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Photochemistry of dicyanopyridines

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Abstract

The photochemistry of a variety of dicyanopyridines (2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dicyanopyridine) in solution at room temperature was investigated. Pulsed UV (308 nm) laser irradiation in deoxygenated acetonitrile yields the triplet state with lifetimes between 4 and 10 μs and absorption bands in the 400 and 320 nm regions. In the presence of added HCl an air-insensitive transient ($\tau \approx$ 10–12 μs, $\lambda_{max} \approx$ 360–380 nm) was observed, suggesting the formation of a protonated excited state.

Irradiation in the presence of amines resulted in the production of the pyridyl radical anion ($\tau \approx$ 40–80 μs, air sensitive, $\lambda_{max} \approx$ 360–380 nm) formed by electron transfer from the amine to the pyridine triplet excited state. Stern–Volmer analysis gave electron transfer rate constants in the range $(1–8) \times 10^{-8}$ M^{-1} s^{-1}.

In methanol solvent, irradiation yielded an air-insensitive transient assigned as the neutral pyridyl radical ($\tau \approx$ 30–200 μs, $\lambda_{max} \approx$ 370–385 nm). The formation of these transients is discussed in the context of previous photochemical electron spin resonance and product studies.

Keywords: Dicyanopyridines; Triplet states; Neutral radicals; Radical anions

1. Introduction

While the utility of heteroaromatic compounds in pharmaceutical and biological applications has resulted in the development of a wide variety of synthetic approaches to their synthesis and numerous studies of their thermal chemistry, the photochemistry of these compounds in solution has received less attention. This is surprising given the mechanistic information that can be gained from such studies.

Previously, two of us (T.C. and B.M.V.) have used a combination of electron spin resonance (ESR) and product analysis to study the photochemically induced reactions of pyridines and quinolines that have been substituted with electron-withdrawing groups such as –CN and –Cl [1–9]. The goal of this research has been to develop photochemical approaches to the synthesis of substituted heteroaromatic molecules that may be difficult to prepare by standard methods.

While it has been possible to propose mechanisms that are consistent with our data, direct confirmation of these mechanisms can possibly be obtained by identifying the transient intermediates produced following pulsed laser excitation. This preliminary report describes the results of laser flash photolysis studies on a series of dicyanopyridines in acetonitrile and methanol solvents (i.e. the solvents used in previous work) and in the presence of added substrates such as amines and acid.

2. Experimental details

2.1. Materials

Spectrophotometric grade acetonitrile (MeCN) was dried and purified by distilling first from P_2O_5 and subsequently from CaH_2. The distilled MeCN was stored and handled under nitrogen. Methanol (MeOH) (Spectrophotometric grade) was used as received. Diethylamine (DEA) and *n*-propylamine were distilled over NaOH under a nitrogen atmosphere and stored under nitrogen in the dark. HCl, 37% in water, was used as received. The dicyanopyridines were either obtained from Aldrich or synthesized from the corresponding carboxylic acid by a previously published procedure [10]. In all cases the pyridines were vacuum sublimed twice prior to use.

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Table 1
Triplet–triplet absorption maxima, triplet lifetimes of pyridines in nitrogen-saturated MeCN and triplet state energies [a]

Compound	λ_{max} (nm)	τ (μs)	E_t (kcal mol^{-1})
3,4-Dicyanopyridine	370, <320	10.0	70.5
2,4-Dicyanopyridine	400, <320	6.0	70.5
2,3-Dicyanopyridine	410, <320	4.0	71.5
2,5-Dicyanopyridine	420, 330	10.0	70.3
2,6-Dicyanopyridine	430, 400, 360	6.0	75.6
3,5-Dicyanopyridine	410, <320	4.0	71.5

[a] Triplet energies measured by phosphorescence emission.

2.2. *Laser flash photolysis*

The laser flash photolysis apparatus has been described in detail previously [11,12]. In a typical experiment samples were irradiated by the UV pulses of a Lumonics EX510 XeCl excimer laser (308 nm, less than 30 mJ per pulse, 8 ns pulse duration). All samples were caused to flow continuously through a specially constructed 7×7 mm^2 quartz cell by a peristaltic pump, thus ensuring that a fresh volume of the sample was irradiated by each laser pulse. Unless otherwise indicated, all samples were deoxygenated prior to irradiation by passing a stream of dry nitrogen through a reservoir containing the sample for 25 min.

2.3. *Cyclic voltammetry*

Reduction potentials were measured in purified dimethylformamide (DMF) with an EG&G Princeton Applied Research potentiostat using an Ag/AgCl reference electrode. The electrode was calibrated using ferrocene as an internal standard (E_{ox}(ferrocene) = 0.43 V vs. the saturated calomel electrode (SCE) in DMF) [13].

3. Results and discussion

3.1. *Triplet and protonated excited states*

Pulsed laser irradiation of all the dicyanopyridines (hereafter referred to as pyridines), with the exception of the 3,4 derivative, in deoxygenated MeCN resulted in the production of two transient species, both absorbing in the 320–450 nm region. (Irradiation of the 3,4 compound yielded only one transient). One of the transients, which was observed for all the pyridines, had an absorption spectrum with two maxima, one in the 400 nm region and the second generally at wavelengths less than 320 nm. This species was efficiently quenched in the presence of oxygen and is therefore tentatively identified as the triplet state of the pyridine. For each of the pyridines Table 1 gives the λ_{max} values for the triplet–triplet absorption as well as the triplet lifetimes, which varied between 4 and 10 μs.

While the decay kinetics at about 430 and 320 nm (triplet state) were the same, the lifetime observed at 360–380 nm was consistently longer (except for the 3,4 compound), indicating the presence of a second transient species. The existence of this species was confirmed by air-quenching experiments. While the 430 and 320 nm decays were quenched by air, the lifetime at 360–380 nm was relatively unaffected. Actually, the absorption at 360–380 nm appears to be due to both the triplet and an air-insensitive species, since the total transient absorption was decreased in the presence of air.

The ratio of the absorption at 380 nm to that of the triplet varied for different pyridines as well as for different samples of the same pyridine. It seems likely that the 380 nm transient is formed either as a result of direct irradiation of a solvent impurity or, more likely, the interaction of an impurity with photoexcited pyridine. In fact, this appears to be confirmed by various attempts we have made to purify the MeCN. Using the solvent "as received" invariably led to a larger 380 nm/triplet ratio than that obtained after treating the MeCN as outlined above.

In attempts to identify the solvent impurity, trace amounts of those materials that are potential MeCN contaminants were added to the pyridine solutions. While the addition of water (a major impurity) did not cause any change in the transient absorption spectrum, addition of trace amounts of acid resulted in the production of a relatively long-lived (slightly longer than the triplet) absorption that was insensitive to the presence of oxygen. This new transient absorbs in the 360–370 nm region and is tentatively assigned as a protonated excited state. Given its spectral and kinetic behavior, it is a possible candidate for the 380 nm transient observed in the absence of added acid. A protonated excited state may be consistent with the behavior reported earlier for 2,4-dicyanopyridine in MeOH. The concentration of the pyridyl radical was significantly enhanced by the addition of HCl. Since no evidence could be found for a protonated ground state [14], a protonated excited state was implicated. As to the nature of the excited state that undergoes protonation, i.e. singlet or triplet, both are sufficiently long lived to be protonated at millimolar acid concentrations. However, given the longer lifetime of the triplet compared with the singlet (about 5–10 μs vs. about 5 ns), the long lifetime of the protonated species and the fact that the triplet is $\pi\pi^*$ in nature, it is more likely that it is the triplet state which is protonated.

3.2. *Electron transfer with amines*

In a recent paper we described the photochemical transformations in solution of 2,4-dicyanopyridine in the presence of aliphatic and aromatic amines [15]. The reaction products included 2-cyanopyridine and 2-cyano-4-aminopyridine or 2-amino-4-cyanopyridine. The mechanism for the substitution reactions was proposed to involve electron transfer from the amine to the photoexcited pyridine, followed by protonation of the pyridine ring nitrogen which is likely facilitated

Table 2
Absorption maxima and lifetimes of pyridine radical anions, reduction potentials of pyridines, bimolecular rate constants for electron transfer quenching of triplet states by DEA and free-energy changes for electron transfer

Compound	λ_{max} (nm)	τ (μs)	$E_{1/2}$ (V)	K_q ($M^{-1}\,s^{-1}$)	ΔG (eV)
3,4-Dicyanopyridine	370	70	−1.23	7.2×10^8	−1.05
2,4-Dicyanopyridine	380, <320	60	−1.28	6.7×10^8	−1.00
2,3-Dicyanopyridine	360, 330	40	−1.35	3.0×10^8	−0.97
2,5-Dicyanopyridine	360, 330	80	−1.38	1.9×10^8	−0.89
2,6-Dicyanopyridine	350	60	−1.61	3.0×10^8	−0.89
3,5-Dicyanopyridine	360	70	−1.54	No quenching	−0.78

by the coulombic attraction of the amine cation radical to the negatively charged nitrogen. Simultaneously with the protonation would be coupling of the resulting aminyl radical to the radical site on the pyridine ring and elimination of HCN. In the production of 2-cyanopyridine, electron transfer is followed by cage escape, followed by elimination of CN and H atom abstraction. Similar results were obtained for the other pyridines [15,16].

In order to establish the validity of the proposed electron transfer step, the pyridines were irradiated in MeCN in the presence of diethylamine (DEA) and in some cases *n*-propylamine. In the presence of DEA a new long-lived transient was observed to grow in with kinetics that were dependent on the DEA concentration. The growth kinetics matched the decay kinetics of the triplet state, indicating interaction between the triplet pyridines and DEA. Table 2 gives the transient absorption maxima and lifetimes for these transients.

When oxygen was introduced into the sample, the decay was enhanced and the total absorption of the new species was efficiently quenched. This lends support for the assignment of this species as the pyridine radical anion formed by electron transfer from the amine. In addition, the effect of oxygen on the yield of the transient is indicative of its triplet origin.

As further confirmation for the presence of anion radical, several of the pyridines were irradiated in the presence of a primary amine, *n*-propylamine. The transient absorption spectra were qualitatively the same using this amine, although larger concentrations were required to produce comparable signals. This is not surprising given the more positive oxidation potential of *n*-propylamine.

Table 3
Pyridyl neutral radical absorption maxima and lifetimes obtained in MeOH

Compound	λ_{max} (nm)	τ (μs)
3,4-Dicyanopyridine	370	180
2,4-Dicyanopyridine	380	100
2,3-Dicyanopyridine	380	30
2,5-Dicyanopyridine	390	30
2,6-Dicyanopyridine	–	–
3,6-Dicyanopyridine	385	>200

By monitoring the triplet decay and/or the growth kinetics of the radical anion as a function of added DEA, it was possible to obtain the bimolecular quenching rate constants for each of the pyridines. Table 2 gives these rate constants as well as the reduction potentials of the pyridines as determined by cyclic voltammetry. The reduction potentials were obtained relative to an Ag/AgCl electrode which was calibrated with a ferrocene internal standard. The values are quoted relative to the SCE. A good correlation was obtained between the ease of electrochemical reduction of the pyridines and the DEA quenching rate constant. It is interesting to note that all the quenching rate constants are considerably less than diffusion controlled even though the free-energy change for electron transfer from DEA to the triplet pyridine, as calculated by the Rehm–Weller equation [1], is considerably negative in each case.

3.3. Neutral radical formation

Irradiation of 2,4-dicyanopyridine in alcohols in the presence of trace amounts of HCl has been shown previously by ESR spectroscopy to lead to the formation of the neutral dicyanopyridyl radical [14]. The suggested mechanism involves coupled proton–electron transfer in the pyridine triplet, T_1, state. Proton transfer to the pyridyl ring nitrogen from the alcohol in an encounter complex was suggested to provide the driving force for electron transfer from the alcohol that would otherwise be endergonic (i.e. the formation of the N–H bond provides the required energy).

We irradiated each of the pyridines in neat MeOH and in all but one case (the 2,6 compound) observed the formation of a single species — a long-lived transient, λ_{max} = 370–380 nm, with kinetics that were insensitive to oxygen. (See Table 3 for the spectroscopic and kinetic data.)

To confirm that the formation of this species was dependent on the presence of methanol, mixtures of MeCN and varying concentrations of MeOH were used. The intensity of the 370 nm absorption increased with increasing MeOH concentration. We assign this absorption to the neutral pyridyl radical.

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[1] The Rehm–Weller equation and DEA oxidation potential can be found in Ref. [17]. The triplet energies were measured previously by phosphorescence spectroscopy (B.M. Vittimberga, unpublished data).

In order to determine the multiplicity of the radical precursor, the intensity of the absorption was determined in the absence and presence of added triplet quenchers including oxygen and dienes. In each case the amount of radical produced was less in the presence of the quencher than in its absence, although it was not entirely quenched. This indicates partial singlet and partial triplet origin for the radical.

This result appears to be contrary to the previous observation that all radical formation was via the triplet [14]. However, in those experiments the alcohol was added to an MeCN solution at relatively low concentrations. At low concentrations the singlet would likely decay to the triplet before it could interact with the MeOH. In the present experiments, however, MeOH is present as solvent and thus would be expected to interact with the singlet before it decays entirely.

4. Summary

Laser photolysis of dicyanopyridines in deoxygenated MeCN leads to the formation of an excited triplet state which absorbs in the 300–400 nm region and decays over a period of several microseconds. Accompanying the formation of the triplet is a second species (except for the 3,4 derivative) which is likely a protonated triplet state formed by reaction with trace amounts of acid.

The triplet state can be reduced by electron transfer from added amines such as DEA and *n*-propylamine. The rate constant for the electron transfer quenching correlates with the reduction potential of the pyridines.

In alcohols the transient behavior is dominated by the formation of a long-lived neutral radical.

Characterization of these transients and the conditions under which they are formed illustrates the variety of reaction pathways available to the pyridines. This will facilitate the use of these compounds in the synthesis of biologically interesting materials.

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