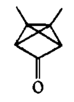
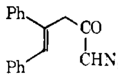
(4) Chemical evidence supporting the formation of a bicyclo[2.1.0]pentanone derivative in the vinylogous Wolff rearrangement is available: Doering and Pomerantz prepared the highly strained cyclobutanone (ii), albeit in low yield, via the copper catalyzed decomposition of diazoketone (i): W. von E. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964);

i



ii

More recently Zimmerman and Little reported that when the copper catalyzed decomposition of iii was carried out in the absence of methanol an intermediate, as yet unidentified, is formed. This intermediate displays an infrared band at 5.60 μ (1785 cm^{-1}). Upon methanolysis ester iv is formed in addition to a variety of other products: H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96**, 4623 (1974).



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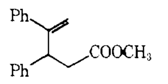

iv

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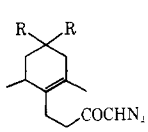

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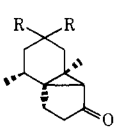

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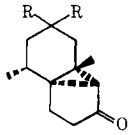

III

a, R = H
b, R = OCH₂CH₂O

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The Photochemical Reactions of Azidopentaamminechromium(III). Evidence for a First Transition Series Coordinated Nitrene Intermediate

Sir:

The recent discovery by Basolo and co-workers of an efficient photoinduced reaction mode involving nitrenes[1] has revived considerable interest in the photochemical reactions of azido complexes of transition metals.[2] In contrast to the redox mode observed in the photolysis of $Co(NH_3)_5N_3^{2+}$,[3] the rhodium(III) and iridium(III) analogues reacted principally via a coordinated nitrene, $M(NH_3)_5NH^{3+}$, pathway.[1] The difference in reaction modes with the heavier metals was attributed to less favorable +2 oxidation states and increased stabilization of the nitrene intermediates by additional dπ-pπ bonding.[1c] As yet, however, nitrene intermediates have not been detected in the photochemical reactions of first transition series azidopentaammine complexes. Analogous to rhodium(III) and iridium(III) complexes, the +2 oxidation state of acidopentaamminechromium(III) is less favorable. Moreover, previous investigations of thermal substitution reactions of $Cr(NH_3)_5N_3^{2+}$ have indicated that the Cr-N bond is unusually stable.[4] With these observations in mind, we have reexamined the 313-nm photolysis of $Cr(NH_3)_5N_3^{2+}$ to determine if nitrene intermediates occur.

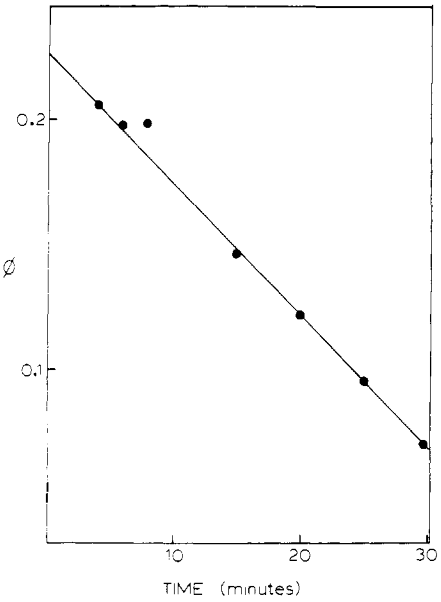

Figure 1. Dependence of the $Cr(NH_3)_5NH_2Cl^{3+}$ quantum yield on irradiation time; initial concentration of $[Cr(NH_3)_5N_3](ClO_4)_2$ is 2.8×10^{-3} M in 0.3 M HCl, $I_0 \sim 10^{-5}$ einstein l.$^{-1}$ min^{-1}.

Previous investigations of the ligand-field photosensitivity of $Cr(NH_3)_5N_3^{2+}$ have established aquation of ammonia as the predominant process,[4] whereas irradiation in the LMCT region, λ ≤330 nm, resulted in a general decline in the ultraviolet absorption spectrum and the evolution of N_2 gas.[5] When acidic or neutral solutions of $Cr(NH_3)_5N_3^{2+}$ are exposed to 313-nm radiation,[6] the quantum yield of dissappearance of $Cr(NH_3)_5N_3^{2+}$, determined from the decrease in absorbance at 280 nm and/or 265 nm, was 0.48; in excellent agreement with the previous determination of 0.45.[5] Also, azide ion was not detected in the photolyte.[7] Contrary to the previous report,[5] however, the inability of the photolyte to reduce $Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, or $Co(NH_3)_5Br^{2+}$ and flash photolysis studies indicate photoredox decomposition is not a major reaction pathway. When degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solutions containing 10^{-4} to 10^{-2} M NaI were exposed to a filtered (10^{-2} M NaI) 210-J flash, 20% of the complex was decomposed and N_2 was formed, yet no transient absorbance of I_2^- was observed.[2a,3b,8] Although the absence of an I_2^- absorbance indicates photoredox does not occur, its absence was further confirmed by flash photolysis. A degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution was exposed to a filtered (10^{-2} M NaI) 250-J flash and analyzed at 740 nm, the absorption maximum of $Cr(H_2O)_6^{2+}$.[9] Sprectra recorded before and after the flash indicated 50% of the complex was decomposed by the flash, but no transient absorbance was observed. Assuming a minimum signal to noise ratio of 2:1, the absence of an absorbance establishes that photoredox accounts for less than 12% of the overall photochemical reaction.

The previous study which proposed a photoredox mechanism reported the yield of N_2 to be essentially the expected 1.5 mol of N_2 per mole of complex decomposed. However, we find the yield of N_2 to be less than 1.5 mol of N_2 per mole of complex decomposed. The amount of gas liberated during the photolysis was quantitated by gas chromatography. A 10^{-3} M $[Cr(NH_3)_5N_3](ClO_4)_2$ solution containing 0.3 M HCl was degassed by repeated freeze-thaw cycles. The spectrum of the solution was recorded before and after photolysis and the number of moles of $Cr(NH_3)_5N_3^{2+}$ decomposed was determined. The noncondensable gas (at liquid N_2 temperature) was quantitatively transferred by a Toepler pump to a Gow Mac gas chromatograph equipped with a 6 ft × 0.25 in. Porapak Q column at room temperature. The GC trace indicated N_2 was the only gaseous product and a series of five experiments yielded 1.1 ± 0.2 mol of N_2 per mole of $Cr(NH_3)_5N_3^{2+}$ decomposed. The apparent excess of nitrogen gas may be due to an inability to account for a possible absorption of the product(s) in determining the number of moles of complex decomposed and/or secondary photolysis[1a] or thermal instability of the primary product of the photochemical reaction (see below).

When 10^{-3} M $[Cr(NH_3)_5N_3](ClO_4)_2$ solutions containing 1.0 M $HClO_4$ are exposed to 313-nm radiation nitrogen is evolved, but the photolyte does not oxidize iodide ion. In 1.0 M HCl, however, 313-nm photolysis of a 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ yielded a photolyte which oxidized iodide to iodine with a quantum yield of 0.23. These results indicate that the initial photochemical product is a chromium nitrene intermediate, $Cr(NH_3)_5NH^{3+}$, which in the presence of HCl is trapped to form the chloramine, known to oxidize iodide to iodine.[1] As indicated by Figure 1, secondary photolysis of $Cr(NH_3)_5NH_2Cl^{3+}$ occurs extensively and, as mentioned above, accounts in part for the high yield of nitrogen relative to the amount of complex decomposed.[1a] Additional experiments also indicate $Cr(NH_3)_5NH_2Cl^{3+}$ is thermally unstable. A 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution containing 1.0 M HCl was photolyzed to 25% consumption of the starting material. The photolyte was then stored in the dark at 25 °C and aliquots taken periodically were tested with iodide ion. After 20 min, the ability of the photolyte to oxidize iodide to iodine had decreased by 20%. This thermal instability precludes the use of conventional ion-exchange chromatography to isolate the $Cr(NH_3)_5NH_2Cl^{3+}$.

Flash photolysis experiments as well as the inability of the photolyte to reduce other acidopentaamminecobalt(III) complexes relegate to a minor role the previously proposed photoredox process. Moreover, the dependence of the yield of $Cr(NH_3)_5NH_2Cl^{3+}$ on the concentration of HCl, Figure 2, extrapolates to a limiting yield of 0.5. The close agreement between the limiting yield and the quantum yield of $Cr(NH_3)_5N_3^{2+}$ decomposition establishes the primary photochemical reaction to be

$$Cr(NH_3)_5N_3^{2+} \xrightarrow[313\text{ nm}]{h\nu} Cr(NH_3)_5N^{2+} + N_2$$

Although the MLCT state of $Cr(NH_3)_5N_3^{2+}$ is expected to be much higher in energy and not important in these experiments, population of this state or one which reacts in a similar manner can give rise to an interesting non-nitrene reaction forming $Cr(NH_3)_5N_2$ and N.[10] The fate of the latter species, N, is the formation of NH_2OH. However, analysis of the photolyte for NH_2OH with α-naphthylamine[11] indicates this reaction pathway does not occur in these experiments.

The initial proposal of a photoredox process for the 313-nm photolysis of $Cr(NH_3)_5N_3^{2+}$ was based, to a significant extent, on the appearance of Co(II) when a weakly acidic, 10^{-4} M $HClO_4$, solution of $Cr(NH_3)_5N_3^{2+}$ was photolyzed in the presence of $Co(NH_3)_5H_2O^{3+}$. Although we have confirmed these observations, the mechanism of the reduction is not clear. Inconsistent with the postulation of Cr(II) as the reducing agent is the observation that only $Co(NH_3)_5H_2O^{3+}$ is reduced whereas $Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(NH_3)_5Br^{2+}$ are not reduced. A number of pieces of evidence, however, suggest that the reductant may be a nitrene product such as $Cr(NH_3)_5NH_2OH^{3+}$ or its conjugate base, $Cr(NH_3)_5NHOH^{2+}$. For example, the yield of Co(II) decreases significantly as the concentration of HCl increases. In the presence of $Co(NH_3)_5H_2O^{3+}$, flash photolysis of $Ir(NH_3)_5N_3^{2+}$ which reacts exclusively via a nitrene intermediate results in a much longer lived transient, $t_{1/2} \sim 0.1$ s, than in the absence of $Co(NH_3)_5H_2O^{3+}$, $t_{1/2} = 50$ ms.[1b]

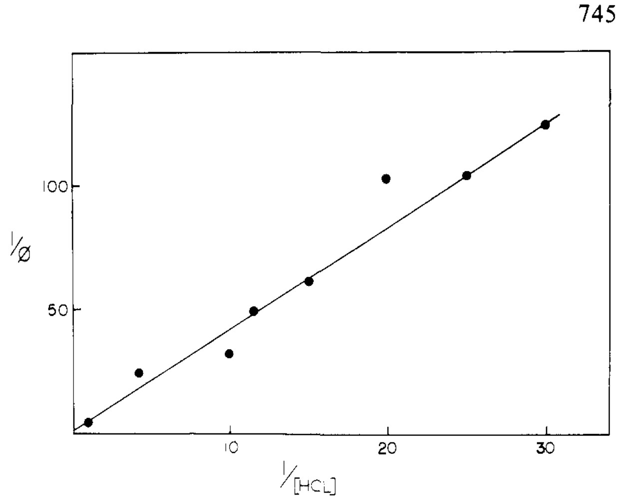

Figure 2. Dependence of the reciprocal of the $Cr(NH_3)_5NH_2Cl^{3+}$ quantum yield on the reciprocal of the HCl concentration. Initial concentration of $[Cr(NH_3)_5N_3](ClO_4)_2$ is 3×10^{-3} M.

A priori, a nitrene reaction pathway, cleavage of an $N-N_2$ bond, is thought to originate in an azide centered excited state.[1b,10] Unlike $Co(NH_3)_5N_3^{2+}$, however, which undergoes photoreduction like other acidopentaamminecobalt(III) complexes, the nitrene reaction pathway of $Cr(NH_3)_5N_3^{2+}$ is quite different from other acidopentaamminechromium(III) complexes.[12] In the cobalt(III) complex, the LMCT state is lower in energy than the azide centered excited state. The difference in behavior of the complexes might then be attributed to an efficient coupling of the LMCT state and the azide excited state of the cobalt complex leading to a lower energy photoredox pathway.[8] With $Cr(NH_3)_5N_3^{2+}$, however, the azide centered excited state may lie lower in energy than the LMCT and MLCT states. An efficient coupling is less likely and the isolated azide excited state would then give rise to exclusively a nitrene reaction pathway.[10]

Acknowledgment. Financial support of this research from the Research Corporation and The Research Foundation of The City University of New York is gratefully acknowledged.

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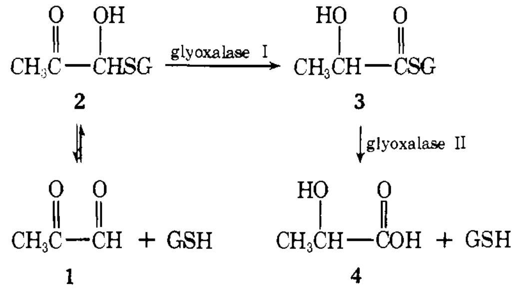
Glyoxalase I Enzyme Studies.[1] 2.[2] Nuclear Magnetic Resonance Evidence for an Enediol-Proton Transfer Mechanism

Sir:

In contrast to the generally accepted 1,2-hydride shift mechanism[3] for the action of glyoxalase I, we wish to present evidence that in the conversion of the α-ketohemithiol acetal **2** (methylglyoxalglutathionylhemithiol acetal) to the α-hydroxythiol ester **3** (*S*-lactoylglutathione) the mechanism involves an enediol-proton transfer rather than a hydride shift. The glyoxalase enzyme system composed of glyoxalase I [*S*-lactoylglutathione methylglyoxal lyase (isomerizing); E.C. 4.4.1.5], the coenzyme glutathione (GSH), and glyoxalase II (S-2-hydroxyacylglutathione hydrolase; E.C. 3.1.2.6) converts methylglyoxal (**1**) to lactic acid (**4**). The role of this enzyme system, which is found widely distributed in cells of all forms of life,[4,5] in metabolism has become a topic of controversy because of its suggested[5] involvement in the regulation of cell division.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}\!-\!\overset{\overset{OH}{|}}{C}HSG} \xrightarrow{\text{glyoxalase I}} \mathrm{CH_3\overset{\overset{HO}{|}}{C}H\!-\!\overset{\overset{O}{\|}}{C}SG}$$

$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}\!-\!\overset{\overset{O}{\|}}{C}H + GSH} \qquad \mathrm{CH_3\overset{\overset{HO}{|}}{C}H\!-\!\overset{\overset{O}{\|}}{C}OH + GSH}$$

Mechanistically, the most intriguing step in the reaction sequence is the rearrangement of the hemithiol acetal **2** to the thiolester **3** for which one might consider either an intramolecular 1,2-hydride shift or an enediol-proton transfer mechanism (originally proposed by Racker).[2,3b,6] Distinguishing the two mechanisms should be straightforward either by detecting the incorporation (or lack of incorporation) of solvent protons into the product or the retention (or loss to the medium) of an isotope of hydrogen when using a properly labeled substrate. Indeed, studies of the former have been reported in deuterium oxide and tritium-enriched water. In each case the 1,2-hydride shift mechanism was proposed because of the lack of detection of deuterium (3% maximum incorporation)[3a] or low incorporation of tritium (less than 4%)[3b] in the lactic acid product, **4**. These results, however, do not rule out the possibility of a fast proton transfer mechanism via an enediol taking place in a highly protected active site. As a matter of fact, the detection of *any* solvent proton incorporation suggests such a possibility. This can be tested by observing incorporation or increased incorporation of solvent protons as the temperature is raised.[7] We report here the results of such a study in which incorporation of solvent protons was detected using NMR spectroscopy. At 25 °C there is incorporation of deuterium (ca. 15%) when the enzyme reaction is run in deuterium oxide. The incorporation increases to ca. 22% when the temperature is raised to 35 °C. These observations clearly demonstrate that

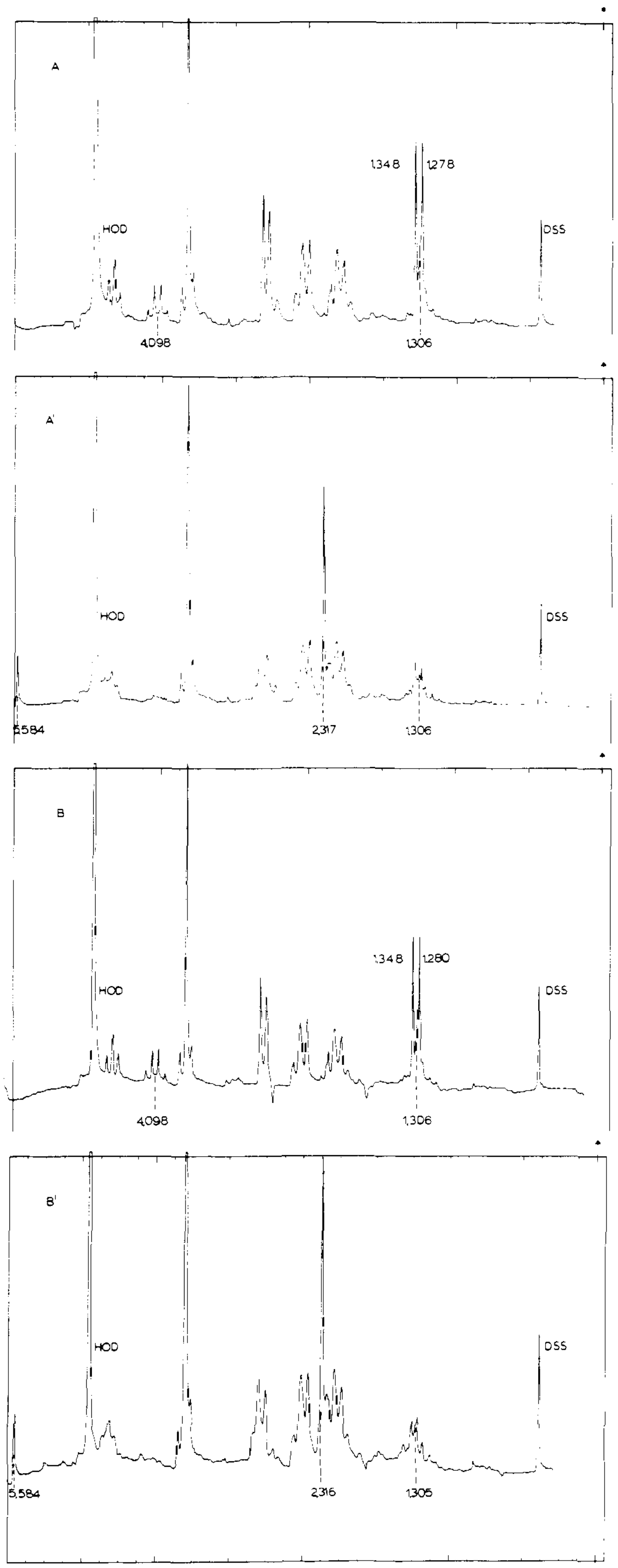


Figure 1. ^{1}H NMR spectra for the glyoxalase I catalyzed conversion of methylglyoxal to lactic acid. Spectra A and B represent the enzyme reaction at 25 and 35 °C, respectively; A' and B' are the corresponding control spectra. Chemical shifts are quoted in parts per million from DSS and the assignments are discussed in the text. The unassigned peaks belong to glutathione.