the 4-picoline and 4-methoxypyridine *N*-oxide complexes, but, since both give triplet state spectra, it seems clear that these complexes are dimeric also.

In analysis of the magnetization studies as well as the inverse susceptibility plots, some interdimer interactions were detected. These interactions are accounted for by the θ value used in the estimation of the molecular field. Some idea of the interdimer exchange may be calculated using the relation[14]

$$J' = \frac{3k\theta}{2zS'(S' + 1)}$$

where J' is the interdimer exchange coupling constant for the z nearest neighbors of a given dimer. Using the effective dimer spin S' of 1 and the two nearest neighbors,[7] values of $-J'$ are found to be $\simeq 0.15$ or 0.8 cm^{-1} for $[Cu(pyO)_2(NO_3)_2]_2$ and 0.30 or 0.04 cm^{-1} for $[Cu(4\text{-}CH_3\text{-}pyO)_2(NO_3)_2]_2$ where the first value was calculated from the magnetization data and the second from the inverse susceptibility data. In any case, a small antiferromagnetic interdimer exchange interaction is apparent.

Conclusions

Three complexes of the form $[Cu(R\text{-}pyO)_2(NO_3)_2]_2$ have been characterized by low-temperature magnetic susceptibility and epr studies. In addition, magnetization studies have been carried out on the unsubstituted and the 4-methyl substituted complexes. Each of the complexes is found to exhibit electronic spin-spin coupling; the interaction leads to a triplet ground state for the unsubstituted and picoline complexes while a singlet state is found to be the ground state for the 4-methoxy complex.

Since the copper(II)-copper(II) separation of 3.458 Å is considered to be too great for any metal-metal bond formation and since a dipole-dipole interaction could not produce singlet-triplet splittings of the observed magnitude, it is not probable that a through space interaction dominates the exchange coupling in any of the complexes studied. Moreover, any direct metal-metal interaction would necessarily be antiferromagnetic according to the Pauli principle; this is not consistent with the two triplet ground-state cases. The copper(II) centers in the complexes studied must be coupled by a superexchange mechanism which is subject to changes in Cu-O-Cu bridge angle in the same way as previously reported[5,19] for oxygen-bridged copper(II) dimers. Further evidence for the superexchange mechanism is manifested by the substituent effects on the exchange energy.

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Photochemical Reaction of the Azidopentaammineiridium(III) Ion. Coordinated Nitrene Intermediate

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 27, 1973*

Abstract: Photolysis of aqueous solutions of $Ir(NH_3)_5N_3^{2+}$ results in the evolution of nitrogen and the formation of a coordinated nitrene intermediate as the only reaction products. For solutions containing hydrochloric acid, the photolysis reaction yields exclusively $Ir(NH_3)_5NH_2Cl^{3+}$. The quantum yields are wavelength dependent and are appreciable for excitation in the ligand-field region of the spectrum. The data are interpreted in terms of a model where a lower energy azido group excited state is the reactive level. An intermediate is observed when $Ir(NH_3)_5N_3^{2+}$ is irradiated in a glass at 77°K or flashed in aqueous solution. The intermediate is attributed to the product of a reaction of the coordinated nitrene and the solvent. A mechanism for the photochemical reaction is proposed.

Metal coordinated nitrene intermediates, M-NH, have been reported for the thermal reactions of azidopentaammine complexes of ruthenium[1] and iridium.[2] Nitrene intermediates also form during the photolysis of hydrazoic acid[3,4] and organic azides.[5,6] However, prior to a recent communication from this laboratory,[7] metal coordinated nitrene intermediates had not been studied nor postulated in the photochemistry of azido metal complexes. Previous investigations on the photodecomposition of azido metal complexes were largely limited to the first-row transition

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metals.[8-11] These reactions are characterized by reduction of the metal ion and nitrogen evolution resulting from secondary reactions of the azide radicals. This paper reports a detailed study of the mechanism of formation of $Ir(NH_3)_5NH_2Cl^{3+}$ from the photolysis of $Ir(NH_3)_5N_3^{2+}$. To further elucidate the role of the coordinated nitrene in the photodecomposition of $Ir(NH_3)_5N_3^{2+}$, the transients generated in the flash photolysis of $Ir(NH_3)_5N_3^{2+}$ under a variety of conditions were investigated.

The results obtained are interpreted in terms of a model where a low energy azido group excited state is the reactive level. The stoichiometric formation of $Ir(NH_3)_5NH_2Cl^{3+}$ is attributed to a stabilization of the coordinated nitrene, due to an increased $d\pi$–$p\pi$ electron donation by transition metals of higher atomic number. Furthermore $Ir(NH_3)_5N_3^{2+}$ has a higher energy charge transfer to metal (CTTM) state than does $Co(NH_3)_5N_3^{2+}$, which leads to photoreduction as its predominant process.[8,10]

Experimental Section

Materials. The complexes $[Ir(NH_3)_5N_3]Cl_2$, $[Ir(NH_3)_5N_3](ClO_4)_2$, $[Ir(NH_3)_5NH_2Cl]Cl_3$, and $[Ir(NH_3)_5NH_2OH](ClO_4)_3$ were prepared by published methods.[2] The elemental analyses of these compounds agreed with the calculated values, and the spectra of the complexes agreed with published spectra.[2,12]

Reagent grade biacetyl (Eastman Kodak Co.) was further purified by fractional distillation, collecting the 89–92° fraction. Practical grade quinoline (Eastman Kodak Co.) was twice fractionally distilled, collecting the 235–238° fraction. The absorption and emission spectra of these compounds agreed with previously published spectra.[13,14] Tris(bipyridine)ruthenium(II) chloride (G. F. Smith Chemical Co., Columbus, Ohio) was used without further purification, since its absorption and emission spectra agreed with the published[15] spectra for this complex.

The results of the photolysis of solutions prepared from water redistilled from alkaline permanganate in a Pyrex apparatus agreed with the results obtained in distilled water. Thus, results reported in this paper were obtained with solutions prepared from distilled water. All other solvents were reagent grade.

Photolysis Procedures. Preliminary experiments for product isolation and gas evolution measurements were described previously.[7] Additional experiments were carried out in a quartz or Pyrex reaction vessel mounted in a Rayonet Reactor or 5 cm from a 550-W Hanovia medium-pressure mercury lamp contained in a quartz immersion well. Wavelength isolation was achieved by use of 254-, 300-, or 350-nm light sources in the Rayonet Reactor. The light from the 550-W mercury lamp was filtered by Pyrex (0% T at 300 nm) or Plexiglass (0% T at 347 nm) filters.

For quantum yield determinations, an optical train was constructed. The light from either a 1000-W Oriel Optics high-pressure xenon or xenon–mercury lamp was focused by means of two quartz lenses through a 14-cm quartz water filter on to the entrance slit of a Bausch and Lomb Model 33-86-08 grating monochromator (1200 groves/mm). The wavelength scale of the monochromator was calibrated with a low-pressure mercury lamp by a procedure adapted from the calibration of a Beckman DU spectrophotometer.[16] Within experimental error, no difference was found between the wavelength transmitted and the monochromator scale reading. The entrance slit, 3.78 mm, and exit slit, 1.40 mm, were calculated from the manufacturers reported dispersion of the grating to yield 90% of the radiation within a 10-nm band pass. The reaction cell, a 10 × 10 × 40 mm quartz spectrophotometer cell, was mounted in a constant-temperature block 5 cm from the exit slit of the monochromator and maintained at 25° with a Haake Model FJ constant-temperature circulator. Since the image of the exit slit did not homogeneously expose the entire reaction cell, the solutions were stirred by 5-mm magnetic stirring bars. Due to the low extinction coefficients at 400 nm, solutions were photolyzed at this wavelength in a 10-cm spectrophotometer cell. Light intensities ($I_0 \sim 10^{-5}$ einstein/(l. min)) were measured by ferrioxalate actinometry[17,18] before and after photolysis, and the average values for each run were used to calculate the quantum yields. The variation in intensity was always less than 5%.

The flash apparatus assembled for these experiments is of the general design described by Porter[19] and was used in a kinetic–spectrophotometric mode. The flash lamp, a Xenon Corp. Novatron 734 lamp powered by a Model 457 micropulser, dissipates a maximum of 100 J at 10 kV. The photolyzing flash has a rise time of 5 μsec, a half-peak duration of 12 μsec, and a total duration of less than 50 μsec. The chemical change, occurring after the flash, is monitored by observing the change in intensity of a collimated beam of light from a 108-W tungsten lamp. The light from the tungsten lamp, powered by an Electro Model N filtered dc power supply, was focused through the center of the reaction cell and light baffle on to the entrance slit of a Bausch and Lomb grating monochromator. The change in intensity of the analyzing beam at a given wavelength is monitored by a EMI 6265B photomultiplier tube. The output of the photomultiplier tube is dropped across a 20 kohm resistor, and the change in voltage as a function of time is displayed on a Tektronic Model 564 storage oscilloscope.

The time resolution of the apparatus, 100 μsec, is due to a saturation of the photomultiplier tube by scattered light from the photolysis flash. The RC time constant of the detection circuit is 0.25 μsec.

The solution to be flashed is contained in a 5-cm fused-quartz spectrophotometer cell which is mounted parallel to, and 1 in. from, the flash lamp. The cell was equipped with a side arm, where the solution could be degassed by repeated freeze–thaw cycles. Since results obtained with solution degassed by freeze–thaw cycles were identical with results obtained with solutions deaerated by N_2 bubbling, the results reported in this paper were obtained with solutions deaerated by N_2 bubbling.

Rate constants for the grow in and decay of the transient were determined from Polaroid photographs of the oscilloscope traces, from the slope of the best straight line drawn through the first- (log A *vs.* time) or second-order ($1/A$ *vs.* 1/time) plot. The spectrum of the transient was obtained by recording the transient signal at various wavelengths and extrapolating the first-order decay plot back to zero time. Except where otherwise indicated, all solutions were discarded after the first flash. The spectrum and kinetic behavior of the transient observed on the above apparatus were identical with results obtained on a Xenon Corp. flash apparatus.[20]

The oxygen dependence of the yield of chloramine was determined by equipping the 10 × 10 × 40 mm reaction cell with an air tight serum cap. The solution was saturated with oxygen, nitrogen, or argon by bubbling the gas through the solution with a syringe needle for 25 min prior to photolysis. During photolysis, the gas was passed over the solution to ensure saturation of the solution. The gas was vented through a second syringe needle inserted through the serum cap.

A series of low-temperature photolyses were carried out in a 0.31-cm quartz cell thermostated to 77°K with liquid nitrogen. The solvent used in these experiments, 4:1 methanol–water, gave a cracked glass. However, the same spectrum of the photolysis products was obtained for a series of identical solutions, indicating that the fractures in the glass did not affect the spectral measurements. Two milliliters of a 10^{-3} M solution of the complex was added to the cell and slowly cooled to 77°K, in order to minimize the amount of cracking. The glasses were irradiated in a Rayonet

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(20) The authors thank Professor J. F. Endicott for the kind use of his flash apparatus to carry out preliminary experiments on the flash photolysis of $[Ir(NH_3)_5N_3](ClO_4)_2$.

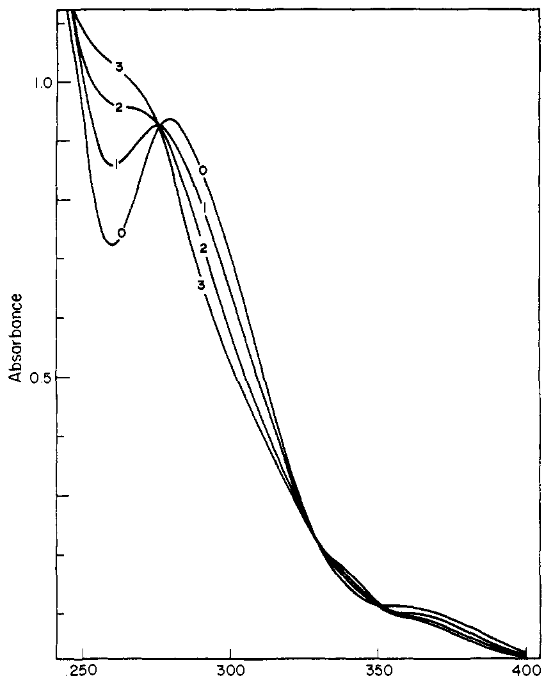

Figure 1. Photolysis of 1.56×10^{-3} *M* [$\mathrm{Ir(NH_3)_5N_3]Cl_2}$ in 0.1*M* HCl with 300 nm radiation in a 1.0-cm cell; 0, 1, 2, and 3 refer to exposure times of 0, 200, 400, and 600 sec, respectively.

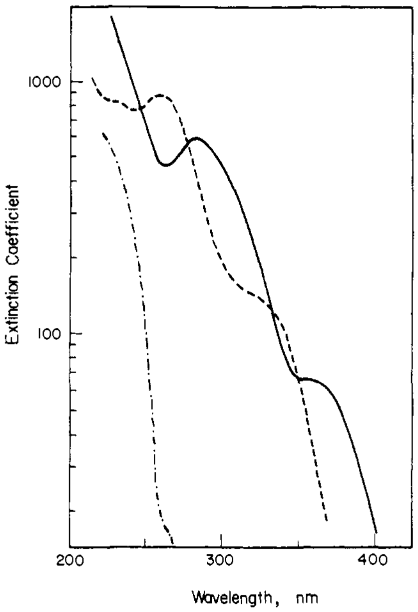

Figure 2. Absorption spectra of $\mathrm{Ir(NH_3)_5N_3^{2+}}$ (—), $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$, (- - -), and $\mathrm{NaN_3}$, (- · · · -) in aqueous solution.

Reactor with 300-nm light, and the spectra were recorded periodically during the photolysis. Care was taken to exactly reproduce the cell position in the spectrophotometer. A base line was determined by recording the spectrum of the solvent cooled to 77°K. Although the cracking in different glasses varied, it remained constant for a given glass and the variation in absorbance was less than 10%.

Analytical Procedure. The isolation and characterization of the products of the photolysis of $\mathrm{Ir(NH_3)_5N_3^{2+}}$ were described previously.[7] The amount of chloramine formed in the photolysis of $\mathrm{Ir(NH_3)_5N_3^{2+}}$ was determined by spectral analysis at 260 and 300 nm. This procedure could be used to approximately 20% consumption of the $\mathrm{Ir(NH_3)_5N_3^{2+}}$, beyond which time erroneous results were obtained due to the photolysis of the product. An alternative approach made use of the quantitative oxidation of iodide ion by the $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ product. The amount of $\mathrm{I_3^-}$ formed after addition of an aliquot of 0.1 *M* KI to an aliquot of the photolyzed solution was determined spectrally at 353 nm. The extinction coefficient of $\mathrm{I_3^-}$ at 353 nm, determined by the addition of known amounts of $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ or $\mathrm{I_2}$ to equivalent aliquots of 0.1 *M* KI, agreed within experimental error and was found to be 2.32×10^4 M^{-1} cm^{-1}. An equivalent aliquot of the unphotolyzed solution was treated in an identical manner. From the difference in absorbance at 353 nm, the concentration of $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ was determined. The decrease in absorbance at 353 nm due to the photolysis of $\mathrm{Ir(NH_3)_5N_3^{2+}}$ was insignificant and did not affect, within experimental error, the calculation of the amount of $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ formed in the photolysis. Analysis by the spectral method yielded values 5-8% larger than those obtained by the iodine method. This difference, however, was within experimental error of the quantum yields obtained by either method.

Azide ion determinations were made by the formation of an $\mathrm{Fe^{3+}\text{-}N_3}$ complex which was determined spectrally at 455 nm, ϵ 2.46×10^3 M^{-1} cm^{-1}.[21] An aliquot of the photolyzed solution, buffered to a pH of 5-6 with a 0.1 *M* NaOH solution, was added to an aliquot of 0.1 *M* $\mathrm{Fe(NO_3)_3}$ and diluted to volume with water. The concentration of $\mathrm{N_3^-}$ was determined from the absorbance at 455 nm, relative to a reference solution prepared in an identical manner with an equivalent aliquot of the unphotolyzed solution. To determine whether any azide ion formed during the photochemical reaction could be detected, a 0.1 *M* HCl solution containing 2.6×10^{-3} *M* [$\mathrm{Ir(NH_3)_5N_3]Cl_2}$ and 10^{-4} *M* $\mathrm{NaN_3}$ was photolyzed with 300-nm light to 5% consumption of the complex. The solution was tested with $\mathrm{Fe^{3+}}$ and, within experimental error, all of the added azide ion was detected.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer, calibrated against polystyrene. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer and/or on a Beckman DU-2 spectrophotometer. Emission and excitation spectra of solid samples, glasses at 77°K, and solutions at 298°K were recorded on a Hitachi MPF-2A fluorescence spectrophotometer. Esr spectra of the photolysis products obtained in a 4:1 methanol-water glass at 77°K were recorded on a Varian E-4 spectrometer. A Beckman expandomatic pH meter equipped with a glass and calomel electrode was used to make pH measurements. This instrument was standardized against a Harleco pH 5 buffer.

Analysis. Carbon, hydrogen, and nitrogen analyses were carried out by Miss H. Beck of this department.

Results

When a 0.1 *M* HCl solution of [$\mathrm{Ir(NH_3)_5N_3]Cl_2}$ was exposed to ultraviolet radiation 1 mol of nitrogen was evolved per mole of complex decomposed. The evolution of nitrogen was not quenched by either iodide ion or acrylamide, both of which quench the evolution of nitrogen for photochemical reactions of azido metal complexes which proceed through an azide radical. Spectra recorded periodically during the photolysis (Figure 1) showed that isosbestic points at 276, 338, and 350 nm were maintained for 22% reaction. Continued photolysis resulted in a loss of the isosbestic points and a general decline of the absorbance throughout the ultraviolet region. Addition of an aliquot of the photolyzed solution, buffered to a pH of 5, to a 0.1 *M* $\mathrm{Fe(NO_3)_3}$ solution indicated free azide ion was not present. However, the photolyzed solution did oxidize iodide ion to iodine. A comparison of the observed spectral changes with spectra of synthetically prepared $\mathrm{Ir(NH_3)_5N_3^{2+}}$ and $\mathrm{Ir(NH_3)_5NH_2Cl^{3+}}$ (Figure 2) and a determination of the amount of nitrogen released established the stoichiometry of the photochemical reaction to be

$$\mathrm{Ir(NH_3)_5N_3^{2+} + 2H^+ + Cl^- + } h\nu \longrightarrow \mathrm{Ir(NH_3)_5NH_2Cl^{3+} + N_2} \qquad (1)$$

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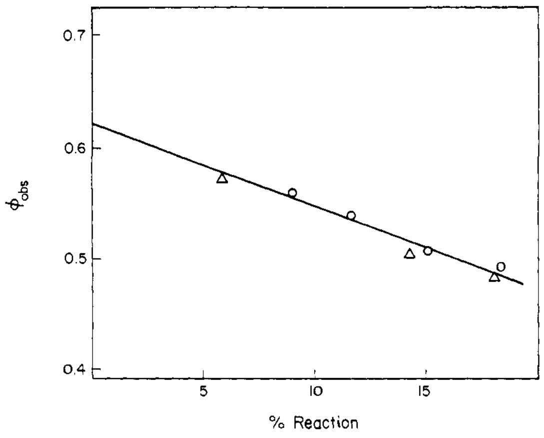

Figure 3. Quantum yields of $Ir(NH_3)_5NH_2Cl^{3+}$ determined at various extents of reaction for the photolysis of a 0.1 *M* HCl solution containing 2.60 × 10^{-3} *M* $[Ir(NH_3)_5N_3]Cl_2$: circles refer to values determined by the spectrophotometric method of analysis; Δ, values obtained by oxidation of I^-.

The spectral changes occurring upon excitation at other wavelengths were identical with those shown in Figure 1; thus this same reaction occurs at all of the wavelengths studied.

The quantum yields of the reaction, summarized in Table I, were obtained by extrapolating the quantum yields observed at various extents of reaction back to 0% reaction. A representative plot of φ_{obsd} at 300 nm as a function of the per cent reaction is shown in Figure 3. The dependence of the yield on the extent of reaction is attributed to secondary photolysis of the product $Ir(NH_3)_5NH_2Cl^{3+}$. Direct photolysis of a 0.1 *M* $HClO_4$ solution containing 10^{-3} *M* $[Ir(NH_3)_5NH_2Cl](ClO_4)_3$ resulted in a general decline in absorbance throughout the ultraviolet region and in the appearance of free chloride ion in the photolyte. The quantum yield of decomposition of $Ir(NH_3)_5NH_2Cl^{3+}$ at 300 nm was found to be 0.66.

Table I. Quantum Yields of $Ir(NH_3)_5NH_2Cl^{3+}$ at Various Wavelengths

$10^3[Ir(NH_3)_5N_3^{2+}]$, *M*	λ_{ex}, nm	$\varphi_{Ir(NH_3)_5NH_2Cl^{3+}}$ [a,b]
2.57	250	0.63
2.60	300	0.61
3.04	350	0.83
2.61	400	0.65

[a] Determined at 25° and in 0.1 *M* HCl. [b] Values obtained from extrapolation of plot of φ_{obsd} *vs.* per cent reaction.

The quantum yields summarized in Table I were found to be independent of the concentration of $Ir(NH_3)_5N_3^{2+}$, over the range 10^{-3}–10^{-2} *M*, and independent of whether the anion was chloride or perchlorate ion provided the concentration of chloride ion, present as NaCl, was 0.1 *M* or greater. Also the quantum yield of $Ir(NH_3)_5NH_2Cl^{3+}$ was not found to be O_2 sensitive. The quantum yields of $Ir(NH_3)_5NH_2Cl^{3+}$ obtained for 0.1 *M* HCl solutions containing 10^{-3} *M* $[Ir(NH_3)_5N_3]Cl_2$ saturated with air, argon, or nitrogen were the same within experimental error.

The quantum yield of $Ir(NH_3)_5NH_2Cl^{3+}$ was found to be independent of the concentration of hydrogen ion. Quantum yields of $Ir(NH_3)_5NH_2Cl^{3+}$ formation at 300 nm, corrected for hydrolysis of the product, for solutions buffered to pH 5 with a sodium acetate–acetic acid buffer and containing 0.1 *M* NaCl were the same as values obtained in 0.1 *M* HCl. However, the yield was found to show a pronounced dependence on the concentration of Cl^-. The dependence of the yield of $Ir(NH_3)_5NH_2Cl^{3+}$ on the concentration of Cl^- was determined by irradiation of a 10^{-3} *M* $[Ir(NH_3)_5N_3](ClO_4)_2$ in 0.1 *M* $HClO_4$ solution. The chloride ion concentration was varied from 0.1 to 4 × 10^{-4} *M*. The latter limit was determined by the concentration of chloride ion in $HClO_4$. The solutions were irradiated at 300 nm and the results of these experiments are shown in Figure 4.

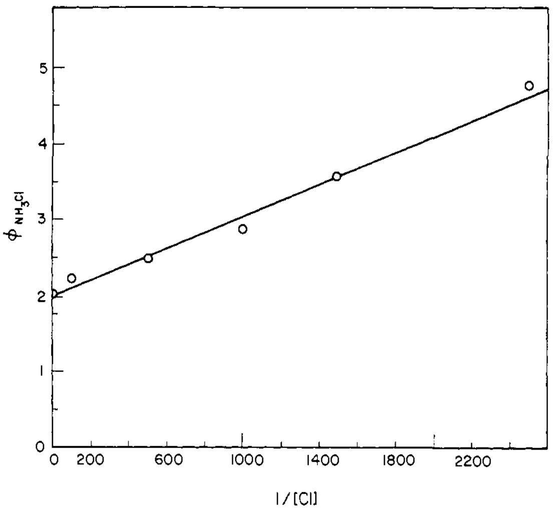

Figure 4. Dependence of the quantum yield for the formation of $Ir(NH_3)_5NH_2Cl^{2+}$, φ_{NH_2Cl}, on chloride ion concentration.

The quantum yields reported in Table I show a maximum value at 350 nm, suggesting that the reactive state may be a metal d–d state or a lower energy state of the complex or azide ligand. To investigate these possibilities a series of sensitization experiments were carried out. The donors used along with the energies of their singlet and triplet states, as well as the energies and spectral assignments of the transitions of $Ir(NH_3)_5N_3^{2+}$, are summarized in Table II.

Table II. Excited-State Energies (kK)

Species	Singlet	Triplet
$Ru(bipy)_3Cl_2$		17.8[a]
Biacetyl	21.5[b]	19.6[b]
Quinolinium ion	32.8[b]	22.0[c]
$Ir(NH_3)_5N_3^{2+}$	27.8 $^1A_{1g}$–$^3T_{1g}$[d] 36.0 $^1A_{1g}$–$^1T_{1g}$[d] 43.0 $^1A_{1g}$–$^1T_{2g}$[d]	

[a] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968). [b] Emission band maxima in 0.1 *M* HCl. [c] G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961). [d] Assignments according to Schmidtke, ref 12.

The results showed that $Ir(NH_3)_5N_3^{2+}$ did not quench the phosphorescence of $Ru(bipy)_3^{2+}$, $K_{sv} < 4$ M^{-1}, a value within experimental error of zero. Nor did $Ir(NH_3)_5N_3^{2+}$ quench the fluorescence of quinolinium ion, $K_{sv} < 10$ M^{-1}. A small amount of $Ir(NH_3)_5NH_2$-

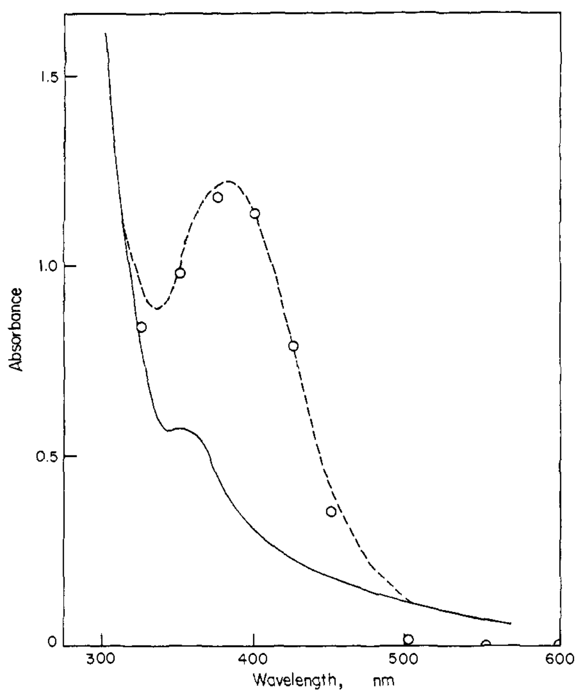

Figure 5. Spectra of 2.83×10^{-3} M $[Ir(NH_3)_5N_3]Cl_2$ (—) and intermediate (- - -) observed on photolysis of a 4:1 methanol-water glass at 77°K. The points ○ represent the relative absorbances (see text) of the intermediate observed on flash photolysis of a 10^{-3} M $[Ir(NH_3)_5N_3](ClO_4)_2$ solution.

Cl^{3+} was formed, $\varphi = 5 \times 10^{-3}$, when quinolium ion was used to sensitize the complex. However, the yield was found to be independent of the concentration of oxygen and approached zero as the path length of the cell was decreased from 5 to 1 cm. Thus, the yield of $Ir(NH_3)_5NH_2Cl^{3+}$ was attributed to a trivial photolysis of the complex due to the fluorescence of quinolinium ion.

With biacetyl as a donor, the results were complicated. It was found that $Ir(NH_3)_5N_3^{2+}$ did quench the phosphorescence of biacetyl in 0.1 M HCl solution, $K_{sv} = 7.7 \times 10^3$ M^{-1}. However, sensitization experiments with 0.1 M HCl solutions containing 0.15 M biacetyl and 1.33×10^{-3} M $[Ir(NH_3)_5N_3]Cl_2$, where 91% of the biacetyl phosphorescence was quenched, did not result in the formation of $Ir(NH_3)_5NH_2Cl^{3+}$, $\varphi^{sen} < 2 \times 10^{-3}$, or azide ion, $\varphi^{sen} < 5 \times 10^{-3}$.

A series of photolyses of $Ir(NH_3)_5N_3^{2+}$ in a 4:1 methanol-water glass at 77°K were carried out to trap reactive intermediates. Photolysis of a glass at 77°K containing 10^{-3} M $[Ir(NH_3)_5N_3]Cl_2$ or $[Ir(NH_3)_5N_3](ClO_4)_2$ resulted in the appearance of a yellow-brown color which disappeared on melting. Identical spectra of the intermediate were obtained with either the chloride or perchlorate salt of $Ir(NH_3)_5N_3^{2+}$ and in acidic, 10^{-3} M HCl, or neutral glasses. The spectrum of the intermediate, shown in Figure 5, was obtained by photolysis at 300 nm of a 4:1 methanol-water glass containing 2.83×10^{-3} M $[Ir(NH_3)_5N_3]Cl_2$ and 10^{-3} M HCl. An estimate of the extinction coefficient of the intermediate was made at 300 nm. The amount of $Ir(NH_3)_5N_3^{2+}$ remaining, after allowing the photolyzed solution to melt, was estimated from the decrease in absorbance at 300 nm. Assuming a one to one stoichiometry between the intermediate and the amount of $Ir(NH_3)_5N_3^{2+}$ consumed, the extinction coefficient at 300 nm was calculated to be 3×10^3 M^{-1} cm^{-1}.

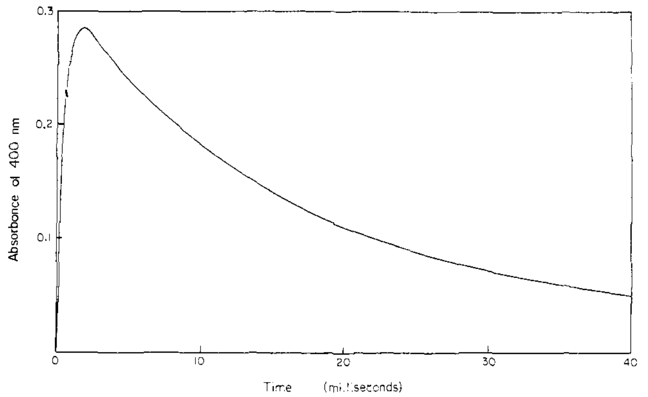

Figure 6. The absorbance-time profile of the transient observed following the flash photolysis of a 10^{-3} M $[Ir(NH_3)_5N_3](ClO_4)_2$ solution.

To characterize the intermediate observed in a glass, a series of flash photolysis experiments were undertaken. The spectrum of the intermediate was obtained by a point by point kinetic method which consisted of separate experiments at different wavelengths. The absorbance, A_0, of the intermediate at various wavelengths was obtained by extrapolating first-order plots of the decay of the intermediate to zero time. The data for these plots were obtained from traces recorded on a time scale where only the decay of the transient was observed. Plots of log absorbance *vs.* time were linear through three or four half-lives. The half-life was taken as the time required for the absorbance to drop to one-half the value of A_0. The half-lives, approximately 17 msec, determined at various wavelengths differed by less than 15%, suggesting that only one intermediate was being observed. The concentration of the intermediate formed in a 71 J flash was determined by flashing a solution containing 10^{-3} M $Ir(NH_3)_5N_3^{2+}$ and 0.1 M HCl. The amount of chloramine formed, 2.52×10^{-5} M, was determined iodiometrically. The absorbance, A_0, of the intermediate at 400 nm was then determined by exposing a 10^{-3} M solution of $Ir(NH_3)_5N_3^{2+}$ to a 71 J flash. The extinction coefficient, assuming a 1:1 stoichiometry and correcting for a small fraction of the intermediate intercepted by perchlorate ion, was calculated to be 2.8×10^3 M^{-1} cm^{-1} at 400-nm. The apparent agreement of the extinction coefficients obtained in a glass and in the flash experiments must be judged with caution since the stoichiometry of the reaction(s) occurring in a glass and in the flash is (are) not known. Furthermore the analyzing beam, 1-cm in diameter, does not analyze the entire reaction cell which is 2-cm in diameter. Thus the optical density of the transient and therefore its extinction coefficient may be larger than those observed. For these reasons the spectra recorded in the glass and flash photolysis experiments are reported in terms of absorbance adjusted such that the absorbances at 400 nm are equal and are plotted in Figure 5 to show their similarity. Unlike $Rh(NH_3)_5N_3^{2+}$ where three intermediates were observed,[22] only one intermediate was observed in the flash photolysis of 10^{-3} M

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[22] G. Ferraudi and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 2371 (1973).

solutions of $Ir(NH_3)_5N_3^{2+}$ at pH 5.5 and 6.5 in the 325–650-nm spectral region.

Figure 6 shows the time dependence of the absorbance which is proportional to the concentration of the intermediate, observed in the flash photolysis of a 10^{-3} *M* $Ir(NH_3)_5N_3^{2+}$ solution. The absorbance of the transient rapidly reaches a maximum in approximately 1–2 msec, then slowly decays in approximately 50 msec.

The rapid rise in absorbance of the transient was investigated on the flash apparatus of Professor Endicott at Wayne State University.[20] The data from plots of absorbance at 400 nm *vs.* time were plotted according to first- and second-order kinetics. The data were best described by second-order kinetics but deviated at long and short times. The intensity dependence of the initial rate was determined by plotting the log of the initial rate *vs.* the log of the charging voltage (intensity is proportional to the square of the charging voltage). The charging voltage was varied from 3.4 to 6.4 kV. The slope of the plot was 3.7 ± 0.5 suggesting a second-order dependence on the intensity. The initial rates of the growth of the absorbance decreased as the concentration of chloride or perchlorate ion increased. However the decrease in rate was not a linear function of the concentration of the ions. The amount of intermediate formed, determined from the absorbance at $t = \infty$, decreased as the concentration of chloride or perchlorate ion increased.

The rate constant of the decay of the transient, $k = 5.1 \times 10^1$ sec^{-1}, was found to be independent of the concentration of the complex over the range 10^{-4}–10^{-3} *M*. However, the amount of intermediate formed per flash, estimated from A_0, decreased as the concentration of $Ir(NH_3)_5N_3^{2+}$ decreased due to a smaller fraction of the flash absorbed. The half-life of the intermediate was also found to be essentially independent of the concentration of added chloride ion but the amount of intermediate observed decreased as the concentration of chloride ion increased. The results of these experiments, as well as the results of similar experiments with perchlorate ion, are summarized in Table III. The data clearly indicate that chloride ion and perchlorate ion scavenge precursors to the observed intermediate.

Table III. Effect of Chloride and Perchlorate Ion on the Decay Kinetics of the Intermediate Observed at 400 nm on Flash Photolysis of 1.0×10^{-3} *M* $[Ir(NH_3)_5N_3](ClO_4)_2$

$[Cl^-]^a$	$[ClO_4^-]^a$	$\tau_{1/2}^b$	A_0^c
0	2.0×10^{-3}	17.5	0.280
1.03×10^{-3}	2.0×10^{-3}	12.0	0.258
5.0×10^{-3}	2.0×10^{-3}	18.0	0.235
2.5×10^{-2}	2.0×10^{-3}	14.0	0.150
5.0×10^{-2}	2.0×10^{-3}	20.1	0.110
0	6.0×10^{-3}	16.5	0.238
0	1.2×10^{-2}	16.8	0.216
0	5.2×10^{-2}	23.4	0.142

[a] Concentration in moles/liter. [b] Half-life in milliseconds. [c] A_0 is the absorbance at 400 nm obtained from extrapolation of the decay to $t = 0$.

As indicated by Figure 7 the amount of intermediate observed at 400 nm on flashing a 10^{-3} *M* $Ir(NH_3)_5N_3^{2+}$ solution at constant ionic strength, 0.01 *M* $NaClO_4$, was a complex function of the pH of the solution. The half-life of the intermediate decreased from 18 to 2.6 msec as the pH of solution increased from 6.0 to 9.7.

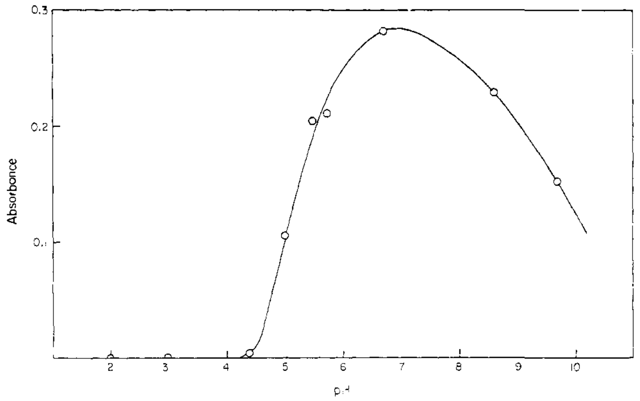

Figure 7. The pH dependence of the initial absorbance, A_0, at 400 nm of the intermediate observed on flash photolysis of 10^{-3} *M* $[Ir(NH_3)_5N_3](ClO_4)_2$.

Discussion

Irradiation of aqueous solutions of $Ir(NH_3)_5N_3^{2+}$ with ultraviolet light results in the evolution of 1 mol of nitrogen per mole of complex decomposed. The yield of nitrogen is not quenched by iodide ion[9,10,23] or acrylamide,[23] and azide ion is not detected in the photolyte. For all wavelengths of irradiation studied, the stoichiometry of the photochemical reaction of the azido complex in hydrochloric acid solution is given by eq 1. These results are readily explained by the formation of a coordinated nitrene intermediate as the primary product of the photochemical event.

The large quantum yields of the photochemical reaction, Table I, and the absence of other reaction modes suggest that a flash photolysis study of $Ir(NH_3)_5N_3^{2+}$ might allow a detailed investigation of the chemistry of the iridium nitrene intermediate. The flash photolytic behavior of $Rh(NH_3)_5N_3^{2+}$ was recently investigated,[22] and the coordinated nitrene was found to undergo a rapid dimerization reaction. The kinetic behavior of the intermediate observed in the flash photolysis of $Ir(NH_3)_5N_3^{2+}$ is essentially the same as that observed in the flash photolysis of $Rh(NH_3)_5N_3^{2+}$. However, unlike $Rh(NH_3)_5N_3^{2+}$ where the spectrum of the dimer is substantially different from the intermediate observed in a 4:1 methanol–water glass at 77°K, the spectra of the intermediates generated in the flash photolysis of $Ir(NH_3)_5N_3^{2+}$ and in a 4:1 methanol–water glass at 77°K are very similar (Figure 5). In a glass, dimerization should not be possible, and the similarity of the spectra suggests that dimerization is not an adequate explanation of the reactions observed in the flash photolysis of $Ir(NH_3)_5N_3^{2+}$. Alternatively, the absorbance–time profile (Figure 6) suggests a mechanistic scheme of the type

$$A \underset{k_{-2}}{\overset{k_2}{\longrightarrow}} B \qquad (2)$$

$$B \xrightarrow{k_3} C \qquad (3)$$

where B is the intermediate with an absorption maximum at 400 nm. Since the half-life of the intermediate

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(23) C. Bartocci and F. Scandola, *Chem. Commun.*, 531 (1970).

is independent of chloride or perchlorate ion concentration and since the amount of intermediate decreases as the concentration of chloride or perchlorate ion increases, the intermediate B is not $Ir(NH_3)_5NH^{3+}$, $Ir(NH_3)_5NH_2^{4+}$, or $Ir(NH_3)_5NHCl^{2+}$. If $Ir(NH_3)_5NH^{3+}$ or $Ir(NH_3)_5NH_2^{4+}$ were the intermediate observed, then its half-life should decrease as the concentration of chloride ion increases. As shown in Table III this is not observed. Nor is the assignment of the intermediate as $Ir(NH_3)_5NHCl^{2+}$ consistent with the data, since the yield of intermediate should increase as the concentration of chloride ion increases which is opposite to what is observed (Table III). The intermediate B is postulated to be a product of the reaction of the coordinated nitrene and water or hydroxide ion to form the conjugate base of the hydroxylamine, $Ir(NH_3)_5NHOH^{2+}$. The reaction with the solvent is in kinetic competition with the more rapid, $t \leq 100$ μsec, scavenging by chloride or perchlorate ion. The rate constant k_3, 5.1×10^1 sec^{-1}, was obtained from the decay of the intermediate. The value of k_2, 2×10^3 sec^{-1}, was obtained by a computer program which reproduced Figure 6. The small value of k_2 suggests that simple scavenging of water by the nitrene is not an adequate explanation or that eq 2 is better represented by an equilibrium process.[24]

The complex pH dependence of the half-life and the amount of intermediate observed (Figure 7) indicate that the intermediate must undergo additional reactions with hydroxide ion. A known sample of $Ir(NH_3)_5NH_2OH^{3+}$ reacts rapidly with hydroxide ion, and an intermediate with an absorption maximum at 400 nm is observed.

A mechanism consistent with the steady state and flash photolysis of $Ir(NH_3)_5N_3^{2+}$ is given by eq 4–11.

$$Ir(NH_3)_5N_3^{2+} + h\nu \xrightarrow{k_4} [Ir(NH_3)_5N_3^{2+}]^* \quad (4)$$

$$[Ir(NH_3)_5N_3^{2+}]^* \xrightarrow{k_5} Ir(NH_3)_5N_3^{2+} + \text{heat} \quad (5)$$

$$[Ir(NH_3)_5N_3^{2+}]^* \xrightarrow{k_6} Ir(NH_3)_5N^{2+} + N_2 \quad (6)$$

$$Ir(NH_3)_5N^{2+} + H^+ \xrightarrow{k_7} Ir(NH_3)_5NH^{3+} \quad (7)$$

$$Ir(NH_3)_5NH^{3+} + Cl^- \xrightarrow{k_8} Ir(NH_3)_5NHCl^{2+} \quad (8)$$

$$Ir(NH_3)_5NH^{3+} + ClO_4^- \xrightarrow{k_9} Ir(NH_3)_5NHOClO_3^{2+} \xrightarrow{k_9'} Ir(NH_3)_5NH_2OH \quad (9)$$

$$Ir(NH_3)_5NH^{3+} + H_2O \xrightarrow{k_{10}} I \longrightarrow P \quad (10)$$

$$Ir(NH_3)_5NHCl^{2+} + H^+ \xrightarrow{k_{11}} Ir(NH_3)_5NH_2Cl^{3+} \quad (11)$$

For eq 10, product I represents the intermediate observed in the flash photolysis.[24a] Neither the steady-state nor the flash photolysis data allow a distinction between chloride ion scavenging the coordinated nitrene, $Ir(NH_3)_5NH^{3+}$, followed by a rapid reaction with hydrogen ion to form the chloramine or protonation of the nitrene prior to addition of chloride ion. However, this does not affect the kinetic analysis, since the quantum yields were found to be independent of pH. Equation 9 represents scavenging by perchlorate ion resulting ultimately in the formation of hydroxylamine. A steady-state analysis of the proposed reaction scheme leads to

$$1/\varphi_{\text{obsd}} = 1/\varphi_{\text{N}} + \frac{k_9[ClO_4^-] + k_{10}[H_3O]}{k_8\varphi_{\text{N}}}\frac{1}{[Cl]} \quad (12)$$

where φ_{N}, the quantum yield of nitrene formation, is given by $k_6/(k_5 + k_6)$ and φ_{obsd} is the observed yield of chloramine. The intercept in Figure 4 yields a value of 0.55 for φ_{N}, a value within experimental error of that observed on direct photolysis in 0.1 *M* HCl solution. This indicates that in 0.1 *M* HCl all the intermediate nitrene is trapped by chloride ion to yield chloramine. The ratio of intercept to slope yields a value of $k_8/(k_9 \cdot [ClO_4] + k_{10}[H_2O])$ of 1740 M^{-1}. Substitution of the value of k_2, 2×10^3 sec^{-1}, obtained from the flash photolysis for $k_9[ClO_4] + k_{10}[H_2O]$ leads to a value of k_8 of 3.5×10^6 M^{-1} sec^{-1}. Although less than diffusion controlled, k_8 indicates that the coordinated nitrene is a very reactive electrophile.

Two pieces of evidence suggest that the coordinated nitrene intermediate may be a singlet. The quantum yield of chloramine formation is independent of oxygen, an efficient scavenger of triplet arylnitrenes.[25] The electrophilicity of iridium nitrene is also characteristic of singlet nitrenes.[2]

The assignment of the ultraviolet absorption bands of $Ir(NH_3)_5N_3^{2+}$ has been made by Schmidtke.[12] The assignments, according to term symbols of the octahedral group, are summarized in Table II. Comparison of the quantum yields determined at various wavelengths (Table I), with these spectral assignments, shows that excitation in the ligand-field region leads to reaction of the azido group and chloramine formation. Spectral studies of hydrazoic acid,[26] alkali metal azides,[27] and alkyl azides[28] indicate that the first allowed singlet state of the azido group is bent, a significant distortion from the linear ground state. This suggests that the thermally equilibrated azide excited state has a significant Stoke's shift from the vertical Franck–Condon transition observed in the absorption spectrum.[29] Deb observed an emission centered at 480 nm from alkali metal azides which he assigned as an azide fluorescence,[27] further suggesting that a thermally equilibrated azido ligand excited state may be very low in energy. It is difficult to associate fission of the nitrogen–nitrogen bond, necessary for the formation of a nitrene intermediate, with reaction from the metal-centered ligand-field excited states. Thus, we propose that the observed reaction takes place from an excited state of the azido ligand which is lower in energy than the ligand-field excited states of the complex. In terms of this model, the wavelength dependence of the quantum yield reflects dif-

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(24) The mechanistic scheme given by eq 2 and 3 is a special case of the more complex situation of two consecutive equilibria. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1963, p 173.

(24a) NOTE ADDED IN PROOF. Although kinetically similar to the flash photolytic behavior of $Rh(NH_3)_5N_3^{2+}$,[22] the similarity of the spectra of the intermediate observed in a glass and in solution suggests that dimerization is not an adequate explanation of the flash photolytic behavior of $Ir(NH_3)_5N_3^{2+}$. Rather a mechanistic scheme of consecutive reactions or equilibria, eq 2 and 3, is proposed where the observed intensity dependence is a complex function of the rate constants describing the reactions or equilibria.

(25) R. A. Abramovitch, *J. Chem. Soc., Chem. Commun.*, 964 (1972).

(26) I. Burak and A. Treinin, *J. Chem. Phys.*, **39**, 189 (1963).

(27) S. K. Deb, *ibid.*, **35**, 2122 (1961).

(28) W. D. Clossen and H. B. Gray, *J. Amer. Chem. Soc.*, **85**, 290 (1963).

(29) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley-Interscience, New York, N. Y., 1968, p 111.

ferences in the efficiency of internal conversion to this excited state. The maximum in the quantum yield observed at 350 nm implies that either a more efficient internal conversion occurs at this wavelength or that the reactive state lies at this energy. The latter possibility is discounted, since an efficient formation of chloramine is also observed at 400 nm. Thermal population of the 350 nm level following excitation at 400 nm seems unlikely, since the quantum yields at these wavelengths were found to be independent of temperature. It is possible that excitation at 350 nm results in an appreciable direct population of an azide excited state, since Gray, *et al.*, have observed a weak absorption ($\epsilon < 20\ M^{-1}\ cm^{-1}$) at approximately 300 nm in alkylazides.[28]

Although the sensitization experiments were undertaken to determine the energy and multiplicity of the reactive level, failure to sensitize the photochemical reaction does not allow conclusions to be drawn regarding the spin or energy of the reactive level.

Conclusion

Unlike the photochemical reactions of first-row transition metal–azidopentaammine complexes, photolysis of azidopentaammineiridium(III) leads exclusively to the formation of the coordinated nitrene intermediate.

This difference in photochemical behavior is attributed to an increased stability of the iridium(III) nitrene intermediate. The size of the outer d orbitals of iridium are larger than for first-row transition metals, permitting greater $d\pi$–$p\pi$ interaction which results in a more stable coordinated nitrene. Furthermore a redox mode of reaction is unfavorable, since the plus two oxidation state of iridium is not stable in its pentaammine complex.

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Critical Evaluation of Molecular Mechanics

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Abstract: The ability of molecular mechanics (empirical force field calculations) to estimate structures and enthalpies of large organic molecules reliably is probed through extensive calculations on alkanes using two significantly different force field models, Allinger's and one described in the present work. Most of the available data are reproduced with an accuracy rivaling that achieved by the experimental methods. Bond lengths are generally calculated within 0.01 Å of the experimental values, except for four-membered rings and small polycyclic systems where 1,3-nonbonded interactions, neglected in our treatment, become important. Bond angles are reproduced with an accuracy of 1–2°; somewhat larger errors (3–5°) are noted for the bridgehead angles at the junction of two four-membered rings. The standard deviation between calculated and experimental heats of formation for a balanced set of acyclic, cyclic, and polycyclic alkanes used in the parameterization of the force field (39 compounds) is 0.83 kcal/mol (present work) and 1.03 kcal/mol (Allinger's force field). Both force fields are applied to the prediction of the heats of formation of 84 alkanes of diverse structural type. While agreement between the two force field calculations is within 2.0 kcal/mol for 55 of the compounds, some large discrepancies are found for molecules composed mainly of CH groups. The largest disagreement is 45.5 kcal/mol calculated for dodecahedrane (20 CH units). The lack of sufficient, reliable experimental data prevents accurate parameterization of the force field for molecules of this type. Calculations on medium-ring cycloalkanes indicate that these systems are more flexible than previously suggested by molecular mechanics. Earlier studies which imposed artificial symmetry constraints during minimization lead to higher energies. Relative energies are determined more reliably than absolute enthalpy calculations since defects in the method tend to cancel. We now support Allinger's conclusion that the molecular mechanics method, in principle, must be considered to be competitive with experimental determination of the structures and enthalpies of molecules.

Quantitative interpretation of organic chemical phenomena requires the availability of accurate thermochemical information. Experimental data are sparse[1] and are not being gathered at a rapid rate. A method is needed whereby such energies can be estimated inexpensively, easily, and with high expectation of accuracy, even when the molecules of interest have not as yet been prepared. At the present time, *molecular mechanics* calculations[2] represent the best approach to a solution of this problem.[3]

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[1] (a) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970; (b) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969; (c) "Bulletin of Thermodynamics and Thermochemistry," E. F. Westrum, Jr., Ed., University of Michigan, issued yearly; (d) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969); (e) M. Kh. Karpet'yants and M. K. Karpet'yants, "Handbook of Thermodynamic Constants of Inorganic and Organic Compounds," Ann Arbor-Humphrey Science Publishers, Ann Arbor, Mich., 1970.

[2] For a review of this computational approach see J. D. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968); Professor S. Lifson (private communication) prefers *Empirical force field calculations* as a descriptive term.

[3] While important progress has been realized in this area using quantum mechanical procedures, difficulties persist in the achievement of the desired degree of accuracy for large organic molecules. For recent reviews, see G. Klopman and B. O'Leary, *Fortsch. Chem. Forsch.*,