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Photoreaction of nitrobenzenes with hydrobromic acid

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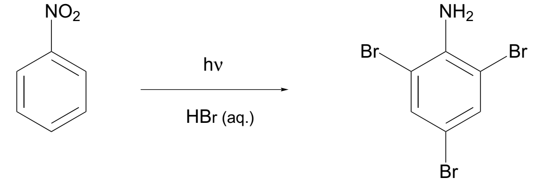
Abstract—Nitrobenzene and three of its derivatives (3-CO_2H, 3-OH, and 4-OH) react efficiently when irradiated (λ >340 nm) in concentrated hydrobromic acid typically to give high yields of 2,4,6-tribromoanilines. The quantum yield ($\Phi = 0.16$ for nitrobenzene) is not changed appreciably by the electron withdrawing carboxy substituent, but is lowered by the electron donating hydroxy substituent. The reactivity suggests that electron transfer from bromide ion to the n,π* triplet is the primary process.

Nitrobenzene is a fundamental molecule whose unique photophysics,[1] photochemistry,[2] and aromatic substitution chemistry[3] continue to attract attention. One of us has reported[4] that nitrobenzenes react photochemically in concentrated hydrochloric acid to give mainly 2,4,6-trichloroanilines. The reaction was established as quite general for nitroaromatics, but the generality for hydrohalic acids has not been established. An attempt to examine this question[4] was thwarted because of absorption of light by hydrobromic acid and hydriodic acid, which photolyze to form bromine and iodine, respectively. We have found that a uranium glass filter, which cuts off radiation below 340 nm, enables us to irradiate nitro compounds without irradiating HBr. We have discovered that a clean, high-yield photoreaction of nitroaromatic compounds occurs in concentrated hydrobromic acid, as shown in Scheme 1.



Scheme 1.

The results of preparative photoreactions are given in Table 1. These reactions were carried out in air-saturated solutions of the nitroaromatic compound in constant-boiling aqueous hydrobromic acid (8.8 M) that had been purified by distillation from powdered tin. Solutions were contained in stoppered Pyrex test tubes enclosed in a uranium glass filter sleeve (Ace Glass Co., λ >340 nm) in a Rayonet RPR-208 reactor fitted with 350 nm broadband lamps. Reaction completion was monitored by the UV absorption of reactants at the λ_{max} of aliquots diluted with water. Workup was usually performed by neutralizing about 95% of the excess HBr with concentrated NaOH, filtering the precipitated photoproduct, washing it with water, and drying it in vacuo. The product from 3-nitrobenzoic acid, however, was captured by extraction with ether after 95% neutralization, and the hydroquinone product from 4-nitrophenol was filtered directly from the reaction medium. Identities were established by comparison of infrared spectra with those of authentic samples. 2,3,6-Tribromo-4-aminophenol had not been reported, and it was characterized.[5]

To grasp the nature of the reaction, it is useful to recognize that the major products are neither oxidized nor reduced from the reactants. The six-electron reduction of the nitro group is balanced by three two-electron oxidations of ring carbons. Noting a slight excess of bromination overall in the case of 4-nitrophenol prompted the question of whether, under our irradiation conditions, we were irradiating the HBr to create electrophilic bromine.

To test this possibility, we irradiated a solution of hydroquinone (0.0055 M) in 8.8 M aq HBr for 96 h.

Keywords: Nitrobenzene; Hydrobromic acid; Hydrobromination; Photochemistry; Tribromoaniline.

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Table 1. Preparative photoreactions of nitrobenzenes in 8.8 M aq HBr

Reactant	Conditions	Products	% Yield
Nitrobenzene	10 mL, 0.025 M, 4 h	2,4,6-Tribromoaniline	96
3-Nitrobenzoic acid	20 mL, 0.010 M, 4 h	2,4,6-Tribromo-3-aminobenzoic acid	86
3-Nitrophenol	20 mL, 0.010 M, 30 h	2,4,6-Tribromo-3-aminophenol	90
4-Nitrophenol	20 mL, 0.020 M, 18 h	2,3,6-Tribromo-4-aminophenol	47
		2,3,5,6-Tetrabromohydroquinone	39

Analysis by NMR of the products extracted into ether revealed a 45:55 ratio of hydroquinone to 2-bromohydroquinone. Since hydroquinone has no absorbance above 340 nm and concentrated aqueous HBr has very slight absorption, light absorption by HBr is the logical source of bromine. The extent of this is about 0.00003 mol/L/h, which could account for 2% of the bromination of the 4-nitrophenol products and 0.12% of the nitrobenzene product. If the competition for light is considered in which reactants absorb at least 97% of the light entering the reaction tube, direct photolysis of HBr is negligible. The probable source of excess bromination in the case of 4-nitrophenol is air oxidation of a hydroquinone to a benzoquinone followed by electrophilic addition of HBr.

The report[6] that nitrosobenzene reacts thermally with hydrohalic acids to give halogenated reduction products including 2,4-dihaloanilines furnishes a clue concerning the reaction sequence. In a reinvestigation of this chemistry, we found that 4-bromonitrosobenzene in an acetic acid solution has its blue-green color discharged immediately on addition of concentrated hydrobromic acid, and that 2,4,6-tribromoaniline is produced in 95% isolated yield. This result is consistent with the reaction sequence shown in Scheme 2. It is likely that the photochemistry generates a bromonitrosobenzene derivative that reacts rapidly and thermally to give the observed products. This offers an explanation for the occurrence of a hydroquinone from 4-nitrophenol as well as the introduction in that case of bromine in the aminophenol meta to the nitrogen function. The expected 3-bromo-4-nitrosophenol has a tautomer, 2-bromobenzoquinone monoxime, that can hydrolyze to give eventually the hydroquinone derivative. The oxime can also undergo electrophilic additions of HBr across the conjugated oxime or imine to generate the observed aminophenol.

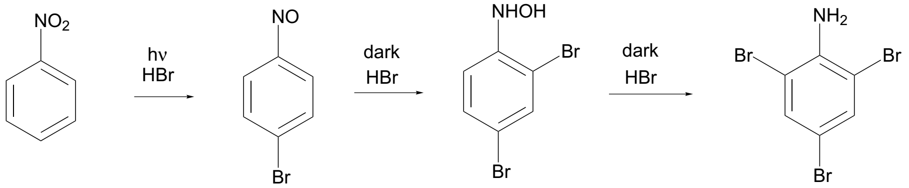
Quantum yields of disappearance of nitroaromatics were determined by monitoring the loss of UV absorbance of diluted samples at the wavelength maximum after first determining the absorbance at completion. Conversions were about 10%, and azoxybenzene in ethanol was the actinometer.[7] Starting material concentrations were sufficient to absorb 98% of the broadband light transmitted through the uranium glass filter into a Pyrex test tube with an internal diameter of 1.4 cm. The quantum yields are reported in Table 2. The effects of substituents on the quantum yields are similar to those for the photoreaction of nitroaromatics with hydrochloric acid:[4] electron withdrawing substituents have little effect on the efficiency, but electron donor substituents reduce the efficiency.

The mechanism proposed[4] for the HCl photoreaction involves electron transfer from halide ion to a predominant n,π* excited state of the nitroaromatic as the primary event, and this is consistent with all that is known for the photoreaction with HBr. Electron donor substituents on nitrobenzenes lower the energy of the π,π* state relative to the close-lying n,π* state, causing the π,π* state, which is unreactive, to become the lower energy state.[4,8] That the range of the suppressive effect of donors on the quantum yield is less than 10-fold in the HBr case compared with 440-fold in the HCl case (for 3-nitroanisole compared with nitrobenzene) adds further support to the electron transfer hypothesis for the HBr case. The free energies for $X^- \rightarrow X + e^-$ in water are 293 kJ/mol for chloride ion and 201 kJ/mol for bromide ion, suggesting that electron abstraction from chloride ion should indeed be much more selective than from bromide ion.

Table 2. Quantum yields of photohydrobromination of nitroaromatics

Compound	M in 8.8 M aq HBr	Quantum yield
Nitrobenzene	0.020	0.16
3-Nitrobenzoic acid[a]	0.020	0.15
3-Nitrophenol	0.010	0.029
4-Nitrophenol	0.020	0.038

[a] Solution was 1:9 (v:v) HOAc: 8.8 M aq HBr.



Scheme 2.

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