

Table II. Coefficients of AO_3 (see 10) in the HOMO and SHOMO of a Linear System of n σ Bonds

n	coeff of AO_3	
	HOMO	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 AO_3 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 n .³⁰ (2) The all-trans (W) arrangement of bonds is the most

(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.

(20) For the case $n = 2$ we predict that $(\pi - \pi)$ -HO- σ -MO mixing and $(\pi + \pi)$ -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 OIT-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 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.²³ 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} In fact, using a more realistic value for the resonance integral between two sp^3 hybrid AO's attached to the same carbon atom ($m\beta$, $m = 0.35^{18c,d}$) 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 firmer quantitative basis.

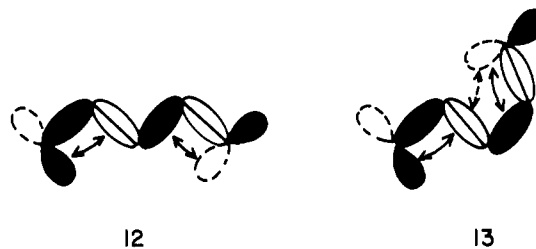
(27) (a) Bieri, G.; Dill, J. D.; Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* 1977, 60, 224. (b) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Ibid.* 1978, 61, 547.

(28) It has been reported that π - π interactions in the series of nonconjugated acyclic dienes $H_2C=CH(CH_2)_mCH=CH_2$ 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 treatment of the level ordering of orbitals interacting through bonds has recently appeared: Verhoeven, J. W.; Pasman, P. *Tetrahedron* 1981, 37, 943.

effective relay of OITB.^{1,15} As mentioned, OITB give a splitting energy of 0.87 eV in **1** but only 0.31 eV in **5**. The $\pi - \pi$ (dashed) and HO- σ -MO's of **1** and **5** are represented in **12** and **13**, respectively. The antibonding interactions between π and allylic



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 - AO_3 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

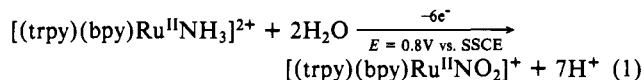
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We have discovered a well-defined reaction in which coordination of ammonia to ruthenium followed by oxidation leads to a rapid, quantitative conversion first to nitrite and then to nitrate. The reaction is remarkable in that it is rapid and involves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

A cyclic voltammogram of an aqueous solution of [(trpy)-(bpy)Ru^{II}NH₃]²⁺ (trpy \equiv 2,2',2''-terpyridine; bpy \equiv 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,



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]⁺,

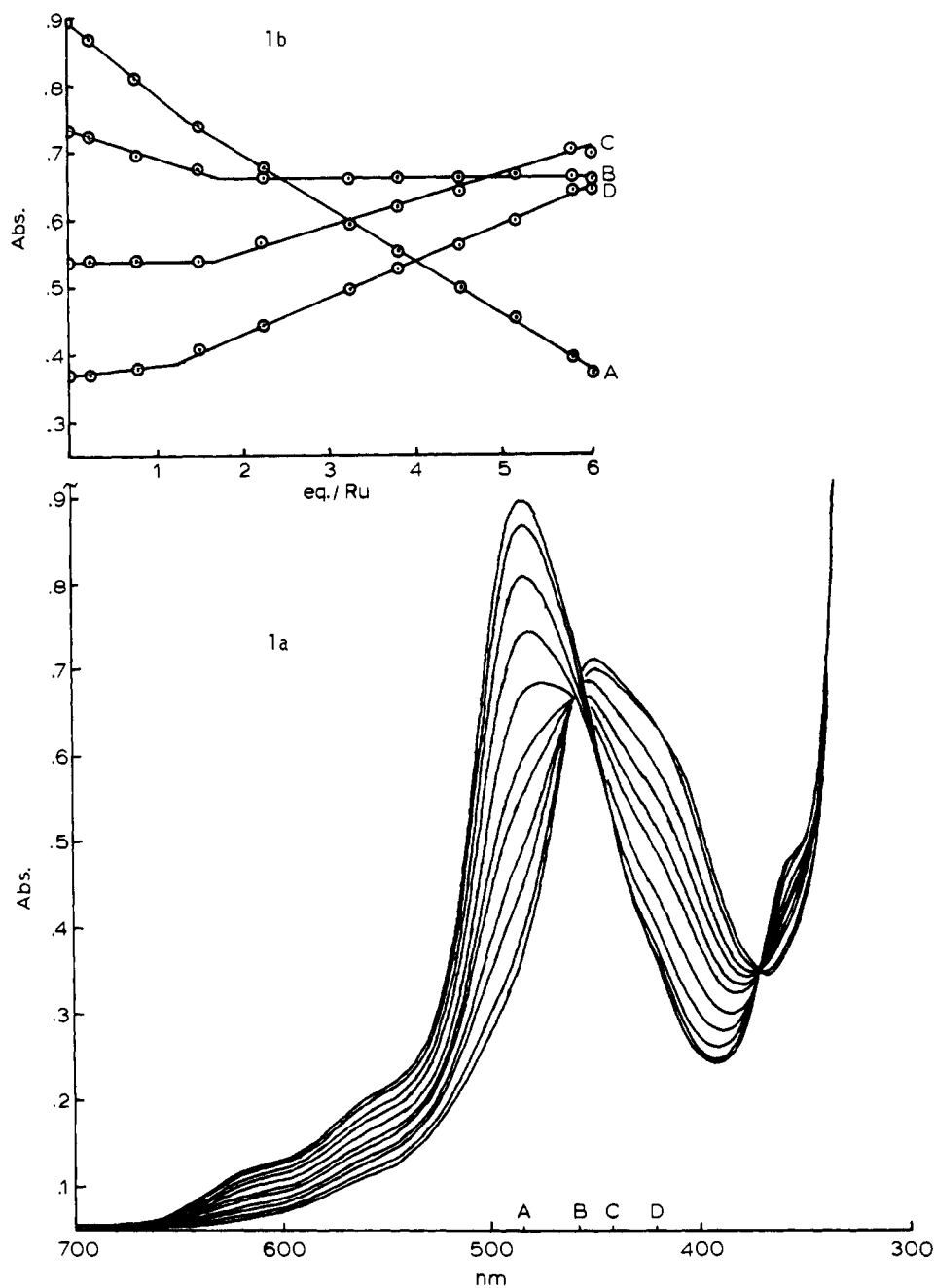
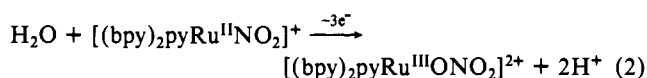


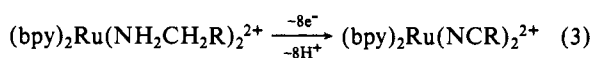
Figure 1. (a) Oxidative spectroelectrochemical titration of $[\text{Ru}(\text{trpy})(\text{bpy})\text{NH}_3]^{2+}$ in water at pH 6.8; 0.1 M in $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$. (b) Plots of absorbance changes vs. extent of oxidative from Figure 1a at several wavelengths. The wavelengths used are indicated on the horizontal axis in Figure 1a.

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



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



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 $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}\text{NH}_3]^{2+}$ in strong acid (pH 0) shows a reversible $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ couple at 0.76 V, suggesting that the first step in the $\text{Ru}^{\text{II}}\text{NH}_3 \rightarrow \text{Ru}^{\text{III}}\text{NO}_2$ conversion is oxidation to $\text{Ru}(\text{III})$. When the pH of a solution containing $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{NH}_3]^{3+}$ is increased from 0 to 4, a rapid reaction occurs which is second order in $\text{Ru}(\text{III})$ ($k \sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$; $T = 25^\circ \text{C}$, pH 4) as shown by the stopped-flow technique. Oxidation of $\text{Ru}(\text{II})$ to $\text{Ru}(\text{III})$ 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.

