Table II. Coefficients of AO₃ (see 10) in the HOMO and SHOMO of a Linear System of $n \sigma$ Bonds

	coeff	of AO ₃
n	НОМО	SHOMO
2	0.37	0.60
3	0.42	0.23
4	0.41	0
5	0.39	0.12
6	0.37	0.18

the HO- σ -MO rather than to the *lowering* of the symmetry adapted $\pi + \pi$ combination through its mixing with LU- σ^* -MO.¹⁹ This result is general for OIT-*n*-B ($n > 2^{20}$) because the data in Table II show that the coefficient of AO₃ in the HO- σ -MO is greater than that in the SHO- σ -MO. Our model also suggests that the splitting energy resulting from π (lone pair) OIT-*n*-B is largely due to the mixing of a symmetry adapted pair of orbitals with the HO- σ -MO.²⁵

The model also makes clear other salient features of OITB: (1) The energy level ordering of the interacted π orbitals depends on the number, n, of intervening bonds: S is below A for even n, and S is above A for odd n.¹ This result immediately follows from the model, because the HO- σ -MO is S for odd n and A for even (2) The all-trans (W) arrangement of bonds is the most $n.^{30}$

(20) For the case n = 2 we predict that $(\pi - \pi)$ -HO- σ -MO mixing and $(\pi - \pi)$ -HO- σ -+ π)-SHO- σ -MO mixing to be comparable. It is therefore interesting to note that Heilbronner and Schmelzer have estimated that in norbornadiene both $\pi + \pi$ and $\pi - \pi$ levels are raised as a result of OlT-2-B and that the former level is raised more than the latter level. Heilbronner, E.; Schmelzer, A. Helv. Chim. Acta 1975, 58, 936.

(21) Even OIT-9-B may be observable $[AO_3(\sigma HOMO) = 0.37, AO_3 - (\sigma SHOMO) = 0.24)]$ and may account for Zimmerman's observations of (σ50000) = 0.24)] and may account for Zimmerman's observations of energy-transfer processes in [2]-rods: Zimmerman, H. E., Goldman, T. D.;
 Hirzel, T. K.; Schmidt, S. P. J. Org. Chem. 1980, 45, 3933.
 (22) The π splitting energy in [4.4.2]propella-3,8-diene is only 0.3 eV.³³
 Although the paper²³ equivocates about the origin of this split we are sure that

it must be due (almost) exclusively to OIT-4-B. The small value of the splitting energy in the propellane compared with that observed for 1 (0.87 eV) could possibly reflect the conformation of the propellane. For example, if the σ framework connecting the π bonds had the cis-trans conformation (as opposed to the trans-trans conformation indicated in the paper²³), then the splitting energy is consistent with that observed for 5 which also has the cis-trans arrangement of σ bonds.

(23) Dougherty, D.; Bloomfield, J. J.; Newkome, G. R.; Arnett, J. F.; McGlynn, S. P. J. Phys. Chem. 1976, 80, 2212.

(24) We draw attention to the nomenclature of interactions between orbitals and the intervening σ framework. The mixing of symmetry adapted combinations of orbitals with the orbitals is called OITB whereas the mixing of a *single* orbital with the σ orbitals is called hyperconjugation.

(25) The assumption that, in OITB, π (or lone pair) interactions occur principally through their mixing with σ orbitals has also been used by Heilbronner and his group in their analysis of photoelectron spectra of molecules exhibiting OITB but in a less explicit manner than described here. We have also learned that, in a letter to Professors D.C. Frost and L. Weiler (Sept 18, 1972), Professor E. Heilbronner described a more general formulation of our ref 16 which is also valid for the case where the molecule lacks symmetry.

(26) The available literature data suggest, however, that OIT-*n*-B are attenuated fairly strongly with increasing $n^{6.28}$ ln fact, using a more realistic value for the resonance integral between two sp³ hybrid AO's attached to the same carbon atom $(m\beta, m = 0.35^{18cd})$ leads to a greater attenuation of OITB-n-B with n. Although the essential features of our model do not suffer from the use of the "C" approximation, the localized orbital technique, as developed by Heilbronner and co-workers,²⁷ would be more appropriate for

placing the model on a fimer quantitative basis. (27) (a) Bieri, G.; Dill, J. D.; Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* 1977, 60, 224. (b) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Ibid.* 1978, 61, 547. (28) It has been reported that π - π interactions in the series of nonconju-

gated acyclic dienes $H_2C=CH(CH_2)_{m-4}CH=CH_2$ with m = 5-9 diminish with increasing m^{29} Although these authors attribute these interactions to through-space effects, their supporting evidence is unconvincing and, until the conformations of these dienes have been determined more rigorously, we are inclined to believe that OITB could be largely responsible for the observations.
(29) Bunzli, J. C.; Burack, A. J.; Frost, D. C. *Tetrahedron* 1973, 29, 3735.
(30) Note Added in Proof. Since submission of this manuscript a similar termination of the similar sector.

treatment of the level ordering of orbitals interacting through bonds has recently appeared: Verhoeven, J. W.; Pasman, P. Tetrahedron 1981, 37, 943.



bond AO's are represented by heavy arrows. In 13, the bonding interactions represented by the dotted arrow cancels out some of the π - σ mixing. (3) Because the splitting energy depends to a large extent on the magnitude of the π -AO₃ interaction, it is evident from the coefficients in Table II that OIT-n-B should decay only weakly with increasing n and should be easily observable for the case $n = 6^{21.26-29}$ We intend to test this prediction by measuring the PES of further "norbornylogs" of 1, which are currently being synthesized in our laboratories.

Finally, we note that OITB involving high-lying π^* MO's should involve mixing with σ^* , rather than σ orbitals, since the π^* levels presumably lie closer to the σ^* MO's than to the σ MO's. Here it is easily shown that the appropriate symmetry adapted pair of π^* MO's is lowered much more, through its mixing with the LU- σ^* -MO, than the other pair of π^* MO's, through its mixing with the SLU- σ^* -MO. We note that the Hoffmann model of OITB¹ represents a special case of our model, since the interacting orbital levels lie about midway between the HO- σ -MO and LU- σ^* -MO (i.e., such as p orbitals in carbon diradicals). In such a case, both σ and σ^* mix strongly with the radical orbitals.

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Oxidation of Coordinated Ammonia to Nitrate

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We have discovered a well-defined reaction in which coordination of ammonia to ruthenium followed by oxidation leads to a rapid, quantitative conversion first to nitrite and then to nitrate. The reaction is remarkable in that it is rapid and involves only a single metal site.

A cyclic voltammogram of an aqueous solution of [(trpy)- $(bpy)Ru^{II}NH_3]^{2+}$ (trpy = 2,2',2"-terpyridine; bpy = 2,2'-bipyridine) at pH 6.8 shows a single irreversible oxidation wave at 0.84 V vs. the saturated sodium chloride calomel electrode (SSCE). Fixed potential electrolysis at 0.8 V results in the loss of six electrons per complex as shown by coulometry. The spectral,

$$[(trpy)(bpy)Ru^{II}NH_3]^{2+} + 2H_2O \xrightarrow[E = 0.8V vs. SSCE]{(trpy)(bpy)Ru^{II}NO_2]^+} + 7H^+ (1)$$

voltammetric, and acid-base properties of the product are identical with those of an authentic sample of [(trpy)(bpy)Ru^{II}NO₂]⁺, thus establishing the stoichiometry shown in eq 1. Since it has been previously shown that further oxidation of [(bpy)₂(py)RuNO₂]⁺,

⁽¹⁹⁾ The simple model predicts that $(E_{\pi-\pi} - E_{\pi})/(E_{\pi} - E_{\pi+\pi}) > 1$. That this ratio is only 0.74 for 1 is probably due to the neglect of small effects such as the additional raising of the basis level by mixing with lower lying σ MO's and the slight depression of the $\pi + \pi$ level through its small mixing with σ^* LUMO.



Figure 1. (a) Oxidative spectroelectrochemical titration of $[Ru(trpy)(bpy)NH_3]^{2+}$ in water at pH 6.8; 0.1 M in $H_2PO_4^{-}/HPO_4^{2-}$. (b) Plots of absorbance changes vs. extent of oxidative from Figure 1a at several wavelengths. The wavelengths used are indicated on the horizontal axis in Figure 1a.

which is closely related to the product of eq 1, occurs to give the analogous nitrato complex (eq 2),¹ when bound to a polypyridyl

$$H_2O + [(bpy)_2pyRu^{II}NO_2]^+ \xrightarrow{236} [(bpy)_2pyRu^{III}ONO_2]^{2+} + 2H^+ (2)$$

complex of ruthenium, ammonia can be induced to undergo a facile, quantitative oxidation to nitrate.

We have begun a series of experiments designed to elucidate the mechanistic details of reaction 1. Earlier work has shown that in related complexes, oxidation of organic amines to imines and nitriles is facile and apparently occurs in a series of net two-electron steps involving oxidative dehydrogenation (eq 3).² In Figure 1

$$(bpy)_2 Ru(NH_2 CH_2 R)_2^{2+} \xrightarrow{-86^-}_{-8H^+} (bpy)_2 Ru(NCR)_2^{2+}$$
 (3)

are shown the results of a spectroelectrochemical titration at several wavelengths. The plots show a change in slope in plots of absorbance change vs. extent of oxidation between one and two oxidizing equivalents and a change in the position of isosbestic points at roughly 2 equiv. The experiment provides clear evidence for the appearance of an intermediate following oxidation by two electrons. We have investigated the details of the early stages of oxidation. A cyclic voltammogram of [(trpy)(bpy)Ru^{II}NH₃]²⁺ in strong acid (pH 0) shows a reversible Ru(III)/Ru(II) couple at 0.76 V, suggesting that the first step in the Ru^{II}NH₃ \rightarrow Ru^{II}NO₂ conversion is oxidation to Ru(III). When the pH of a solution containing [(trpy)(bpy)Ru^{III}NH₃]³⁺ is increased from 0 to 4, a rapid reaction occurs which is second order in Ru(III) ($k \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$; T = 25 °C, pH 4) as shown by the stopped-flow technique. Oxidation of Ru(II) to Ru(III) leads to a bleaching

⁽¹⁾ Keene, F. R.; Salmon, D. J.; Meyer, T. J. J. Am. Chem. Soc. 1977, 99, 2384. Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. Inorg. Chem. 1980, 19, 1896.

⁽²⁾ Keene, F. R.; Salmon, D. J.; Meyer, T. J. J. Am. Chem. Soc. 1976, 98, 1884. Brown, G. M.; Weaver, T. F.; Keene, F. R.; Meyer, T. J. Inorg. Chem. 1976, 15, 190.

$$[(trpy)(bpy)Ru^{II}NH_{3}]^{2+} \xrightarrow{-2e^{-}}_{-2H^{+}} [(trpy)(bpy)Ru^{IV} = NH]^{2+} \xrightarrow{H_{2}O} [(trpy)(bpy)Ru^{II}NH_{2}OH]^{2+} \xrightarrow{-4e^{-}+H_{2}O, -4H^{+}} |_{-4e^{-}, -3H^{+}} [(trpy)(bpy)Ru^{II}NO_{2}]^{2+} \xrightarrow{-3e^{-}}_{+H_{2}O, -2H^{+}} [(trpy)(bpy)Ru^{II}NO_{2}]^{+} \xrightarrow{+H_{2}O, -2H^{+}}_{-H_{2}O, +2H^{+}} [(trpy)(bpy)Ru^{II}NO_{2}]^{3+}$$

in the visible region because of the loss of bands arising from $d\pi(Ru(II)) \rightarrow \pi^*(bpy)$ transitions. For the rapid reaction observed by the stopped-flow technique, the observed absorbance changes are consistent with the reappearance of $\sim 50\%$ of the stoichiometric amount of [(trpy)(bpy)Ru^{III}NH₃]²⁺. The rapid reaction is followed by a slower reaction that follows first-order kinetics ($k = 5 \times 10^{-3} \text{ s}^{-1}$ at 25 °C) independent of pH over the range 2-10. At the end of the slow reaction nearly the total absorbance of the initial solution before oxidation is recovered but with slight changes in spectral detail. Oxidation of the solution at 0.8 V at the end of the slow reaction occurs with n = 5 to give [(trpy)(bpy)Ru^{II}NO₂]⁺ quantitatively.

Although complete details are lacking, our surmise is that following oxidation to Ru(III) a disproportionation occurs to give [(trpy)(bpy)Ru^{II}NH₃]²⁺ and the Ru(IV) imido complex [(trpy)(bpy)Ru^{IV}=NH]²⁺. The reaction is entirely analogous to the disproportionation in eq 4^3 and the proposed imido complex

$$2[(trpy)(bpy)Ru^{III} OH]^{2+} \xrightarrow[K = 5 \times 10^{-3}]{} [(trpy)(bpy)Ru^{IV} O]^{2+} + [(trpy)(bpy)RuOH_2]^{2+} (4)$$

is isoelectronic with the oxo complex $[(trpy)(bpy)Ru^{IV}=O]^{2+}$. There is precedence for the suggested disproportionation from the work of Taube and Rudd⁴ who suggested that disproportionation occurs following the addition of base to solutions containing $[Ru(NH_3)_5py]^{3+}$. Following the rapid disproportionation, the slow step appears to involve the pH independent attack of H₂O on the coordinated imide to give the related hydroxylamine complex (eq 5). This conclusion is supported by the observed spectral changes;

$$[(trpy)(bpy)Ru^{IV} = NH]^{2+} + H_2O \xrightarrow{\kappa} [(trpy)(bpy)Ru^{II}NH_2OH]^{2+} (5)$$

[(trpy)(bpy)RuNH₂OH]²⁺ is expected to be closely related spectrally to [(trpy)(bpy)Ru^{II}NH₃]²⁺.

The results described above appear to establish, at least in preliminary detail, the initial two-electron stage of the ammonia to nitrate oxidation. We have no mechanistic details for the second stage, which is a four-electron oxidation, except for the nature of the initial product of oxidation. If the ammine complex is oxidized at pH 4.9 rather than pH 6.8, the initial product is the nitrosyl complex, [(trpy)(bpy)Ru^{II}NO]³⁺, rather than the nitro complex. An acid-base equilibrium exists between the nitrosyl and nitro complexes (eq 6),¹ and although the nitro complex is

$$[(trpy)(bpy)Ru^{II}NO_2]^+ +$$

$$2H^{+} \stackrel{\mathbb{A}}{\longrightarrow} [(trpy)(bpy)Ru^{II}NO]^{3+} + H_{2}O (6)$$

the thermodynamically favored form at pH 4.9, conversion of the nitrosyl to the nitro is slow at this pH.

As previously mentioned, the final stage of the ammonia to nitrate conversion is the two-electron oxidation of bound nitrite to nitrate which has been studied in some detail.¹ A set of reactions describing oxidative conversion of ammonia to nitrate suggested by the results described both here and earlier are shown in the scheme below. The evidence for direct oxidation of the Ru(IV) imido intermediate comes from cyclic voltammetry where the irreversible oxidation leading to the RuNO2 product occurs rapidly on the time scale for attack by water.

It seems clear that our results and results reported earlier on the oxidation of amines coordinated to ruthenium³ or osmium⁵

both presage an extensive chemistry. One benefit of this chemistry may be the insight that it brings to the design of catalytic reagents for multiple electron-transfer reactions.

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Synthesis Applications of Aza-Cope Rearrangements.^{1a} A Stereoselective Synthesis of cis-3a-Aryloctahydroindoles and a New Short Entry to Amaryllidaceae Alkaloids

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The use of "directed" cationic aza-Cope rearrangements (2azonia[3,3]sigmatropic rearrangements) for the synthesis of a variety of heterocyclic systems, under mild conditions, has been described in recent reports from this laboratory.^{1a,2} An unusual annulation sequence which exploits this chemistry is illustrated in eq 1. This sequence, which would accomplish a "ring-enlarging

$$\begin{array}{c} HO \stackrel{R^{3}}{\underset{(CH_{2})n}{H} H} \\ (CH_{2})n \\ H \\ H \\ R^{1} \\ H \\ R^{1}$$

pyrrolidine annulation", would be of particular importance in synthesis if the widely occurring^{3,4} cis-3a-aryloctahydroindole ring system (cis-2, n = 1, $R^3 = Ar$) could be prepared in this fashion. If the amine and vinyl groups are oriented trans in the cyclopentyl precursor 1 (n = 1), this sequence should stereorationally lead to the formation of only the cis-octahydroindole ring system, since pericyclic rearrangement via only a single "chair-type" transition state is possible for systems of this type (eq 2).5-8 A cis-octa-



^{(1) (}a) Part 5 in the series. For part 4, see: Overman, L. E.; Yokomatsu, T. J. Org. Chem. 1980, 45, 5229. (b) Camille and Henry Dreyfus Teacher-Scholar, 1976-1981.

⁽³⁾ Thompson, M. S.; Meyer, T. J., manuscript in preparation. Moyer,
B. A.; Meyer, T. J. *Inorg. Chem.* 1981, 20, 436.
(4) Rudd, De F. P.; Taube, H. *Inorg. Chem.* 1971, 10, 1543.
(5) Buhr, J. D.; Taube, H. *Inorg. Chem.* 1979, 18, 2208.

^{(2) (}a) Overman, L. E.; Kakimoto, M. J. Am. Chem. Soc. 1979, 101, 1310. (b) Overman, L. E.; Kakimoto, M.; Okawara, M. Tetrahedron Lett. 1979,

^{4041. (}c) Overman, L. E.; Fukaya, C. J. Am. Chem. Soc. 1980, 102, 1454. (3) This ring system is found, for example, in alkaloids of the mesembrine,

Amaryllidaceae, Aspidosperma, and Strychnos familes.
 (4) Cf.: Dalton, D. R. "The Alkaloids. The Fundamental Chemistry"; Marcel Dekker: New York, 1979.

⁽⁵⁾ This prediction assumes that intramolecular Mannich ring closure of the presumed azacyclononadiene intermediate 3 would be more rapid than any loss of stereochemical integrity of this intermediate.