the formation of an ion pair between dry electron and Na$^+$ cation in the spur. The radius of the spur is usually thought to be ~20 Å, and the distance between two Na$^+$ cations (assuming the ion radius ~ 0.98 Å) is calculated to be 5.1 and 6.6 Å for 18 and 8 M NaOH solutions, respectively. Thus, one can expect that the combination of dry electron with Na$^+$ cation in the spur is one of the most probable reaction routes for the irradiation of such highly concentrated NaOH aqueous solutions.

Other possible explanations for this result are the reaction of localized electron with scavenger by tunneling[17] or the formation of *encounter pair*[18] between e_{aq}^- and scavenger. A more detailed mechanism of the fast reaction of dry electrons with alkali metal cations may be given by obtaining the C_{37} value for the solution containing various kinds of metal cations as a function of a series of scavengers. This work suggests that the nanosecond pulse radiolysis technique would be applicable to the study of the fast reaction of dry electrons with metal cations.

Conclusion

We have shown that excess electrons are localized in the shallow traps associated with Na$^+$ cations initially after pulse irradiation. This ion pair was also observed in the irradiated aqueous solutions of NaOH at room temperature. The ion pair is thought to be formed in the spur very early in the radiation of concentrated NaOH aqueous solutions.

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Reaction of OH with Pyridine. Pulse-Radiolytic and Product-Analysis Studies

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The products obtained from the reaction of OH radicals, generated radiolytically, with pyridine under conditions where the intermediate 1-azahydroxycyclohexadienyl radicals are oxidized to isomeric hydroxypyridines have been examined by high-performance liquid chromatographic methods. From product-analysis data, the initial radiation chemical yields of *o*-, *m*-, and *p*-hydroxypyridines are 1.0, 3.8, and 0.3, respectively. The high yield of *m*-hydroxypyridine exemplifies the electrophilic nature of OH. The low yield of *p*-hydroxypyridine is attributed to the failure to quantitatively oxidize the 1-aza-*p*-hydroxycyclohexadienyl radical by the more powerful oxidant such as $IrCl_6^{2-}$. The isomeric OH adducts of pyridine exhibit selectivity in reactivity with the two oxidants examined, and their reducing strength follows the order meta > ortho > para. From optical pulse radiolysis the second-order rate constant for the electron-transfer processes between hexachloroiridate and meta and ortho pyridine–OH adducts was determined to be 5.8×10^8 M^{-1} s^{-1}.

Introduction

It has been shown recently that derivatives of benzene exhibit selectivity in the addition of OH to various positions in the ring.[1–15] This selectivity seems to result from the electrophilicity of OH.[12–15] similar trends in the addition of OH to the heterocycles have been implicated,[16,17] though product analyses of hydroxy derivatives have not been carried out in detail. Moveover, hydroxylations of nitrogen heterocycles lead to biologically important metabolites, and in some enzymatic processes hydroxylation proceeds via hydroxyl radical.

Recently Steenken and O'Neill[15] have shown by ESR investigations that, for pyridine and substituted pyridine derivatives, OH adds predominantly to the least electron deficient positions of the pyridine ring, position 3 or 5. We have undertaken detailed investigations of the yields of hydroxy derivatives obtained after oxidizing 1-azahydroxycyclohexadienyl radical isomers by either a mild oxidant $Fe(CN)_6^{3-}$ or a more powerful oxidant $IrCl_6^{2-}$. Separation of isomeric hydroxypyridines from pyridine and the oxidant was carried out by high-performance liquid chromatography. In order to obtain kinetic information about the reactivities of the OH adducts with the oxidants, we carried out optical pulse radiolytic investigations on a microsecond time scale.

Experimental Section

Pyridine obtained from Aldrich was distilled before use. All of the isomeric hydroxypyridines obtained from Aldrich were recrystallized before use. Potassium hexachloroiridate(IV), potassium hexacyanoferrate(III), and potassium hexachloroiridate(III) were obtained from G. F.

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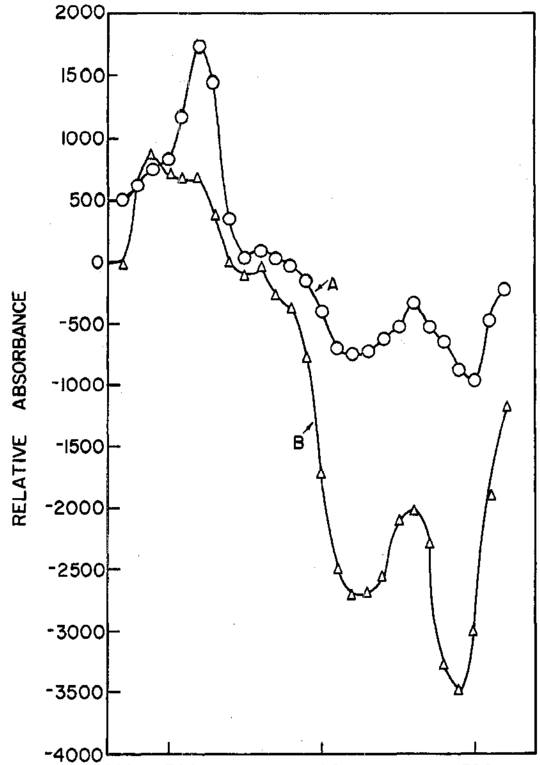


Figure 1. The spectra observed (A) 2 μs and (B) 100 μs after the pulse in a nitrous oxide saturated solution containing 5 mM pyridine and 0.4 mM hexachloroiridate at pH 7.0 (buffered with phosphate).

Smith (Columbus, OH) and used as received. For product-analysis studies, water was triply distilled including distillation from basic permanganate and acid dichromate solutions. All solutions were buffered with 2 mM phosphate.

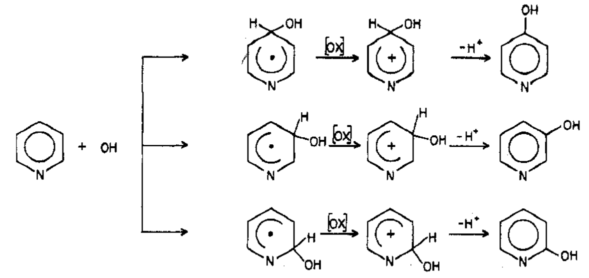
For pulse-radiolysis studies, aqueous solutions containing appropriate quantities of substrate were saturated with N_2O in order to convert e_{aq}^- to OH and were irradiated with 5-ns electron pulses from an Arco LP7 linear accelerator. The dose per pulse was ~2 × 10^{16} eV g^{-1} which corresponds to an initial concentration of ~2 μM. The data aquisition was carried out by the computer-controlled pulse-radiolysis apparatus described earlier.[18]

For product-analysis studies, 2–5 mM solutions of pyridine containing 0.4 mM of oxidant were saturated with N_2O and irradiated by using dose rates of 3.12 × 10^{17} eV g^{-1} min^{-1} as determined by Fricke dosimetry. The conversion of the products was kept below 10% of the initial concentration of the oxidant. The irradiated solutions were analyzed by using the liquid-chromatography apparatus described earlier.[19] The isomeric hydroxypyridines were detected optically or fluorimetrically. Details of separation and detection have been described elsewhere.[20]

Results and Discussion

The optical absorption spectra measured 2 and 100 μs after the pulse of a 5.0 mM solution of pyridine containing 0.1 mM $IrCl_6^{2-}$ at pH 7.05 are shown in Figure 1, a and b, respectively. At 320 nm, a rapid increase in absorbance followed by a slow decrease was observed. As seen from Figure 1b, at all wavelengths between 350 and 500 nm, bleaching of initial absorbance was observed. The rate of bleaching observed at 490 nm, the absorption maximum of $IrCl_6^{2-}$, agreed within 5% with the rate of decrease in absorbance monitored at 320 nm. Since e^- is converted to hydroxyl radical, the species that are present immediately after the pulse are H and OH. Both H and OH add to pyridine with second-order rate constants 6.5 × 10^8 and 3 × 10^9 M^{-1} s^{-1}, respecitvely.[21,22] The rapid initial increase in absorbance corresponds to the addition of OH to pyridine to produce isomeric 1-azahydroxycyclohexadienyl radicals readily as shown in Scheme I. These radicals being good reductants readily transfer electrons to $IrCl_6^{2-}$, a strong oxidant. The absorbance due to the reduced form of the oxidant is very low (<5%) between 300 and 550 nm, as compared to $IrCl_6^{2-}$, and hence bleaching of the absorbance was observed as is shown in Figure 1b. A typical absorbance vs. time profile fitted to a single exponential process is shown in Figure 2. From the time dependence of the decrease in absorption at 490 nm, a second-order rate constant 5.8 × 10^8 M^{-1} s^{-1}, an average obtained by varying four different concentrations in the range 0.1–0.4 nm, was obtained. All traces fit well only with a single exponential process.

Scheme I



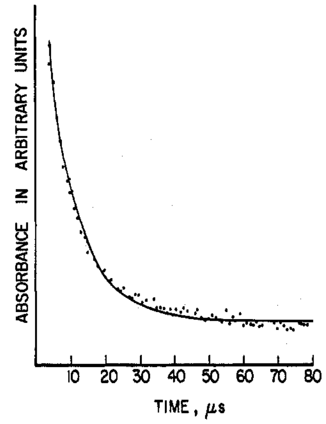


Figure 2. The decay of the absorption of $IrCl_6^{2-}$ at 490 nm after pulse irradiation of a N_2O-saturated 5 mM pyridine with 0.16 mM $IrCl_6^{2-}$ at pH 7.0 (buffered with phosphate). The pathlength of the optical cell was 1.0 cm. The agreement between the observed points (·) and the calculated line fitted to a single exponential decay process was within ±5%.

In order to calibrate the total yield of hexachloroiridate $(^{-}G_{\mathrm{IrCl_6}^{2-}})$ obtained from the reaction of isomeric 1-azahydroxycyclohexadienyl radicals with hexachloroiridate(IV), we measured the bleach in optical density at 490 nm on pulse irradiating N_2O-saturated 0.01 M formate solutions containing 0.1 mM potassium hexachloroiridate(IV). In the formate system, OH is quantitatively converted to CO_2^-, which reduces $IrCl_6^{2-}$ to form $IrCl_6^{3-}$ and CO_2. After correcting for the contribution from H atoms, the decrease in absorbance of $IrCl_6^{2-}$, within 100 μs after the pulse in the pyridine system, corresponds with 85% of the total yield of OH. This indicates that not all pyridine–OH adducts transfer electrons to $IrCl_6^{2-}$. The alternative pathway for the decay of the pyridine–OH adducts in via dimerization of the radicals. As will be seen later, only the para OH adduct of pyridine does not react with $IrCl_6^{2-}$ within 100 μs after the pulse.

The second-order rate constant obtained for electron-transfer reaction between pyridine–OH adducts and $IrCl_6^{2-}$

TABLE I: Yields of Hydroxypyridines Produced by Reaction of OH with Pyridine in the Presence and the Absence of Oxidants[a]

oxidant	3-hydroxy-pyridine	2-hydroxy-pyridine	4-hydroxy-pyridine
none	0.13 ± 0.02	0.4 ± 0.05	0.20 ± 0.04
$K_3Fe(CN)_6$ (0.4 mM)	3.75 ± 0.2	0.43 ± 0.04	0.29 ± 0.05
Na_2IrCl_6 (0.4 mM)	3.0[b]	0.97 ± 0.08	0.3 ± 0.05

[a] The concentration of pyridine was 4-5 mM; pH 7.65. [b] Not quantitatively determinable because of thermal reaction between 3-hydroxypyridine and hexachloroiridate. After the correction for the product lost due to thermal reaction yields a value of 3.8 in agreement with the ferricyanide system.

TABLE II: Rate Constants for Electron Transfer from Isomeric 1-Azahydroxycyclohexadienyl Radicals to Oxidants

oxidant	$k_{(ox)_o}$, $M^{-1}\,s^{-1}$	$k_{(ox)_m}$, $M^{-1}\,s^{-1}$	$k_{(ox)_p}$, $M^{-1}\,s^{-1}$
$K_3Fe(CN)_6$	$<5 \times 10^4$[a]	5×10^6–10^4[b]	$\leqslant 5 \times 10^4$[a]
Na_2IrCl_6	5.7×10^8[c]	5.7×10^8	$\leqslant 5 \times 10^4$[a]

[a] These estimates are based on the product analysis data from Table I. [b] Based on a combination of data from product analysis and pulse radiolysis. [c] Obtained from optical pulse radiolysis kinetics (see text).

is lower than that of hydroxycyclohexadienyl radicals (2.7 × $10^9\ M^{-1}\ s^{-1}$).[23] This difference indicates that 1-azahydroxycyclohexadienyl radical is a poorer reductant than hydroxycyclohexadienyl radical.

In a similar study oxidation of OH adduct of pyridine by 1 mM $Fe(CN)_6^{3-}$ showed no observable change in absorbance at 420 nm, the absorption maximum of $Fe(CN)_6^{3-}$, in several hundred microseconds. Hence, an upper limit for the rate constant for the reaction

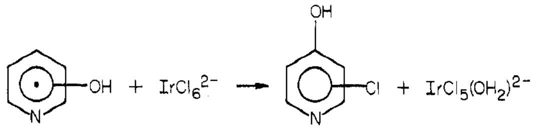
$$C_5H_5NOH + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-} + C_5H_5NOH^+$$

is estimated to be $5 \times 10^6\ M^{-1}\ s^{-1}$.

The yields of *o*-, *m*-, and *p*-hydroxypridines obtained after γ radiolysis of aqueous solutions containing pyridine (4–5 mM) in the presence and the absence of oxidants are shown in Table I. The rate constant for electron transfer from isomeric 1-azahydroxycyclohexadienyl radicals to the oxidants investigated is shown in Table II.

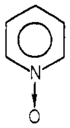
It can be seen from Table I that, in the absence of oxidant, the yields of the three isomeric hydroxypyridines are low and roughly the same. On the other hand, in the presence of $Fe(CN)_6^{3-}$, a pronounced increase in the yield of 3-hydroxypyridine was obtained. In the presence of $IrCl_6^{2-}$, the yield of 2-hydroxypyridine increased by a factor of 2.2 as compared to the value obtained in the presence of the weaker oxidant, $Fe(CN)_6^{3-}$. Because of facile thermal reaction between $IrCl_6^{2-}$ and 3-hydroxypyridine, the yield of 3-hydroxypyridine could not be determined quantitatively; hence a lower value for the yield of 3-hydroxypyridine was found and reported in Table I. Contrary to the pronounced increase in the yield of 2-hydroxypyridine in the presence of $IrCl_6^{2-}$, the yield of 4-hydroxypyridine remained roughly the same.

In certain thermal reactions of alkyl cleavages from organomercurials by an electron-transfer process with $IrCl_6^{2-}$, Kochi[24] observed some contribution due to the chlorine atom transfer from $IrCl_6^{2-}$ to form chloroalkanes and $IrCl_5(OH_2)^{2-}$. The occurence of chlorine atom transfer in the oxidation of pyridine–OH adducts by $IrCl_6^{2-}$ as shown by the equation

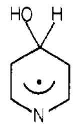


was checked by testing for the formation of $IrCl_5(OH_2)^{2-}$. After oxidation of γ-radiolyzed product with chlorine,[25] the presence of $IrCl_5(OH_2)^-$ was not observed. Hence, no chlorine atom transfer occurs under our experimental conditions.

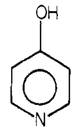
In order to find out the contribution from the addition of OH directly to pyridine nitrogen, we tested the formation of any pyridine *N*-oxide (I) by liquid chromatography



I



II



III

and found none.

The initial yield of hydroxyl radicals expected for a N_2O-saturated aqueous solution containing 5 mM pyridine and 0.4 mM $IrCl_6^{2-}$ is 5.5.[26] The total product yield observed was ~5.0. Since a substantial increase in the yield of only 2-hydroxypyridine was observed with $IrCl_6^{2-}$ as oxidant and not that of 4-hydroxypyridine, the missing 10% of the yield can be attributed to nonquantitative conversion of the radical II to the product III. In the optical pulse radiolysis studies, the decrease in absorbance of $IrCl_6^{2-}$ corresponded only to 85% of *G*(OH). This would be consistent if the para OH adduct of pyridine was not oxidized by $IrCl_6^{2-}$.

The second-order rate constants reported in Table II for the reaction of isomeric 1-azahydroxycyclohexadienyl radicals with $IrCl_6^{2-}$ are much higher than with the weaker oxidant, $Fe(CN)_6^{3-}$. The meta isomer transfers electrons readily with both of the oxidants whereas the ortho and para isomers are not oxidized by $Fe(CN)_6^{3-}$; moreover, the para isomer is not oxidized even by $IrCl_6^{2-}$. The selectivity in the reactivities of these isomers reflects their reducing power, which follows the order meta > ortho > para.

Product-analysis studies show that the initial yields of ortho:meta:para OH adducts of pyridine are in the ratio of 8:68:14, respectively. The high value of addition to the meta position is in reasonable agreement with the initial yield of the meta OH adduct of pyridine, 80%, estimated by ESR techniques by Steenken and O'Neill.[15] These results show that because of its electrophilic nature, OH radical adds predominantly to the least electron-deficient position of the pyridine ring. The isomeric 1-azacyclohexadienyl radicals exhibit remarkable selectivity in reactivity toward hexachloroiridate and ferricyanide.

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(26) From the reported rate constants[19,20] for N_2O-saturated solutions containing 5 mM pyridine and 0–4 mM $IrCl_6^{2-}$, the total OH yield expected would be only 5.5 instead of 6.0 because of the small loss of e_{aq}^- to $IrCl_6^{2-}$.

Role of Proflavin as a Photosensitizer for the Light-Induced Hydrogen Evolution from Water

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Primary photoprocesses involved in the photoreduction of proflavin by electron donors such as EDTA and also its role as a photosensitizer in the photoreduction of methyl viologen were examined by continuous and flash photolysis techniques. While photolysis with EDTA alone results in irreversible photoreduction product, in the presence of methyl viologen, there is redox sensitization. Both processes are shown to proceed via anion radicals of proflavin. Laser photolysis studies also provide direct evidence for the occurrence of extensive photoionization from the singlet and triplet excited states.

Introduction

Visible light induced photoproduction of H_2 from water via photoredox reactions of the type

$$DH + A \xrightarrow[h\nu]{\text{sensitizer}} D + A^- + H^+ \qquad (1)$$

$$2A^- + 2H_2O \xrightarrow[\text{catalyst}]{\text{redox}} 2A + H_2\uparrow + 2OH^- \qquad (2)$$

is currently being examined in several laboratories[1-4] as a viable means of solar energy conversion and storage. Efficient photosensitizers reported to date are the metal complex $Ru(bpy)_3^{2+}$ (ref 5–8) and the acridine dyes such as proflavin.[9-10] Popular schemes involve photosensitized reduction of the acceptor (A) methyl viologen (MV^{2+}) with electron donors (DH) such as EDTA or triethanolamine and subsequent water reduction to H_2 (reaction 2) achieved with the aid of redox catalysts[5-12] derived from noble metals Pt or Au. Earlier we have investigated mechanisms of such sensitized reductions with chlorophyll *a*[13] and $Ru(bpy)_3^{2+}$ (ref 6) as sensitizers. Recent results reported[9,10] with proflavin are interesting (intriguing?) for several reasons: (i) a rather high quantum yield for MV^+ ($\phi = 0.60$) formation with EDTA as the electron donor, (ii) unusual stability and high turnovers of the sensitizer under photolysis conditions (compared to irreversible photoreductions), (iii) significant pH dependence of H_2 yields on the nature of donor, and (iv) the possibility of a reductive cycle operating in the MV^{2+} reduction. So we have investigated the mechanism of photoreduction of proflavin with EDTA and also the photosensitized reduction of MV^{2+} by both continuous and laser flash photolysis techniques. Our results which form the basis of this report also present direct evidence for extensive photoionization of the dye from the singlet excited state.

Materials and Methods

Proflavin (3,6-diaminoacridine) employed was the hemisulfate salt (BDH). Most of the studies employed the commercial sample as such since control experiments with the purified sample gave similar results. EDTA-sodium salt (Fluka) and methyl viologen (BDH) were used as received. To allow for the rapid establishment of the acid–base equilibria, all studies were carried out in buffer solutions (phthalate or phosphates), and the solutions were thoroughly degassed by bubbling with white spot N_2 (O_2 level < 10 ppm) for at least 15 min.

Continuous photolysis experiments were carried out with a 450-W Xe lamp, used in conjunction with water (IR heat) and UV-cutoff (≤400 nm) glass filters. For some studies, Balzer's K-45 interference filters (20-nm band-pass around 440 nm) were employed. Flash photolysis experiments employed 25-ns, 347.1-nm ruby laser pulses of a J. K. laser's 2000 Series system, with a conventional flash kinetic photoelectric detection with a pulsed Xe-lamp source. An 1P28 photomultiplier was used for UV–visible transients, and for near-IR ($\lambda \geq 600$ nm) an ITT 400 fast photodiode was employed. Since intensive photolysis caused by analyzing light was observed on solutions containing EDTA, a 495-nm cutoff filter before analyzing light was used, and only transients absorbing above 500 nm were monitored. Colloidal Pt–PVA was prepared according to the methods reported earlier.[12] H_2 yields were measured on a Gow-Mac gas chromatograph with thermal conductivity detector and Ar carrier gas.

Results and Discussion

I. Continuous Photolysis Studies. (*a*) *Acid–Base Equilibria in the Ground State.* Proflavin has three amino nitrogens, each of which can take up a proton. So, de-

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