as shown in eq 5 and 6, should make an *ab initio* calculation useful in the differentiation.

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Production of a Dinitrogen Complex *via* the Attack of Nitric Oxide upon a Metal-Ammine Complex

Sir:

We wish to report a novel preparation of the now familiar $Ru(NH_3)_5N_2^{2+}$ ion. Some previous methods of preparation have included direct substitution by N_2 into $Ru(NH_3)_5OH_2^{2+}$[1] and the use of such nitrogen-containing compounds as N_2H_4,[2] N_2O,[3] and NO^+.[4] While pursuing our interests in the chemistry of nitrosylammineruthenium complexes,[5] we have now discovered that saturation of alkaline solutions (pH >9) of $Ru(NH_3)_6^{3+}$ with nitric oxide results in the rapid and quantitative formation of $Ru(NH_3)_5N_2^{2+}$.

Solutions of $Ru(NH_3)_6^{3+}$ (2.96×10^{-3} *M*) were saturated with argon using an all-glass system. Argon-purged solutions of NaOH (0.01 *M*) were then introduced into the reaction flask with a Teflon needle. The gas flow could be switched rapidly to NO, which had been vigorously scrubbed through towers of molecular sieve, solid KOH, and 5 *M* NaOH.[6] All gases were passed through a final, common scrubber of 0.1 *M* NaCl (room temperature, ~1 atm). At the conclusion of the NO gas flow, argon was readmitted to the system (~20 min) to remove residual NO. The product solution was acidified (HCl or HBr) and $Ru(NH_3)_5N_2^{2+}$ was analyzed by the characteristic uv spectrum (λ_{max}, 221 nm (ϵ 1.8×10^4 M^{-1} cm^{-1}))[7] (97%) and by gas chromatographic techniques (molecular sieve column)[6] using Fe^{3+} to liberate N_2 (95 ± 5%). The complex isolated as the bromide salt (>75% yield) displayed the identical ir spectrum as alternative preparations of $[Ru(NH_3)_5N_2]Br_2$. Rotary evaporation to dryness of the product solution (acidified with HCl) indicated no products other than $[Ru(NH_3)_5N_2]Cl_2$ as identified by ir and uv-visible spectroscopy.

Treatment of NO with $Ru(NH_3)_6^{3+}$ in acid media results in the quantitative, facile production of $Ru(NH_3)_5NO^{3+}$.[5a] For the most part, substitution or redox reactions of ruthenium ammines have been confined to studies in acid media. Only recently, Rudd and Taube[8] have suggested that some Ru(III) pentaammines undergo disproportionation in alkaline media. Using $Ru(NH_3)_5Cl^{2+}$ (3.38×10^{-3} *M*) and a NO saturated (15 min) solution of 0.01 *M* NaOH, we did not observe any $Ru(NH_3)_5N_2^{2+}$. Instead, at least 82% of the product was identified[6] as $[Ru(NH_3)_4(NO)(OH)]^{2+}$.

From Latimer[9] one can calculate that NO is thermodynamically capable of undergoing disproportionation in alkaline solution into NO_2^- and N_2. The rapidity of the reaction negated the possibility of N_2 (from the disproportionation of NO)[9] being the source of our dinitrogen product.[10] With $Ru(NH_3)_6^{3+}$ or $Ru(NH_3)_6^{2+}$ (2.96×10^{-3} *M*), NaOH (0.01 *M*), and $NaNO_2$ (4.7×10^{-3} *M*), no $Ru(NH_3)_5N_2^{2+}$ was observed. In addition, the reaction of $Ru(NH_3)_6^{2+}$ (2.96×10^{-3} *M*) with NO in 0.01 *M* solutions of NaOH did not produce the dinitrogen complex.

The reaction was studied as a function of pH using the following buffer solutions: pH 6–8, $H_2PO_4^-$–OH^-; pH 8–9.2, Borax–HCl; pH 9.2–10.8, Borax–OH^-; pH 11.5–12, HPO_4^{2-}–OH^-. A small volume of $Ru(NH_3)_6^{3+}$ solution was added to the buffer solutions which had been saturated with NO. Using gas chromatography and the uv spectrum of the product, $Ru(NH_3)_5N_2^{2+}$, no dinitrogen complex was detected at pH 6, 31% at pH 7.5, 41% at pH 7.76, 100% at pH 8.45 and 9.03. Both a 0.01 *M* NaOH solution and a HPO_4^{2-}–OH^- buffer (pH 12) gave quantitative yields of $Ru(NH_3)_5N_2^{2+}$.

Attempts at measuring the rate of the reaction have been complicated because of the rapidity of the reaction. Preliminary kinetic studies performed by injecting $Ru(NH_3)_6^{3+}$ solutions (1×10^{-3} *M*) into alkaline NO solutions indicate that the rate increased markedly while increasing the pH of buffer solution (pH 7.0 → 9.0).

In order to gain further insight into the mechanism of our reaction, N-15 labeled NO (99% enriched, Mallinckrodt Nuclear) was used in place of the tank NO. The experiment was performed using a vacuum line to admit controlled amounts of NO into the reaction vessel containing frozen 0.01 *M* NaOH and solid $[Ru(NH_3)_6]Br_3$ (contained in a side arm mounted on the reaction vessel). The NaOH solution and NO were allowed to thaw (5 min) with vigorous stirring. The $[Ru(NH_3)_6]Br_3$ was then tipped into the solution. After 20 min the NO was pumped off, the solution was evaporated to dryness, and the residue was washed with absolute methanol to remove NaBr. The labeled sample produced only a single, strong band at 2080 ± 5 cm^{-1}. The unlabeled sample produced a band at 2114 ± 5 cm^{-1}. The doubly labeled complex, $Ru(NH_3)_5{}^{30}N_2^{2+}$ has recently been prepared as the bromide salt[11] and gives a band at 2035 ± 10 cm^{-1}. Earlier work[6,12] producing equilibrium mixtures of $Ru(NH_3)_5{}^{29}N_2^{2+}$ demonstrated that the dinitrogen stretch occurs at 2075 ± 10 cm^{-1}.

The evidence presented above suggests that nitrogen(II) as NO (rather than nitrogen(III), or N_2) attacks the metal-ammine complex. The dependence of the product yield on pH points to the possibility of amide

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(1) D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967).

(2) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(3) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6874 (1969).

(4) H. Scheidegger, J. N. Armor, and H. Taube, *ibid.*, **90**, 3263 (1968).

(5) (a) J. N. Armor, H. Scheidegger, and H. Taube, *ibid.*, **90**, 5928 (1968); (b) work in progress by S. Pell and J. N. Armor.

(6) J. N. Armor, Ph.D. Thesis, Stanford University, May 1970.

(7) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 6170 (1970).

(8) DeF. P. Rudd and H. Taube, *Inorg. Chem.*, **10**, 1543 (1971).

(9) W. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, p 104.

(10) No nitrite ion (λ_{max}, 208 nm, intense, in acidic solution) was observed in our product solutions.

(11) J. N. Armor, unpublished results.

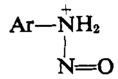
(12) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970).

formation

$$Ru(NH_3)_6^{3+} = Ru(NH_3)_5(NH_2)^{2+} + H^+$$

During the course of our work, D. Waysbort and G. Navon[13] reported the pK_a for the above deprotonation reaction as 12.4. If their value is correct,[14] it suggests that the production of $Ru(NH_3)_5N_2^{2+}$ is extremely fast (in order to obtain yields of 100% $Ru(NH_3)_5N_2^{2+}$ even at pH 9).

Once the amide is formed, it is easy to see how NO could attack the bound NH_2^-. In a similar manner it has been suggested that N_2O_3 can attack arylamines to yield intermediate arylnitrosoamines



$$Ar{-}\overset{+}{N}H_2{-}N{=}O$$

which leads to the formation of diazonium salts.[15]

The marked reactivity of $Ru(NH_3)_6^{3+}$ in alkaline solution parallels the observation[16] that while substitution by $S_2O_3^{2-}$ or SPO_3^{3-} onto $Ru(NH_3)_6^{3+}$ is slow in acid solution, the reactions in alkaline solution proceed rapidly with the production of a sulfamate complex: $Ru(NH_3)_5NHSO_3^+$. We are carrying out further work to find additional examples of the reactivity of $Ru(NH_3)_6^{3+}$ in alkaline media.

Besides being experimentally very simple to carry out, this reaction offers a clean, rapid, and high-yield

$$Ru(NH_3)_6^{3+} + NO + OH^- \longrightarrow Ru(NH_3)_5N_2^{2+} + 2H_2O$$

method of producing $Ru(NH_3)_5N_2^{2+}$ without having to reduce the Ru(III) center with external reducing agents.

Acknowledgment. Financial support for this work was provided by an EPDA, Part E Fellowship to Steven Pell and by a Boston University Graduate School award to John N. Armor.

[13] D. Waysbort and G. Navon, *Chem. Commun.*, 1410 (1971).

[14] Previously unpublished results (submitted for publication) lead us to accept with some reservations the conclusions of Waysbort and Navon.

[15] C. Noller, "Textbook of Organic Chemistry," W. B. Saunders, Philadelphia, Pa., 1966, p 430.

[16] J. N. Armor and H. Taube, *Inorg. Chem.*, 10, 1570 (1971).

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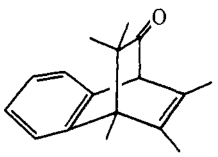
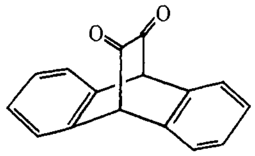
New Enone Photochemistry

Sir:

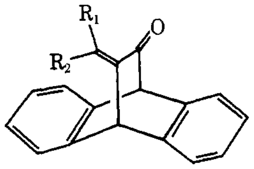
Retro Diels–Alder reactions of ethanoanthracenes and similar bridged aromatics have provided a useful synthetic route to molecules which may be otherwise inaccessible or at least difficult to obtain.[1] Elimination of the ethano bridge can be accomplished thermally or photochemically, but when the bridge contains a carbonyl group so that the eliminated molecule is a ketene, the photochemical path is much the more facile. For example, **1** readily gave dimethylketene and 1,2,3,4-tetramethylnaphthalene photochemically, whereas the thermal reaction required temperatures of 450–550°.[2] Similarly the α-diketone **2** gave anthracene and carbon monoxide photochemically, though it melts without decomposition at 200° and was recovered (80%) on being heated to 350°.[3]



1



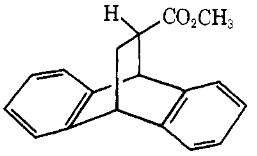
2



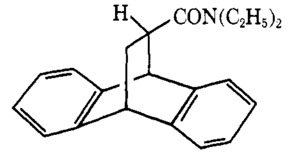
3a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Ph$

It is not yet known, in the photolysis of **2**, whether the ethano bridge is eliminated as O=C=C=O (oxoketene or bis(carbon monoxide)) which subsequently falls apart, or whether the carbon monoxide is formed directly.[4] To probe this question further, we have synthesized and irradiated several monomethylene analogs of **2** (*i.e.*, **3a** and **3b**). We found, as had been hoped, that products derived from methyleneketenes can be obtained (depending on the substituents R_1 and R_2), but we also discovered an interesting new photoisomerization of enones.

The α-methylene ketone **3a**[5] was irradiated in methanol solution (10^{-3} *M*, Hanovia 450-W lamp, Pyrex, 1 hr), anticipating that if cleavage to anthracene and methyleneketene were to occur, the latter would be trapped as methyl acrylate. Instead the main reaction product, isolated in 93% yield, was the ester **4** (identical in all respects with an authentic sample).[6] Less than 1% of anthracene and its photodimer, both of which are easily detected, were produced.



4



5

The formation of **4** from **3a** can be rationalized by a Norrish type I cleavage, rotation of the carbonyl group and electron delocalization, 180° C–C bond rotation and rebonding to form a ketene intermediate A.[7] Con-

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[1] For a review, see H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); see also J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966).

[2] R. K. Murray, Jr., and H. Hart, *Tetrahedron Lett.*, 4995 (1968); A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, **89**, 4554 (1967).

[3] J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Lett.*, 125 (1969).

[4] The mass spectral fragmentation pattern of **2** indicated that $C_2O_2^+$ was formed, but attempts to trap the neutral molecule were unsuccessful.[3] Low-temperature irradiations of **2** have thus far failed to give unequivocal evidence for C_2O_2: H. Hart and D. L. Dean, unpublished results.

[5] E. I. Snyder and R. A. Clement, *J. Amer. Chem. Soc.*, **82**, 1424 (1960).

[6] R. K. Hill and G. R. Newkome, *J. Org. Chem.*, 34, 740 (1969).

[7] An alternate path, cleavage to methyleneketene which then readds at the terminal carbon–carbon double bond faster than it reacts with methanol, seems unlikely in view of the results with **3b** (*vide infra*). The question of 180° rotation is being tested with bridgehead labeled compounds. Other mechanistic details (excited state multiplicity, whether A is a discrete reaction product or whether the nucleophilic