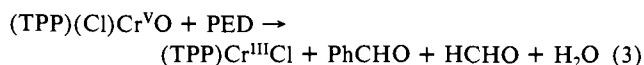
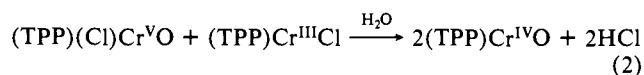
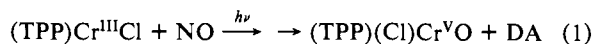


irradiated by room fluorescent light. Another identical solution was stored in the dark. At given intervals of time, 200- μ L aliquots of the irradiated reaction solution were transferred under N_2 to 2-mL cap-sealed bottles with a gas-tight syringe and these samples were stored on dry ice. Each sample was carefully (to avoid light) analyzed by HPLC.⁶ The results are shown in Figure 1. Inspection of Figure 1 shows that the plots of the yields of benzaldehyde and DA vs. irradiation time exhibit the shape anticipated for an autocatalytic reaction. Analysis of the reaction solution stored in the dark after 4.5 h showed that no benzaldehyde or DA had been formed. Irradiation of this solution provided a quantitative yield of benzaldehyde and DA after 40 min. In a separate experiment, a solution of (TPP)Cr^{III}Cl (8.0×10^{-6} M) and NO (1.1×10^{-4} M) in CH_2Cl_2 was subjected to intermittent exposure to room fluorescent light followed by monitoring in the dark at 429 nm. It was found that the reaction continued for up to 2 min in the dark after each period of light exposure. In order to determine if DA, a product of oxygen transfer from NO, might play a role as an autocatalytic agent, the experiment of Figure 1 was repeated with the inclusion of 1.2×10^{-3} M DA. The time course for this reaction was followed by HPLC analysis of benzaldehyde and is included in Figure 1. By inspection of the figure there is seen to be a shortening of the lag phase and a small rate enhancement. DA seems to play some minor role in the photoinduced autocatalysis.

That (TPP)Cr^{IV}O is not the oxidant for the rapid reaction with PED reported above is shown by the following experiments. The formation of benzaldehyde was followed by HPLC after mixing of a solution composed of (TPP)Cr^{IV}O (4.52×10^{-4} M) and a 100-fold excess of PED in CH_2Cl_2 . After 24 h there still remained more than 50% of unreacted (TPP)Cr^{IV}O. This result establishes that the oxidation of PED by ground-state TPPCr^{IV}O is far too slow to be a competent component of the mechanism of the photocatalytic reaction, since the photocatalytic reactions of Figure 1 go to completion in a short period of time. The species (TPP)Cr^{IV}O is a rather stable oxo metalloporphyrin as shown by the fact that it has been isolated and characterized by X-ray crystallography.⁷ Though this species is known to oxidize alcohols to aldehydes the rate of reaction with PED is, as shown, quite slow. The species (TPP)(Cl)Cr^VO is a much stronger oxidizing agent⁸ than (TPP)Cr^{IV}O and is stable in CH_2Cl_2 for a few hours at room temperature.⁹ Controlled-potential oxidation of (TPP)Cr^{IV}O was used to provide a stable CH_2Cl_2 solution of (TPP)(ClO₄)Cr^VO (4.4×10^{-5} M). To this solution there was added PED (to a concentration of 6.2×10^{-4} M) and the decrease in (TPP)(ClO₄)Cr^VO (412 nm) and increase in (TPP)Cr^{III}ClO₄ (450 nm) was followed at 30 °C in the dark. The reaction was found to obey the first-order rate law ($k_{obsd} = 6.7 \times 10^{-2} s^{-1}$) and the isobestic points at 374 and 439 nm established the absence of any accumulated intermediate. The oxidation of PED produced quantitative yields of benzaldehyde (95% by HPLC)⁶ and formaldehyde (100% by Nash procedure).¹⁰ The rapid rate of reaction of PED with the oxo-Cr^V porphyrin species allows this reaction to be a competent component of the photocatalysis of PED oxidation by NO.

We have shown (loc. cit.) that both (TPP)Cr^{IV}O and (TPP)(Cl)Cr^VO are present following the irradiation of solutions of (TPP)Cr^{III}Cl and NO. The formation of (TPP)Cr^{IV}O is known³ to occur by disproportionation of (TPP)Cr^{III}Cl with (TPP)(Cl)Cr^VO. High monooxygen donation potential compounds react with (TPP)Cr^{III}Cl to afford principally (TPP)(Cl)Cr^VO and low monooxygen donation potential compounds can only afford (TPP)Cr^{IV}O.

Since in the photocatalytic reaction the spectra of the spent reaction solution is that of both (TPP)(Cl)Cr^VO and (TPP)Cr^{IV}O and the reaction of percarboxylic acids with (TPP)Cr^{III}Cl provides a similar composition of Cr(IV) and Cr(V) species,¹ we may conclude that the photocatalytic oxygen transfer from NO to (TPP)Cr^{III}Cl is as efficient as the oxygen transfer from percarboxylic acids to (TPP)Cr^{III}Cl in the dark. Though the nature of the photoautocatalysis is not understood the essence of the overall oxidation of PED may be expressed as shown in eq 1-3.



In summary, unlike the facile and dark transfer from NO to iron(III) and manganese(III) *meso*-tetraphenylporphyrins, the oxygen transfer to chromium(III) occurs only by photocatalysis. While aniline *N*-oxides have been shown to undergo photoinitialized deoxygenation,¹¹ it has been demonstrated previously that *p*-cyano-*N,N*-dimethylaniline *N*-oxide does not react with our trap (PED).³ While the product of the photocatalysis oxidizes PED very rapidly, (TPP)Cr^{IV}O does not; and since (TPP)(Cl)Cr^VO does, the latter must be the initial product of oxygen transfer and, thus, is converted to (TPP)Cr^{IV}O by comproportionation with (TPP)Cr^{III}Cl.

Acknowledgment. This work was supported by a grant from the National Institutes of Health and The American Cancer Society.

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A Vinyltrimethylenemethane Intermediate in the 1,3-Sigmatropic Rearrangement of the 6-Methylenebicyclo[3.1.0]hex-2-enyl System

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Because the barriers to internal rotation and cyclization of biradicals usually are very small,¹⁻⁵ the identification of these species as true intermediates in thermal rearrangements has been difficult. We conjectured that a stabilizing structural alteration of the biradical should deepen the local potential minimum and facilitate detection of the intermediate. This paper describes the experimental consequences of such an alteration, in which the putative partially conjugated biradical **1** of the bicyclo[3.1.0]hex-2-ene rearrangement⁶⁻⁸ is converted to the fully conjugated vinyltrimethylenemethane (VTMM) species **2** derived from 6-

(6) HPLC was performed as described in ref 1c. The retention time of each product follows: benzaldehyde (5.5 min), DA (8-9 min), and *p*-cyano-*N*-methylaniline (20 min).

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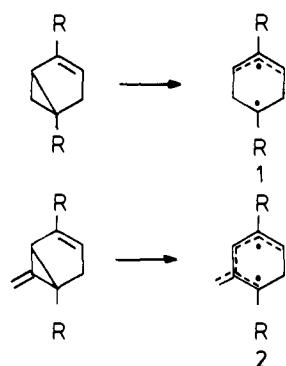
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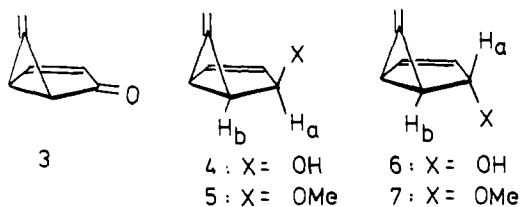
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methylenebicyclo[3.1.0]hex-2-enes^{9,10}

Reduction of ketone **3**¹¹ to the syn alcohol **4** with DIBALH^{12a} followed by methylation gave the syn methyl ether **5**.^{13,14} Acid-catalyzed equilibration of the syn-anti (**4-6**) alcohol mixture



obtained by Luche reduction^{12b} of **3** gave the more stable anti alcohol **6**, which upon methylation gave anti methyl ether **7**.¹⁵

Heating either **5** or **7** in benzene (54–140 °C) led to a highly stereoselective rearrangement to the endo and exo cyclopropyl methyl ethers **8** and **9**¹⁶ (Scheme I) in a ratio of ~30:1.¹⁷ Control experiments demonstrated that **8** and **9** do not interconvert under these conditions. A hypothesis of two pairs of competitive pathways from **5** and **7**, without a common intermediate, would imply identical competition ratios in systems with entirely different geometric requirements for reactive atomic motions. More probably, both **5** and **7** give the common VTMM **10** by cleavage of the bridge bond. The rearrangement of the anti compound **7** is about 16 times faster than that of the syn isomer **5** at 100 °C: $k'_7 = 10^{13.4} \exp(-24\,700(\text{cal/mol})/2.3RT)$, $k'_5 = 10^{13.3} \exp(-26\,600(\text{cal/mol})/2.3RT)$. Double epimerization $5 \rightarrow 7$ would have been difficult to observe during pyrolysis because $k'_7 \gg k'_5$; if prominent, the reverse process, $7 \rightarrow 5$, should have been observable but was not seen.

With a common intermediate **10**, the phenomenological ratio k'_7/k'_5 is the same as the mechanistic ratio k_7/k_5 (Scheme I). When combined with the constraints of microscopic reversibility and the information (above) that $k_{\text{eq}} = [7]/[5]$ probably is greater than unity, the data indicate a high degree of stereoselectivity in the ring-closure reactions of the biradical intermediate **10**: $k_{-7}/k_{-5} \geq 16$ and $k_{-8}/k_{-9} \approx 21$.

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(13) New substances were characterized by elemental composition and by mass and NMR spectroscopy.

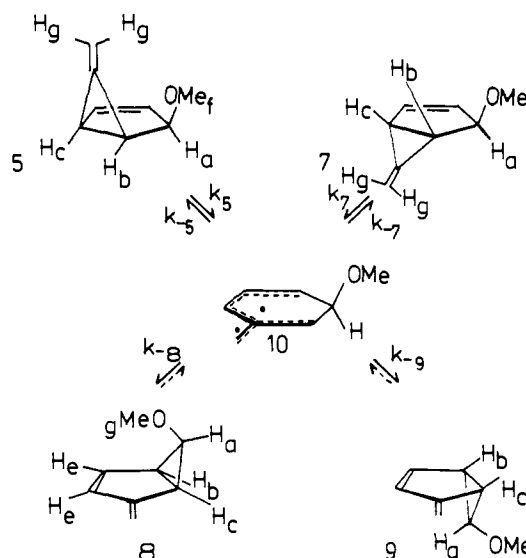
(14) Stereochemistry was assigned to **5** by NMR coupling constant ($J_{AB} = 6.8$ Hz) and by nuclear Overhauser enhancement (NOE) measurements (250 or 500 MHz, difference display, irradiated nucleus \rightarrow signal enhancement): $H_a \rightarrow H_b$, 11%; $H_b \rightarrow H_a$, 9%; $H_f \rightarrow H_b$, 4%; $H_f \rightarrow H_g$, 4%.

(15) Stereochemistry of **7** assigned by $J_{AB} < 0.5$ Hz; NOE $H_a \rightarrow H_b$, 4%; $H_f \rightarrow H_b$, 10%; $H_b \rightarrow H_a$, 3%; $H_b \rightarrow H_f$, 7%.

(16) Compound **8**: $J_{AB} \approx J_{AC} = 6.5$ Hz; NOE $H_b + H_c \rightarrow H_a$, 13%; $H_a \rightarrow H_b + H_c$, 15%; $H_g \rightarrow H_e$, 3%. Compound **9**: $J_{AB} \approx J_{AC} < 0.5$ Hz.

(17) This ratio was weakly temperature-sensitive: ~30 at 54 °C, ~21 at 100 °C.

Scheme I



The previously observed^{11b} rearrangement of the cyclopropanone ethylene ketal **11** to the cyclopropanone ethylene ketal **12** in benzene is characterized by the Arrhenius expression $k'_{11} = 10^{12.1} \exp(-27\,700(\text{cal/mol})/2.3RT)$. We now have observed a similar rearrangement of the dimethyl ketal **19**: $k'_{19} = 10^{12.4} \exp(-27\,800(\text{cal/mol})/2.3RT)$. The latter process also occurs at about the same rate in EtOH or CD₃OH, but ketal exchange does not occur to a significant extent under these conditions. This finding argues against a hypothetical ionization mechanism passing over an α -methoxycarbonium ion intermediate and supports a purely intramolecular thermal pathway.

Pyrolysis of optically active (–)-ethylene ketal **11**,¹⁹ [α]₃₆₅ –1176°, 66 ± 2% ee,²⁰ in benzene at 88.1 °C for 24.33 h resulted in 78 ± 2% conversion to optically inactive cyclopropanone ketal **12**, >99% racemic.²¹ Recovered **11** had 88% of its original enantiomeric excess. This result is most readily interpreted with an achiral biradical intermediate **13**, having an effectively planar carbon skeleton, which cyclizes competitively to racemic **12** and **11** in the ratio of about 7:1.¹⁸ The possibility of an independent pathway for the small amount of enantiomerization of **11** cannot be ruled out but requires an extra hypothesis.

Similarly, either diastereomeric 2,3-butanediol ketal **14** or **15** in benzene at 108 °C afforded the same (~1:1) mixture of cyclopropanone ketals **16** and **17**, as would be expected from the proposed common intermediate **18**.

Although the actual magnitudes of the ring-closure barriers in biradicals of the VTMM type (**2**, **10**, **13**, **18**) are not known, the present results suggest that each of these species lies in a local minimum deep enough to compel all of the reactive trajectories to pass through it. The conformational⁶ and dynamic²² effects

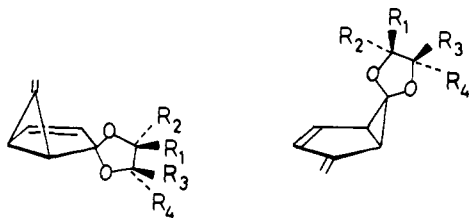
(18) Direct evidence on the geometry of **10** and **18** is not available, but analogy to the case of **13** suggests that **10** and **18** each also have an effectively planar carbon skeleton. The experiments are noncommittal on whether the exocyclic methylene hydrogens of **10**, **13**, and **18** effectively lie in the carbon plane or flank it symmetrically.

(19) (a) Synthesized as before¹¹ with optical activation of the synthetic intermediate 6-chloro-6-methylbicyclo[3.1.0]hexan-2-one by the sulfoximine-mediated resolution method of Johnson. (b) Johnson, C. R.; Zeller, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 4021.

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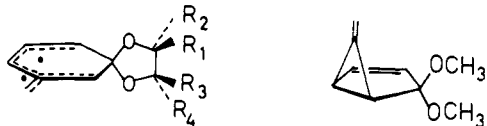
(21) The optical rotation expected for complete preservation of ee was determined by diimide reduction of **12** to (inter alia) *syn*-2-methylbicyclo[3.1.0]hexan-6-one ethylene ketal, which in turn was prepared optically pure, [α]₃₆₅ ± 219°, from (+)-3-methylcyclohexanone, using the synthetic method of Guisti: Guisti, G.; Morales, C. *Bull. Soc. Chim. Fr.* **1973**, *1*, 382.

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11: $R_1, R_2, R_3, R_4 = H$
 14: $R_1, R_4 = H; R_2, R_3 = CH_3$
 15: $R_1, R_4 = CH_3; R_2, R_3 = H$

12: $R_1, R_2, R_3, R_4 = H$
 16: $R_1, R_4 = CH_3; R_2, R_3 = H$
 17: $R_1, R_4 = H; R_2, R_3 = CH_3$



13: $R_1, R_2, R_3, R_4 = H$
 18: $R_1, R_4 = CH_3; R_2, R_3 = H$

19

that may be important in other thermal reactions do not seem to be detectable here.

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Kinetics and Mechanism of Nitrate Reduction by a Dimeric Aquamolybdenum(III) Complex in Aqueous Solution. Direct Evidence for an Oxo-Group Transfer

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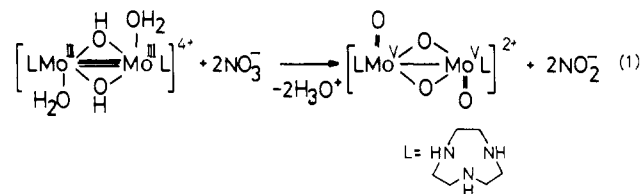
Received August 22, 1985

The molybdoenzyme *E. coli* nitrate reductase catalyzes the reduction of nitrate to nitrite at an active site of mononuclear Mo(IV) (or Mo(V)) center.¹ In the past a number of monomeric oxomolybdenum(V) complexes have been found to reduce nitrate to NO₂ in nonaqueous solvents.² The formation of a (nitrate)-molybdenum(V) precursor complex has been proposed in the rate-determining step with subsequent intramolecular one-electron transfer and oxo-group transfer to produce dioxomolybdenum(VI) species and NO₂. The mononuclear hexa-aquamolybdenum(III) cation has been shown to reduce NO₃⁻ to NO₂⁻ in aqueous solution generating the aquamolybdenum(V) dimer, [Mo₂O₄(H₂O)₆]²⁺.³ Formally, this reaction involves a two-electron transfer which could be an oxo-transfer reaction. The transfer of an oxygen atom from the inert nitrate ion to the respective molybdenum centers has not been previously demonstrated experimentally.

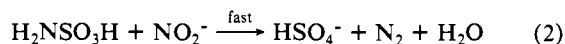
We here wish to report the kinetics and mechanism of the reaction of the diamagnetic, green bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum(III)](4+) cation^{4,5} with

nitrate in acidic aqueous solution.

The reaction of the bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclononane)molybdenum(III)](4+) cation^{4,5} with nitrate under strictly oxygen-free conditions yields quantitatively purple anti-[L₂Mo₂O₄]²⁺ and nitrite (eq 1).



The formation of NO₂⁻ during the above reaction was proven in situ when the reaction was carried out in the presence of sulfanilic acid and α-naphthylamine in acidic aqueous solution both of which do not react with either the Mo(III) dimer or the Mo(V) dimer in the absence of nitrate. The generation of the known deep-red azo dye is good evidence for the presence of NO₂⁻. The stoichiometry of the above reaction was determined spectrophotometrically (Job's method) using amidosulfonic acid as effective nitrite scavenger (eq 2)⁶ and quantitative determination



of the gaseous nitrogen evolved. One nitrate is consumed per molybdenum(III) center.

The kinetics of the reaction between [L₂Mo₂(μ-OH)₂(H₂O)₂]⁴⁺ and nitrate (pseudo-first-order conditions; excess NO₃⁻) were determined spectrophotometrically at 380 nm using eight different solutions containing varying amounts of NO₃⁻ ([NO₃⁻] = 0.01–0.40 M; [Mo^{III}]₂ = 4 × 10⁻⁴ M), methanesulfonic acid ([H⁺] = 0.1 M), and amidosulfonic acid ([H₂NSO₃H] = 5.2 × 10⁻³ M). The ionic strength was adjusted to 0.5 M by using sodium methanesulfonate as innocent electrolyte. Plots of absorbance changes, log(A_t - A_∞), against time, t, were linear for at least 4 half-lives.⁷ The final spectrum, after the reaction with nitrate was complete, corresponded exactly to that of anti-[L₂Mo₂O₄]²⁺.⁸ Scan spectra recorded during the reaction revealed the presence of two isosbestic points at 335 and 473 nm. Variation of [Mo^{III}]₂ ((1.4–4.0) × 10⁻⁴ M) did not affect the pseudo-first-order rate constants, k_{obsd}. Values of the second-order rate constant, k (M⁻¹

$$-d[Mo^{III}]_2/dt = d[Mo^V]_2/dt = k[Mo^{III}]_2[NO_3^-] \quad (3)$$

s⁻¹), obtained by a least-squares treatment of data are 0.023 (10 °C), 0.042 (17 °C), and 0.10 (25 °C). Activation parameters for k are ΔH[‡] = 69 ± 4 kJ mol⁻¹ and ΔS[‡] = -33 ± 12 J mol⁻¹ K⁻¹. It is noted that a small but reproducible linear dependence of the rate on [H⁺] is observed. Thus in going from [H⁺] = 0.05 to 0.30 M ([NO₃⁻] = 0.05 M, [Mo^{III}]₂ = 2 × 10⁻⁴ M, [H₂NSO₃H] = 5 × 10⁻³ M, 25 °C, I = 0.5 M (NaCH₃SO₃)) the value of k_{obsd}

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(5) In all experiments described here solid samples of diamagnetic, green [L₂Mo₂^{III}(μ-OH)₂(OH)₂](PF₆)₂·H₂O were used as starting material (L = 1,4,7-triazacyclononane). This salt was prepared from [L₂Mo₂(μ-OH)₂(μ-CO₃)]I₂·H₂O^{4a} (2.5 g) in deoxygenated aqueous HPF₆ (0.5 M, 50 mL) at room temperature. Desired product 1.5 g, precipitated slowly at 0 °C. Anal. Calcd for C₁₂H₃₃O₄N₆Mo₂P₂F₁₂: C, 17.44; H, 4.39; N, 10.77. Found: C, 17.3; H, 4.1; N, 9.9.

(6) Oxygen-free aqueous solutions of the Mo^{III}₂ dimer do not react with H₂NSO₃H.

(7) Kinetic runs performed in the absence of H₂NSO₃H under otherwise identical conditions were not found to follow strictly first-order kinetics and the final absorption spectrum indicated the presence of small amounts of other products than anti-[L₂Mo₂O₄]²⁺. In a few preliminary, separate experiments it was confirmed that the Mo(III) dimer reacts rapidly with nitrite and NO generating yellow solutions, from which yellow-greenish solids were obtained (IR bands at 1780 and 1630 cm⁻¹ are indicative of dinitrosylmolybdenum species).

(8) The rate of the previously reported irreversible, H⁺-catalyzed anti → syn isomerization⁹ of the product anti-[L₂Mo₂O₄]²⁺ is much slower under our experimental conditions and does not interfere with the spectrophotometric product analyses measured directly after the reduction of nitrate is complete.

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