1-Oxa-3-methylcyclohex-3-en-2-one. Under a dry nitrogen atmosphere, 5.0 mL of n-BuLi (2.4 M in hexane) was added to a stirred solution of diisopropylamine (1.96 g, 19.3 mM) in 60 mL of dry THF at −78 °C. The reaction mixture was allowed to warm to 25 °C, stirred for an additional 0.5 h, and then cooled to −78 °C. δ-Valerolactone (2.00 g, 20 mM) in 50 mL of dry THF was added over an hour to the cold solution and stirred for another 0.5 h. Phenylselenyl bromide (PhSeBr) in 7 mL of dry THF was added rapidly to the cold stirred enolate solution (immediate discoloration), and the cold reaction mixture was diluted with Et_2O. The ether solution was washed with 10% HCl, saturated $NaHCO_3$, and saturated NaCl. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude material (1.7 g) was dissolved in 20 mL of THF and 0.5 mL of AcOH at 0 °C. Hydrogen peroxide (30 mL, 30%) was added to the cold solution over 0.5 h and then stirred for an additional 0.5 h. The reaction mixture was poured into cold saturated $NaHCO_3$ and extracted with Et_2O. The organic layer was washed with H_2O and saturated NaCl and dried ($MgSO_4$), and the solvent was removed in vacuo. Vacuum distillation afforded a colorless liquid (0.56 g, 25%): bp 54–66 °C (0.4 mm); ^1H NMR (CCl_4) δ 1.85 (s, 3 H, CH_3), 2.25–2.50 (m, 2 H), 4.30 (t, 2 H), 6.53 (m, 1 H); IR (film) ν 1703 (C=O) cm^{-1}; MS (70 eV), m/e (relative abundance) 112 (67), 94 (11), 82 (62), 67 (41), 66 (11), 55 (18), 54 (100), 53 (37), 43 (16), 41 (24), 39 (94).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.38.

3-Oxabicyclo[4.4.0^{1,6}]decen-2-one. Peroxide **3** (10 mg, 0.05 mM) was added to a solution of p-toluenesulfonic acid (8 mg) in 10 mL of benzene and heated at reflux for 27 h. The reaction mixture was diluted with Et_2O, washed with 10% $NaHCO_3$ and saturated NaCl and dried ($MgSO_4$). The solvent was removed in vacuo, and the crude lactone was purified by column chromatography (silica gel, Et_2O) to yield 4 mg (52%) of lactone: ^1H NMR (CCl_4) δ 1.65 (m, 4 H), 2.20 (m, 6 H), 4.25 (t, 2 H); IR (CCl_4) ν 1720 (C=O) cm^{-1}; MS, m/e (relative abundance) 152 (67), 134 (19), 122 (10), 107 (62), 106 (23), 93 (22), 91 (42), 80 (12), 79 (100), 78 (10), 77 (28), 67 (13), 65 (13).

Anal. Calcd for $C_9H_{12}O_2$: 152.0837. Found: 152.0828.

Acknowledgment. This work was supported by the Office of Naval Research and by the National Science Foundation.

Registry No. **1**, 83115-69-9; **2**, 83115-67-7; **3**, 83115-68-8; **5**, 72649-02-6; DPEA, 10075-85-1; DPA, 1499-10-1; DBA, 523-27-3; TOSMIC, 36635-61-7; O_2, 7782-44-7; PhSeBr, 34837-55-3; perylene, 198-55-0; acetic acid, 64-19-7; methanol, 67-56-1; diethylmalonic acid, 105-53-3; 2-methyl-2-cyclopropylmalonic acid, 83115-70-2; cyclopropylmalonic acid, 5617-88-9; 4-cyanospiro[5.2]octane, 83115-71-3; spiro[5.2]octan-4-one, 2205-98-3; spiro[5.2]octane-4-carboxylic acid, 83115-72-4; spiro[5.2]octane-4,4-dicarboxylic acid, 83115-73-5; δ-valerolactone, 542-28-9; 3-methyl-1-oxa-3-phenylselenylcyclohexan-2-one, 83115-74-6; 3-oxabicyclo[4.4.0]-1(6)-decen-2-one, 83115-75-7.

Mechanism of the Water-Catalyzed Photoisomerization of *p*-Nitrobenzaldehyde

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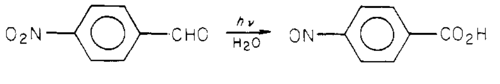
Received June 25, 1982

p-Nitrobenzaldehyde is observed to photoisomerize cleanly to p-nitrosobenzoic acid in aqueous solutions but to be photostable in pure acetonitrile or acetic acid. The dimethyl acetal of p-nitrobenzaldehyde is photostable in water. The quantum yield (0.034 at 254 nm in 99% H_2O/1% CH_3CN) depends upon the water concentration in mixtures of acetonitrile and water but is unaffected by pH in the range of 0–10, by the concentration of starting material, and by free radical trapping agents such as dioxane, methanol, or oxygen in aqueous solution. The reaction is sensitized efficiently by sodium anthraquinone-2-sulfonate (E_T = 62 kcal/mol) and quenched by the triplet quencher 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. Deuterium isotope effects were determined for the solvent ($\Phi_{H_2O}/\Phi_{D_2O} = 1.37 \pm 0.05$) and for the formyl hydrogen ($\Phi_{\alpha\text{-H}}/\Phi_{\alpha\text{-D}} = 1.05 \pm 0.10$). Photoisomerization in water containing 0.01–0.10 M ammonia causes p-nitrosobenzamide to appear as a photoproduct. This result implicates a quinoid ketene intermediate. The new evidence reported allows elimination of a number of plausible mechanisms for the photoisomerizaton, including two mechanisms proposed previously. A mechanism is proposed for which the primary process is exciplex formation involving electron transfer from water to the nitrophenyl triplet n,π* state, this interaction being followed by a rapid proton transfer from $H_2O^{+\cdot}$ to its geminate radical, p-$O_2NC_6H_4CHO^{-\cdot}$.

ortho-Nitrobenzaldehyde has long been known to undergo clean and efficient photoisomerization to o-nitrosobenzoic acid[2,3] in a variety of media including the solid state.[4] The meta and para isomers have been reported to be stable to the analogous photoisomerization, though other products are formed on irradiation in alcohol.[2] The finding that p-nitrobenzaldehyde in water is cleanly photoisomerized to p-nitrosobenzoic acid[5] was therefore unexpected. The reaction was an exception to a rule formulated by Sachs and Hilpert[6] that photosensitivity of aromatic nitro compounds is associated with an ortho arrangement of nitro and aliphatic C–H groups.



When the nitro and formyl groups are situated ortho, the lowest energy triplet state is of n,π* configuration and is that associated with the nitrophenyl chromophore.[7,8] The primary process leading to photoisomerization is hydrogen abstraction from formyl by a nitro oxygen atom.

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[1] Address correspondence to this author at Grinnell College.

[2] Ciamician, G.; Silber, P. *Chem. Ber.* **1901**, *34*, 2040–2043.

[3] Leighton, P.; Lucy, F. A. *J. Chem. Phys.* **1934**, *2*, 756–766.

[4] Cowell, G. W.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 1106–1110.

[5] Wubbels, G. G.; Hautala, R. R.; Letsinger, R. L. *Tetrahedron Lett.* **1970**, 1689–1691.

[6] Sachs, F.; Hilpert, S. *Chem. Ber.* **1904**, *37*, 3425–3428.

[7] Morrison, H. A. In "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Wiley-Interscience: New York, 1969; Part I, pp 165–213.

[8] Filby, W. C.; Guenther, K. *Z. Phys. Chem.* (*Frankfurt am Main*) **1975**, *95*, 289–292.

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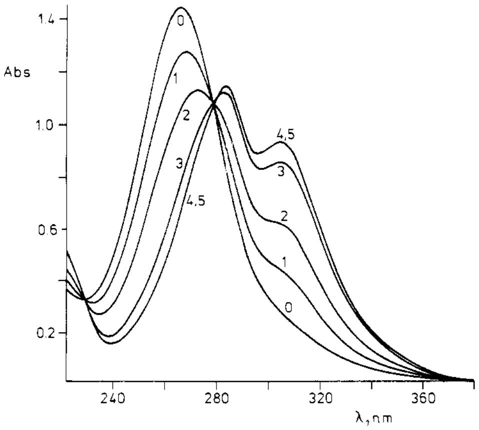

Figure 1. Ultraviolet spectra for photoisomerization at 313 nm of *p*-nitrobenzaldehyde (1.0×10^{-4} M) to *p*-nitrosobenzoic acid in water (1% CH_3CN) containing 0.01 M H_2SO_4 at irradiation times as indicated: 0 = 0 min, 1 = 5 min, 2 = 10 min, 3 = 40 min, 4 = 85 min, 5 = 110 min.

Since a process of this kind is geometrically impossible for the para isomer, its photoisomerization presented an interesting mechanistic puzzle. We thought the reaction worthy of study because it was clean, and it was completely lacking in precedent. Furthermore, since water was required in the reaction medium[5] and yet the stoichiometry required no net change for water, we surmised that a catalytic action of water was involved, which also had no precedent. Additional interest in the reaction has arisen because *p*-nitrobenzaldehyde has been found to be a photodegradation product of chloramphenicol.[9]

We now report a mechanistic study of this novel reaction. The results support the conclusion that the mechanism involves initial electron transfer from water and that the electron-deficient radical so formed abstracts the formyl hydrogen.

Results

Photorearrangement of *p*-nitrobenzaldehyde to *p*-nitrosobenzoic acid in water is very clean as indicated by isosbestic points at 279 and 227 nm and by the coincidence of product maxima at 284 (ε 11 500) and 305 nm (ε 9359) in an exhaustively irradiated solution (see Figure 1) with those of an authentic sample of *p*-nitrosobenzoic acid at the same acidity. The quantum yield at 313 nm in water/acetonitrile (92:8 v:v) was determined with a merry-go-round apparatus to be 0.045 at conversions less than 10%. At 254 nm, the quantum yield in water/acetonitrile (99:1 v:v) was determined by a different method to be 0.034. Long irradiation of *p*-nitrobenzaldehyde in pure acetic acid or acetonitrile caused no photochemistry as judged by UV spectra of the sample.

Several conditions were varied and shown to have little or no effect on either the photochemistry or the efficiency. These included the following: (i) varying the starting material concentraton from 5.0×10^{-4} to 5.0×10^{-3} M did not change the quantum yield; (ii) conducting the reaction in water saturated with benzene produced no traces of phenol detectable by gas chromatography; (iii) the presence of organic solvents such as 10% dioxane, 10% methanol, 25% *tert*-butyl alcohol, 20% acetic acid, and 20% acetonitrile slightly affected the efficiency but did not change the product absorptions in the UV spectrum at conversions less than 50%; extended irradiation of the solutions containing dioxane, methanol, or *tert*-butyl alcohol caused slow degradation of the product absorptions and the isosbestic points; (iv) the presence of 0.01 M KI had no effect on the efficiency or the product, but high concentrations of NaCl (3–6 M) and NaBr (1–3 M) decreased the efficiency; (v) varying the acidity of the medium from pH 10 to 1 M H_2SO_4 had no effect on the product or the efficiency; (vi) solutions purged of dissolved air by flushing with nitrogen showed no change in product or efficiency.

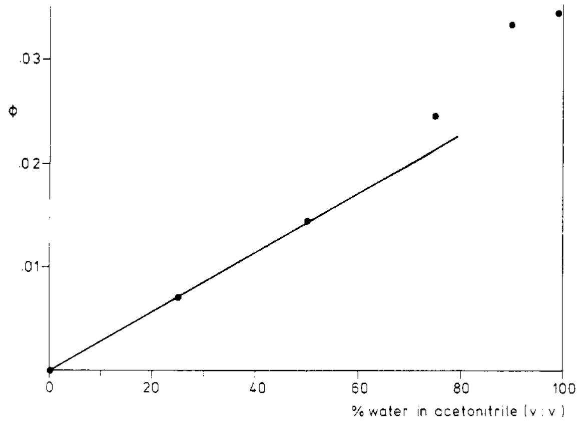

Figure 2. Dependence of the efficiency of photoisomerization of *p*-nitrobenzaldehyde at 254 nm on the water concentration in mixtures of acetonitrile and water (all 0.01 M H_2SO_4).

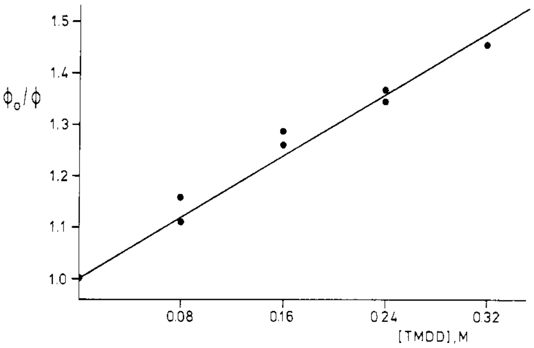

Figure 3. Quenching of photoisomerization at 366 nm of *p*-nitrobenzaldehyde in 50% CH_3CN/H_2O by 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide.

The dependence of the quantum efficiency on the concentration of water in mixtures with acetonitrile is shown in Figure 2. In the acetonitrile-rich solutions, linear dependence of efficiency on the water concentraton is observed. In the water-rich media, the points deviate above the linear correlation line, suggesting that a small solvent effect on the efficiency occurs in this region.

The reaction could be sensitized and quenched by substances specific for triplet excited states. Sodium 9,10-anthraquinone-2-sulfonate[10] caused photoisomerization of *p*-nitrobenzaldehyde in 4:1 H_2O/CH_3CN to occur cleanly with an efficiency 1.19 times greater than that of the comparable direct reaction under conditions in which the sensitizer absorbed 96% of the incident light at 313 nm. 3,3,4,4-Tetramethyl-1,2-diazetine 1,2-dioxide, a quencher specific for triplet states,[11] quenched the photoisomerization at 366 nm when present at rather high concentrations in 50% CH_3CN/H_2O. The Stern–Volmer plot is shown in Figure 3.

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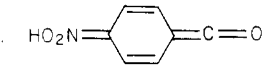
[9] Reisch, J.; Weidmann, K. G. *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1971**, *304*, 911–919.

[10] This sensitizer undergoes intersystem crossing to the triplet with unit efficiency and has a triplet energy (phosphorescence in MeOH–EtOH at 77 K) of 62.1 kcal/mol: Dearman, H. H.; Chan, A. *J. Chem. Phys.* **1966**, *44*, 416–417.

[11] Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077–5078.

Deuterium isotope effects on the efficiency of photoisomerization were determined for the solvent and also for the formyl hydrogen. The photoreaction at 254 nm in 99:1 H_2O/CH_3CN is 1.37 ± 0.05 times as efficient as is the reaction in 99:1 D_2O/CH_3CN. The α-deuterio-*p*-nitrobenzaldehyde was prepared by H–D exchange of the dithiane derivative in EtONa–EtOD. The efficiency of photoisomerization of the α-protio aldehyde is 1.05 ± 0.10 times that of the α-deuterio compound in 9:1 H_2O/CH_3CN at 313 nm.

In our original report of this reaction,[5] we suggested without evidence that the *aci*-nitroketene (shown below)



would be a plausible intermediate in the photoisomerization. In order to obtain evidence for this intermediate, we conducted the photoisomerization in the presence of ammonia, supposing that the product would be *p*-nitrosobenzamide if the ketene were attacked by ammonia. Analysis of the products of photoisomerization in the presence of ammonia by reverse-phase high-pressure liquid chromatography revealed that the amide is indeed formed when ammonia is present. This conclusion is based on enhancement of the suspected *p*-nitrosobenzamide peak with an authentic sample. At ammonia concentrations of 0.01, 0.05, and 0.1 M, the yields of the amide were 7.9%, 40%, and 63%. Ammonia at these concentrations did not affect appreciably the efficiency of disappearance of *p*-nitrobenzaldehyde. Moreover, ammonia at 0.1 M did not change appreciably the absorbance of *p*-nitrobenzaldehyde in water [λ_{max} 267 nm (ϵ 14 400)], but ammonia at 1.0 M caused the absorptivity at λ_{max} 267 nm to decrease by 15%. These data indicate that imine formation may be appreciable at ammonia concentrations above 0.1 M but that the imine comprises less than a few percent of the sample at the lower ammonia concentraitons.

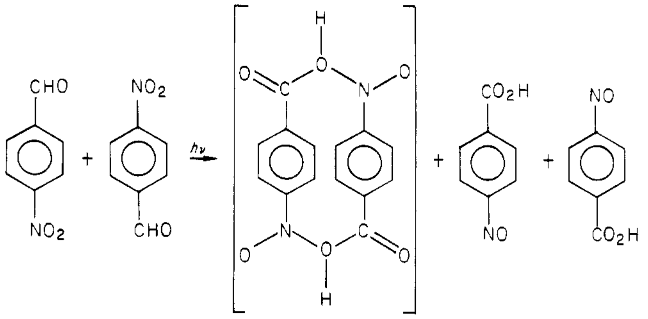
At 0.1 M ammonia, a side reaction is evident which gives a product absorbing noticeably at 415 nm. When ammonia is present at a 1 M concentration, this photo reaction appears to be predominant. Preparative-scale reactions at 1 M ammonia yielded only amorphous solids as products which could not be characterized. We suspect that the reaction is direct photoamination,[12] which would give aminonitrobenzaldehydes. Such substances are reported to form imine-linked polymers on isolation.[13]

The diethyl acetal of *o*-nitrobenzaldehyde is reported to undergo photoisomerization to ethyl *o*-nitrosobenzoate[14] in a reacton analogous to that of the free aldehyde. We examined the possibility that the para acetal in water might react analogously to *p*-nitrobenzaldehyde. Irradiation of the dimethyl acetal of *p*-nitrobenzaldehyde in water [λ_{max} 267 nm (ϵ 9700)] for a period twice that required for the reaction of *p*-nitrobenzaldehyde to reach completion caused no change in the UV spectrum. This result agrees with an earlier observation[15] that photolysis of the para diethyl acetal in ethanol did not cause isomerization.

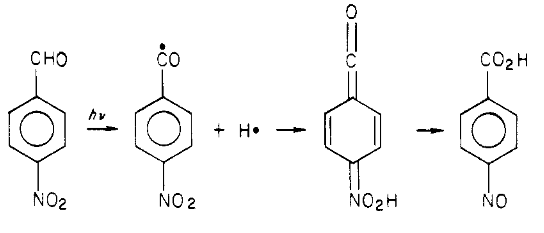
Discussion

p-Nitrobenzaldehyde is a photodegradation product of the antibiotic chloramphenicol, and the mechanism of its photoisomerization in water to *p*-nitrosobenzoic acid has therefore attracted attention.[9,16,17] We wish to examine in view of our experimental findings two photoisomerization mechanisms already proposed in the literature[16] and also to consider several other plausible mechanisms based on primary photochemical processes reported for aryl aldehydes[18] and nitro compounds.[7]

Scheme I



Scheme II



Reisch and Weidmann[16] proposed that excited *p*-nitrobenzaldehyde reacts in a complex, bimolecular primary process with a ground-state molecule of *p*-nitrobenzaldehyde (Scheme I). The proposal may be objected to on the ground that it would appear to require an improbably clean sequence of excitation, hydrogen abstraction, and radical coupling followed by a second identical sequence in order to form the dimeric complex. On experimental grounds, we believe it can be eliminated by our observation that the quantum yield is invariant over a 10-fold range of concentration of *p*-nitrobenzaldehyde. Furethermore, the absence of a kinetic isotope effect for deuterium at the α-position suggests that the formyl C–H bond is not broken in the primary process. Finally, the mechanism provides no role for water and no opportunity for the intervention of ammonia.

Reisch and Weidmann[16] also suggested that in the presence of methanol, the reaction proceeds by photochemical formation of the dimethyl acetal, which subsequently photoisomerizes to methyl *p*-nitrosobenzoate. The basis for this suggestion was analogy to a proposed mechanism for photoisomerization of *o*-nitrobenzaldehyde in the presence of alcohols.[7] One could envision an analogous pathway for the reaction in water involving preliminary formation of the hydrate of the aldehyde. That the extinction coefficient at the λ_{max} of *p*-nitrobenzaldehyde in water (ϵ 14 400) is virtually the same as that reported for the compound in isopropyl alcohol[19] and hexane[20] suggests that very little of the hydrate is present in water.[21] This suggests that the hydrate could not ac-

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(12) van Vliet, A.; Kronenberg, M. E.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1970**, *26*, 1061–1067.

(13) Borsche, W.; Sell, F. *Chem. Ber.* **1950**, *83*, 78–87.

(14) Bamberger, E.; Elger, F. *Justus Liebigs Ann. Chem.* **1909**, *371*, 319–365.

(15) Tanasescu, I. *Bull. Soc. Chim. Fr.* **1926**, *29*, 1443–1455.

(16) Reisch, J.; Weidmann, K. G. *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1971**, *304*, 906–910.

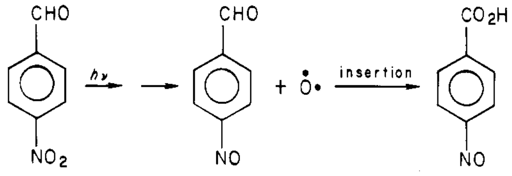
(17) Green, R. G.; Sutcliffe, L. H.; Preston, P. N. *Spectrochim. Acta, Part A* **1975**, *31A*, 1543–1544.

(18) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966.

(19) Petrow, V.; Stephenson, O.; Sturgeon, B. *J. Chem. Soc.* **1953**, 4066.

(20) Forbes, W. F. *Can. J. Chem.* **1958**, *36*, 1350.

Scheme III



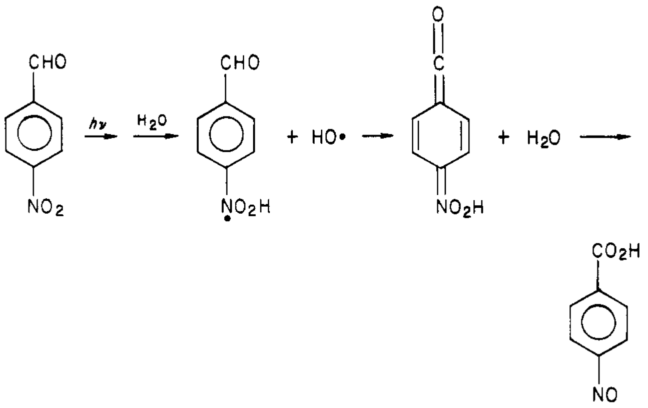
count for the photochemistry because it could not compete adequately with the aldehyde for light absorption. In addition, the observation that the dimethyl acetal is photochemically inert in water vitiates the suggestion that the acetal,[16] or the corresponding hydrate, is an intermediate in the photoisomerization.

A pathway initiated by α cleavage of the C–H bond of the formyl group[18] could be imagined (Scheme II), despite the lack of positive evidence that α cleavage occurs significantly for unsubstituted benzaldehyde in solution.[22,23] This pathway conflicts with several pieces of experimental evidence. The α-deuterium isotope effect on the quantum yield is within the experimental error of unity. The possibility seems remote that α cleavage, in competition with rapid radiationless decay of the excited state,[24] could occur without showing a significant primary kinetic isotope effect. Furthermore, the sensitization experiment clearly implicates a triplet excited state of energy below 62 kcal/mol. Unsubstituted benzaldehyde has a triplet n,π* state energy of 71.7 kcal/mol,[25] and the energy of the state would be expected to be perturbed little by an electron-withdrawing para substituent.[26] The nitrobenzene n,π* triplet lies at about 60 kcal/mol[27,28] and would also be expected to be little affected by the *p*-formyl group. That sensitization supplying 62 kcal/mol proceeds with an efficiency slightly greater than that of the comparable direct photoreaction appears to exclude any photochemistry starting from the carbonyl excited state and implicates the nitro triplet n,π* state as the reactive excited state.

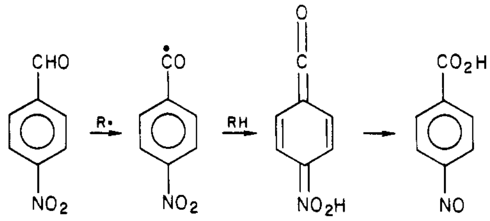
Aromatic nitro compounds have been claimed to undergo photochemical oxygen atom fission in gas and liquid phases,[18] although an alternative to this conclusion has been suggested.[7] If the nitro group of photoexcited *p*-nitrobenzaldehyde were to undergo such a fission, a plausible mechanism for isomerization could be envisioned as shown in Scheme III.

Several pieces of evidence conflict with the proposal in Scheme III. That no photoisomerization could be observed on extended irradiation of *p*-nitrobenzaldehyde in acetonitrile or acetic acid casts doubt on the mechanism and suggests that water plays a significant role in the reaction. The latter conclusion is strongly supported by results in Figure 2 and also by the small but significant isotope effect observed for D_2O vs. H_2O ($\Phi_{H_2O}/\Phi_{D_2O} = 1.37 \pm 0.05$), which would be difficult to rationalize by Scheme III. The mechanism also provides no means of rationalizing the intervention of ammonia which causes the amide to appear as a product.

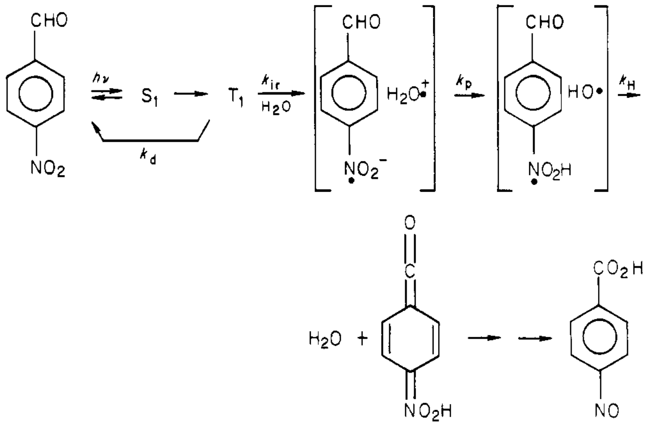
Scheme IV



Scheme V



Scheme VI



The primary process of hydrogen abstraction by nitro compounds is extensively documented;[29] it could initiate photoisomerization by the mechanism of Scheme IV. Whereas abstraction of hydroxyl hydrogens is not commonly observed, there is evidence that energetic one-electron oxidants such as persulfate,[30] *tert*-butoxy,[31] and photoexcited quinones[32] react in this fashion with alcohols, that *tert*-butoxy[33] and photoexcited ketones[34] abstract hydrogen from phenols, and that triplet *p*-benzoquinone abstracts an electron or a hydrogen atom from water.[35]

The mechanism of Scheme IV, assumed to involve a simple hydrogen abstraction in the primary process, con-

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(21) In alcohol solvents such as methanol or ethanol, formation of the hemiacetal or acetal could proceed appreciably, as suggested by the lower extinction coefficient (11 500) reported for the aldehyde in ethanol. Forbes, W. F.; Mueller, W. A. *J. Am. Chem. Soc.* **1957**, *79*, 6495. Patai, S.; Israeli, Y. *J. Chem. Soc.* **1960**, 2025–2030.

(22) Cocivera, M.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 1772–1774.

(23) Closs, G. L.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 7229–7231.

(24) Hautala, R. R.; Mayer, T. *Tetrahedron Lett.* **1977**, 2499–2502.

(25) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3.

(26) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614.

(27) Cowley, D. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1576–1580.

(28) Brinen, J. S.; Singh, B. *J. Am. Chem. Soc.* **1971**, *93*, 6623–6629.

(29) Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 49–85.

(30) Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *Proc. R. Soc. London* **1973**, *322*, 151.

(31) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 630–632.

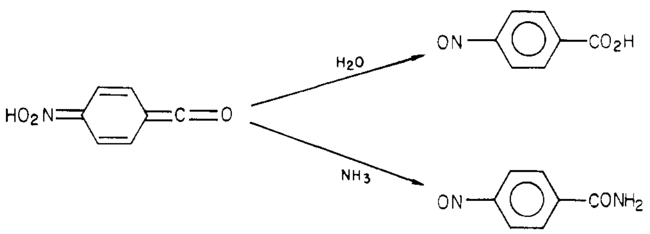
(32) McLauchlan, K. A.; Sealy, R. C. *J. Chem. Soc., Chem. Commun.* **1976**, 115.

(33) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162–4166.

(34) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154–4162.

(35) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103–1104.

Scheme VII



flicts with the small observed isotope effect for D_2O. Since the hydrogen abstraction would occur in competition with rapid radiationless decay, it would be expected to show a primary isotope effect such that Φ_{H_2O}/Φ_{D_2O} would be >2[31,36] rather than 1.37 which is observed.

Photoisomerization could also be formulated as a free radical chain reaction (Scheme V). In this case the photochemistry would serve merely to generate the chain-carrying radicals. That there are no nongeminate free radicals of consequence to the mechanism, e.g., hydroxyl or *p*-nitrobenzoyl, is shown by the fact that the reaction proceeds normally in the presence of oxygen or the good hydrogen donor dioxane. The hydroxyl radical reacts with dioxane with a rate constant of 5×10^9 M^{-1} s^{-1}.[37]

We propose for this photoisomerization the mechanism shown in Scheme VI. Several pieces of evidence provide specific support for the mechanism, the major features of which are electron transfer from water to the triplet state to form a radical ion pair or an exciplex, proton transfer within this species, abstraction of the formyl hydrogen by the geminate hydroxyl radical to form the quinoid intermediate, and thermal addition and elimination reactions leading to the observed product.

Ammonia in the concentration range of 0.01–0.1 M causes *p*-nitrosobenzamide to appear as a photoproduct. That the chemical yield of this substance increases with increasing ammonia concentration while the quantum yield of disappearance of *p*-nitrobenzaldehyde stays roughly constant indicates that ammonia does not participate in the primary photochemistry and that it intervenes by attacking an irreversibly formed intermediate. A likely intermediate to accomodate these facts is the *aci*-nitroketene which was suggested as an intermediate in our previous report.[5] Competition in attack by ammonia and water on this intermediate (Scheme VII) would account well for our observations.

The two geminate radical pairs in the mechanism (Scheme VI) are shown in brackets for the experimental reason that the geminate radicals appear to react only with each other, i.e. the electrophilic radicals $H_2O^{+}\cdot$ and $HO\cdot$ cannot be trapped by the highly reactive trapping agent, dioxane, at high concentration. Though we have no further evidence concerning the nature of these species, it seems likely that both correspond to exciplexes.

Our evidence based on sensitization and quenching for involvement of the triplet n,π* state of the nitrophenyl chromophore is unequivocal. That the sensitized reaction is more efficient than the direct reaction is probably a consequence of the quantum yield of intersystem crossing for the nitro aromatic chromophore which appears to be around 0.7 for comparable systems.[38] Enhancements of the efficiency of rearrangement of the ortho isomer (Φ = 0.50) by use of a heavy-atom additive (xenon) or a triplet sensitizer has been reported recently,[8] the enhancements being attributed to modest efficiency (ca. 0.6) of intersystem crossing.

For reasons presented below, it appears that the photoisomerization of the para isomer is irreversible after the electron-transfer step, k_{ir} (Scheme VI). In this case, the quantum yield expression shown in eq 1 would apply,

$$\frac{1}{\Phi} = \frac{1}{\Phi_{isc}}\left(1 + \frac{k_d}{k_{ir}[H_2O]}\right) \qquad (1)$$

which predicts a linear relationship between $1/\Phi$ and $1/[H_2O]$. Owing to the zero intercept of the left-hand, linear portion of Figure 2 (values for 0–50% water), the relationship is also linear when plotted as $1/\Phi$ vs. $1/[H_2O]$; the slope of this plot ($k_d/\Phi_{isc}k_{ir}$) is 2000 mol/L. For $\Phi_{isc} = 0.7$, this result indicates that $k_d/k_{ir} \simeq 1400$ (at 254 nm).

Additional kinetic information can be derived from the quenching results (Figure 3) at 366 nm. TMDD quenching of T_1 in Scheme VI should occur according to eq 2. With

$$\Phi/\Phi_q = 1 + \frac{k_q[Q]}{k_d + k_{ir}[H_2O]} \qquad (2)$$

$\Phi_{isc} = 0.7$,[38] $k_q = 2.5 \times 10^9$ M^{-1} s^{-1},[39] $[H_2O] = 27.8$ M, and $\Phi = 0.02$, k_d and k_{ir} are calculated by eq 1 and 2 to be 1.6×10^9 s^{-1} and 1.7×10^6 M^{-1} s^{-1}, respectively. The ratio k_d/k_{ir} obtained by this estimation (970) is in fair agreement with that estimated above. The value of k_d agrees with previous findings that radiationless decay of triplet nitrobenzenes is rapid: the lifetime of triplet nitrobenzene in 2-propanol is estimated at 1 ns,[38] and that of 3,5-dinitroanisole in organic media is less than 10 ns.[39]

An independent value for comparison to k_{ir} is difficult to obtain. By using the thermochemical data shown for eq 3–5, one may estimate that eq 6 is endergonic (vs. NHE)

$$OH^- = \cdot OH + e^- \quad \Delta G° = 45.4 \text{ kcal/mol}^{40} \qquad (3)$$

$$\cdot OH + H_3O^+ = H_2O^{+}\cdot + H_2O \quad \Delta G° = 4.1 \text{ kcal/mol}^{41} \qquad (4)$$

$$H_2O + H_2O = OH^- + H_3O^+ \quad \Delta G° = 21.7 \text{ kcal/mol} \qquad (5)$$

$$H_2O = H_2O^+ + e^- \quad \Delta G° = 71.2 \text{ kcal/mol} \qquad (6)$$

by about 71 kcal/mol (all species are aqueous). $E_{1/2}$ for *p*-nitrobenzaldehyde in acetonitrile is −1.1 V (vs. NHE)[42] and is about 0.5 V less negative in alkaline water.[43] Thus we estimate eq 7 to be endergonic by 14 kcal/mol. The

$$p\text{-}O_2NC_6H_4CHO + e^- = p\text{-}O_2NC_6H_4CHO^{-}\cdot \qquad (7)$$

sum of eq 6 and 7 is the proposed primary process, but in the ground state. Allowing for the energy of excitation (ca. 60 kcal/mol), we estimate that complete electron transfer would be endergonic by about 25 ± 10 kcal/mol. At this energy gap, the rate constant of 1.7×10^6 M^{-1} s^{-1} is too large to be ascribed to complete electron transfer such as that reported for singlets by Rehm and Weller.[44] In order

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(36) Moore, W. M.; Ketchum, M. D. *J. Phys. Chem.* **1964**, *68*, 214–217.

(37) Walling, C.; El-Taliawi, G. M.; Johnson, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 133–139.

(38) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 1949–1952.

(39) Varma, C. A. G. O.; Plantenga, F. L.; van den Ende, C. A. M.; van Zeyl, P. H. M.; Tamminga, J. J.; Cornelisse, J. *J. Chem. Phys.* **1977**, *22*, 475–483.

(40) Frank, A. J.; Grätzel, M.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 593–602. These authors estimate ΔG° for eq 6 at 78.4 ± 11.5 kcal/mol. Delahay, P.; van Burg, K. *Chem. Phys. Lett.* **1981**, *83*, 250–254; these authors estimate 76.1 ± 6.9 kcal/mol.

(41) The pK_a of $H_2O^{+}\cdot$ may be estimated to be about three units below that of hydronium ion: Simic, M.; Hayon, E. *J. Am. Chem. Soc.* **1971**, *93*, 5982–5986.

(42) Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 1852.

(43) Volke, J. *J. Electroanal. Chem.* **1965**, *10*, 344.

to rationalize the rate constant, one must invoke binding energy of an exciplex intermediate to lower the energy gap or a merged transition state involving partial electron transfer and hydrogen atom transfer.[45,46] The problem is similar to that encountered in photoreduction of ketones by amines in which the endergonicity of full electron tranfer is considerably larger than the apparent activation energy for the electron-transfer interaction step.[45]

The observed isotope effect for water ($\Phi_{H_2O}/\Phi_{D_2O} = 1.37$) is readily reconciled with the proposed electron-transfer interaction. A small isotope effect in the same direction as that observed is apparent in the vertical ionization potentials of D_2O and H_2O (12.64 and 12.61 eV, respectively).[47] An analogous reaction is electron transfer from amines or sulfides to one-electron acceptors. The isotope effect of hydrogen bound to the donor atom or to a neighboring atom on the rate constants of these reactions is expected to be small and positive;[48] electron-transfer interactions of primary amines (RNH_2 vs. RND_2) with photoexcited benzophenone as the oxidant showed isotope effects in the range of 1.9–1.4.[46] Hydrogen abstraction by benzophenone from 2-propanol, a process which does not involve significant electron transfer, shows a normal primary isotope effect ($k_H/k_D = 2.8$).[36] We conclude that the isotope effect observed is consistent with expectations for an electron-transfer process. That it is so small suggests that the subsequent proton transfer step, which has an intrinsic isotopic rate differential of $k_H/k_D \geq 3$ but which is not observed here, involves an intermediate which does not revert to starting material. If the proton transfer competed with reversal of the electron transfer, one would expect to see a correspondingly significant isotope effect.

That the isotope effect for the formyl hydrogen is unity suggests that the intermediate involved in that hydrogen abstraction step, k_H, is also incapable of reversion to starting material. Again an intrinsic hydrogen isotope effect on the abstraction reaction ($k_H/k_D \geq 3$) is expected and may be assumed to occur; we conclude that the intermediate involved is already committed to becoming the product and that the isotope effect is therefore invisible.

We expect the proton-transfer step, k_p, to be spontaneous and to proceed in a period of $\sim 10^{-10}$ s. This conclusion is based on the pK_a values of the species involved; *p*-$OHC{-}C_6H_4{-}NO_2H\cdot$ may be estimated to have a pK_a of about 2.5,[49] and $H_2O^{+\cdot}$ is estimated to have a pK_a less than −1.[41] The facility expected for this reaction explains why we were unable to perturb the system by varying the acidity of the medium in the pH range of 10–0.

The failure of *p*-nitrobenzaldehyde dimethyl acetal to photoisomerize in water was initially puzzling since a reaction analogous to that of *p*-nitrobenzaldehyde seems possible. We see two plausible explanations. The absence of the formyl group increases the difficulty of reduction of the nitro compound. Using the reduction potentials of the $ArNO_2^-/ArNO_2$ couples for nitrobenzene and *p*-nitrobenzaldehyde as guides,[42] loss of the formyl group would increase the energy barrier for electron transfer by about 7 kcal/mol. Also, the group, $CH(OCH_3)_2$, might differ substantially from CHO as a hydrogen atom donor in the proposed geminate radical pair. Among other things, one would expect CHO to be coplanar with the aromatic ring, whereas $CH(OCH_3)_2$ should be conformationally unrestricted.

Finally, it should be noted that the photoisomerization mechanism amounts to a novel form of catalysis of an excited-state reaction that we have termed electron hole transfer catalysis.[50] In this case the electron hole on the nitro oxygen atom in the n,π^* state is transfered to an oxygen orbital of water. That mobile electron hole becomes filled by the abstraction of the formyl hydrogen. Thus, the primary events, through the agency of electron hole transfer catalysis, are analogous to those proposed for the ortho isomer.[7,8] We regard water as catalyst because it appears in the reciprocal quantum yield expression (eq 1) to a higher reciprocal power than it appears in the stoichiometry. It is clear by inspection that water is also a catalyst for the ground-state conversion of the quinoid intermediate to the final product.

Experimental Section

Ultraviolet spectral measurements were made on Beckman DU, DB-G, or 5260 spectrophotometers. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer; NMR spectra were recorded on a Perkin-Elmer R12B or R600 FT spectrometer, both at 60 MHz. Liquid chromatography was carried out with an Altex 310 unit equipped with a Lichrosorb RP18 column (3.2 mm × 25 cm) and a UV detector operated at 254 nm. Gas chromatography was carried out with a Hewlett-Packard 5750 chromatograph equipped with 10% SE-30 columns on Chromosorb Q (0.25 in. × 10 ft). Quantitative gas chromatography was carried out with a Gow-Mac 750 fid chromatograph equipped with a $^1/_8$ in × 6 ft column of DC 200 on Chromosorb W and a Columbia Supergrator III electronic integrator.

p-Nitrobenzaldehyde was Eastman Kodak material which was washed with aqueous NaOH and recrystallized twice from $EtOH{-}H_2O$. Acetonitrile was spectrograde material from the Aldrich Chemical Co. D_2O was 99.8 atom of D from Aldrich. Sodium anthraquinone-2-sulfonate (Eastman) was dissolved in water and washed with ether and chloroform. It was then recrystallized twice from water by using Norite. Ethanol-*d* was prepared by a published procedure.[51]

3,3,4,4-Tetramethyl-1,2-diazetine 1,2-dioxide was prepared by reported procedures from 2-nitropropane.[11,52,53] It showed ϵ = 0.108 at 366 nm in 50% $CH_3CN{-}H_2O$; it is soluble in this solvent to the extent of about 0.4 M at room temperature. The dimethyl acetal of *p*-nitrobenzaldehyde was prepared by refluxing the aldehyde in excess methanol containing a few drops of H_2SO_4. The material boiling at 168 °C (20 mm) was homogeneous on TLC and was used without further purification.

***p*-Nitrobenzaldehyde-*α*-*d*.**[54] *p*-Nitrobenzaldehyde (1.51 g, 0.01 mol), 1,3-propanedithiol (1.08 g, 0.01 mol), benzene (50 mL), and a few crystals of *p*-toluenesulfonic acid were refluxed overnight in a flask equipped with a Dean–Stark trap. The benzene solution was washed with dilute NaOH and then water, dried over $MgSO_4$, and evaporated. The product dithiane was crystallized from the residue with 200 mL of methanol after treatment with charcoal (2.07 g, mp 141–142 °C). It was recrystallized from benzene–hexane.

The dithiane (0.70 g) was stirred overnight in 20 mL of EtOD containing a small amount of NaOEt. The NMR spectrum of the solution acidified with 2 drops of HOAc showed complete loss of the methine hydrogen resonance at 512 ppm ($CDCl_3$). Workup was performed by removing the EtOD in vacuo, taking up the

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(44) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834–839.

(45) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141–161.

(46) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048–1054.

(47) NSRDS-NBS: "Ionization Potentials, Appearance Potentials, and Heats of Formaiton of Gaseous Positive Ions"; U. S. Government Printing Office: Washington, DC, June 26, 1969.

(48) Pryor, W. A.; Hendrickson, W. H. *J. Am. Chem. Soc.* **1975**, *97*, 1582.

(49) Hayon, E.; Simic, M. *Acc. Chem. Res.* **1974**, *7*, 114.

(50) Wubbels, G. G.; Monaco, W. J.; Johnson, D. E.; Meredith, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 1036–1037.

(51) Pasto, D. J.; Meyer, G. R. *J. Org. Chem.* **1968**, *33*, 1257.

(52) Lamchen, M.; Mittag, T. W. *J. Chem. Soc. C* **1966**, 2300–2303.

(53) Sayre, R. *J. Am. Chem. Soc.* **1955**, *77*, 6689–6690.

(54) Procedures for preparing the dithiane and hydrolyzing it are adapted from: Seebach, D.; Erickson, B. W.; Singh, G. *J. Org. Chem.* **1966**, *31*, 4303–4304.

residue in 20 mL of benzene, and crystallizing the product by adding hexane (0.524 g, mp 139–141 °C).

The deuterated dithiane (0.524 g) was refluxed overnight with 0.49 g of HgO, 25 mL of a 9:1 solution of $MeOH/H_2O$, and 5 mL of a 9:1 $MeOH/H_2O$ solution of $HgCl_2$ (1.36 g). A white precipitate was filtered off; the solution was concentrated in vacuo to ~5 mL, diluted with 100 mL of CH_2Cl_2/hexane (1:1), and extracted with portions (3 × 40 mL) of half-saturated NH_4OAc(aq). The organic layer was washed with saturated NaCl(aq) and dried, and the solvent was removed in vacuo. The residue was crystallized from hexane, giving light yellow crystals: 0.039 g; mp 65–95 °C. It was recrystallized from hexane. The NMR spectrum in $CDCl_3$ was identical with that of *p*-nitrobenzaldehyde except for the complete absence of the resonance due to the formyl hydrogen at δ 10.2.

***p*-Nitrosobenzamide.** A number of attempts to prepare this compound from *p*-aminobenzamide by adaptations of the procedure reported for the ortho isomer[55] with peroxyacetic acid as the oxidant were unsuccessful. It was prepared successfully by the following procedure. To *p*-aminobenzamide (0.100 g, 0.734 mmol) in 20 mL of CH_3CN at 60 °C was added *m*-chloroperbenzoic acid (0.310 g of 80–90% material, Aldrich) in 5 mL of CH_3CN. After 10 min, the mixture was filtered to remove a yellow solid (0.025 g, mp 340–350 °C), and the green filtrate was poured into 2% aqueous NaOH (100 mL) and extracted with 100 mL of EtOAc. The organic layer was washed with water, dried over Na_2SO_4, and evaporated to ~5 mL in vacuo. The crystals present were collected and washed with EtOAc: 0.0354 g; mp 335–345 dec; UV (5% Me_2SO–H_2O) λ_{max} 285 nm (ϵ 10 700), 307 (10 000); IR λ_{max} 3450, 3150, 1710, 1410, 1380, 1250 cm^{-1}. Anal Calcd for $C_7H_6N_2O_2$: C, 56.00; H, 4.03; N, 18.46. Found: C, 56.35; H, 4.14; N, 18.54. The product appears to become resinous when isolated as crystals, causing difficulty in its characterization.

Irradiations. Qualitative examinations of photoreactions in cuvets were carried out by irradiating the samples with Pyrex-filtered light from a 1200-W General Electric UA-11 mercury lamp. These reactions were monitored by scanning the UV spectra of the solutions.

Quantitative irradiations in 1.00-cm quartz cuvets at 254 nm were carried out by using unfiltered light from a Hanau 2346 low-pressure mercury lamp mounted in a box equipped with a shutter and a cell holder. The solutions in acetonitrile–water contained 0.01 M H_2SO_4 and ca. 2.5×10^{-4} M *p*-nitrobenzaldehyde. Analysis was carried out on aliquots diluted fivefold with 0.01 M H_2SO_4 by determining the absorbance at 268 nm (ϵ reactant, 14 400; ϵ product, 7100). The solvent isotope effect was determined for solutions containing 99% D_2O or H_2O, 1% CH_3CN, 0.01 M H_2SO_4, and 2.5×10^{-4} M *p*-nitrobenzaldehyde. These reactions were monitored by the absorance increase of the undiluted samples at 305 nm (ϵ reactant, 2800; ϵ product, 9350). The actinometer for these reactions was a solution of *m*-nitroanisole (2.5×10^{-4} M) and NaOH (0.01 M) in air-saturated 2% methanol–water,[56] which was monitored at 390 and 254 nm ($\Phi = 0.21$). Calculation of the photon flux involves corrections for product absorption and for the transmitted light.[56]

Quantitative irradiations at 313 nm were carried out by using a merry-go-round apparatus (Southern New England Ultraviolet Co., Model MGR-500) and a 200-W mercury lamp (Hanovia) in a tap-water-cooled quartz immersion well. The 313-nm radiation was isolated by using a 1-cm path of 0.002 M $K_2Cr_2O_7$ in aqueous 5% K_2CO_3 and 3 mm of Pyrex 7740 glass. The immersion well was washed before each run with 250 mL of concentrated hydrochloric acid to remove iron oxide contaminants. Samples of 3–5 mL were contained in 15 mm o.d. Pyrex tubes equipped with Ace Glass Co. vacuum seals.[57] The actinometer was 0.100 M valerophenone in benzene.[58] Actinometer solutions were degassed by three freeze–pump–thaw cycles to pressures of 10^{-3} mm and were analyzed with a dodecane internal standard by gas chromatography. The reactions of the *p*-nitrobenzaldehyde samples (typically 1.25×10^{-3}M) were monitored by the absorbance decrease at 267 nm of aliquots diluted 25-fold with 0.1 M aqueous H_2SO_4. The extinction coefficient of *p*-nitrosobenzoic acid at 267 nm varies somewhat with pH; in 0.1 M aqueous H_2SO_4 it is 6700. Reactions were typically carried to conversions of about 10%.

The quenching by 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide was carried out with the merry-go-round apparatus by using 366-nm radiaton from a 450-W mercury lamp (Hanovia) which was isolated by using a combination of Corning filters No. 0-52 and 7-54. The progress of reactions (0.015 M starting material) was monitored by the absorbance increase at 313 nm of aliquots diluted 50-fold with 0.01 M aqueous H_2SO_4. The extinction coefficient of *p*-nitrosobenzoic acid at 313 nm in this medium is 8300. Reaction solutions were prepared so as to make the water cocentration 27.8 M; i.e., the final dilution to the mark was made with acetonitrile.

Photoisomerization in Aqueous Ammonia Solutions. Solutions of *p*-nitrobenzaldehyde (1.05×10^{-4}M) in aqueous ammonia (0.01, 0.05, and 0.1 M) were irradiated at 313 nm to approximately 50% conversions on the merry-go-round. The liquid chromatographs of solutions (20 μL) injected directly (20% CH_3CN/H_2O eluant) showed peaks at 1.7, 2.5, and 8.4 min (1.2 mL/min flow rate). We attribute the first peak to the unidentified photoamination product since it was very small for the 0.01 M ammonia solution and increased in size in proportion to increases in the ammonia concentration. The second peak was enhanced by authentic *p*-nitrosobenzamide, and the third peak was enhanced by *p*-nitrobenzaldehyde. Quantitative assessment of the latter two substances was carried out by manually measuring the peak areas (height times width at half-height) and comparing with the peak areas obtained for injections of authentic samples at known concentraitons.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge the support of the National Science Foundation for Undergraduate Research Participation grants and for funds to purchase a Beckman 5260 UV–vis spectrophotometer used in this research. G.G.W. thanks the National Science Foundation for a Science Faculty Professional Development award and colleagues at the University of Leyden for their hospitality and provision of facilities for preparing the manuscript and for the experiments at 254 nm. We thank Professor A. Hummel for pointing out ref 40.

Note Added in Proof. The photoisomerization reported here may be related mechanistically to the photoredox reactions in water of *m*-nitrobenzyl alcohol and *m*-nitrophenylacetaldehyde reported by Wan and Yates.[59]

Registry No. *p*-Nitrobenzaldehyde, 555-16-8; *p*-nitrobenzaldehyde dimethyl acetal, 881-67-4; *p*-nitrosobenzoic acid, 619-68-1; sodium anthroquinone-2-sulfonate, 131-08-8; 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide, 34493-89-5; deuterium, 7782-39-0; *p*-ntirosobenzamide, 54441-14-4.

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(55) Ibne-Rasa, K. M.; Koubek, E. *J. Org. Chem.* **1963**, *28*, 3240–3241.

(56) De Jongh, R. O. Ph.D. Thesis, University of Leyden, Leyden, Netherlands, 1965, pp 25–29.

(57) Wubbels, G. G. *J. Chem. Educ.* **1977**, *54*, 49.

(58) Wagner, P. J.; Kamppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495–7499.

(59) Wan, P.; Yates, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1023–1024; **1982**, 275–276.