

## FLASH PHOTOLYSIS STUDY OF 5-NITROQUINOLINE

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### Summary

Flash photolysis of 5-nitroquinoline in 50% isopropyl alcohol-water solutions containing hydrochloric acid provides evidence that electron transfer to its  $\pi, \pi^*$  triplet is the primary process leading to the known photoreduction, which terminates in formation of a chlorinated 5-amino-quinoline. A transient having a wavelength maximum at 550 nm and a lifetime of  $5.3 \pm 0.3$  ms is assigned as the 5-nitro-quinolinium radical anion. A second absorption appearing at 410 nm with a lifetime of  $1.1 \pm 0.1$  ms is believed to arise from an irreversible reaction of the protonated radical anion with the solvent. A comparison of the flash data with photochemical quantum yields suggests that both transients contribute to the observed photoreduction.

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### Introduction

In a recent photochemical study from this laboratory we reported the photoreduction of 5-nitroquinoline to 5-amino-6,8-dichloroquinoline in 50% isopropyl alcohol-water solutions containing hydrochloric acid [1]. The quantum yield for 313 nm photolysis increases with HCl concentration and levels off at a maximum value of  $5.44 \pm 0.16 \times 10^{-2}$  when  $[\text{HCl}] \geq 1 \text{ M}$ . The contribution of the chloride ion as an electron donor to the triplet state of aromatic nitro compounds has been demonstrated in steady state and flash photolysis experiments with nitrobenzene and 4-nitropyridine [2 - 4]. In order to evaluate the importance of this process in the photoreduction of 5-nitroquinoline we have undertaken a flash photolysis study of this molecule in alcoholic and acidic solutions with the aim of trying to identify triplets, anions and neutral radicals that may account for the acid dependent photochemical behavior of this molecule. Triplet-triplet absorption has been reported for 1-nitronaphthalene [5 - 8] using conventional flash and laser flash photolysis and the measured triplet lifetime, 1.5 - 5  $\mu\text{s}$ , at room temperature is consistent with our estimate of  $\leq 4 \times 10^5 \text{ s}^{-1}$  for the deactivation rate constant deduced from energy transfer experiments [9]. Reports, however, differ as to where the triplet absorption maximum appears in the visible wavelength region, *i.e.* 450 [5] to 580 nm [7]. The absorption spectra of 1- and 2-nitro-

naphthalene anions have been reported to exhibit maxima at 605 and 480 nm, respectively [10]. Although the absorption spectrum of neither the triplet nor the radical anion of 5-nitroquinoline is known we felt that a comparison of photochemical and flash photolysis data might provide the needed correlation to assign any observed transients.

## Experimental

### *Materials*

5-Nitroquinoline obtained from Aldrich Chemical Co. was recrystallized twice from pentane and once from benzene before using. Spectrograde cyclohexane, isopropyl alcohol and EPA were used as received. Glass distilled water and reagent grade HCl were used for aqueous solutions.

### *Equipment*

The flash photolysis apparatus employed two xenon flash lamps in series with the sample between them and experiments were performed with an energy input of  $\sim 100$  J. The lamp profile was approximately  $40 \mu\text{s}$  wide. Transient absorptions were monitored with a 200 W tungsten-iodine lamp, an Aminco scanning monochromator coupled with an RCA 1P28 photomultiplier, and the photomultiplier signal was displayed on a Tektronix 545B oscilloscope equipped with a type 1A5 plug-in. Kinetic analyses were performed on a computer.

Experiments were performed with 1 cm o.d.  $\times$  12 cm long quartz cells. Solutions typically  $4 \times 10^{-4}$  M in 5-nitroquinoline, were vacuum degassed at least three times and then sealed off at pressures  $< 5 \times 10^{-4}$  Torr.

## Results

Flash photolysis of 5-nitroquinoline did not result in any triplet-triplet absorption for any of the solutions studied, which suggests that the triplet is too short lived ( $< 40 \mu\text{s}$ ) or that its absorption lies outside the scanned region (400 - 630 nm). Since the triplet lifetime of 1-nitro-naphthalene at room temperature is  $\sim 3 \mu\text{s}$  [5 - 8] it is not unexpected that no triplet was observed in the resolution time of our apparatus. That the triplet is populated can readily be discerned from the phosphorescence yield of 5-nitroquinoline in EPA at 77 K, which was measured and found to be 0.27. The distinct 0-0 band, vibrational structure and similarity to naphthalene and nitronaphthalene phosphorescence provide evidence that the lowest triplet is indeed  $\pi, \pi^*$ . Flash photolysis of 5-nitroquinoline in degassed EPA, cyclohexane and ethyl alcohol at room temperature also yielded no transients. The photochemically active medium where reduction occurs with 313 nm photolysis is 50% isopropyl alcohol-water containing HCl, and flash photolysis of these solutions do

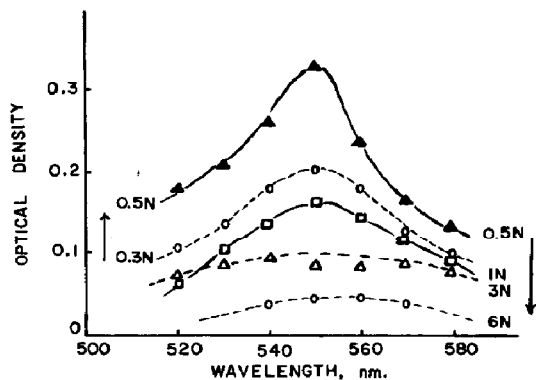
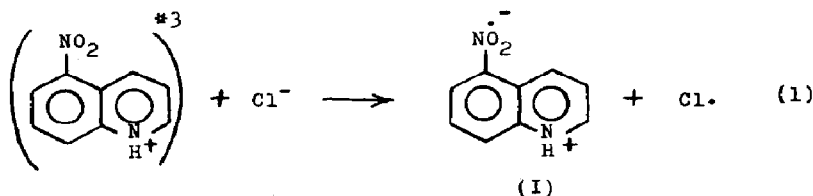


Fig. 1. Transient absorption in the flash photolysis of degassed  $4 \times 10^{-4} M$  5-nitroquinoline in 50% isopropyl alcohol-water as a function of HCl concentration. Transient lifetime was determined to be 5.3 ms in the acid range 0.5 - 3 N HCl. This transient is absent in neat isopropyl alcohol, 50% isopropyl alcohol-water containing 6 N  $H_2SO_4$  and in 12 N HCl.

result in the production of transients exhibiting first order decay kinetics, and whose appearance depends upon the acid used and its concentration. In particular the flash photolysis of  $4 \times 10^{-4} M$  5-nitroquinoline in 50% isopropyl alcohol-water containing HCl results in two absorption peaks in the visible wavelength region, which appear at 550 nm and 410 nm.

The optical density behavior of the 550 nm transient is interesting in that it increases up to  $[HCl] \sim 0.5 M$  and then decreases rapidly for increasing acidic solutions. The absorption spectrum in 50% isopropyl alcohol-water with varying HCl concentration is shown in Fig. 1. That this transient is absent in neat isopropyl alcohol or in 50% isopropyl alcohol-water with 6 N  $H_2SO_4$  underlines the importance of the chloride ion as an electron donor. It has already been shown that chloride ions and protons must both be present for the enhanced photoreduction of aromatic nitro compounds [11, 12]. This transient is absent in air-saturated solutions and further supports the view that it is the neutral 5-nitroquinolinium radical (I) generated via electron transfer, *i.e.*



The lifetime of this transient, which decays via first order kinetics, remains constant at  $5.3 \pm 0.3$  ms for the range 0.5 - 3 N HCl.

The second transient observed in 50% isopropyl alcohol-water solutions containing HCl as well as  $H_2SO_4$  appears with a wavelength maximum at 410 nm, exhibits first order kinetics, and has a lifetime of  $1.1 \pm 0.1$  ms in the acid range 0.5 - 3 N HCl. In contrast to the rise and fall in the optical density of the 550 nm transient in the range 0.02 - 6 M HCl, however, the optical density at 410 nm increases continuously. In fact, it also appears in

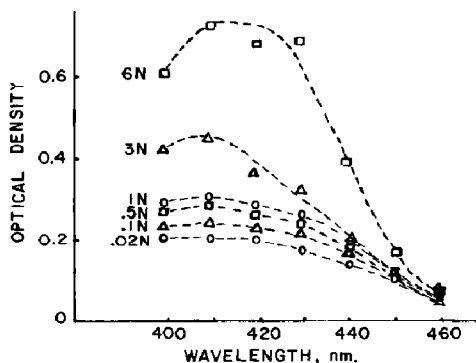


Fig. 2. Transient absorption in the flash photolysis of degassed  $4 \times 10^{-4} M$  5-nitroquinoline in 50% isopropyl alcohol-water as a function of HCl concentration. Transient lifetime was determined to be 1.1 ms in the acid range 0.5 - 3 N HCl.

air-saturated concentrated HCl, although about half as intense as in 50% isopropyl alcohol-water with 6 N HCl, about one-fourth as intense in 50% isopropyl alcohol-water with 6 N  $H_2SO_4$  and barely noticeable in neat isopropyl alcohol. A summary of the absorption behavior of the 410 nm transient in 50% isopropyl alcohol-water is shown in Fig. 2. Since this absorption is observed in 12 M HCl as well as in 50% isopropyl alcohol-water with 6 M HCl, it appears that isopropyl alcohol is not necessary for its formation, or that this absorption represents more than one species. On the other hand, flash data for  $4 \times 10^{-4} M$  5-nitroquinoline in which the percentage isopropyl alcohol was varied between 50 and 90% while [HCl] was held constant at 0.5 M, indicate that increasing alcoholic concentration favors more 410 nm transient and is accompanied by a concomitant decrease at 550 nm. Flashing air-saturated solutions result in approximately 50% decrease in its optical density. It is noteworthy that although the photoreduction quantum yield is constant when [HCl] > 0.5 M, the 550 nm absorption decreases while that of the 410 nm increases.

The presence of triplets in 5-nitroquinoline is certainly evident from its photochemical behavior, and from its naphthalene-like phosphorescence spectrum which we have measured in 50% isopropyl alcohol-water, 0.5 M in HCl, at 77 K (Fig. 3). Nitronaphthalenes and nitroquinolines phosphoresce from  $\pi, \pi^*$  [3] while nitrobenzene and 4-nitropyridine, possessing a lowest  $n, \pi^*$  triplet do not phosphoresce. The phosphorescence yield in this medium was estimated to be 0.12 relative to the value of 0.051 for naphthalene in EPA [13]. Although the phosphorescence yield for 5-nitroquinoline is larger in EPA,  $\Phi_p = 0.27$ , the phosphorescence spectrum and thus the energy of the lowest triplet is not significantly affected by the presence of HCl and  $H_2SO_4$ . From the prominent 0-0 band the triplet state energy of 5-nitroquinoline is estimated to be 58 kcal, which is comparable to the  $\pi, \pi^*$  [3] energy of naphthalene and 1- and 2-nitronaphthalene [14].

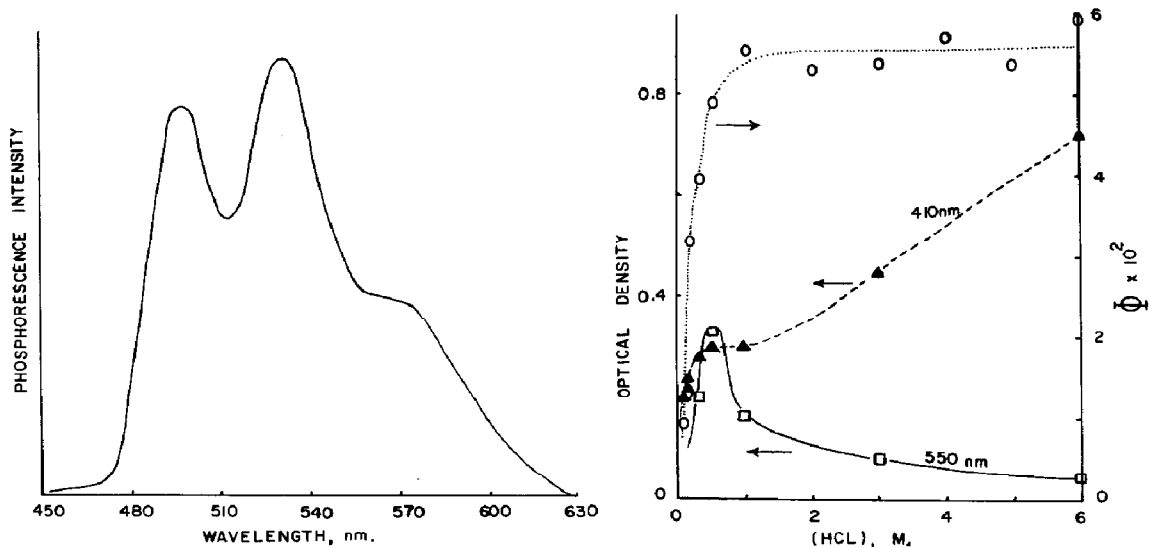


Fig. 3. Phosphorescence spectrum of  $4 \times 10^{-4} M$  5-nitro quinoline in 50% isopropyl alcohol-water with 0.5 M HCl; 77 K, 313 nm excitation.

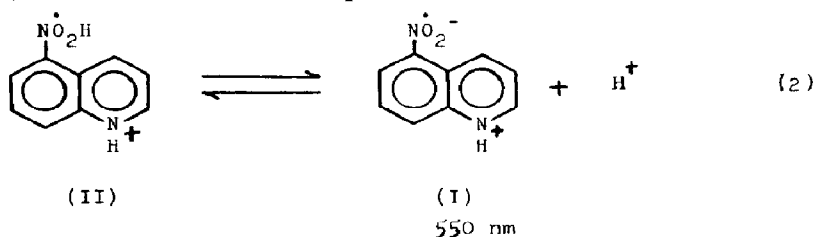
Fig. 4. Flash absorption data for 5-nitroquinoline in 50% isopropyl alcohol-water as a function of HCl concentration for the 410 nm ( $\blacktriangle$ ) and the 550 nm ( $\square$ ) transient. The 313 nm disappearance quantum yields ( $\circ$ ) are also given in order to provide a comparison between steady state and flash photolysis data.

## Discussion

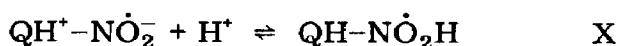
In view of the necessity of HCl and isopropyl alcohol for formation of the 550 nm transient, we assign its absorption spectrum to the neutral radical (I) generated by electron transfer from the chloride ion as indicated in reaction (1). The decreasing intensity when  $[HCl] > 0.5$  is most likely due to protonation of the 5-nitroquinolinium anion. A similar electron transfer reaction has already been observed with the nitrobenzene and 4-nitropyridine triplet [4]. Furthermore, its sensitivity to air and the fact that the 1- and 2-nitronaphthalene radical anions are known to absorb at 605 nm and 480 nm, respectively, supports this assignment [10].

The assignment of the 410 nm transient, which most likely does not involve a primary photochemical process, is more difficult since it can be observed in 50% isopropyl alcohol-water with 6 N  $H_2SO_4$ , 6 N HCl, and in 12 M HCl, in the absence of alcohol. In Fig. 4 are summarized the photochemical quantum yield behavior in 50% isopropyl alcohol-water for the disappearance of 5-nitroquinoline [1] and the optical density of the 410 nm and 550 nm transients as a function of HCl concentration. It is evident that for solutions in which  $[HCl] > 0.5 M$ , the quantum yield remains constant [1] but the optical density of the 550 nm transient decreases while that at 410 nm increases. In the acid range less than 0.5 M the intensity of both transients is increasing as is the photochemical quantum yield. It thus appears that they both contribute to the observed photoreduction.

The first order decay constant for the 550 nm and 410 nm transients each remains constant in the acid range 0.5 - 3 N HCl, which indicates that the protonated form of the 5-nitroquinolinium anion (II) cannot be the 410 nm transient, *i.e.*, the observation that decay kinetics are different for two species in rapid equilibrium with each other precludes the assignment of (II) for the 410 nm absorption.



We believe that the protonation of the neutral radical (I) to produce (II) must be rapidly followed by an irreversible reaction involving the solvent, *i.e.*,



to produce some radical species X, which is the origin of the 410 nm transient.

From the acid dependence of the 550 nm absorption we can estimate the  $\text{p}K_a$  value for dissociation of (II) to be close to zero. Henglein *et al.* [15] have reported that the analogous process involving nitrobenzene,  $\text{PhNO}_2\text{H} \rightleftharpoons \text{PhNO}_2^- + \text{H}^+$  has a  $\text{p}K_a = 3.2$ . The approximate three orders of magnitude increase in the dissociation constant for the protonated radical (II) in 5-nitroquinoline relative to protonated nitrobenzene anion is probably due to the protonated ring nitrogen in the heterocyclic. In the 5-nitroquinolinium triplet electron transfer yields a neutral radical while with nitrobenzene an anion radical is formed. In the ground state protonation of the quinoline nitrogen appears to be essentially complete at  $[\text{H}^+] \approx 0.5 \text{ M}$  as can be seen by the quantum yield data summarized in Fig. 4. Our results support the view that the 410 absorption is not the result of a primary process involving the 5-nitroquinoline triplet state, but probably the result of an irreversible process involving the protonated anion and the solvent. The possibility that this absorption may involve the singlet state is rejected since its lifetime can be estimated to be  $< 10^{-10} \text{ s}$ .

Although we are unable to assign the 410 transient, whose intensity is enhanced by the presence of isopropyl alcohol and acid, flash photolysis data support the view that the photoreduction of 5-nitroquinoline occurs via at least two transients. Only one transient was observed with nitrobenzene while with 4-nitropyridine evidence for the 4-nitropyridinium anion and its protonated form have been given [4]. In the photoreduction of 1-nitronaphthalene in concentrated HCl, the quantum yield is known to be  $3.3 \times 10^{-3}$  which is significantly lower than the value of  $12.8 \times 10^{-3}$  observed in 50% isopropyl alcohol-water with 6 M HCl [16], indicating that the alcohol is essential to its photoreduction. With 5-nitroquinoline, however, the dis-

appearance quantum yield of  $5.7 \pm 0.5 \times 10^{-2}$  in air saturated, concentrated HCl, is essentially identical to the value  $5.9 \pm 0.5 \times 10^{-2}$  reported for 50% isopropyl alcohol-water with 6 M HCl [16], indicating that the alcohol is essential to its photoreduction. With 5-nitroquinoline, however, the disappearance quantum yield of  $5.7 \pm 0.5 \times 10^{-2}$  in air saturated, concentrated HCl, is essentially identical to the value  $5.9 \pm 0.5 \times 10^{-2}$  reported for 50% isopropyl alcohol-water containing 6 M HCl [1]. Thus alcohol appears not to be necessary for the photoreduction of 5-nitroquinoline as it is for 1-nitronaphthalene. The fact that the 410 absorption in 12 M HCl is relatively weak when compared with the quantum yield measured suggests that the photochemical mechanism might be different in the absence of alcohol. The relatively large phosphorescence yield for 5-nitroquinoline suggests that its triplet-triplet absorption should be readily observed in laser flash photolysis.

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