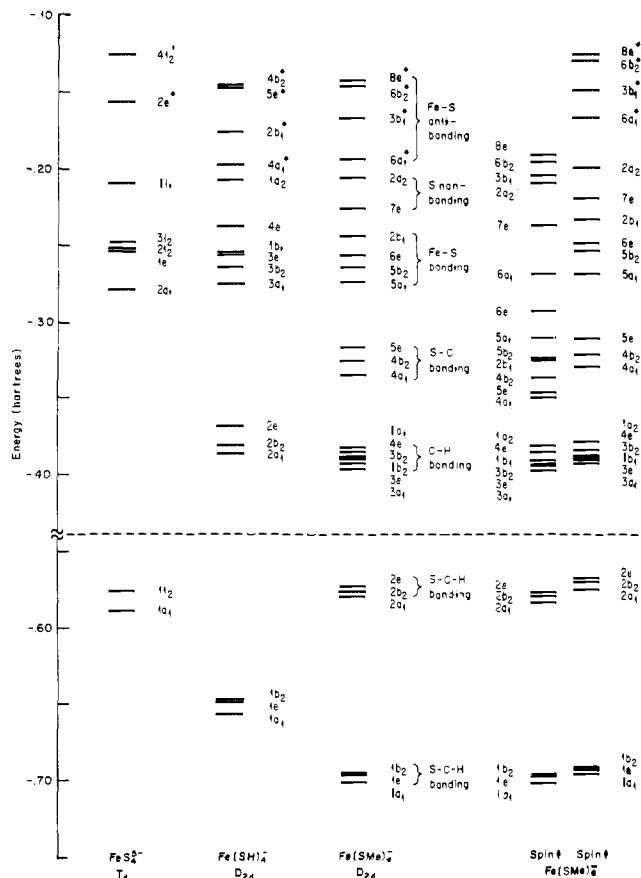


Figure 1. SCF- $X\alpha$ -SW ground state energy levels for oxidized rubredoxin models. All levels are fully occupied except those marked with an asterisk, which are half-filled in the spin-restricted diagrams and empty in the spin-polarized diagram.

levels, since the Fe-S/S-C level mixing observed in the spin-polarized calculation for the former has no analog in the latter. Further, we feel that no model more complicated than $\text{Fe}(\text{SCH}_3)_4^-$ should be required to discuss most properties of the FeS_4 core in oxidized rubredoxin, since substitution of cysteinyl for methyl groups should have major effects only on orbitals below -0.35 hartree, none of which have significant density in the Fe-S region.

Finally, it is clearly necessary to do calculations on such highly paramagnetic systems in spin-polarized form if one wishes to avoid being misled even qualitatively about metal vs. ligand character of important orbitals.

Our further studies of rubredoxin will include calculations on models for the reduced form,¹⁶ investigation of effects of shortening one Fe-S bond, and transition-state calculations of electronic spectra for comparison with experiment. In the last area we would only say at present that the lowest *allowed* transition of $\text{Fe}(\text{SCH}_3)_4^-$ should be $2a_2^\downarrow \rightarrow 6a_1^\downarrow$, corresponding to massive S \rightarrow Fe charge transfer.

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Calorimetric Evaluation of Enthalpies of Formation of Some Bridged-Ring Hydrocarbons. Comparison with Data from Empirical Force Field Calculations

Sir:

Enthalpies of formation of polycyclic hydrocarbons of diverse structure and moderate size (up to ca. 20 carbon atoms) are now accessible via empirical force field calculations¹⁻³ in a few minutes using modern computers. In contrast, experimental determination of the enthalpies of formation of such compounds via synthesis, purification, and combustion calorimetry usually takes many months of effort. Furthermore, the force field approach can be used to probe the enthalpies and structures of unknown molecules. The general acceptance of data from this source and their use in the quantitative interpretation of chemical phenomena depend on their reliability. A recent critical evaluation¹ of the use of two general force fields, those of Schleyer¹ and Allinger,² lists the enthalpies of formation and strain energies of some 84 hydrocarbons, mainly of the bridged-ring type, none of which has been measured experimentally. Ac-

cordingly, we have selected nine compounds for an experimental evaluation of the reliability of the force field data. For comparative purposes, the list includes two compounds, adamantane (1) and diamantane (6), for which experimental ΔH_f° values were already available.

Adamantane (1),^{4a} 1- and 2-methyladamantane (2)^{4b} and (3),^{4c} 1,3,5,7-tetramethyladamantane (4),^{4b} protoadamantane (5),^{4d} diamantane (6),^{4e} and 4-, 3-, and 1-methyl-diamantane (7),^{4b} (8),^{4f} and (9)^{4b} were subjected to rigorous purification, to 99.99 mol%, by recrystallization, vacuum sublimation, and, with the exception of tetramethyladamantane (4) which was redistilled and resublimed several times, multiple zone-refining. Combustions were carried out in the "Belfast" Mark I aneroid bomb,⁵ yielding the solid phase enthalpies of formation, ΔH_f° (c), listed in Table I.

Since the molecular mechanics data relate to the gas phase at 25°, it was essential to have available a quick, reliable method of measuring enthalpies of sublimation. Such a method involving the use of a commercial gas chromatograph and a gas flow technique has now been developed⁶ and the ΔH_{sub}° data obtained in this way are listed in Table I. The value for adamantane is in excellent agreement with literature values: 14.26 vs. 14.45,³ 14.18,⁷ and 14.00 kcal mol⁻¹.⁸

Within the error limits our gas phase enthalpy of formation, ΔH_f° (g), of adamantane is in complete agreement with two of three earlier determinations: 31.76 \pm 0.32 vs. 30.65 \pm 0.98,³ 30.57 \pm 0.90,⁹ and 32.96 \pm 0.19 kcal mol⁻¹.⁷ whereas that of diamantane, 32.60 \pm 0.58 kcal mol⁻¹, differs appreciably from an earlier value of 36.65 \pm 2.00 kcal mol⁻¹¹⁰ in which ΔH_{sub}° was estimated from the enthalpies of fusion and vaporization, corrected to 25° using assumed molar heat capacities, and now shown to be incorrect. Comparison of the experimental ΔH_f° (g) data for compounds (1-9) with the Schleyer (S), ΔH_f° , and Allinger (A), ΔH_f° , results reveals the following features. (i) Both force fields overestimate the thermochemical stability of all nine compounds, Allinger's more so than Schleyer's. Nevertheless, if the errors in the calculated data are taken to be $\pm 1-2$ kcal mol⁻¹, there is a notable measure of agreement between ΔH_f° (g) exptl. and (S) ΔH_f° for compounds (1-5). (ii) Although both force fields predict that the strain energy of tetramethyladamantane (2 kcal mol⁻¹) is less than that of adamantane (6-7 kcal mol⁻¹), they overemphasize the stabilizing influence of the four methyl groups. Using our ΔH_f° (g) value the strain energy of tetramethyladamantane becomes 5 kcal mol⁻¹. (iii) The enthalpies of the four diamantyl systems are calculated less reliably than

Table I^c

	1	2	3	4	5	6	7	8	9
	Experimental								
$-\Delta H_f^\circ$ (C)	46.02 \pm 0.09	56.72 \pm 0.30	51.80 \pm 0.29	86.54 \pm 0.46	36.04 \pm 0.41	55.53 \pm 0.55	62.51 \pm 0.17	62.24 \pm 0.48	59.12 \pm 0.78
ΔH_{sub}°	14.26	16.15	16.14	19.39	15.50	22.93	18.98	24.64	19.27
$-\Delta H_f^\circ$ (g)	31.76 \pm 0.32	40.57 \pm 0.34	35.66 \pm 0.62	67.15 \pm 0.50	20.54 \pm 0.60	32.60 \pm 0.58	43.53 \pm 0.30	37.60 \pm 0.58	39.85 \pm 0.85
	Molecular Mechanics								
(S) $-\Delta H_f^\circ$ ^a	32.50	41.82	37.94	70.26	21.13	37.37	46.82	42.91	43.56
(A) $-\Delta H_f^\circ$ ^b	33.82	42.89	39.04	70.21	22.63	38.13	47.21	43.35	44.43
(S) $\Delta\Delta H_f^\circ$	0.74	1.25	2.28	3.11	0.59	4.77	3.29	5.31	3.71
(A) $\Delta\Delta H_f^\circ$	2.06	2.32	3.38	3.06	2.09	5.53	3.68	5.75	4.58

^aCalculated ΔH_f° data from the Schleyer force field in ref 1. ^bCalculated ΔH_f° data from ref 1 obtained with the Allinger force field in ref 2. ^cData are in kilocalories per mole.