Nitrobenzene Photochemistry. II.
Protonation in the Excited State[1]

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Abstract: Quantum yield studies at 366 mμ of nitrobenzene in isopropyl alcohol–water mixtures containing hydrochloric acid indicate that protonation of nitrobenzene in the excited state (triplet) enhances the photochemical disappearance of nitrobenzene, which occurs by two competing reactions: (1) hydrogen abstraction from isopropyl alcohol and (2) chloride ion attack on the aromatic ring. The quantum yield results for the hydrogen abstraction reaction in 50% isopropyl alcohol–water solutions suggest that the nitrobenzene triplet begins to protonate when $[H^+] \approx 3$ *M*. This unexpected behavior indicates that nitrobenzene is a stronger base in the excited state relative to the ground state. Ultraviolet spectra indicate that protonation in the ground state is not important for the concentration range of acid studied (0–12 *M* HCl). The quantum yield for nitrobenzene disappearance in 12 *M* HCl is $\Phi = 0.30$.

The quantum yield for the disappearance of nitrobenzene in isopropyl alcohol at 366 mμ has recently been determined to be 1.14×10^{-2} in degassed solutions.[1] The process proceeds by the n,π* triplet which results in hydrogen abstraction and the formation of phenylhydroxylamine, C_6H_5NHOH. The rearrangement of phenylhydroxylamine in hydrochloric acid to *o*- and *p*-chloroanilines is well known.[2] Evidence for involvement of the triplet has been demonstrated by energy-transfer experiments using perfluoronaphthalene as an acceptor.[3]

Another reaction of photoexcited nitrobenzene was recently reported by Letsinger, *et al.*,[4] who observed the rapid disappearance of nitrobenzene in concentrated HCl, and chloride ion attack was postulated. They isolated 2,4,6-trichloroaniline and 2,4-dichloroaniline as products.

In attempting to increase the low quantum yield of disappearance for nitrobenzene in isopropyl alcohol we became interested in studying the effect of protons on the excited state(s) of nitrobenzene, and the importance of the hydrogen atom abstraction reaction relative to the chloride ion attack on the aromatic ring. With the aim of following the two competing processes and elucidating the photochemical behavior of nitrobenzene a quantum yield study was undertaken.

Experimental Section

Materials. Reagent grade nitrobenzene was vacuum distilled prior to use in these experiments. A sample of zone-refined nitrobenzene was also used with no significant differences in behavior. Spectrograde isopropyl alcohol was used as a solvent. Acid solutions were prepared from reagent grade HCl and H_2SO_4 and quartz-distilled water. Low-temperature glasses for emission spectra were prepared from spectrograde methylcyclohexane and EPA.

Apparatus. In all experiments, the 366-mμ light was isolated from a high-pressure Osram 100W/2 mercury lamp with a Corning combination filter CS7-83. Light intensities were determined with the potassium ferrioxalate actinometer described by Hatchard and Parker.[5] Solutions were degassed at $<10^{-4}$ mm and sealed off. In the acid runs there were no significant differences between the disappearance quantum yield for air-saturated solutions and degassed solutions. In pure isopropyl alcohol, however, the quantum yield for air-saturated solutions is 30% lower than for degassed solutions. The lack of oxygen effect in acid runs is not unexpected since the protonated triplet reacts faster than the unprotonated triplet, thereby accounting for the larger quantum yields in acid solutions. Other details and analytical procedures have been described elsewhere.[1]

Phosphorescence emissions at 77°K in methylcyclohexane and EPA glasses were recorded with an Aminco grating monochromator equipped with a rotating motor shutter assembly and a 1P21 photomultiplier tube. The phosphorescence of benzophenone was used as a reference ($\phi_p = 1$).

The ultraviolet spectrum of nitrobenzene in sulfuric acid solutions was recorded with a Bausch and Lomb 505 spectrophotometer.

Results

The quantum yield data reported in this work were obtained from two sets of experiments. The first consideration was to obtain data in 50% isopropyl alcohol–water solutions containing varying amounts of HCl. The results are recorded as curve 1 in Figure 1, which indicates that there is a striking increase in the disappearance yield when (H^+) exceeds 3 *M*. It is noteworthy that the disappearance yield for nitrobenzene increases by a factor of 36 when the concentration of HCl was varied from 0 to 6 *M*.

The second set of data was obtained by excluding isopropyl alcohol (approximately 1% to dissolve nitrobenzene) and following the photochemical disappearance of nitrobenzene in aqueous HCl. The results appear as curve 2 in Figure 1, where the striking increase in quantum yield of disappearance occurs in the vicinity of 6 *M* HCl. The steep rise at 6 *M* HCl is in agreement with results reported by Letsinger, *et al.*[4] The largest disappearance yield which we observed occurred in 12 *M* HCl where $\Phi = 0.30$. This is a considerable increase from 4.0×10^{-3}, which is obtained in 50% isopropyl alcohol–water solutions containing no HCl. In view of the observation that decreasing the alcohol concentration with water by a factor of 2 lowers the quantum yield for the disappearance of nitrobenzene by the same amount, it does not appear that a solvent effect is important in this study.

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[1] Part I: R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966).

[2] H. E. Heller, E. D. Hughes, and C. K. Ingold, *Nature*, **168**, 909 (1951).

[3] J. K. Brown and W. G. Williams, *Chem. Commun.*, **14**, 495 (1966).

[4] R. L. Letsinger and G. O. Wubbels, *J. Am. Chem. Soc.*, **88**, 5041 (1966).

[5] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

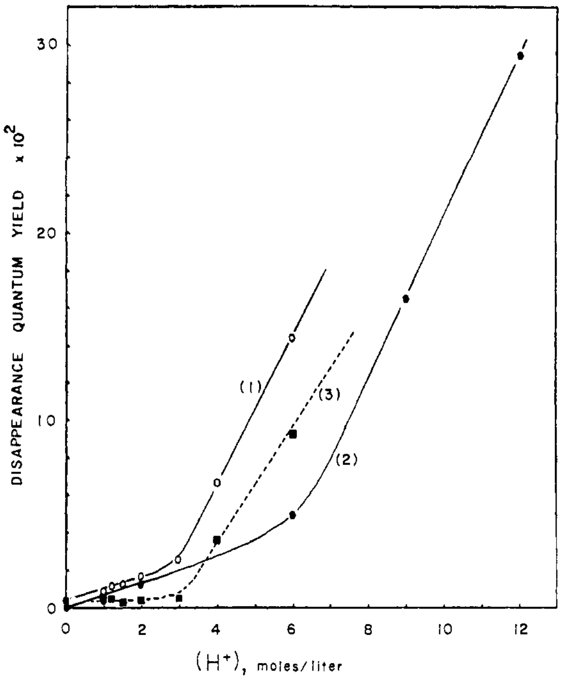

Figure 1. Nitrobenzene photochemical disappearance quantum yields at 366 mμ: (1) results obtained in 50% isopropyl alcohol–water solutions with increasing concentration of HCl; (2) results obtained with aqueous solutions of nitrobenzene with increasing concentration of HCl; (3) constructed from results 1 − 2, represents the hydrogen abstraction part of the total quantum yield, with increasing (H^+). The concentration of nitrobenzene was generally in the range 10^{-2} *M*.

Table I. Photochemical Disappearance Quantum Yields of Nitrobenzene at 366 mμ in 6 *M* HCl with Varying Amounts of Isopropyl Alcohol (100% Isopropyl Alcohol ≈ 13 *M*)

Isopropyl alcohol concn, %	Φ (total)
1	0.040 ± 0.009
10	0.105 ± 0.005
25	0.18 ± 0.01
50	0.14 ± 0.03

The hydrogen abstraction part of the quantum yield was obtained by taking the difference between curves 1 and 2 and is presented as curve 3 in Figure 1. The first hydrogen abstraction process is represented by

$$C_6H_5NO_2{}^{*3} + (CH_3)_2CHOH \longrightarrow C_6H_5N\dot{O}_2H + (CH_3)_2\dot{C}OH$$

which terminates with the production of acetone. The presence of acetone in our experiments was confirmed by gas chromatography.

The hydrogen abstraction part of the total quantum yield has an unusual behavior in that there is no dependence on hydrogen ion concentration until 3 *M*. When (H^+) > 3 *M*, there is a striking increase in the disappearance yield, which is proportional to the hydrogen ion concentration.

Since the hydrogen abstraction occurs in the absence of acid, we were also concerned with the importance of nitrobenzene disappearance by chloride ion attack in the absence of protons. Photolysis of nitrobenzene in a degassed solution of 2 *M* LiCl results in a disappearance yield $\leq 5 \times 10^{-4}$, which emphasizes the importance of protons for the chloride ion attack.

In an effort to obtain a better understanding of the photochemical disappearance yield of nitrobenzene in acid solutions and the importance of hydrogen abstraction from isopropyl alcohol, quantum yields were also measured for 6 *M* HCl solutions with varying amounts of isopropyl alcohol. The results, which are presented in Table I, show an increasing yield with increasing alcohol concentration; however, more importantly, there is a leveling off of the quantum yield which does not distinguish between 25 and 50% isopropyl alcohol in 6 *M* HCl solutions. The limiting quantum yield $\Phi = 0.16 \pm 0.03$ suggests that all the available protonated triplets in solution are reacting; however, the disappearance yield includes reaction of unprotonated and protonated forms. This deduction follows from the fact that in the absence of HCl, $\Phi = 4 \times 10^{-3}$ for 50% isopropyl alcohol–water solutions; *i.e.*, the contribution to the quantum yield from the unprotonated triplet is not important in acid solutions.

From the ultraviolet absorption spectra of nitrobenzene in HCl solutions, it can be concluded that protonation in the ground state is not important. The absorption peak which appears at 269 mμ in neutral and weakly acidic solutions shifts with increasing acidity to longer wavelengths. In 36 *N* H_2SO_4, the absorption peak occurs at 288 mμ. It is reasonable to attribute the shift to lower energies to a solvent effect, since no isosbestic point was observed in the spectra. Brand, *et al.*,[6] have reported a $pK_a = -11.26$ for the dissociation of nitrobenzene in sulfuric acid, $C_6H_5NO_2H^+ = C_6H_5NO_2 + H^+$. The evidence is convincing that nitrobenzene is a very weak base in the ground state and that excitation of the protonated species does not occur.

It has been predicted[7] that for n,π* transitions, the intersystem crossing yield is large; however, we have not been able to observe any significant phosphorescence from a degassed sample of nitrobenzene in a methylcyclohexane glass at 77°K. The only reported phosphorescence from nitrobenzene is the work of Lewis and Kasha,[8] who reported 474 mμ for the 0–0 band of the nitrobenzene triplet. By comparison to benzophenone which exhibits a high phosphorescence efficiency ($\phi_p = 1$), the phosphorescence yield for nitrobenzene at 77°K is $\leq 10^{-3}$. It would appear that the nitrobenzene triplet deactivates rapidly or the yield of triplet is small. From our disappearance yields (pure isopropyl alcohol) in air-saturated and degassed solutions, the Stern–Volmer equation, $\Phi^0/\Phi = 1 + k_q\tau_T \cdot (O_2)$, using 10^{-3} *M* for the concentration of oxygen in solution,[9] indicates that the lifetime of the nitrobenzene triplet at room temperature is approximately 3.5×10^{-7} sec. Although this estimate makes the assumption that oxygen reacts directly with the triplet, the result implies that radiationless decay is extremely rapid.

Discussion

The results in Figure 1 exhibit proton dependence for two competing reactions: (1) hydrogen abstraction from the alcohol and (2) chloride ion attack on the aromatic ring. It is surprising that the hydrogen ab-

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(6) J. C. D. Brand, W. C. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).

(7) M. Kasha, *Radiation Res. Suppl.* 2, 268 (1960).

(8) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(9) P. Zuman, "Organic Polarographic Analysis," The Macmillan Co., New York, N. Y., 1964, p 69.

straction reaction shows no acid dependence until 3 *M* and then increases rapidly when $(H^+) > 3$ *M*.

It is an inviting possibility to explain the increased extent of hydrogen abstraction as well as the increasing chloride ion attack as arising from the increased lifetime and reactivity of the protonated excited state (triplet). Protonation of either singlet or triplet would account for the behavior illustrated in Figure 1; however, the singlet is not favored since nitrobenzene does not fluoresce and also has an estimated radiative n,π^* singlet lifetime of *ca.* 10^{-6} sec, which is determined from the integrated absorption curve. Consequently, the singlet lifetime can be estimated to be *ca.* 10^{-10} sec. Since the triplet lives longer, protonation is more likely in this state.

In pure isopropyl alcohol the disappearance of nitrobenzene (N) occurs by hydrogen abstraction from the solvent by the triplet, whereas in acid solutions the reactions given in (1–4) are suggested.

$$^3N^* + (CH_3)_2CHOH \longrightarrow \dot{N}H + (CH_3)_2\dot{C}OH \quad (1)$$

$$^3N + H^+ \longrightarrow {}^3NH^{+*} \quad (2)$$

$$^3NH^{+*} + (CH_3)_2CHOH \longrightarrow \dot{N}H + (CH_3)_2\dot{C}OH + H^+ \quad (3)$$

$$Cl^- + {}^3NH^{+*} \longrightarrow \text{products (chloroanilines)} \quad (4)$$

The steady-state expression for the quantum yield of disappearance of nitrobenzene in 50% isopropyl alcohol–water solutions, with respect to the hydrogen abstraction reaction, leads to the expression

$$\Phi_{-C_6H_5NO_2}(\text{H abstract}) = \phi_T\tau_T[k_H(\text{IPA}) + k_{pr}(H^+)]$$

where ϕ_T is the yield of triplet and τ_T is the lifetime of the nitrobenzene triplet in acid solutions, $[k_{dt} + k_H(\text{IPA}) + k_{pr}(H^+) + k_x(Cl^-)]^{-1}$, which is largely controlled by k_{dt}, radiationless decay of triplet, in neutral and acidic solutions. Rate constants k_H, k_{pr}, and k_x are for hydrogen abstraction, protonation of the nitrobenzene triplet, and chloride ion attack on the aromatic ring, respectively. The expression assumes that those triplets which protonate react.

Although variation of triplet lifetime with hydrogen ion concentration is predicted from the steady-state treatment, it appears that the lifetime is not significantly changed in acid solutions. This conclusion arises from the fact that in 6 *M* HCl, the hydrogen abstraction disappearance yield is approximately 0.1 as can be seen from curve 3 in Figure 1. This value represents a small fraction of the available triplets in an n,π^* system, since the intersystem crossing yield is expected to be high.[7] Thus it is reasonable to consider k_{dt} as the determining factor in the lifetime of the nitrobenzene triplet. Low-temperature emission studies at 77°K in neutral and acid media also suggest that radiationless decay of the triplet remains important.

In acid solutions >3 *M*, where protonation in the excited state occurs, the hydrogen abstraction process can be completed by an electron transfer and a proton release from the positively charged solvent radical, *i.e.*, reaction 3.

From the slope of the curve 3 in Figure 1 and the value of 4×10^{-3} for $\Phi_{-C_6H_5NO_2}$(H abstract) in the absence of acid, it is determined that $k_{pr}/k_H \approx 44$, which indicates that the hydrogen abstraction reaction involving the protonated form of nitrobenzene in the excited state is much more important than the participation of the unprotonated species in acid solutions. It would appear that nitrobenzene is a stronger base in the excited state relative to the ground state.

A significant question which arises from our results is whether or not the protonation step in the excited state produces a higher triplet yield than is obtained in the absence of acid. If the triplet yield remained constant, the quantum yield is expected to reach an upper limit. Our data do not distinguish this possibility, since no leveling effect is observed in the concentration range of HCl studied.

An analogy exists between the photochemistry and electrochemistry of nitrobenzene, since in both cases phenylhydroxylamine is obtained. Polarographically an increase of acidity lowers the half-wave potential, which corresponds to a faster reduction; photochemically, this is observed as an increasing quantum yield.