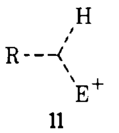
volysis of bicyclo[2.2.2]octyl-2-*p*-bromobenzenesulfonate has been reported to afford a 65:35 ratio of unrearranged (**7**) to rearranged products (**8**).[11] The formation of a preponderance of the tertiary bridgehead cation is significant in that it provides a clear example when σ nucleophilicity is more important than the stability of the resulting carbenium ion in electrophilic attack at a C–H bond. The importance of σ basicity in this electrophilic addition is further exemplified by the facile oxidation of adamantane (**9**), which is readily converted (5 h) to *N*-(1-adamantyl)acetamide in 88% yield. In contrast, norbornane (**10**) gave only *N*-(*exo*-2-norbornyl)acetamide (78%), with no evidence of involvement of the highly destabilized 1-norbornyl cation. The relative ease of hydrogen transfer from the bridgehead positions of **5, 9,** and **10** does reflect the stability of the incipient tertiary cations.[12]

Rate-limiting hydrogen transfer to NO_2^+ is further supported by an observable primary deuterium kinetic isotope effect. Previously reported oxidative hydride transfer reactions have exhibited a k_H/k_D range from 1.6 to 11.7 for organic substrates.[13] The isotope effect is expected to be largest when hydrogen is half transferred in a linear transition state, where the summation of vibrational energy differences will be maximized (eq 3). Oxidation of 1-adamantane-d_1 with NO_2BF_4 in acetonitrile was accompanied by a kinetic isotope effect of 1.86 at 20 °C. The same experiment with nitrosonium tetrafluoroborate resulted in a k_H/k_D of 2.30 at 82 °C.[14] The higher temperature for $NOBF_4$ was required because of the substantially diminished efficacy of NO^+ as an electrophilic reagent in this solvent system.[15] Both salts are most likely highly solvated by the donor solvent, which both increases the selectivity of the oxidant and stabilizes carbenium ion formation.

$$R{-}H + E^+ \rightarrow [R{-}{-}{-}H{-}{-}{-}E]^+ \rightarrow R^+ + H{-}E \qquad (3)$$

Our data demonstrate that the nitronium ion is a fairly discriminant oxidant (in acetonitrile), whose reactivity is influenced by both σ basicity and incipient carbenium ion stability. This selectivity would tend to exclude a reactant-like transition state. The formation of bridgehead acetamide **6** as the major product from **5** argues against a late transition state with appreciable carbenium ion character. In order to explain the relatively small k_H/k_D, we therefore invoke the nonlinear transition state **11**. Such a "triangular"[3,16] transition state would be expected to exhibit a smaller iostope effect, since less energetic bending vibrational modes may be the major contributor to the observed isotope effect. Significantly, kinetic isotope effects for hydrocarbon nitration with nascent protonated NO_2^+ ($O{=}N^{2+}{-}OH$) generated in concentrated HNO_3/H_2SO_4 are also small ($k_H/k_D = 2.0$).[17] This suggests that similar transition states may be involved. Olah initially suggested that nitronium ion nitration of alkanes with NO_2PF_6 proceeds via a three-center bond transition state (**11**) involving the electron pair of the σ C–H bond and an empty p orbital of the bent nitronium ion. The apparent dichotomy between these studies,[3,17] which afford nitroalkanes (nitration), and the present results may be attributed to our use of acetonitrile solvent, a very efficient carbenium ion trap. Control experiments have rigorously excluded nitroalkanes as the kinetic product in acetonitrile.[18,19]



11

In summary, this study has provided the most effective method to date for functionalizing hydrocarbons with nitronium salts. This is the first example of rate-limiting hydrogen transfer to a nitronium salt that affords a carbenium ion intermediate. Evidence is presented that the transition state closely resembles that for nitration with the donor solvent strongly influencing cation formation.

Acknowledgment. Support of this work by the National Science Foundation (CHE 76 21992) is gratefully acknowledged. R.D.B. wishes to thank Professor Roald Hoffmann for his generous hospitality during his sabbatical leave at Cornell, where this manuscript was written.

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(9) In a typical experiment, 10 mmol of substrate in 20 mL of dry CH_3CN was added to 13 mmol of NO_2BF_4 under a nitrogen atmosphere. After the solution was stirred at room temperature for 1 to 16 h, the reaction was quenched by the addition of water and the acetamide product was isolated by simple extraction.

(10) The ^{13}C and ^1H NMR and mass spectral data for **6, 7,** and **8** were consistent with their assigned structures. In addition, **7** and **8** were converted to their respective quarternary ammonium hydroxides and subjected to Hoffmann pyrolysis. Isolation of bicyclo[2.2.2]oct-2-ene and bicyclo[3.2.1]oct-2-ene confirmed the skeletal structures of **7** and **8**. All other acetamides reported were independently synthesized.

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(18) The formation of 1-nitroadamantane (<1%) could not be detected by GLC during the oxidation of adamantane. 2-Nitropropane, 2-methyl-2-nitropropane, and 1-nitroadamantane were found to be inert to NO_2BF_4 in CH_3CN at 25 °C for 1.5 h. Equimolar mixtures of 2-methyl-2-nitropropane and *tert*-butyl bromide showed >95% reaction of the bromide with no measurable loss of nitroalkane. Inclusion of $HClO_4$ effected a 32% loss of nitro compound. Equimolar mixtures of 1-nitroadamantane and adamantane (or 1-bromoadamantane) and 1.3 equiv of NO_2BF_4 in CH_3CN at 25 °C showed <20% loss of nitroadamantane in 5.5 h. Complete reaction of adamantane (or its bromide) and formation of the corresponding acetamide were noted.

(19) We have also observed this dichotomy with NO_2OCOCF_3, formed in situ by the reaction of NH_4NO_3 and trifluoroacetic anhydride in trifluoroacetic acid. Cyclooctane gave the trifluoroacetate, the nitrate, and nitrocyclooctane.

(20) Lubruzol Fellowship, 1974–1976.

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Received July 18, 1978

Primary Processes in the Photochemistry of $Co(NH_3)_5Cl^{2+}$

Sir:

Extensive photochemical studies of Co(III) complexes have been carried out.[1] In particular the charge-transfer photochemistry has been examined thoroughly.[2] Since, however, in most cases only final products and quantum yields have been determined, little is known of the first intermediates that are the precursors of the photoredox products. The 254-nm photochemistry of $Co(NH_3)_5Cl^{2+}$ leads to formation of Co^{2+} (quantum yield $\phi = 0.25$) and a small amount of N_2 but no Cl_2.[3] Besides this main reaction a photoaquation reaction leading to $Co(NH_3)_4(H_2O)Cl^{2+}$ has been described.[4] As first intermediates of this charge-transfer (CTTM) photochemistry, a radical pair ($(Co^{II}(NH_3)_5Cl\cdot)^{2+}$) has been postulated[5] which may rearrange (photoaquation) or split off a radical (photoredox reaction). In the latter case a Co(II) complex and a radical, possibly Cl·, NH_3^+, or NH_2Cl^-,[6] is formed. All of these intermediates are unstable and decay in the microsecond time scale. The kinetics of loss of the last three NH_3 ligands from $Co^{II}(NH_3)_5^{2+}$ have been measured by a pulse radiolytic technique;[7] the earlier steps of decomposition of the Co(II) complex, however, were too fast to allow resolution. A knowledge of the kinetics of the first steps of the photoredox reactions would help to answer the important question as to whether the CTTM excited state forms a high- or low-spin Co(II) complex.

A new method of measuring such processes is to combine the fast optical and conductivity detection methods known from pulse radiolysis[8] with photolysis by short laser pulses. A neodym-yag laser (system 2000, JK-Laser Ltd.) combined with Nd-glass amplifier (Korad K1) and two frequency doublers delivered light pulses of 265 nm (4.45 eV) of 20-ns duration and 2-mJ power into a quartz cell through which the solution was flowing. The details of the fast kinetic spectroscopy instrumentation has been described elsewhere.[8] The cell contained two pairs of platinum electrodes and the laser beam was incident on the solution between the two electrodes of one pair; the second pair served as reference. Care was taken that the laser light did not illuminate the electrodes. A 2-ms pulse of 100 V was applied to the electrode pairs and the difference in current was measured (180-Ω working resistor, 180-Ω cable impedance, 20-MHz oscilloscope) when the laser impinged on the solution.

For measurements at times longer than 10 µs, the ac conductivity was used.[8] The optical and conductivity time-dependence data were digitized and evaluated on a PDP 11/40 computer.[9]

In Figure 1a the upper trace shows the behavior of the optical absorption at 370 nm of a 1.6×10^{-4} M $[Co(NH_3)_5Cl]Cl_2$ solution containing additional 5×10^{-3} M HCl (the solution had been purged with Ar to remove oxygen and CO_2). Immediately after the laser pulse, the absorption increases and reaches a plateau after 50 ns. This increase was slower at lower Cl^- concentration. Measurements of the absorption on the plateau at different wavelengths showed the typical spectrum of the Cl_2^-.[10] The reactions observed may therefore be formulated as

$$Co(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Co(NH_3)_5^{2+} + Cl\cdot \quad (1)$$

$$Cl\cdot + Cl^- \rightarrow Cl_2^- \quad (2)$$

(the possibility of another mechanism[6] will be discussed later). With the known extinction coefficient of Cl_2^- [10] (ϵ 8.8×10^3 M^{-1} cm^{-1}), the quantum yield $\phi = 0.2 \pm 0.05$ could be estimated. From the rate of increase a rate constant of $k_2 = 1.4 \times 10^{10}$ M^{-1} s^{-1} was measured which corresponds within experimental error to the known rate.[10] Reaction 1 must be faster than 5×10^7 s^{-1}.

The conductivity shows a small buildup during the laser pulse followed by a decay below the initial conductivity level. The small increase is attributed to the photoaquation reaction[5]

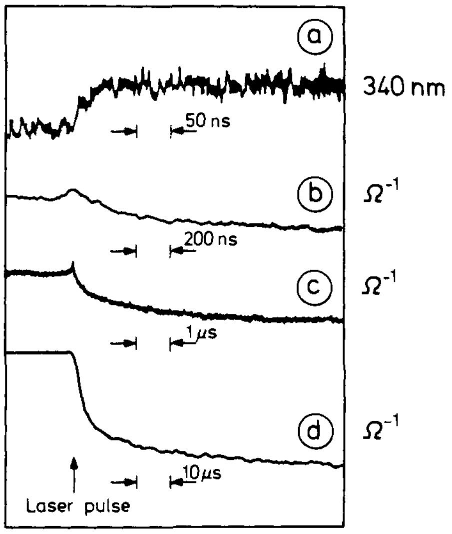

Figure 1. Optical absorption and conductivity changes after laser irradiation in a solution of 2×10^{-4} M $Co(NH_3)_5Cl^{2+}$ with (a) 5×10^{-3} M HCl and (b-d) 1×10^{-3} M HCl.

$$Co(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Co(NH_3)_5H_2O^{3+} + Cl^- \quad (3)$$

which is expected to cause an increase in conductivity owing to the formation of a Cl^- (equivalent conductivity $\Lambda = 76.3$ Ω^{-1} M^{-1} cm^2 at 25 °C) and an additional charge of the complex ($\Delta\Lambda \approx 60$ Ω^{-1} M^{-1} cm^2). Another photoaquation mechanism

$$Co(NH_3)_5Cl^{2+} + H^+ \xrightarrow{h\nu} Co(NH_3)_4(H_2O)Cl^{2+} + NH_4^+ \quad (4)$$

postulated by Moggi et al.[4] would cause an immediate decrease of the conductivity because a proton ($\Lambda = 349.8$ Ω^{-1} M^{-1} cm^2) is consumed and an NH_4^+ ($\Lambda = 73.4$ Ω^{-1} M^{-1} cm^2) is formed. The expected change in conductivity would be $\Delta\Lambda = 120$ for reaction 3 and $\Delta\Lambda = -300$ for 4. The observed increase indicates that reaction 3 proceeds to a much higher extent than 4. If reaction 4 is neglected, the quantum yield for 3 can be estimated as $\phi = 0.3$. A further reaction which could give rise to an increase of this magnitude would be the photodissociation of ion pairs such as $[Co(NH_3)_5Cl]Cl^+$ which may be present in solution. We do not, however, consider this to be an important pathway since the same behavior was observed using $[Co(NH_3)_5Cl](ClO_4)_2$ without free chloride.

The decay following the initial increase corresponds to a change in equivalent conductivity of $\Delta\Lambda \approx 600$ Ω^{-1} M^{-1} cm^2 as calculated from the amount of Cl_2^- (and consequently $Co^{II}(NH_3)_5^{2+}$) formed in the laser pulse. This relative high change is best explained by the consumption of two protons by protonation of two NH_3 molecules. Kinetic analysis shows that the decay is composed of two first-order reactions with rate constants $k_5 = 4.1 \times 10^6$ s^{-1} and $k_6 = 4.8 \times 10^5$ s^{-1}. We attribute the observed reactions to the detachment of two NH_3 ligands from the reduced Co complex:

$$Co(NH_3)_5 \rightarrow Co(NH_3)_4 + NH_3 \quad (5)$$

$$Co(NH_3)_4 \rightarrow Co(NH_3)_3 + NH_3 \quad (6)$$

The free ligand positions in the complexes are taken up by H_2O, but this cannot be detected and is neglected here. The NH_3 liberated is protonated immediately ($k = 4.3 \times 10^{10}$ M^{-1} s^{-1},[11] $t_{1/2} = 25$ ns at the pH of the solution), and this loss of H_3O^+ causes the decay of the conductivity.

At longer times (Figure 1d) the decay proceeds further. This conductivity change corresponds to the consumption of three more H_3O^+ by NH_3 and the rates correspond very well to those observed in the pulse radiolytic reduction of Co complexes[7] ($k = 6 \times 10^4, 1 \times 10^4, 1.5 \times 10^3\ s^{-1}$).

The conclusions drawn from these findings are as follows. The primary step in the charge-transfer photochemistry of $Co(NH_3)_5Cl^{2+}$ is oxidation of the Cl^- and elimination of the Cl atom. The intermediate observed by flash photolysis in the microsecond time scale and interpreted as NH_2Cl^- [6] may be the product of a reaction of this highly reactive Cl atom with the released ammonia or it could be $ClOH^-$ from reaction of Cl· with water[10] (at pH values higher than 3), which has a spectrum similar to that of Cl_2^- but with a lower extinction coefficient. Our observations show that the Cl atom is quickly complexed with Cl^- to Cl_2^-. The reduced Co complex releases the NH_3 ligands in five successive steps. The rates of these steps decrease by a factor of roughly 7 for each NH_3 eliminated. This observation leads to the conclusion that a particularly stable complex with four NH_3 ligands in a plane as would be expected for a low-spin Co(II) complex by analogy to the stable macrocyclic Co(II) complexes[12] is not present, and that the spin relaxation to the stable form of free Co(II) takes place in $<10^{-7}$ s. Measurements of the elimination of first NH_3 from $Co(NH_3)_6^{2+}$ will be reported in a further paper.[13]

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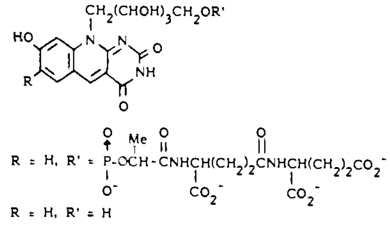
Received March 12, 1979

Synthesis of 7,8-Didemethyl-8-hydroxy-5-deazariboflavin and Confirmation of Its Identity with the Deazaisoalloxazine Chromophore of *Methanobacterium* Redox Coenzyme F_{420}

Sir:

Methane-producing bacteria contain at least two novel coenzymes which participate in the eight-electron reduction of CO_2 to CH_4 at the expense of H_2 oxidation: coenzyme M (β-mercaptoethanesulfonate),[1] proposed as a one-carbon carrier during CO_2 reduction, and factor 420,[2] a fluorescent redox cofactor which is an immediate acceptor of electrons from a methanogen hydrogenase. Reduced F_{420}, in turn, is a mobile reductant for cellular NADP. Wolfe and colleagues have isolated F_{420} and recently proposed that it has structure **1**,[3] based on spectroscopic evidence and similarity to known 8-hydroxyflavin[4] and 5-deazaflavin chromophores.[5,6] Factor 420 would then be the first example of a naturally occurring 5-deazaisoalloxazine, and independent structural corroboration, by synthesis, seems in order.

We report here the syntheses of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**2a**)[7] and 8-demethyl-8-hydroxy-5-deazariboflavin (**2b**)[7] as well as experiments confirming that **2a** is identical with the riboflavin level derivative (FO)[3] obtained by acid hydrolysis of factor 420.[3]

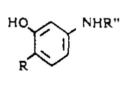


1 R = H, R' = $P(\rightarrow O)(O^-)$-OCH(Me)-C(=O)NHCH(CO_2^-)$(CH_2)_2$C(=O)NHCH(CO_2^-)$(CH_2)_2CO_2^-$

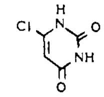
2a R = H, R' = H

2b R = Me, R' = H

Syntheses of **2a,b** represent modifications of our earlier method for the preparation of 5-deazariboflavin.[8] Condensation of **3a** with ribose (MeOH, reflux, 4 h) gave a 79% yield of **4a** (mp 144 °C dec), which was unstable and was used directly. Attempted hydrogenation of **4a** in the presence of Raney Ni or Pd catalyst resulted in reduction of the aromatic ring as a major side reaction. However, treatment of **4a** (1 equiv) with $NaBH_3CN$ (4.8 equiv) in MeOH containing a small amount of AcOH (20 °C, 16 h) gave satisfactory reduction. After destruction of excess borohydride, chromatography on AG 50W-X8 cation-exchange resin (elution with 1% NH_4OH) afforded an 80% yield of **5a**: mp 133–135 °C dec; NMR[9] (Me_2SO-d_6) δ 5.9–6.2 (m, 3 H), 6.7–7.1 (m, 1 H), 8.87 (s, 1 H)). Compound **5a** (3 equiv) was reacted with 6-chlorouracil (**6**)[10] (1 equiv) in a small volume of H_2O (reflux, 14 h). The resulting solution was applied to a column of AG 50W-X8 resin. Elution with H_2O yielded **7a** (46% based on **6**, 70% based on recovered **5a**) as a glass which was suitable for use in the next reaction: NMR(Me_2SO-d_6) δ 4.08 (s, 1 H), 6.6–6.9 (m, 3 H), 7.1–7.4 (m, 1 H, partly superimposed on broad NH hump).



3 R'' = H
4 R'' = D-ribosyl
5 R'' = D-ribityl



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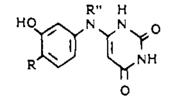
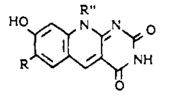


7 R'' = D-ribityl



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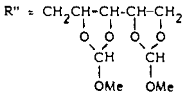
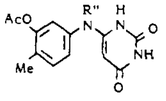
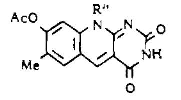


R'' = CH_2CH-CH-CH-CH_2



9
R'' = $CH_2(CHOAc)_3CH_2OAc$



10
R'' = $CH_2(CHOAc)_3CH_2OAc$

a R = H; **b** R = Me

Cyclization of **7a** was accomplished by treatment with a large excess of trimethyl orthoformate in the presence of *p*-toluenesulfonic acid catalyst (reflux, 18 h). The product **8a** precipitated from the reaction mixture in 41% yield and was obtained as a golden yellow, fluorescent solid (mp >251 °C dec).[11] Treatment with 1 N HCl (steam bath, 0.5 h) converted **8a** into **2a** (83%), obtained as golden yellow crystals (mp 284–286 °C dec).[12]

The synthesis of **2b** was carried out by a modification of the above route. In contrast to **4a**, **4b** was successfully converted into **5b** (mp 119–122 °C (after LC)); NMR(Me_2SO-d_6) δ 1.90 (s, 3 H), 5.9–6.1 (m, 2 H), 6.70 (d, J = 8 Hz, 1 H), 8.60 (s, 1 H)) by hydrogenation (600 psi of H_2, Raney Ni, 70 °C,