(2R,3R,4R), (2R,3S,4S), (2S,3R,4R), and (2S,3S,4S) isomers showed a doublet²² for H-6_{ax} at δ 2.30 ($J \sim 12$ Hz) (cf. Figure 1c). This arises from the (2S,5S,6R)- $[5,6-^2H_2]$ imine hexahydropyrimidine and its enantiomer (cf. Scheme IIc). Again, these resonances were satisfactorily reproduced by computer-assisted simulation (cf. Figure 2c).

The signals of H-6_{ax} of dideuterated imine hexahydropyrimidines (cf. Scheme II) derived from dideuterated spermidines were broadened and shifted upfield (ca. 12 Hz) compared to H-6_{ax} in 4, presumably because of effects from deuterium(s). A further compliction is that these signals overlap those for H-1'ax, which appears as two octets separated by 7 Hz in the spectrum of each dideuterated imine hexahydropyrimidine (cf. Figure 1a-c).23 These complexities necessitated the synthesis of a reference sample of one of the dideuterated imine hexahydropyrimidines. This was achieved from $(E)-[1,2^{-2}H_2]$ ethene via (2S,3R)/(2R,3S)-3aminopropionitrile (cf. Scheme III). The key step in this sequence is the conversion of [1,2-2H₂]2-(trifluoroacetamido)ethanol O-ptoluenesulfonate into [1,2-2H₂]-1-cyano-2-(trifluoroacetamido)ethane with retention of configuration at the reacting deuterio-methylene group.²⁴ The synthetic [1',2'-2H₂]spermidine was reacted with ≥2 mol equiv ethanal in deuteriochloroform to give (5R,6R)- $[5,6-{}_{2}H_{2}]$ -4 + (5S,6S)- $[5,6-{}^{2}H_{2}]$ -4 and their enantiomers. The 61.4-MHz ²H NMR spectrum of this mixture showed four broad singlets of equal intensity at δ 1.66 and 3.03, corresponding to the (5R,6R)-isomer and its enantiomer, and at δ 1.52 and 2.33, for the (5S,6S)-isomer and its enantiomer. The 400-MHz ¹H NMR spectrum was very similar (peak for peak matching; cf. Figure 1d) to the dideuterioimine hexahydropyrimidine derived from (2R,3R,4S)/(2R,3S,4R)/(2S,3R,4S)/(2S,3S,4R)-[3,4-²H₂]methionines (cf. Scheme II). In particular, the resonance for H-6_{ax} was a broad singlet²¹ at δ 2.30, superimposed on resonances from H-1'ax (cf. Figures 1d,b, 2b).

A recent kinetic study of spermidine synthase from E. coli concluded5a that a Ping-Pong Bi-Bi mechanism operates, via an intermediate aminopropylated enzyme. If this were correct, the stereochemical course of spermidine synthase should be an overall retention via two inversion steps. The contrasting conclusion from the present study is that spermidine synthase operates by a sequential Bi-Bi mechanism exhibiting the stereochemistry of a classical $S_N 2$ reaction, i.e., inversion.²⁵ It is therefore analogous to enzymic transmethylation with adenosylmethionine, for which inversion at the sulfonium methyl has been conclusively demonstrated.²⁶ Recently, transadenosylation of methionine to form adenosylmethionine has also been shown to occur with inversion of configuration at the reacting methylene group.2

Acknowledgment. We thank SERC for financial support, Drs. E. Curzon and O. W. Howarth for high-field NMR spectra

(22) This resonance is expected to be a doublet (J = 12 Hz) of 1:1:1 triplets

(Regional NMR Service, University of Warwick), Dr. D. C. Billington for the preparation of dideuterated methionines and Dr. P. Bigler (Universität Bern, Institut für Organische Chemie) for computer-assisted simulations or NMR spectra. A helpful discussion with Professor S. J. Gould, University of Connecticut, is greatfully acknowledged.

Interconversion of Nitrite and Ammonia: Progress toward a Model for Nitrite Reductase

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Recently, we reported that for the complex [Ru(trpy)(bpy)-NH₃]²⁺ (trpy is 2,2',2"-terpyridine; bpy is 2,2'-bipyridine), the coordinated ammonia is oxidized rapidly and quantitatively to give the corresponding nitrosyl complex [Ru(trpy)(bpy)NO]³⁺, which is in acid-base equilibrium with the nitro complex [Ru(trpy)-(bpy)NO₂]⁺ and the two are present in equal amounts at pH 2.34¹

$$[Ru(trpy)(bpy)NH_{3}]^{2+} \xrightarrow{-6e^{-}}$$

$$1 \qquad \qquad +H_{2}O, -5H^{+}$$

$$[Ru(trpy)(bpy)NO]^{3+} \xrightarrow{+H_{2}O, +2H^{+}} [Ru(trpy)(bpy)NO_{2}]^{+} (1)$$

We report here that the reverse reaction, the reduction of coordinated nitrosyl to coordinated ammonia, occurs for a variety of polypyridyl complexes of both ruthenium and osmium and that the mechanism involves a series of facile one-electron-transfer steps, as initially suggested by Armor for the reduction of [Ru-(NH₃)₅NO₁^{3+,2} We also report the *catalytic* reduction of nitrite to ammonia, based on the water-soluble metalloporphyrin Fe(I-I)TPPS (TPPS = meso-tetrakis(p-sulfonatophenyl)porphine).³

In Figure 1 is shown a cyclic voltammogram for [Ru(trpy)-(bpy)NO](BF₄)₃ in aqueous solution buffered at pH 4.68.⁴ The first reduction, wave A, at $E_{1/2} = 0.19 \text{ V}$ vs. SSCE, 4 is a reversible, pH-independent one-electron transfer to an orbital largely $\pi^*(NO)$ in character (eq 2).⁵ The second reduction, wave B (at E_p^c =

$$[Ru(trpy)(bpy)NO]^{3+} \xrightarrow{+e^{-}} [Ru(trpy)(bpy)\dot{N}O]^{2+}$$
(2)

-0.36 V), is also a pH-independent, one-electron reduction, while the third reduction, wave C (at $E_p^c = -0.57 \text{ V}$), is pH dependent. Coulometry⁵ past the third wave (E = -0.6 V) results in a quantitative, six-electron (n = 5.9) reduction of the nitrosyl complex 2 to the ammine complex 1 as shown in eq 3.

$$[Ru(trpy)(bpy)NO]^{3+} + 6e^- + 5H^+ \rightarrow$$

$$[Ru(trpy)(bpy)NH_3]^{2+} + H_2O$$
 (3)

However, clear evidence for reduced intermediates can be obtained by cyclic voltammetry. Cycling through the first reduction (wave A) and to the onset of the second wave (wave B), results in the appearance of an oxidative wave (wave I) due to an intermediate (I) having $E_p^a(I) = +0.38 \text{ V}$. Cycling past both waves A and B to the onset of the third reduction (wave C) results in the loss of the oxidative wave for intermediate (I) and the appearance of an oxidative wave (wave II) for a second intermediate

⁽J = 2 Hz), ignoring vicinal $H_{ax}^{-}D_{eq}$ coupling (cf. ref 21). (23) This is believed to arise from an isotope effect of deuterium vs. hydrogen transmitted from axial H or D through the nitrogen lone pair (axial) to H-2 (axial) and H-1'_{ax} [N.B. in the spectra of dideuterated samples of 4 H-2 appears as two quartets of similar intensity separated by 7 Hz].

⁽²⁴⁾ This sequence was established with unlabeled compounds (new compounds gave spectroscopic data and combustion analyses in accord with their assigned structures); 2-(trifluoromethyl)-\(\Delta^2\)-oxazoline (Tanaka, K.; Shreeve, J. M. Inorg. Chem. 1980, 19, 2612 and refs cited therein) was isolated from treatment of 2-(trifluoroacetamido)ethanol O-p-toluenesulphonate with NaCN/Me₂SO or KOH/CH₂Cl₂; exposure of this oxazoline to excess of NaCN in Me₂SO (1 week/room temperature) converts it into 1-cyano-2-(trifluoroacetamido)ethane; we thank Dr. D. J. Robins for experimental details concerning steps viii and ix of Scheme III [cf.: Khan, H. A.; Robins, D. J. J. Chem. Soc. Chem. Commun. 1981, 554]; mass spectral analyses showed deuterated intermediates to contain $\geq 90\%$ [2H_2] species. (25) For a comment on the kinetic analysis of ref 5a see footnote 11 of ref

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⁽⁴⁾ Note from eq 1 that at pH 4.68 the dominant form in the nitro-nitrosyl acid-base system is the nitro complex. However, on the time scale of our experiments, the nitrosyl - nitro interconversion is slow and it is possible to observe the electrochemical properties of the nitrosyl complex without interference from the nitro complex.

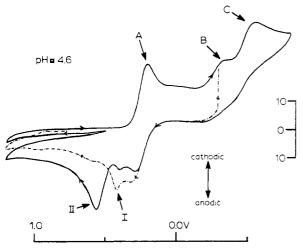


Figure 1. Cyclic voltammograms of [(terpy)(bpy)Ru(NO)](BF₄)₃ in pH 4.6 aqueous buffer (10.5 with added Na₂SO₄) at a carbon paste working electrode. Scan rate is 100 mV/s, the potential scale is in volts and the vertical current scale is in microamps.

Scheme Ia

a trpy = 2,2',2''-terpyridine, bpy = 2,2'-bipyridine.

(II) having $E_p^a(II) = +0.55 \text{ V}$. In more acidic solutions (pH <2.6), waves B and C overlap, waves I and II are not observed, and the only product from reductive cycling through combined waves B and C is the ammine complex 1.

When the observations described above are combined with the earlier results1 on the oxidation of the ammine complex [Ru-(trpy)(bpy)NH₃]²⁺, a reasonable mechanism for the interconversion of nitrite and ammonia emerges and is shown in Scheme I. Reasonable guesses are made in Scheme I as to the nature of intermediates I and II. From pH dependence studies, oxidation of I involves the loss of a proton since $E_p^a(I)$ varies linearly with pH (slope = -50 mV/pH) over the pH range 2.66-4.68. The proton dependence is consistent with proton-electron loss from [Ru(trpy)(bpy)NHO]⁺ (postulated to be I) to give [Ru(trpy)-(bpy)NO]²⁺, followed by rapid oxidation to give [Ru(trpy)-(bpy)NO]³⁺. Related complexes containing the bound NHO group such as OsCl₂(CO)(NHO)(PPh₃)₂⁷ and Co(das)₂Cl(NHO)⁸

(das = o-phenylenebis(dimethylarsine)), have been isolated and characterized. From the pH dependence of wave C, where $E_p^c(C)$ varies linearly with pH (slope = 73 mV/pH) over the pH range 3.12-5.29, and relative voltammetric peak heights, the second intermediate results from a net one-electron, one-proton reduction of intermediate I, $[Ru(trpy)(bpy)NHO]^+$, which suggests that intermediate II is $[Ru(trpy)(bpy)N]^{2+}$ or [Ru(trpy)(bpy)-NH₂O]²⁺. The apparent buildup of [Ru(trpy)(bpy)NH]²⁺ (8) by oxidation of $[Ru(trpy)(bpy)NH_3]^{2+}$ and the buildup of $[Ru(trpy)(bpy)N]^{2+}$ (7) by the reduction of $[Ru(trpy)(bpy)NO]^{3+}$ shows that the interconversion between the "Ru(V) nitrido" (7) and the "Ru(IV) imido" (8) intermediates is the slow step in the overall nitrite to ammonia interconversion. If the intermediate is, in fact, [Ru(trpy)(bpy)N]2+, the slowness of the step may be associated with the necessity of a proton-coupled electron transfer, as observed earlier in the comproportionation reaction between [Ru^{IV}(bpy)₂(py)O]²⁺ and [Ru^{II}(bpy)₂(py)(H₂O)]²⁺.9

The generality of the reduction of coordinated nitrosyl to am-

monia is shown by the reactions in eq 4-7, all of which are quantitative as shown by coulometry and product characterization studies.

$$\begin{array}{c} \textit{cis-}[\text{Ru}(\text{bpy})_2(\text{NO})\text{Cl}]^{2+} \xrightarrow{+6\text{e}^-} \\ & \textit{cis-}[\text{Ru}(\text{bpy})_2(\text{NH}_3)(\text{H}_2\text{O})]^{2+} + \text{Cl}^- \ (4) \end{array}$$

$$cis$$
-[Ru(bpy)₂(NO)py]³⁺ $\xrightarrow{+6e^-}$ cis -[Ru(bpy)₂(NH₃)py]²⁺ + H₂O (5)

$$[Os(trpy)(bpy)NO]^{3+} \xrightarrow{+6e^{-}} [Os(trpy)(bpy)NH_{3}]^{2+} + H_{2}O$$
(6)

$$cis$$
-[Ru(bpy)₂(NO)(NO₂)]²⁺ $\xrightarrow{+12e^-}$
 cis -[Ru(bpy)₂(NH₃)₂]²⁺ + 3H₂O (7)

Neither the ruthenium complexes nor the osmium complex in eq 1 and 4-7 reduces nitrite/nitrosyl catalytically to ammonia, due to the stability of the ammine complexes toward substitution. However, we have made a preliminary investigation of the catalytic reduction of nitrite to ammonia based on the water-soluble metalloporphyrin Fe(II)TPPS. To a dilute solution of sodium nitrite (0.03 M) in a pH 6.5 phosphate buffer solution (0.5 M Na₂HPO₄, 0.5 M KH₂PO₄) was added a catalytic amount of Fe(II)TPPS (0.0005 M). The solution was electrolyzed at -0.9 V, where clearly enhanced (3×) catalytic currents were observed compared to those of a solution where the catalyst was not added. The total charge passed in the partial electrolysis (101.2 C) corresponded to a catalytic turnover of 140 for the catalyst on a per electron basis or of 23 on the basis of a net six-electron event. Free ammonia was detected in the electrolyzed solution by GC analysis, where the amount (~ 0.0054 M) of ammonia corresponded to approximately 50% of the coulombs passed, based on a six-electron reduction.

Nitrosyl complexes of iron porphyrins have been previously prepared. 10 Olson, et al. have recently shown that Fe(TPP)NO undergoes a reversible one-electron reduction in CH₂Cl₂.¹¹ It is quite conceivable that the mechanism for the catalytic reduction is closely related to the series of reactions in Scheme I. The sequence of events would involve the axial binding of nitrite to Fe(II)TPPS, nitro to nitrosyl conversion, and entry into the redox cycle of Scheme I. The advantage of the iron system from the

⁽⁵⁾ All potentials are reported vs. the saturated sodium chloride calomel electrode, which is +0.234 V with respect to the normal hydrogen electrode. (See: Bard, A. J., Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980.). Coulometric reductions were performed by using a gas-tight electrochemical cell with a mercury pool as a working electrode, a platinum gauze as an auxilliary electrode, and a saturated sodium chloride calomel electrode as a reference.

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catalytic point of view is the axial lability of Fe(II)TPPS, which provides the release of bound ammonia following its formation and the subsequent reentry of Fe(II)TPPS into the nitrite reduction cycle.

As a last point, it is important to note that the active site in the nitrite reductase enzymes¹² is though to be based on an iron heme unit. The results reported here may provide mechanistic insight into the chemical details of the operation of this enzyme

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Registry No. 1, 58452-44-1; **2**, 83006-31-9; **3**, 78913-50-5; cis-[Ru-(bpy)₂(NO)Cl]²⁺, 31847-83-3; cis-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-31-9; **3**, 78913-50-5; cis-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-31-9; **3**, 78913-50-5; cis-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-31-9; **3**, 78913-50-5; cis-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-31-9; **3**, 78913-50-5; cis-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-31-9; cis-[Ru(bpy)₂(NH₃O)(H₂O)(H₃O)(32-0; $cis-[Ru(bpy)_2(NO)py]^{3+}$, 47713-31-5; $cis-[Ru(bpy)_2(NH_3)py]^{2+}$, 83006-33-1; [Os(trpy)(bpy)NO]³⁺, 83006-34-2; [Os(trpy)(bpy)NH₃]²⁺, 83006-35-3; *cis*-[Ru(bpy)₂(NO)(NO₂)]²⁺, 47637-63-8; *cis*-[Ru(bpy)₂- $(NH_3)_2]^{2+}$, 56993-98-7; Fe(II)TPPS, 83006-36-4; NO_2^- , 14797-65-0; NH₃, 7664-41-7; nitrite reductase, 9080-03-9.

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Transfer of O₂ from Triphenyl Phosphite Ozonide to Alkyl-Substituted Olefins

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Two general mechanisms have been recognized for phosphite ozonide reactions with olefins. In the first of these, the ozonide decomposes to phosphate and singlet oxygen1 followed by normal singlet oxygen reactions (reaction 1). At temperatures lower than those required for this unimolecular decomposition, one can frequently observe a direct bimolecular reaction² between ozonide and olefin that results in the delivery of O₂ to the olefin (reaction

$$(C_6H_5O)_3PO_3 \xrightarrow{-30 \text{ °C}} (C_6H_5O)_3PO + {}^1O_2 \xrightarrow{} HOO \xrightarrow{} (C_6H_5O)_3PO_3 + \underbrace{}^{-70 \text{ °C}} HOO \xrightarrow{} (C_6H_5O)_3PO_3 (2)$$

Results from Bartlett's laboratory^{2b,c,3} make it clear that the mechanistic details of pathways 1 and 2 can differ dramatically. With the vinyl ethers below, Bartlett and co-workers favor a [2] + 2]cycloaddition pathway3 for the singlet oxygen reaction (reaction 3) and a two-step pathway2b,c with a long-lived zwitterionic intermediate in the direct reaction (reaction 4). We point out in this communication that the direct reaction of phosphite ozonides with tetramethylethylenes is, in contrast, very similar to that of singlet oxygen.

Isotope effect differences in the reactions of the isomeric tetramethylethylenes- d_6 have provided sensitive tests of mechanism in the singlet oxygen reaction⁴ and the reactions of azoenophiles.⁵

We have repeated these isotope effect mapping experiments with triphenyl phosphite ozonide (TPPO) and tetramethylethylenes- d_6 . The results are presented in Table I.

In the case of the TPPO-mediated direct delivery of O_2 , as in the free singlet oxygen case, also shown in Table I, it is obvious that only cis relationships of C-H and C-D bonds lead to an isotope competition. This previously led us to propose an olefin-bisecting approach⁴ of ¹O₂, a situation that must be very closely duplicated in the reaction of phosphite ozonides with olefins. An economical view of the TPPO-alkene reaction could be represented by transition state 4, the geometrically equivalent 5; or conceivably, the ozonide is sufficiently energetic to produce perepoxide 6.

As in singlet oxygen chemistry, the present experiments do not discriminate among geometrically equivalent pathways (4, 5, or 6 for example). A number of mechanisms can be eliminated, however, most prominently the zwitterionic pathway suggested by structure 7. As we have previously pointed out in arguments

concerning ${}^{1}O_{2}$, such intermediates would predict equal k_{H}/k_{D} effects for olefins 2 and 3 (Table I), contrary to our findings. Since strong evidence supports zwitterions in phosphite ozonide-vinyl ether reactions2b (see reaction 4), it is clear that a unified mechanism for ozonide-olefin reactions will be elusive. The situation is thus completely analogous to free singlet oxygen chemistry. Jefford and co-workers⁷ in particular have generated strong evidence for zwitterions in ¹O₂ reactions with unsymmetrical, electron-rich systems such as methoxynorbornene, while other evidence⁴ makes it highly unlikely that zwitterions (or di-

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