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Contribution from the Department of Biochemistry,
The Ohio State University, Columbus, Ohio 43210

Mechanism of Formation of Bis(pyridine)oxoosmium(VI) Esters. Effect of Pyridine Activity on the Apparent Rate Law

Robert L. Clark and E. J. Behrman*

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In previous work from this laboratory,[1] we suggested that the kinetics of formation of the title compounds could be explained by a three-term rate law

$$v = k_0[\mathrm{OsO_4}][\mathrm{S}] + k_1\beta_1[\mathrm{OsO_4}][\mathrm{S}][\mathrm{py}] + k_2\beta_2[\mathrm{OsO_4}][\mathrm{S}][\mathrm{py}]^2$$

where py = pyridine and S = substrate.

In accordance with this proposal, linear plots of $(k_\psi - k_0[\mathrm{S}])/[\mathrm{S}][\mathrm{py}]$ vs. [py] were observed under pseudo-first-order conditions (OsO_4 concentration limiting) from which values of $k_1\beta_1$ and $k_2\beta_2$ were evaluated. Estimates of β_1 and β_2 were obtained from absorbance changes of OsO_4–pyridine mixtures as a function of pyridine concentration.

However, discrepancies appeared on closer analysis of our data: (1) plots of the absorbance changes of OsO_4–pyridine mixtures which assumed the existence of both $OsO_4{\cdot}py$ and $OsO_4{\cdot}2py$ were not linear over the entire concentration range;[1] (2) the square term in pyridine concentration assumed importance in the kinetic analysis at lower concentrations than required by the data on complex formation; (3) examination of the ir and Raman spectra of concentrated solutions of OsO_4 and pyridine showed no bands other than those attributable to OsO_4, $OsO_4{\cdot}py$, and pyridine.[2]

This situation is resolved by our observation that plots of the square of pyridine activity[3] vs. k_ψ are linear over the entire pyridine concentration range investigated (Figure 1). We conclude that there is no significant term which is first order in pyridine and that the fit of the data to the three-term rate law is an algebraic consequence of the fact that as the quantity of pyridine increases, the $(k_\psi - k_0[\mathrm{S}])/[\mathrm{S}]a_{\mathrm{py}}$ term becomes increasingly larger than the corresponding term in [py], while the a_{py} term itself becomes increasingly smaller than the [py] term (Figure 2). Kirby and Jencks[4] have previously observed apparent self-association of pyridine with consequent kinetic deviations. The rate law is thus

$$v = k_0[\mathrm{OsO_4}][\mathrm{S}] + k_2'[\mathrm{OsO_4}][\mathrm{S}]a_{\mathrm{py}}^2$$

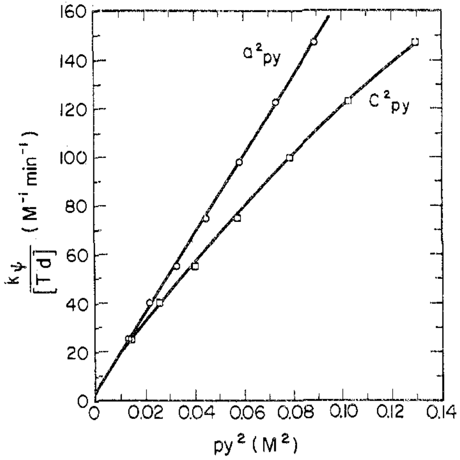


Figure 1. Kinetics of the reaction of osmium tetroxide with thymidine (Td) as a function of the quantity of pyridine present. The data are taken from ref 1a, Figures 3 and 4. C^2_{py} is the square of pyridine concentration; a^2_{py} is the square of pyridine activity.

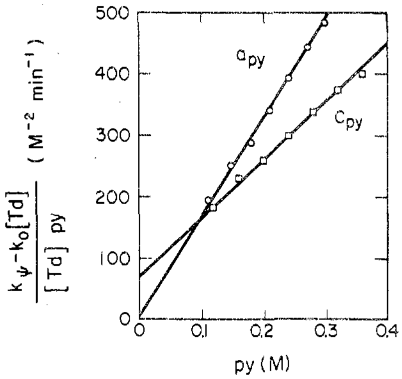
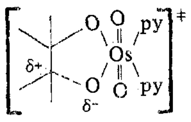
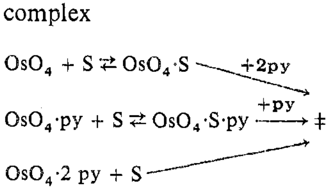


Figure 2. Linear plots of $k_\psi/[\mathrm{py}]$ vs. [py] using either pyridine concentration or activity. Note the y intercept for the concentration plot which gave rise to the spurious k_1 term. The data are taken from ref 1a, Figures 3 and 4.

This rate law is in accordance with an activated complex which contains two pyridine ligands



We write this species with partial bond formation to account for the high stereospecificity of the reaction.[5] We cannot, however, with the data at hand, adequately distinguish among the possible pathways which might lead to this activated complex



Our preference is for the second pathway which also fits Burton's data[6] on the ammonia–OsO_4 reaction and our observations on the α,α'-dipyridyl–OsO_4 system. Burton[6] observed only 1:1 complex formation between OsO_4 and ammonia but second-order kinetic dependence on ammonia concentration over the same range. The activity coefficient of ammonia, in contrast to that of pyridine, is essentially constant and equal to 1 under Burton's conditions.[7] We find that although the α,α'-dipyridyl–OsO_4 stability constant is very small, the rate of reaction with an olefin is much greater than in the presence of an equivalent amount of pyridine.

We have reevaluated β_1 and β_2 at 30° from the pyridine activity data and the absorbance changes of ref 1a, Table IV, using a nonlinear regression program. If the initial estimates for β_1 and β_2 of 0.24 and 0.05, respectively, for the lowest pyridine concentration are smoothly increased to the values 0.36 and 0.075 at 3.0 *M* pyridine, the observed absorbance changes fit to within 10% of the calculated values (ϵ_1 3800, ϵ_2 10,000 at 340 nm). That β values should increase with increasing pyridine concentration is not unreasonable in view of our observation that 1 *M p*-dioxane, which complexes OsO_4 only very weakly, increases the observed stability constant for the OsO_4–pyridine system by about 10%. This effect of solvent polarity is observed more dramatically in CCl_4 in which β_1 is about 12.[8]

The nature of the $OsO_4{\cdot}2py$ complex is not clear. Contact charge transfer[9] may occur as weak complexes between OsO_4 and aromatic molecules are known.[10]

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Registry No. OsO_4, 20816-12-0; pyridine, 110-86-1.

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Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Bis[bis(1,2-ethanedithiolato)ferrate(III)] Dianion, a μ_2-Thiolato Dimer. Synthesis and Properties

T. Herskovitz, B. V. DePamphilis, W. O. Gillum,
and R. H. Holm*

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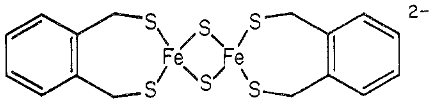
In the course of developing preparative routes to 2-Fe complexes which might serve as synthetic analogs[1] of the active sites of iron–sulfur proteins such as plant ferredoxins, adrenodoxin, and putidaredoxin,[2] the reactions of Fe(III) salts, sodium hydrosulfide, and various dithiols have been investigated. With *o*-xylene-α,α'-dithiol the centrosymmetric μ_2-sulfido-bridged dimer dianion **1** containing tetrahedrally coordinated Fe(III) is obtained. Its structure and electronic properties[3,4] reveal it to be a good representation of the oxidized forms of 2-Fe proteins. Under similar conditions with 1,2-ethanedithiol a dianionic complex has been isolated which contains no sulfide. This species has been identified as bis[bis(1,2-ethanedithiolato)ferrate(III)] dianion, $[Fe_2(edt)_4]^{2-}$ (**2**), whose structure[5] is schematically represented below. The complex is centrosymmetric with distorted trigonal-bipyramidal coordination, a planar and nearly square Fe_2S_2 bridging unit, and an Fe···Fe separation of 3.410 (3) Å. $[Fe_2(edt)_4]^{2-}$ is one of a small number[4] of centrosymmetric Fe(II) or Fe(III) dimers bridged by sulfur atoms included in chelate rings of the half-dimer. Of these, the dimeric Fe(II) complexes derived from *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)ethylenediamine, $[FeL]_2$, and *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)-1,3-propanediamine, $[FeL']_2$,[6] are structurally quite similar to **2**. In view of the current interest in Fe–S coordination compounds[7] and our own concern with various types of iron–thiolate complexes,[1] the X-ray structural characterization of $[Fe_2(edt)_4]^{2-}$ has been augmented by examination of certain chemical and electronic properties, which are reported herein.



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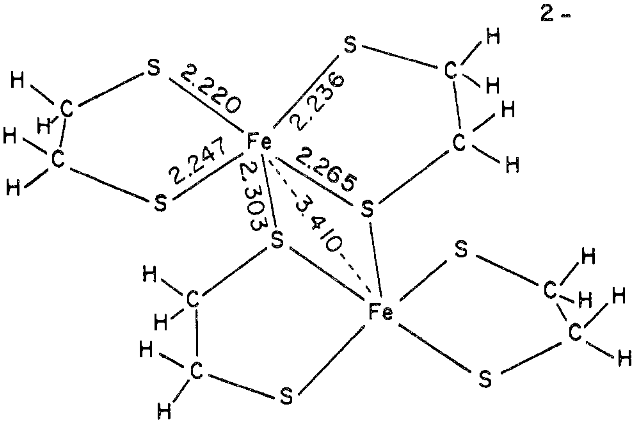

2

Experimental Section

Preparation of Compounds. All manipulations were performed with degassed solvents under a pure dinitrogen atmosphere.

$(n\text{-}Bu_4N)_2[Fe_2(S_2C_2H_4)_4]$. To a methanolic solution of 3.6 ml (42 mmol) of 1,2-ethanedithiol and 4.5 g (84 mmol) of sodium methoxide was added 8.24 g (20 mmol) of ferric chloride in methanol. An immediate dark red-brown color developed which became red-violet after the addition of ferric chloride was complete. Following stirring for 36 hr the reaction mixture was filtered and the collected solid was washed with water, leaving a small residue. The filtrate and wash were combined and treated with 9.2 g (29 mmol) of tetra-*n*-butylammonium bromide in water, yielding a precipitate of small black crystals. Two recrystallizations of this material from acetonitrile afforded the product in 35–50% yield as large, beautifully crystalline black blocks, mp 185–187°. Anal. Calcd for $C_{40}H_{88}N_2S_8Fe_2$: C, 49.76; H, 9.20; N, 2.90; S, 26.57; Fe, 11.57. Found: C, 49.90; H, 9.04; N, 2.95; S, 26.62; Fe, 11.68.

$[(CH_3)_3(PhCH_2)N]_2[Fe_2(S_2C_2H_4)_4]$. The above procedure was used with trimethylbenzylammonium bromide as the precipitant. The pure product was obtained as a black, finely crystalline solid, mp 196–198°. Anal. Calcd for $C_{28}H_{48}N_2S_8Fe_2$: C, 43.07; H, 6.20; N, 3.59; S, 32.85; Fe, 14.30. Found: C, 43.01; H, 6.27; N, 3.63; S, 32.57; Fe, 14.22.