Photochemical n $\longrightarrow$ π^* Excitation of Nitrobenzene

R. Hurley and A. C. Testa

Contribution from the Department of Chemistry, St. John's University, Jamaica, New York 11432. *Received May 4, 1966*

Abstract: The photochemistry of nitrobenzene in isopropyl alcohol has been studied at 366 mμ. Evidence for hydrogen abstraction from isopropyl alcohol, following n $\rightarrow$ π^* excitation of nitrobenzene, is presented. Results are consistent with the triplet state of nitrobenzene being the reactive species. Phenylhydroxylamine is generated as the initial product, which oxidizes in air to nitrosobenzene and couples with the latter to form azoxybenzene. The quantum yield for the disappearance of nitrobenzene in degassed solutions was determined to be $1.14 \pm 0.08 \times 10^{-2}$. The over-all photochemical reduction of nitrobenzene involves four hydrogen atom abstractions, as evidenced by the ratio of acetone formation to nitrobenzene disappearance.

Oxygen atom transfer has been reported by Hastings and Matsen[1] to explain the vapor phase photochemistry of nitrobenzene, which results in nitrosobenzene and *p*-nitrophenol. Chapman[2] has reported the photoisomerization of the aromatic nitro group to nitrite ester. Other photochemical studies[2-5] of aromatic nitro compounds have been reported with emphasis on addition reactions to olefins; however, it is surprising that quantum yield studies for such compounds are lacking. Rebbert and Slagg[6] have reported the photochemistry of nitroalkanes, and the quantum yields for these molecules were found to be small compared to unity. With the aim of understanding the photochemistry of aromatic nitro compounds, a quantum yield study of nitrobenzene was undertaken.

By analogy to the n $\rightarrow$ π^* excitation of benzophenone, which results in hydrogen atom abstraction from alcoholic solvents,[7-10] the n $\rightarrow$ π^* transition of nitrobenzene at 340 mμ[11,12] may be expected to undergo a similar reaction. In the photochemistry of benzophenone, the population of the triplet occurs with unit efficiency,[8] and in isopropyl alcohol, the quantum yield for the disappearance of benzophenone approaches 2.[7] Presumably, the existence of this hydrogen abstraction following excitation of nitrobenzene in isopropyl alcohol could provide evidence concerning the excited states involved in the photochemical behavior of nitrobenzene.

Hydrogen-abstraction processes by aromatic nitro compounds were suggested in the pyrolysis of such compounds[13] and in the photoinduced paramagnetism of nitrobenzene in tetrahydrofuran.[14] Recently Mauser and Heitzer[15] reported on a related hydrogen-abstraction process for the photochemistry of nitrosobenzene in methanol.

The polarographic reduction of nitrobenzene in neutral solutions[16] is represented by the following overall process.

$$C_6H_5NO_2 + 4H^+ + 4e \longrightarrow C_6H_5NHOH + H_2O$$

If hydrogen abstraction by nitrobenzene can be induced photochemically, it becomes tempting to speculate on the final product obtained, in addition to considering the relationship, if any, between photochemical and electrochemical excitation. A relationship between photochemistry and mass spectrometry was recently demonstrated for small ring compounds.[17]

Experimental Section

Materials. Reagent grade nitrobenzene was vacuum-distilled prior to use in these experiments. Spectrograde isopropyl alcohol and benzene were used as solvents. Azoxybenzene was obtained from Chemical Procurement, Inc. (College Point, N. Y.) and recrystallized from ethanol.

Apparatus. In all experiments, the 366-mμ light was isolated from a high-pressure Osram 100 W/2 mercury lamp with a Corning combination filter CS 7-83. The lamp was placed at the focal point (2.5 in.) of a quartz lens in order to produce a parallel beam of light across the sample. A 1P28 photomultiplier tube was mounted behind the cell block, which contained the sample, to monitor light intensities and to determine the per cent transmission.

Quartz spectrophotometric cells (1 cm) were used for air-saturated experiments, but for degassed runs the cells were extended with a graded seal to be attached to a vacuum line. Each sample was degassed at least three times with alternate cycles of freezing and vacuum boiling, and then sealed off. Experiments were performed at 35 ± 1°.

Intensity determinations were made with the potassium ferrioxalate actinometer described by Hatchard and Parker.[18]

Analytical Procedures. The disappearance of nitrobenzene was determined by measuring optical densities of photolyzed solutions at 320 and 366 mμ, after allowing the phenylhydroxylamine produced to convert quantitatively to azoxybenzene. The extinction coefficients used in this work are: nitrobenzene, ϵ_{366} 76.8 and ϵ_{320} 237; azoxybenzene, ϵ_{366} 2.83×10^3 and $\epsilon_{320} = 1.50 \times 10^4$. A second procedure for following nitrobenzene disappearance was by polarographic analysis in 50% ethanol-water solutions containing acetic acid-sodium acetate buffer. The agreement of quantum yields results for the two methods was satisfactory.

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A Beckman DU spectrophotometer was used for quantitative absorbance measurements and a Bausch and Lomb 505 spectrophotometer was used to follow the conversion of phenylhydroxylamine to nitrosobenzene and the coupling reaction, resulting in azoxybenzene; *vide infra*.

The presence of acetone in photolyzed solutions was obtained by gas chromatographic analysis using a 6-ft, 0.25-in. o.d. column of 20% Carbowax 20M on 80–100 mesh Gas Chrom CLA (from Applied Science Laboratories, State College, Pa.). The column was operated at 50° with a helium flow rate of 116 cc/min.

Results

In air-saturated solutions, the photolysis of nitrobenzene in isopropyl alcohol results in phenylhydroxylamine, which was characterized by its ultraviolet spectrum (absorption peaks at 238 and 281 mμ) and confirmed by observing its conversion in the dark to nitrosobenzene (absorption peaks at 281 and 306 mμ). The quantum yield for the disappearance of nitrobenzene in air-saturated solutions was determined to be $0.87 \pm 0.1 \times 10^{-2}$. By comparison to benzene where hydrogen abstraction is not very likely, a degassed solution of 5.55×10^{-2} *M* nitrobenzene in benzene photolyzed for 2763 min at 366 mμ exhibited no photochemical activity.

The results obtained indicate that the photochemistry of nitrobenzene in air-saturated solutions of isopropyl alcohol is complicated by dark reactions, which involve the oxidation of phenylhydroxylamine to nitrosobenzene, together with a coupling reaction to form azoxybenzene. It was observed that prolonged exposure of nitrobenzene at 366 mμ in air-saturated solutions of isopropyl alcohol produces a yellow color, which was identified by ultraviolet absorption to be azoxybenzene. Ogata, *et al.*,[19,20] have reported the oxidation of phenylhydroxylamine to be represented as follows.

$$C_6H_5NHOH + {}^1/_2O_2 \longrightarrow C_6H_5NO + H_2O$$

$$C_6H_5NHOH + C_6H_5NO \longrightarrow C_6H_5\text{-}N(O){=}NC_6H_5 + H_2O$$

Russell and Geels[21] have found that, when C_6H_5-NHOH and C_6H_5NO are each greater than 5×10^{-3} *M*, the conversion to azoxybenzene is essentially complete. We have found this conversion to azoxybenzene to be quantitative when concentrations of phenylhydroxylamine and nitrosobenzene are each greater than 2 m*M*, but in dilute solutions, *ca.* 10^{-5} *M*, phenylhydroxylamine converts to nitrosobenzene, with no evidence of azoxybenzene. For concentrations between these extremes, mixtures of nitrosobenzene and azoxybenzene are obtained. Our photolysis runs were designed to produce sufficient phenylhydroxylamine to convert quantitatively to azoxybenzene.

In view of the dark reactions present in air-saturated solutions, degassed runs of nitrobenzene in isopropyl alcohol were performed in cells which were sealed off under vacuum prior to ultraviolet excitation. In these runs the phenylhydroxylamine concentration produced remained constant, and the quantum yields for the disappearance of nitrobenzene were determined to be $1.14 \pm 0.1 \times 10^{-2}$. This result is approximately 30% higher than the air-saturated values, and may be interpreted in terms of less quenching of the triplet state.

Noteworthy of our results was the observation that acetone was generated during the photolysis. In fact, it was determined by gas chromatography that the ratio of acetone formation to disappearance of nitrobenzene is 2.0 ± 0.3. The presence of acetone provides direct evidence for the hydrogen-abstraction reaction by photoexcited nitrobenzene from isopropyl alcohol. Thus the photoreduction of nitrobenzene involves four hydrogen atoms in agreement with the electrochemical reduction.

A summary of quantum yield runs for the disappearance of nitrobenzene in isopropyl alcohol is given in Table I. Photolysis times varied from 1300 to 5400 min with no significant effect on the quantum yields.

Table I. Quantum Yield Results for the Disappearance of Nitrobenzene in Isopropyl Alcohol at 366 mμ and 35 ± 1°

$C_6H_5NO_2$ concn, *M*	Intensity $\times 10^{-15}$, quanta/sec	Quantum yield $\times 10^2$
1.45×10^{-2} air satd	4.80	0.84 ± 0.12
	4.15	
3.20×10^{-2} air satd	4.40	
	4.35	0.97 ± 0.19
	4.30	
2.67×10^{-1} air satd	4.51	0.80 ± 0.11
3.32×10^{-2} degassed	4.22	1.13 ± 0.09
1.60×10^{-2} degassed	4.07	1.15 ± 0.06
	4.07	

Discussion

Simple aromatic nitro compounds do not fluoresce; however, their phosphorescence has been reported.[22,23] In view of this it seems reasonable to expect that the reactive state in this system is the nitrobenzene triplet, which abstracts a hydrogen atom from isopropyl alcohol as a primary step. It was stated earlier in this work that the hydrogen abstraction reaction is observed in the photochemistry of benzophenone, where it has been shown that the triplet is the reactive state. In nitrobenzene the low quantum yield for disappearance is accounted for by either inefficient intersystem crossing, or by the rate constant for the hydrogen abstraction competing with the lifetime of the triplet. As a possible precursor to phenylhydroxylamine, it is noteworthy that recently the presence of phenyl nitroxide, C_6H_5-NOH, was detected by electron spin resonance during the thermal reduction of nitrobenzene by amines.[21,24] A final hydrogen abstraction from the solvent by phenyl nitroxide would produce phenylhydroxylamine.

In view of the four hydrogen abstractions involved in the photoreduction of nitrobenzene, it is difficult to postulate a detailed mechanism. The following sequence of reactions appears to afford a satisfactory explanation of the photochemical behavior of nitrobenzene in isopropyl alcohol.

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$$C_6H_5NO_2 + h\nu \longrightarrow C_6H_5NO_2^{*(1)} \quad \text{excitation to singlet} \quad (1)$$

$$C_6H_5NO_2^{*(1)} \rightsquigarrow C_6H_5NO_2 \quad \text{radiationless decay} \quad (2)$$

$$C_6H_5NO_2^{*(1)} \rightsquigarrow C_6H_5NO_2^{*(3)} \quad \text{intersystem crossing} \quad (3)$$

$$C_6H_5NO_2^{*(3)} \rightsquigarrow C_6H_5NO_2 \quad \text{radiationless decay} \quad (4)$$

$$C_6H_5NO_2^{*(3)} + CH_3CH(OH)CH_3 \longrightarrow C_6H_5N\dot{O}_2H + CH_3\dot{C}(OH)CH_3 \quad \text{hydrogen abstraction} \quad (5)$$

$$C_6H_5NO_2^{*(3)} + O_2 \longrightarrow C_6H_5NO_2 + O_2 \quad \text{oxygen quenching} \quad (6)$$

$$C_6H_5N\dot{O}_2H + CH_3\dot{C}(OH)CH_3 \longrightarrow C_6H_5N(\dot{O}H)_2 + CH_3COCH_3 \quad \text{hydrogen abstraction} \quad (7)$$

$$C_6H_5N(\dot{O}H)_2 + CH_3CH(OH)CH_3 \longrightarrow C_6H_5\dot{N}OH + H_2O + CH_3\dot{C}(OH)CH_3 \quad \text{hydrogen abstraction} \quad (8)$$

$$C_6H_5\dot{N}OH + CH_3\dot{C}(OH)CH_3 \longrightarrow C_6H_5NHOH + CH_3COCH_3 \quad \text{hydrogen abstraction} \quad (9)$$

In addition to eq 1–9, the oxidation of phenylhydroxylamine occurs as a dark reaction, producing nitrosobenzene and azoxybenzene (*vide supra*). The four hydrogen-atom abstractions, eq 5 and 8 from the solvent and eq 6 and 7 from radicals, have analogy to similar processes in the photochemistry of benzophenone.[7] A steady-state approximation for degassed solutions leads to a simple expression for the disappearance quantum yield of nitrobenzene

$$\Phi = \frac{\phi_T}{[1 + k_4/k_5(\mathrm{IPA})]}$$

where $\phi_T = k_3/(k_2 + k_3)$ is the yield of nitrobenzene triplets, and (IPA) is the concentration of isopropyl alcohol. The low quantum yields obtained experimentally indicate that (a) the yield of nitrobenzene triplets is small, and/or (b) the ratio $k_4/k_5(\mathrm{IPA})$ is large compared to unity. The above expression for the quantum yield assumes that every $C_6H_5N\dot{O}_2H$ radical produced becomes a phenylhydroxylamine molecule.

In air-saturated solutions, quenching of the triplet by oxygen must be included, *i.e.*, eq 6, and the quantum yield expression becomes

$$\Phi = \frac{\phi_T}{\left[1 + \dfrac{k_4 + k_6(O_2)}{k_5(\mathrm{IPA})}\right]}$$

Thus when oxygen concentration is increased, the quantum yield decreases. Our results are in qualitative agreement with the predicted behavior. Reactions 1–6 above also occur in the photochemistry of benzophenone, where the quantum yield for disappearance is significantly higher than it is for nitrobenzene. For benzophenone $k_4/k_5(\mathrm{IPA}) \approx 3 \times 10^{-2}$, where the hydrogen abstraction rate constant, k_5, is $1.28 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$,[25] and the deactivation rate constant of the triplet, k_4, is $5.3 \times 10^5\ \mathrm{sec}^{-1}$.[10] Apparently in the photochemistry of nitrobenzene, $k_4/k_5(\mathrm{IPA}) > 3 \times 10^{-2}$, which effectively shows that the lifetime of the nitrobenzene triplet competes favorably with hydrogen abstraction. Since oxygen only changes the quantum yield by approximately 30%, it is reasonable to expect $k_4 > k_6(O_2)$. If oxygen quenching of the triplet is assumed to be diffusion controlled,[9] $k_6 \sim 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, and $(O_2) \sim 10^{-3}\ M$, the deactivation rate constant of the nitrobenzene triplet $k_4 > 10^6\ \mathrm{sec}^{-1}$. This is not an unreasonable estimate since the triplet of nitrobenzene has not been reported from flash photolysis experiments. It is also noteworthy that whereas in benzophenone the O–O bands for singlet (77 kcal) and triplet (69 kcal) correspond to an energy spacing $(E_S - E_T) = 8$ kcal, in nitrobenzene the triplet (60 kcal)[26] and singlet (~77 kcal) correspond to $(E_S - E_T) \sim 17$ kcal. The larger splitting in nitrobenzene should favor less intersystem crossing relative to benzophenone.

In conclusion, it appears that the combination of less intersystem crossing and a large deactivation rate constant for the nitrobenzene triplet accounts for the low quantum yield of disapppearance in isopropyl alcohol, relative to values reported for benzophenone.

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