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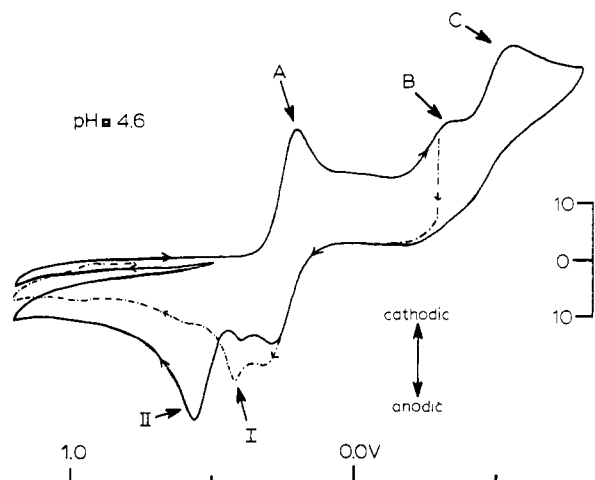
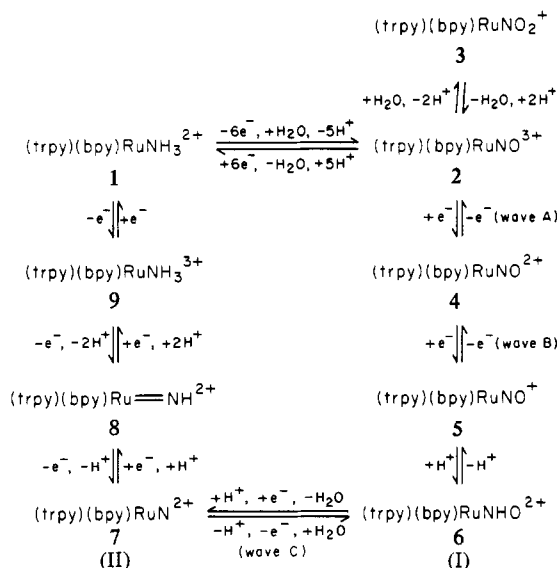


Figure 1. Cyclic voltammograms of $[(\text{terpy})(\text{bpy})\text{Ru}(\text{NO})](\text{BF}_4)_3$ in pH 4.6 aqueous buffer (I 0.5 with added Na_2SO_4) at a carbon paste working electrode. Scan rate is 100 mV/s, the potential scale is in volts and the vertical current scale is in microamps.

Scheme I^a



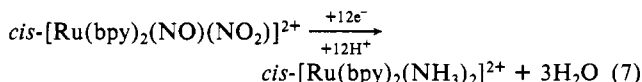
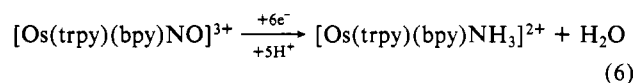
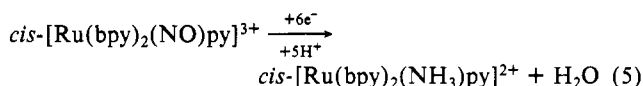
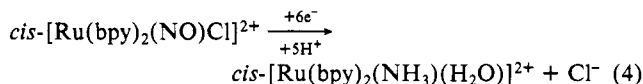
^a trpy = 2,2',2''-terpyridine, bpy = 2,2'-bipyridine.

(II) having $E_p^a(\text{II}) = +0.55$ 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 $[\text{Ru}(\text{trpy})(\text{bpy})\text{NH}_3]^{2+}$, 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 $E_p^a(\text{I})$ 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 $[\text{Ru}(\text{trpy})(\text{bpy})\text{NHO}]^+$ (postulated to be I) to give $[\text{Ru}(\text{trpy})(\text{bpy})\text{NO}]^{2+}$, followed by rapid oxidation to give $[\text{Ru}(\text{trpy})(\text{bpy})\text{NO}]^{3+}$. Related complexes containing the bound NHO group such as $\text{OsCl}_2(\text{CO})(\text{NHO})(\text{PPh}_3)_2$ ⁷ and $\text{Co}(\text{das})_2\text{Cl}(\text{NHO})$ ⁸

(das = *o*-phenylenebis(dimethylarsine)), have been isolated and characterized. From the pH dependence of wave C, where $E_p^c(\text{C})$ 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, $[\text{Ru}(\text{trpy})(\text{bpy})\text{NHO}]^+$, which suggests that intermediate II is $[\text{Ru}(\text{trpy})(\text{bpy})\text{N}]^{2+}$ or $[\text{Ru}(\text{trpy})(\text{bpy})\text{NH}_2\text{O}]^{2+}$. The apparent buildup of $[\text{Ru}(\text{trpy})(\text{bpy})\text{NH}]^{2+}$ (**8**) by oxidation of $[\text{Ru}(\text{trpy})(\text{bpy})\text{NH}_3]^{2+}$ and the buildup of $[\text{Ru}(\text{trpy})(\text{bpy})\text{N}]^{2+}$ (**7**) by the reduction of $[\text{Ru}(\text{trpy})(\text{bpy})\text{NO}]^{3+}$ 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, $[\text{Ru}(\text{trpy})(\text{bpy})\text{N}]^{2+}$, the slowness of the step may be associated with the necessity of a proton-coupled electron transfer, as observed earlier in the disproportionation reaction between $[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})\text{O}]^{2+}$ and $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{py})(\text{H}_2\text{O})]^{2+}$.⁹

The generality of the reduction of coordinated nitrosyl to ammonia is shown by the reactions in eq 4–7, all of which are quantitative as shown by coulometry and product characterization studies.



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 $\text{Fe}(\text{II})\text{TPPS}$. To a dilute solution of sodium nitrite (0.03 M) in a pH 6.5 phosphate buffer solution (0.5 M Na_2HPO_4 , 0.5 M KH_2PO_4) was added a catalytic amount of $\text{Fe}(\text{II})\text{TPPS}$ (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 $\text{Fe}(\text{TPP})\text{NO}$ undergoes a reversible one-electron reduction in CH_2Cl_2 .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 $\text{Fe}(\text{II})\text{TPPS}$, nitro to nitrosyl conversion, and entry into the redox cycle of Scheme I. The advantage of the iron system from the

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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 thought 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 system.

Acknowledgments are made to the National Institutes of Health under Grant No. 2-ROI-GH15238-15 and to the National Science Foundation under Grant No. CHE-8002433 for support of this research.

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⁺, 83006-32-0; *cis*-[Ru(bpy)₂(NO)py]³⁺, 47713-31-5; *cis*-[Ru(bpy)₂(NH₃)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(NH₃)₂]²⁺, 56993-98-7; Fe(II)TPPS, 83006-36-4; NO₂⁻, 14797-65-0; NH₃, 7664-41-7; nitrite reductase, 9080-03-9.

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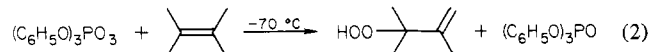
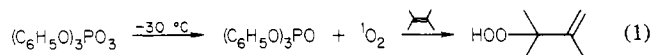
Transfer of O₂ from Triphenyl Phosphite Ozonide to Alkyl-Substituted Olefins

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Received May 10, 1982

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 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 pathway^{2b,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.

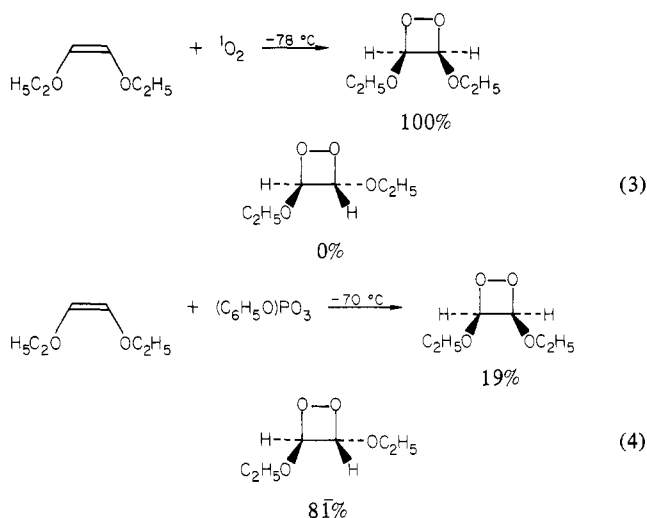
Isotope effect differences in the reactions of the isomeric tetramethylethylenes-*d*₆ have provided sensitive tests of mechanism in the singlet oxygen reaction⁴ and the reactions of azoenophiles.⁵

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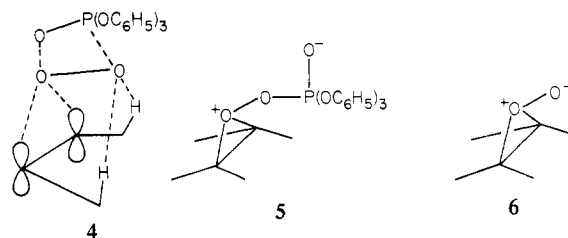
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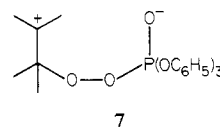


We have repeated these isotope effect mapping experiments with triphenyl phosphite ozonide (TPPO) and tetramethylethylenes-*d*₆. The results are presented in Table I.

In the case of the TPPO-mediated direct delivery of O₂, 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 ¹O₂, 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 reactions^{2b} (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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