J. Am. Chem. Soc. 1986, 108, 6435-6437

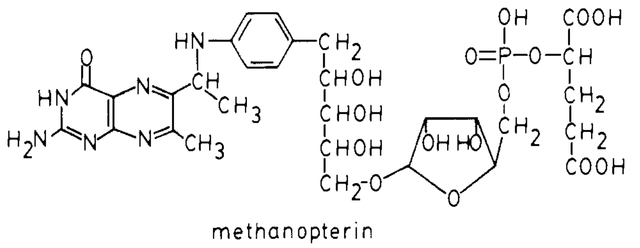

Figure 1. Chemical structure of methanopterin.

resulting diisopropylidene diethyl dithioacetal pentose derivatives were converted into the respective di-*O*-isopropylidene aldehydes (step c) by cleavage in the presence of mercury chloride and cadmium carbonate as described by English[13] with the exception that the chloroform extract of the reaction mixture was washed with 10% KI to remove the mercury salts[14] and the products were purified by chromatography on silica gel.[12] The resulting aldehydes were coupled at −78 °C in diethyl ether with [*N*,*N*-bis(trimethylsilyl)-*p*-anilinyl]lithium which was prepared from *p*-bromo-*N*,*N*-bis(trimethylsilyl)aniline (step d) as described by Pratt.[15] After 12 h, the reaction mixtures were warmed to room temperature, treated with methanol saturated with ammonium chloride, and washed with water. The resulting 1,2,3,4-di-*O*-isopropylidene-5-(*p*-aminophenyl)-1,2,3,4,5-pentahydroxypentanes were then reduced with an excess of $LiAlH_4$ (5×) at 80 °C in ether in a sealed tube for 48 h[16] followed by acid hydrolysis with 1 M HCl for 1 h at 100 °C to give the final product which was purified by preparative thin-layer chromatography.

Samples of 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane were isolated by the oxidative cleavage of tetrahydromethanopterin isolated from *Methanobacterium formicicum* and rumen isolate 10-16B as previously described.[6,17]

The synthetic products, as well as the samples isolated from the methanogenic bacteria, were converted into their pentatrifluoroacetyl derivatives by heating at 60 °C for 2 h with an equal mixture of methylene chloride and trifluoroacetic anhydride (v/v). After evaporation of the solvents, the derivatives were dissolved in methylene chloride and separated by gas chromatography on a 0.32 × 305 cm glass column packed with 3% SP-2100. When the temperature was programmed from 150 °C at 6 °C/min the retention times for the ribose, arabinose, xylose, and lyxose isomers were 3.64, 3.74, 3.81, and 4.02 min, respectively. The sample isolated from the methanogenic bacteria had a retention time of 3.64 min and cochromatographed with the ribose-derived standard. This same order has been observed for the elution of the trifluoroacetyl derivatives of the pentitols during gas chromatography.[18,19]

The mass spectrum of the derivatized synthetic sample which was derived from D-ribose was recorded at 70 eV on a VG 70-70E-HF gas chromatograph–mass spectrometer and was identical with that of the derivative of the 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane isolated from the bacteria. The major observed ions (their observed intensities are in parentheses) were at m/z 69 (44), 107 (24), 132 (14), 202 (100), 226 (55), 252 (32), 240 (16), 366 (7), 393 (19), and M^+ 707 (15). The mass spectrum of the pentatrifluoroacetyl derivative for each of the other stereoisomers was essentially identical with that of the ribose isomer except for small variations in the intensities of the m/z 69 and 107 ions.

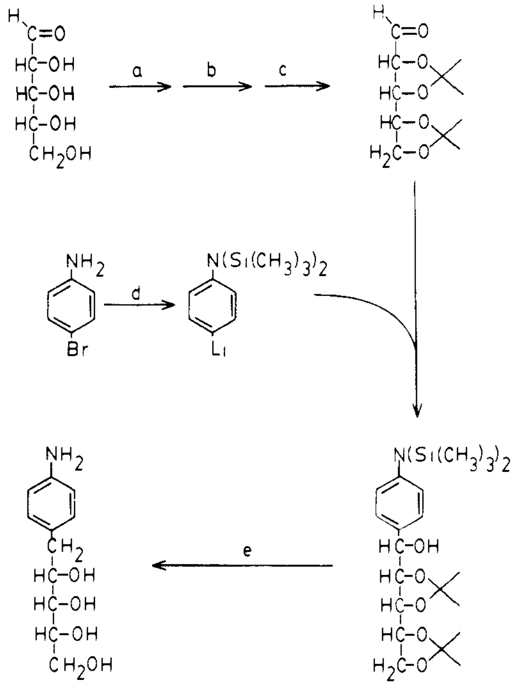

Figure 2. Synthetic scheme for the synthesis of 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane of known stereochemistry starting from pentoses.

This work establishes methanopterin to be the third example of a coenzyme in nature having a polyol side chain with the ribitol stereochemistry, the other examples being riboflavin[20] and coenzyme F_{420}.[21]

Acknowledgment. I thank Kim Harich for running the mass spectra, Donna Reed for assistance in growing the bacteria, and Linda D. White for editing the manuscript.

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Multiple Intermediates Generate Fluorophore-Derived Light in the Oxalate/Peroxide Chemiluminescence System[1]

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We have obtained evidence for new mechanistic features of the reaction[2] of bis(2,4,6-trichlorophenyl) oxalate (TCPO) with hydrogen peroxide and triethylamine (TEA) in the presence of 9,10-diphenylanthracene (DPA) in ethyl acetate as solvent. Chemiluminescence is generated by at least two intermediate compounds X and Y which produce the same singlet excited state

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(1) This research was supported by funds provided by Oread Laboratories, Inc., and the Kansas Advanced Technology Commission.

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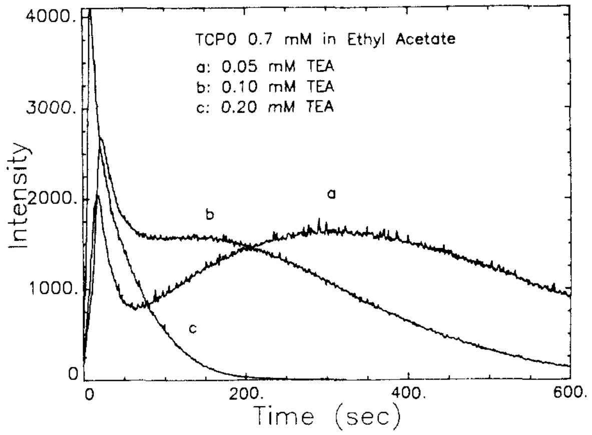


Figure 1. Intensity of emitted light (430 nm) as a function of the time after mixing in a system consisting of 0.7 mM bis(2,4,6-trichlorophenyl) oxalate, 2 mM hdyrogen peroxide, and 50 μM 9,10-diphenylanthracene in ethyl acetate, with triethylamine at the indicated concentrations.

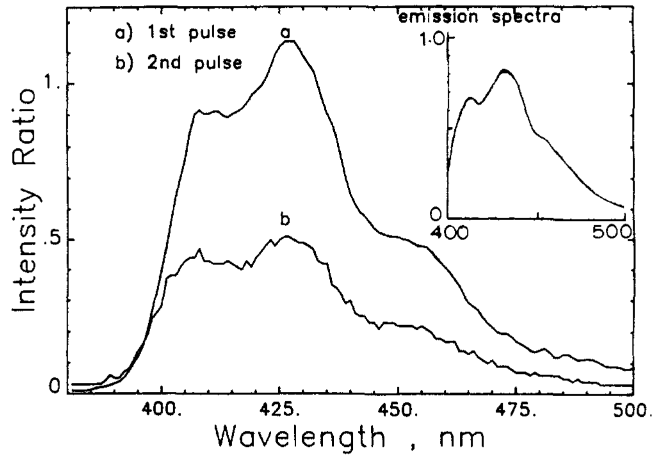


Figure 2. Spectra of the emitted light at two points during the experiment of Figure 1a. Spectrum a was collected at 75 s after mixing, spectrum b at 300 s after mixing. The two are identical with each other and with the fluorescence spectrum of the singlet excited state of 9,10-diphenylanthracene, which is shown in the inset (Roberts, R. G.; Hirt, R. C. *Appl. Spectrosc.* **1967**, *21*, 250).

of DPA. At least one intermediate Z, which does not generate light, occurs between X and Y.

Figure 1 shows typical time courses for the intensity of the light emitted by this system. Curves a and b exhibit two maxima. This apparent oscillatory character is reminiscent of nonlinear kinetic systems, but its origin is probably simpler because (a) truly periodic behavior of the intensity has never been observed and (b) there exists a model consistent with the data, in which two intermediate substances, generated in series, each produces one of the light pulses.

Figure 2 shows the spectrum of the emitted light at a point in the first pulse and at a point during the second pulse. The two spectra are identical with the emission spectrum of the singlet excited state of DPA, shown in the inset. Therefore all the fluorescence emitted in the reaction is derived from the same source, the singlet excited state of DPA.

The light intensity/time courses, shown in Figure 1 for three concentrations of triethylamine, can be compared with computer simulations (Figure 3) based on the mechanistic model of Scheme I. The two-pulse intensity/time profile at low triethylamine concentration requires at least two intermediates which lead to the generation of light (X and Y in Scheme I). At high concentrations of the amine, where the emission passes through only a single maximum, the decay of intensity is bi- or tri-exponential, still requiring the incorporation of the same two intermediates.

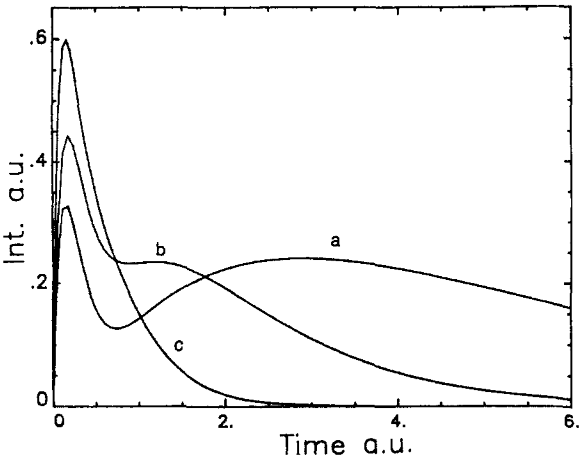
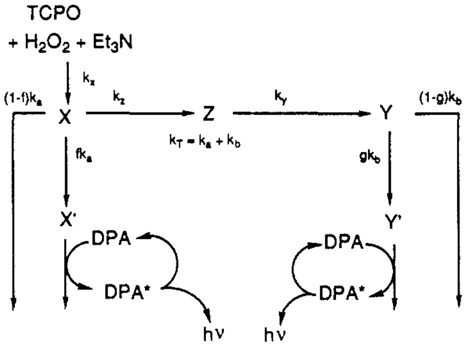


Figure 3. Simulations of intensity/time courses from the kinetic laws shown in Scheme I. The rate constants were selected to give curves resembling those in Figure 1. However, an exact simulation with physically significant constants is not expected because Scheme I is certainly mechanistically oversimplified. For example, a chemiluminescent quantum yield of unity is assumed. Also, control experiments indicate that the trichlorophenol generated during the reaction affects the rate, either by complexing with triethylamine or by direct effects. It also is a mild quencher and will thus affect the amount of light emitted. Curves otherwise more complex than those in Figure 1 are observed under some conditions, signaling kinetic complications not dealt with in Scheme I. Therefore the constants for modeling were arbitrarily chosen simply to indicate the versatility of the model in reproducing the forms of the intensity/time courses. The values employed (arbitrary units of reciprocal time; $f = g = 1$; k_x, k_z, k_y, k_a, k_b) were the following: (a) 6, 6.5, 0.3, 1, 0.5; (b) 7, 4.5, 0.8, 0.5, 1.45; (c) 12, 3.5, 2.4, 0.5, 0.5.

Scheme I. Minimal Mechanism for the Generation of Light in the TCPO/H_2O_2/TEA System[a]



$$I = \frac{dh\nu}{dt} = fk_a[x] + gk_b[Y]$$

$$I = [OX]_0 \left\{ \frac{fk_a}{(k_T-k_x)} (e^{-k_xt} - e^{-k_Tt}) + \frac{g\,k_bk_xk_yk_z}{(k_T-k_x)} \times \left[\frac{(e^{-k_xt} - e^{-k_bt})}{(k_y-k_x)(k_b-k_x)} + \frac{(e^{-k_Tt} - e^{-k_bt})}{(k_y-k_T)(k_b-k_x)} \right] + \frac{g\,k_bk_xk_yk_z}{(k_T-k_y)} \left[\frac{(e^{-k_yt} - e^{-k_bt})}{(k_y-k_x)(k_b-k_y)} \right] \right\}$$

[a] The kinetic expressions derivable from the mechanism are shown at the bottom. $[OX]_0$ means initial concentration of TCPO. See ref 5 for structural hypotheses for X, Y, and Z.

The rate constants for the decay of light intensity (from a fit of the intensity/time curves) are independent of DPA concentration from 1.25 μM to 1.5 mM (in agreement with previous work[4]). This shows that the luminescent state DPA* is generated either (a) rapidly by species X′ and Y′ produced in a slower step from X and Y or (b) directly from X and Y but in a process which

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[4] Catherall, C. L. R.; Palmer, T. F.; Cundall, R. B. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 823, 837.

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.

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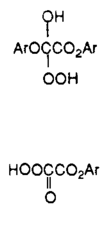
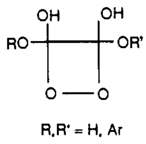
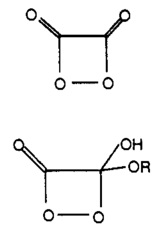
(5) Our current structural hypotheses are these:



X



Z



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

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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]

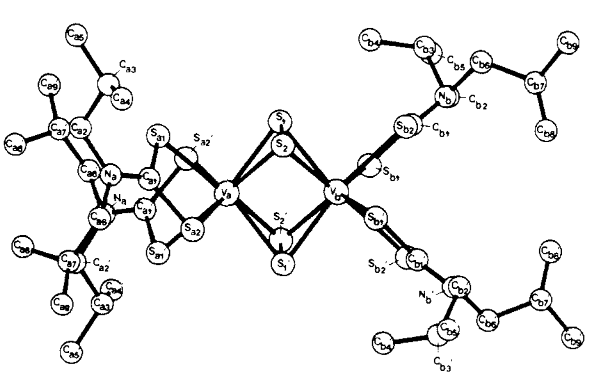

Figure 1. ORTEP drawing of $V_2(\mu\text{-}S_2)_2[(C_4H_9)_2NCS_2]_4$ (**2**). Bond lengths (Å): V_a–V_b 2.851 (1), S_1–S_2 1.998 (2), V_a–S_1 2.402 (2), V_a–S_2 2.403 (1), V_a–S_{a1} 2.492 (1), V_a–S_{a2} 2.501 (2).

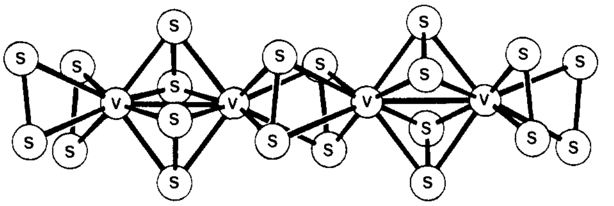

Figure 2. Part of the $(VS_4)_n$ chain in patronite, showing two V–V pairs.[22]

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]

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(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 $(NH_4)_3VS_4$.

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