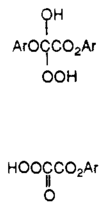
is a negligible part of the total decay of X and Y. Below about 1 mM DPA, the light yield increases with DPA concentration, as previously observed.[4]

At lower concentrations of triethylamine, the light appears in distinct pulses, so that the appearance of the second intermediate Y is not coincident with the disappearance of X. There must be a storage point along the reaction pathway between them. The storage point between the two intermediates X and Y we denote Z. It is not possible to simulate the observed two-pulse intensity/time profile on the basis of the system portrayed in Scheme I *unless* a discrete species Z is included. The system as shown generates the curves in Figure 3 with the parameters indicated in the figure caption.

The mechanism of Scheme I constitutes a major revision of previous ideas about this reaction.[3,4] Current work is directed toward a more precise kinetic definition of the reaction and toward the testing of structural hypotheses[5] for X, Y, and Z. The applicability of Scheme I is not limited to the TCPO/TEA system in ethyl acetate. The new mechanism also accounts for observations similar to those described here, which we have made with other oxalate esters, other base catalysts, and other solvent systems.

---

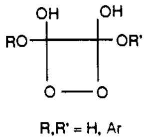
[5] Our current structural hypotheses are these:



$ArOC(OH)(OOH)CO_2Ar$

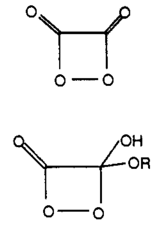
$HOOC(=O)CO_2Ar$

X



R,R' = H, Ar

Z



R = H, Ar

Y

Z should be a poor electron acceptor compared to X and Y and its structure is therefore consistent with its failure to generate light. The structures of X and Y are also consistent with the observation that one equivalent of the phenol is released early in the reaction and the second equivalent more slowly.

Induced Redox Reactivity of Tetrathiovanadate(V): Synthesis of the Vanadium(IV) Dimer $V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4$ and Its Structural Relationship to the V/S Mineral Patronite

Thomas R. Halbert,* Linda L. Hutchings, R. Rhodes, and Edward I. Stiefel*

Exxon Research and Engineering Company
Corporate Research Science Laboratories
Clinton Township, Annandale, New Jersey 08801

Received March 27, 1986

Induced internal electron transfer reactions involving tetrathiometalate anions of Mo and W have recently been established.[1-3] The $M(VI)S_4^{2-}$ (M = Mo, W) anions react with *oxidants* to yield products with the metals in *lower* oxidation states. For example, reaction of $Mo(VI)S_4^{2-}$ with thiuram disulfides yields $Mo(V)(S_2)(R_2NCS_2)_3$.[2] Reducing equivalents for the reduction of Mo(VI) to Mo(V) come from oxidation of bound sulfide to disulfide. Diagonal relationships in the periodic table[4] suggest that VS_4^{3-} and MoS_4^{2-} might undergo similar reactions. Indeed internal redox reactions might afford a new route to lower valent vanadium sulfur complexes. Such complexes are currently rare, although interest in their synthesis is increasing.[5-11]

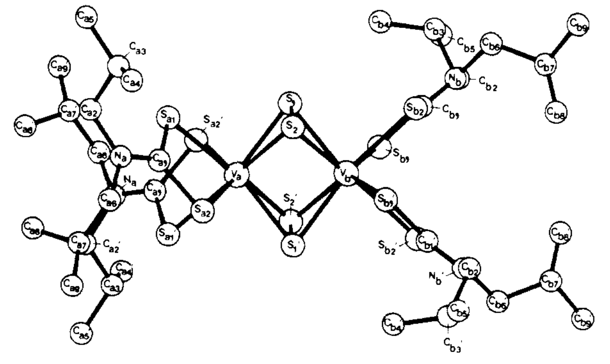


Figure 1. ORTEP drawing of $V_2(\mu\text{-}S_2)_2[(C_4H_9)_2NCS_2]_4$ (**2**). Bond lengths (Å): $V_a\text{–}V_b$ 2.851 (1), $S_1\text{–}S_2$ 1.998 (2), $V_a\text{–}S_1$ 2.402 (2), $V_a\text{–}S_2$ 2.403 (1), $V_a\text{–}S_{a1}$ 2.492 (1), $V_a\text{–}S_{a2}$ 2.501 (2).

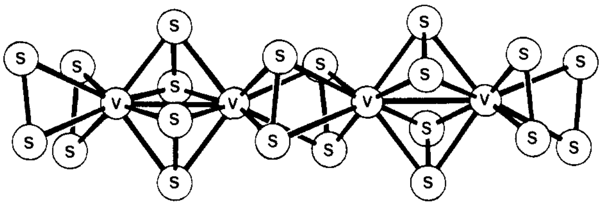


Figure 2. Part of the $(VS_4)_n$ chain in patronite, showing two V–V pairs.[22]

In comparison with $(NH_4)_2MoS_4$, the salt $(NH_4)_3VS_4$[12,13] has found relatively little use as a starting material in inorganic syntheses.[7,13,14] It dissolves in aqueous base to give deep violet solutions, which decompose quickly to brown oxygen-containing materials. Dissolution of $(NH_4)_3VS_4$ in dry, deoxygenated DMF yields only brown polymeric vanadium sulfides. Attempts to exchange the ammonium ion for tetraalkylammonium ions (e.g., tetrabutylammonium) were heretofore unsuccesful. However, when a *dry* solution of tricaprylylmethylammonium chloride in toluene containing 2% DMF is stirred with $(NH_4)_3VS_4$ in an inert atmosphere, the desired metathetical reaction slowly occurs, yielding a deep violet solution of tris(tricaprylylmethylammonium) tetrathiovanadate and a precipitate of ammonium chloride, which is separated via filtration.[15] This solution is indefinitely stable under inert atmosphere.

Treatment of a VS_4^{3-} solution prepared as above with solid tetraisobutylthiuram disulfide causes an immediate color change from violet to brown. Silica gel chromatography of the reaction solution permitted isolation of the major product, a yellow-brown material which readily crystallized from toluene/hexane.[16]

---

[1] Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

[2] Pan, W.-H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Commun.* **1985**, 927.

[3] Cohen, S. A; Stiefel, E. I. *Inorg. Chem.* **1986**, *25*, 4657.

[4] Greenwood, N. A.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 32.

[5] Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1151.

[6] Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321.

[7] Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731.

[8] Szeymies, D.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 804.

[9] Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297.

[10] Koch, S. A.; Chebolu, V. *Organometallics* **1983**, *2*, 350.

[11] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 184.

[12] Krüss, G.; Ohnmais, K. *Chem. Ber.* **1890**, *23*, 2547.

[13] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.

[14] Kovacs, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 340.

[15] A degassed solution containing 18 g of tricaprylmethylammonium chloride (Aliquat 336, Aldrich, 44.5 mmol) dissolved in 150 mL of toluene/2% DMF was allowed to stand over activated 4A molecular sieves for 4 h under inert atmosphere and then filtered. Solid $(NH_4)_3VS_4$ (3.46 g, 14.8 mmol) was added to the filtrate, and the mixture was stirred for 72 h. Precipitated NH_4Cl was removed via filtration, leaving an air- and moisture-sensitive violet solution approximately 0.1 M in VS_4^{3-}. UV-vis λ_{max} 326, 364, 538 nm (reported[13] for $(NH_4)_3VS_4$ in 1 M aqueous NaOH: 265, 349, 394, 544 nm).

[16] Solid tetraisobutylthiuram disulfide (0.54 g, 1.3 mmol) was added to 5 mL of 0.1 M $Aliquat_3VS_4$ in toluene/2%DMF under inert atmosphere. After it was stirred 1 h, the solution was chromatographed on silica gel (10:1 hexane/THF eluent). Solvent was removed from the major yellow-brown band and the product recrystallized from toluene/hexane to give 113 mg of yellow brown crystals. Yield 22% based on starting $(NH_4)_3VS_4$.

0002-7863/86/1508-6437$01.50/0

Spectroscopic and analytical data[17] suggested that this product was a novel vanadium(IV) dimer **2** formed via the induced internal redox reaction indicated in eq 1. The detailed nature of **2** was

$$2VS_4^{3-}\ (\mathbf{1}) + 2(i\text{-}Bu_2NCS_2)_2 \rightarrow V^{IV}_2(S_2)_2(i\text{-}Bu_2NCS_2)_4\ (\mathbf{2}) + S_x^{2-} \quad (1)$$

established by single-crystal X-ray diffraction.[18,19] Crystals of **2** obtained via evaporation of THF/hexane solutions consist of discrete molecular vanadium(IV) dimers (Figure 1). The vanadium atoms lie on a crystallographic C_2 axis. The V–V distance of 2.851 (1) Å and the observed room temperature diamagnetism of the complex are consistent with the presence of a vanadium–vanadium bond. The vanadium atoms are bridged by two symmetry-related μ-η^2-S_2 ligands, forming a $M_2(\mu\text{-}\eta^2\text{-}S_2)_2$ core similar to that previously found in $Mo_2(S_2)_6^{2-}$ and $Mo_2(S_2)_2Cl_6$.[20,21] The coordination sphere of each vanadium is completed by two bidentate dithiocarbamate ligands. The arrangement of the ligands is simply described as a distorted octahedron, with each S_2^{2-} ligand occupying a single vertex. Although other *molecular* vanadium dimers with S_2 bridges are known,[5,6] the only other $V_2(\mu\text{-}\eta^2\text{-}S_2)_2$ core that has been structurally characterized occurs in the mineral patronite (VS_4). Patronite consists of linear chains of vanadium(IV) ions bridged by S_2^{2-} ligands,[22,23] illustrated in Figure 2. The vanadium ions in patronite associate in pairs with V–V distances alternating between 2.83 and 3.22 Å. There is a remarkable correspondence between the structural parameters of the core in **2** and the core about the tight V–V pairs in patronite. The V–V distances are nearly identical (2.851 (1) Å for **2** vs. 2.83 Å for patronite), as are the S–S distances within the S_2^{2-} ligands (1.998 (2) Å in **2** vs. an average of 2.03 Å in patronite) and the average V–S distances (2.405 Å in **2** vs. 2.40 Å in patronite).

The virtual congruence of the $V_2(S_2)_2$ units in **2** and in patronite presents a vivid confirmation of the persistence of structural units through molecular and solid-state systems. Moreover, the synthesis of **2** by an induced internal redox process reemphasizes the utility of this novel synthetic strategy.

Acknowledgment. We thank Dr. J. Carter Cook for field desorption mass spectra, which were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029).

Supplementary Material Available: Crystallographic details, including tables of atomic coordinates, thermal parameters, bond lengths, and bond angles, for $V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4$ (14 pages); table of structure factors for $V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4$ (14 pages). Ordering information is given on any current masthead page.

---

(17) IR spectrum (KBr pellet): 1485 (s), 1468 (sh), 1438 (m), 1424 (m), 1390 (m), 1370 (sh), 1360 (m), 1341 (m), 1290 (w), 1245 (s), 1205 (m), 1150 (s), 1097 (m), 1003 (m), 940 (w), 922 (m), 882 (w), 809 (m), 630 (m), 620 (w), 590 (m), 535 (vw), 440 (vw), 378 (m) cm^{-1}. Field desorption mass spectrum, base peak corresponds to molecular ion $V_2S_{12}C_{36}H_{72}N_4^+$: *m/z* obsd (calcd) 1046, 100 (100); 1047, 59 (53); 1048, 79 (67); 1049, 33 (30); 1050, 27 (20); 1051, 8 (8). Anal. Calcd for $V_2S_{12}C_{36}H_{72}N_4$: C, 41.27; H, 6.93; N, 5.35; V, 9.72. Found: C, 42.48; H, 7.40; N, 5.22; V, 9.35. UV–vis λ_{max} (ϵ, 1 mol^{-1}/cm^{-1}): 298 (61 000), 474 (5450).

(18) The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., Lincoln, NE 68501.

(19) Crystal data: Space group *C*2/*c* (No. 15), with a = 30.268 (6) Å, b = 17.484 (1) Å, c = 17.523 (4) Å, β = 143.38 (1)°, and Z = 4. Calculated density 1.258 g cm^{-3}. The structure was solved by a combination of direct methods and difference Fourier techniques. $R_F = 0.038$, $R_{wF} = 0.038$ for 3135 independent reflections with $I > 3\sigma(I)$ and $3° < 2\theta < 50.7°$ (Mo Kα radiation). Anisotropic thermal parameters were used for all non-hydrogen atoms.

(20) Müller, A.; Nolte, W.-O.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 279.

(21) Marcoll, J.; Rabenau, A.; Mootz, *D.*; Wunderlich, H. *Rev. Chim. Miner.* **1974**, *11*, 607.

(22) Allman, R.; Baumann, I.; Kutoglu, A.; Rosch, H.; Hellner, E. *Naturwissenschaften* **1964**, *51*, 263. The atomic position reported for S2 (0.763, 0.096, 0.234) is physically unreasonable, lying within 0.3 Å of S_1. The position (0.763, –0.096, 0.234) was used for this figure; this gives a structure qualitatively in agreement with that published, though the reported V–S_2 bond lengths are still not reproduced.

(23) Klemm, W.; Schnering, H. G. *Naturwissenschaften* **1965**, *52*, 12.

NAD(P)$^+$-NAD(P)H Models. 61. An Interconversion between Central and Axial Chiralities as an Evidence for a Functional Model of Chemical Evolution of an Enzyme

Atsuyoshi Ohno,* Meguru Ohara, and Shinzaburo Oka

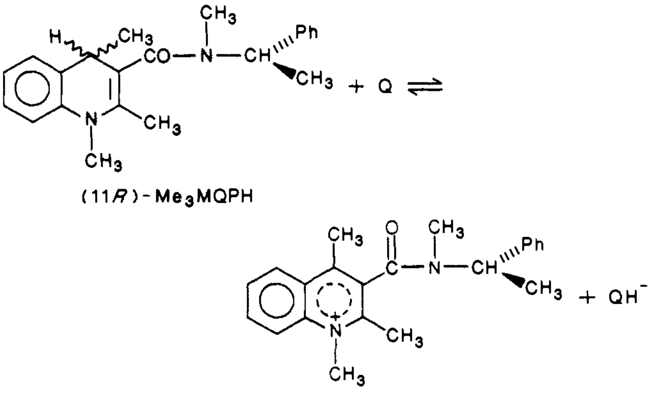
Institute for Chemical Research, Kyoto University
Uji, Kyoto-Fu 611, Japan

Received March 24, 1986

It is well-known that NAD(P)$^+$-dependent dehydrogenases discriminate between the *re* and *si* faces of the coenzyme. Two important and interesting hypotheses were proposed recently to explain the existence of these two opposite stereospecificities. One of the hypotheses proposes that the hydride transfer takes place on the less reactive *re* face of coenzyme when the natural substrate has a thermodynamically unstable carbonyl group and vice versa. The proposal is based on the assumption that during billions of years of chemical evolution, the enzyme has reached the optimal state to catalyze both directions of a reversible reaction most efficiently.[1] Although the proposal was immediately subjected to argument,[2] the basic idea involved in the proposal seems worthy of consideration.[3]

The other hypothesis proposed by Buck and his co-workers is mainly based on quantum-mechanical calculations.[4] The carbonyl oxygen in the carbamoyl group at the 3-positon of the enzyme-bound (dihydro)nicotinamide ring is set on the *re* or *si* face of the coenzyme due to prohibited rotation, and a hydride transfers on the face occupied by the carbonyl oxygen. That is, at the transition state of the redox reaction, the migrating hydrogen and the carbonyl oxygen are set in *syn* configuration. X-ray analysis and other physical measurements as well as chemical reactions with well-designed nicotinamide derivatives supported this proposal.[5-7]

In our previous paper, we described how 3-[*N*-methyl-*N*-(*R*)-(α-methylbenzyl)carbamoyl]-1,2,4-trimethyl-1,4-dihydroquinoline [(11*R*)-Me$_3$MQPh] and its corresponding quinolinium salt [(11*R*)-Me$_3$MQP$^+$] stereospecifically interconvert, in agreement with Buck's proposal. The former compound has a central chirality at the 4-position of the dihydroquinoline ring but its side-chain carbonyl group can rotate freely, whereas in the latter



(11*R*)-Me$_3$MQPH

(11*R*)-Me$_3$MQP$^+$

Q = quinone

---

(1) Nambiar, K. P.; Stauffer, D. M.; Lolodziej, P. A.; Benner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 5886–5890.

(2) Oppenheimer, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3032–3033.

(3) Benner, S. A.; Nambiar, K. P.; Chambers, G. K. *J. Am. Chem. Soc.* **1985**, *107*, 5513–5517.

(4) Donkersloot, M. C. A.; Buck, H. M. *J. Am. Chem. Soc.* **1981**, *103*, 6554–6558.

(5) van Lier, P. M.; Donkersloot, M. C. A.; Koster, A. S.; van Hooff, H. J. G.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 119–120.

(6) de Kok, P. M. T.; Buck, H. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1009–1010.

(7) Ohno, A.; Kashiwagi, M.; Ishihara, Y.; Ushida, S.; Oka, S. *Tetrahedron* **1986**, *42*, 961–973.

0002-7863/86/1508-6438$01.50/0