$H_3)_3](PF_6)$[5] by using conditions similar to those described above for the synthesis of **2**. The anions of **2** and **3** are assumed to be isostructural on the basis of their extremely similar IR spectra.[6b,11b] Although compounds **2** and **3** are both stable toward atmospheric dioxygen and moisture, compound **3** alone is light sensitive. We are currently exploring its mechanism of photochemical decomposition.

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Hydrogen Evolution from Homogeneous Reaction Systems Containing Reduced Mo–Fe–S Clusters

Sir:

While there has recently been extensive research on light-driven hydrogen evolution systems,[1] the problem of effecting, and elucidating the molecular mechanism of, spontaneous hydrogen evolution from protic molecules in strictly homogeneous systems remains largely unresolved. In a biological context the prominent cases are the hydrogenase enzymes,[2] which, with one known exception,[3] contain Fe–S clusters as the only prosthetic groups. On the basis of core extrusion studies three such enzymes appear to contain 1–3 Fe_4S_4 sites,[4–7] and in another case EPR results indicate the presence of both Fe_4S_4 and Fe_2S_2 sites.[8] We describe here certain observations which may prove useful in designing and interpreting thermal hydrogen evolution systems of biological and abiological types.

Because those hydrogenases which operate in the H_2-evolving direction do so in the presence of reductants ($E_m \leq -400$ mV) sufficient to elicit EPR signals reasonably attributable to the $[Fe_4S_4]^{1+}$ core oxidation level in at least several enzymes,[2,5,8] reactions of the reduced cluster $[Fe_4S_4(SPh)_4]^{3-}$[9] with protic acids in aprotic media were investigated. In nearly all systems tested, weak acids such as HOAc present in stoichiometric to large excess amounts effected partial or complete oxidation to $[Fe_4S_4(SPh)_4]^{2-}$ (detected after addition of $Et_3N/PhSH$[10]) but gave no H_2 detectable by GC.[13] Stronger acids tended to decompose clusters. However, the system 2.0 mM $[Fe_4S_4(SPh)_4]^{3-}$ in *N*,*N*-dimethylacetamide (DMA) with initial PhSH/cluster molar ratios (*X*) of 240–480:1 afforded after 24 h 11–31% yields of H_2[11] on the basis of assumed reaction 1. While this system may be

$$2[Fe_4S_4(SPh)_4]^{3-} + 2PhSH \rightarrow 2[Fe_4S_4(SPh)_4]^{2-} + 2PhS^- + H_2 \quad (1)$$

regarded as a preliminary step toward development of a synthetic hydrogenase, the rather low yields obtained thus far encouraged an alternative approach to homogeneous H_2 evolution.

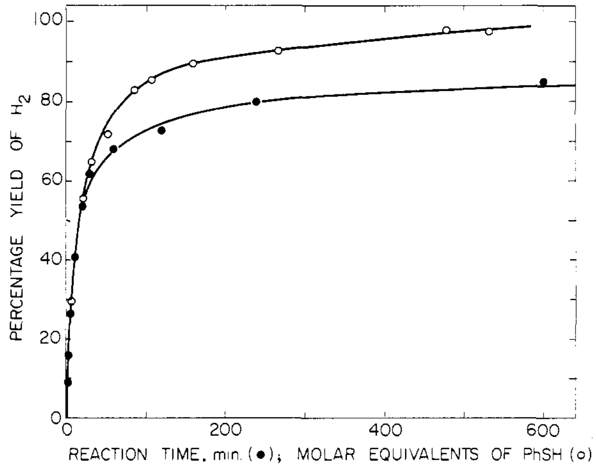

Figure 1. Percent yield of H_2 at ~25 °C from $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]/PhSH$ reaction systems in DMA solutions as dependent upon initial PhSH/cluster molar ratios and time. (○) 1.02 mM $[Mo_2Fe_6S_8(SPh)_9]^{5-}$, ratios 0 to 532:1, sampled after 24-h reaction time. (●) 1.14 mM $[Mo_2Fe_6S_8(SPh)_9]^{5-}$, ratio 379:1, 0–600 min after thiol addition; reactions quenched by addition of 50 μL of a 1 M PhSSPh solution in DMA. The same abscissa applies to both curves.

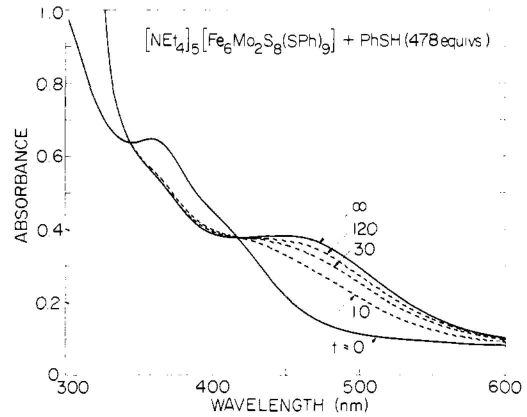

Figure 2. Absorption spectral changes accompanying H_2 evolution from a reaction system initially containing 1.02 mM $(Et_4N)_5[Mo_2Fe_6S_8(SPh)_9]$ (λ_{max} 358 (ϵ_M 62 600), ~405 nm, sh (ϵ_M 42 000)) and a PhSH/cluster molar ratio of 478:1. Spectra at various times *t* (min) after thiol addition are shown; the system at $t = 0$ contains no thiol. The spectrum at $t = \infty$ (~420 min) corresponds to that of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ (λ_{max} 347 (ϵ_M 53 000), 449 nm (ϵ_M 37 000)) measured separately, except that the 347-nm band is obscured by PhSH absorption.

Catalysis by hydrogenase of the exchange reaction $H_2 + HDO \rightleftarrows HD + H_2O$ has been widely interpreted as implicating an enzyme-bound hydride intermediate,[2,14] thus suggesting for more efficient H_2 evolution the utilization of a reactant molecule capable

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[1] See: M. Kirch, J.-M. Lehn, and J.-P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979), and references therein.

[2] L. E. Mortenson and J.-S. Chen in "Microbial Iron Metabolism," J. B. Neilands, Ed., Academic Press, New York, 1974, Chapter 11.

[3] *A. eutrophus* hydrogenase contains an FMN prosthetic group also: K. Schneider and H. G. Schlegel, *Biochem. Biophys. Res. Commun.*, **84**, 564 (1978).

[4] W. O. Gillum, L. E. Mortenson, J.-S. Chen, and R. H. Holm, *J. Am. Chem. Soc.*, **99**, 584 (1977).

[5] D. L. Erbes, R. H. Burris, and W. H. Orme-Johnson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4795 (1975).

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[8] K. Schneider, R. Cammack, H. G. Schlegel, and D. O. Hall, *Biochim. Biophys. Acta*, **578**, 445 (1979).

[9] J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, **16**, 2565 (1977).

[10] R. W. Johnson and R. H. Holm, *J. Am. Chem. Soc.*, **100**, 5338 (1978).

[11] Measurements: H_2 in the argon gas phase was determined by gas chromatography as described elsewhere;[12] redox potentials were obtained by differential pulse polarography (glassy carbon electrode, Ag/AgCl reference electrode); isomer shifts from Mössbauer spectroscopy are mean values of overlapping quadrupole doublets relative to Fe metal at 80 K. DMA was purified by reduced pressure distillation from CaH_2 and then sodium metal + acenaphthalene ($C_{12}H_8$). Thiols were freshly distilled.

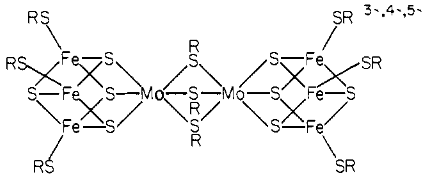
[12] R. R. Eady, B. E. Smith, R. A. Cook, and J. R. Postgate, *Biochem. J.*, **128**, 655 (1972).

[13] Oxidation of reduced cluster without stoichiometric reduction of potential substrate also occurs in the system $[Fe_4S_4(SPh)_4]^{3-}/HOAc/C_2H_2$, which produces ethylene in ≤60% yield: R. S. McMillan, J. Renaud, J. G. Reynolds, and R. H. Holm, *J. Inorg. Biochem.*, **11**, 213 (1979). The nature of this nonproductive oxidative reaction is unknown.

[14] T. Yagi, M. Tsuda, and H. Inokuchi, *J. Biochem.* (*Tokyo*), **73**, 1069 (1973).

0002-7863/80/1502-7600$01.00/0

of two-electron transfer to a (protic) substrate. Simple consideration of hydrogen reduction potentials[15] supports this view. Soluble stable molecules that can deliver two electrons at low potentials are uncommon, but recent syntheses of Mo–Fe–S "double-cubane" clusters,[16,17] possible models of the Mo site in nitrogenase,[17] provide an entry to this class of electron carriers. Oxidized cluster **1** (R = Ph[16]) has evidenced no H_2 evolution capability. However, in DMA solution it undergoes successive reversible reductions to $[Mo_2Fe_6S_8(SPh)_9]^{4-}$ (**2**) and $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ (**3**) at half-wave potentials $E_1 = -1.00$ V and $E_2 = -1.21$ V.[11] Anaerobic reaction of a solution of 1 equiv of $(n\text{-}Bu_4N)_3$ (**1**) and 10 equiv of Et_4NBr in acetonitrile with 3 equiv of 0.5 M $Na^+C_{12}H_8^-$ in HMPA followed by cooling to −10 °C afforded, after recrystallization (acetonitrile) of the separated solid, black, extremely air-sensitive crystals of analytically pure $(Et_4N)_5$ (**3**). The larger ^{57}Fe isomer shift[11] of the doubly reduced cluster **3** (0.41 mm/s) vs. **1** (0.32 mm/s) at 80 K signifies increased Fe(II) electronic character in **3** and therewith reduction of its individual clusters.



1 (3–), **2** (4–), **3** (5–)

Reaction systems composed of preisolated $(Et_4N)_5$ (**3**) and excess PhSH in DMA under an argon atmosphere spontaneously evolve H_2[11] and remain homogeneous over the period of reaction. Pertinent H_2 yield and time course results for several systems are shown in Figure 1. Spectrophotometric monitoring of reaction systems such as that in Figure 2 demonstrate that the final cluster species at cessation of H_2 production is **1**. The overall process is proposed to be reaction 2, on which basis H_2 yields are expressed.

$$[Mo_2Fe_6S_8(SPh)_9]^{5-} + 2PhSH \rightarrow [Mo_2Fe_6S_8(SPh)_9]^{3-} + 2PhS^- + H_2 \quad (2)$$

With sufficient ratios X and reaction times H_2 evolution is essentially quantitative (Figure 1). Thus in the system with X = 379:1 after 10 h and in those with X = 266–532:1 after 24 h, 85% and 93–98%, respectively, of the theoretical amount of H_2 based on the two-electron oxidation of **3** are produced. In comparison, 1.03 and 1.10 mM solutions of the one-electron reductant **2**, generated by the stoichiometric reaction **1** + **3** ⇄ 2 **2** ($K_{equil} = 10^{3.55}$ from $E_{1,2}$) with X = 379:1, reacted more slowly and less efficiently. After ~70 min (vs. 20 min for the comparable system containing 1.14 mM **3**) a 50% H_2 yield was obtained, which increased to only ~60% after 16 h, although oxidation of **2** to **1** was complete.[13] It is possible that some of the H_2 evolved originates from a rapid pathway involving the small amount (initially ~1.5%) of **3** present in the equilibrium mixture.

The foregoing results demonstrate that one sufficient condition for homogeneous, essentially quantitative H_2 evolution is utilization of a low potential two-electron reductant[18] which, inter alia, may be capable of stabilizing hydride at a metal site. The variation in behavior between $[Fe_4S_4(SPh)_4]^{3-}$ and **3** is unlikely to arise from different one-electron reducing abilities inasmuch as their first reduction potentials differ by only 14 mV in DMA solution.[11] Further research will involve kinetic studies of **3** and other reduced clusters with thiols, other acids, and additional two-electron substrates. Present results indicate that **3** can produce H_2 from other thiols (e.g., 79% yield from $PhCH_2SH$ after 24 h with X = 430:1) but less satisfactorily from certain other acids such as HOAc (25% after 20 h with X = 1100:1) which may also effect ligand substitution, observed with Fe–S clusters,[10] and/or cluster degradation.

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(15) At pH 7: $H^+ + e^- \rightarrow H$, −2.5 V; $2H^+ + 2e^- \rightarrow H_2$, −0.41 V.

(16) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, **740** (1978); G. Christou and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, in press.

(17) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979); T. E. Wolff, P. P. Power, R. B. Frankel, and R. H. Holm, *ibid.*, **102**, 4694 (1980).

(18) H_2 evolution from H_2O in a heterogeneous system containing the two-electron reductant $Ru(bipy)_3{}^0$ has recently been demonstrated: H. D. Abruña, A. Y. Teng, G. J. Samuels, and T. J. Meyer, *J. Am. Chem. Soc.*, **101**, 6745 (1979).

(19) U.K. Science Research Council/NATO Postdoctoral Fellow, 1980.

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Ion Pairing and Solvent Effects in the Reactivity of Anions toward Free Radicals[1]

Sir:

We have reported that the photostimulated $S_{RN}1$ reaction (Scheme I) between 2-chloro-2-nitropropane and enolate anions is sensitive to the nature of the solvent and the counterion.[2] Since it is often dangerous to infer reactivity from the rate or yield of a radical chain process, we have examined the relative reactivity of a series of anions in competitive $S_{RN}1$ reactions to ascertain the importance of ion-pairing effects (Scheme II). Relative reactivities of the anions (k_A/k_B) toward the intermediate 2-nitro-2-propyl radicals were evaluated from product analysis.[3]

Scheme I. $S_{RN}1$ Mechanism

$$Me_2C(X)NO_2{}^{-\cdot} \rightarrow Me_2\dot{C}NO_2 + X^-$$

$$Me_2\dot{C}NO_2 + A^- \rightarrow Me_2C(NO_2)A^{-\cdot}$$

$$Me_2C(NO_2)A^{-\cdot} + Me_2C(X)NO_2 \rightarrow Me_2C(NO_2)A + Me_2C(X)NO_2{}^{-\cdot}$$

$$X = Cl,\ p\text{-}MePhSO_2,\ NO_2$$

Scheme II. Competitive $S_{RN}1$ Reactions

$$Me_2\dot{C}NO_2 + A^- \xrightarrow{k_A} Me_2C(NO_2)A^{-\cdot} \xrightarrow{-e^-} Me_2C(NO_2)A$$

$$Me_2\dot{C}NO_2 + B^- \xrightarrow{k_B} Me_2C(NO_2)B^{-\cdot} \xrightarrow{-e^-} Me_2C(NO_2)B$$

$$A^-,\ B^- = Me_2C{=}NO_2{}^-,\ (EtO_2C)_2CH^-,\ (EtO_2C)_2CMe^-,\ (EtO)_2PO^-,\ (EtO)_2PS^-$$

Table I gives the relative reactivities[4] of a series of anions relative to $Me_2C{=}NO_2{}^-$ in the presence of K^+[2.2.2]-cryptand

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(1) Electron Transfer Processes. 23. This work was supported by Grant CHE-7823866 from the National Science Foundation.

(2) Russell, G. A.; Jawdosiuk, M.; Ros, F. *J. Am. Chem. Soc.* **1979**, *101*, 3378.

(3) Pure samples of the products (2,3-dimethyl-2,3-dinitrobutane, diethyl methyl(2-nitroisopropyl)malonate, diethyl isopropylidenemalonate, diethyl 2-nitroisopropylphosphonate, and diethyl 2-nitroisopropylthiophosphonate) were used as references for ^1H NMR analysis. A molar ratio of $Me_2C(X)NO_2{:}A^-{:}B^-$ of 1:1:1 was generally used. The anions were generated in situ with equivalent amounts of lithium or potassium *tert*-butoxide. Reactions were conducted at 25 °C with sunlamp irradiation and were complete in 90 min. The overall yields of products were usually 80–100%.

(4) By use of the integrated equation, $k_A/k_B = \log (1 - [P_A]/[A^-]_0)/\log (1 - [P_B]/[B^-]_0)$. With A^- equal to $(EtO_2C)_2CH^-$, a molar ratio of $Me_2C(X)NO_2{:}A^-{:}B^-$ of 1:2:1 was employed in order to eliminate participation of $B^- = Me_2C{=}NO_2{}^-$ in the elimination of HNO_2 from the intermediate diethyl (2-nitroisopropyl)malonate. In this case the rate expression employed was $k_A/k_B = \log (1 - [EtO_2C)_2C{=}CMe_2]/2[(EtO_2C)_2CH^-]_0)/[2 \log (1 - [O_2NCMe_2CMe_2NO_2]/[Me_2C{=}NO_2{}^-]_0)]$.

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