Reactivity of the 3-Nitroanisole Triplet: Methanol Inhibition of Photohydroxylation

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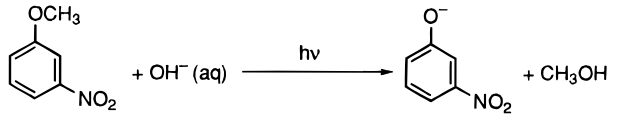
The reactivity of the triplet state of 3-nitroanisole (**1**) toward a series of quenchers has been investigated in water and water alcohol mixtures. The triplet is a relatively efficient hydrogen abstractor, a very efficient electron acceptor, but a poor electron donor. Hydroxide quenches the triplet state via nucleophillic aromatic substitution. Methanol inhibition of the S_N2 Ar* reaction of hydroxide with triplet **1** in water at pH 12 was examined by steady-state and time-resolved methods. HPLC measurements show that a product in addition to 3-nitrophenolate is formed in trace amounts (≤1% of total material) when methanol is present. 2-Propanol, *tert*-butyl alcohol, and trifluoroethanol do not quench the reaction nor does their presence lead to formation of additional products. Methanol quenching of the reaction follows Stern−Volmer behavior with $K_{SV} = 0.36 \pm 0.03$ M^{-1} leading to a rate constant of $(2.3 \pm 0.2) \times 10^6$ M^{-1} s^{-1} for methanol quenching of product formation. Transient absorption studies show that methanol quenches triplet **1** at pH 11.5 with a rate constant of $(1.8 \pm 0.1) \times 10^6$ M^{-1} s^{-1}. In the absence of hydroxide, methanol does not quench the triplet state. The results are explained in terms of formation of low concentrations of methoxide in alkaline solution.

Introduction

Photosubstitution of 3-nitroanisole (**1**) by aqueous hydroxide is believed to proceed via the so-called S_N2 Ar* mechanism.[1,2] The nucleophile attacks the nitroanisole triplet state at the methoxy-substituted carbon yielding an anionic σ-complex which thermally decays to yield the photosubstitution product, 3-nitrophenolate (**2**), and methanol.[1,2]



2, ϕ = 0.22 if [OH^-] > 1mM

The quantum yield is dependent on the hydroxide concentration but reaches a maximum value of 0.22 at [OH^-] 1 mM.[1] *tert*-Butyl alcohol has no effect on the yield of photosubstitution product at less than 90% *tert*-butyl alcohol by volume.[1,3] This has been used as evidence to support the S_N2 Ar* mechanism.[1,3] By contrast, aqueous methanol markedly reduces the product yield at concentrations less than ca. 20% methanol by volume.[4−6] Although this behavior of methanol has been noted on several occasions [4−6] the process by which methanol interferes with the photosubstitution has not been investigated. In this report we examine the influence of methanol on the photohydroxylation making use of both time-resolved and steady-state methods. In this context we have also carried out a detailed examination of the triplet's reactivity in hydrogen bonding solvents.

Experimental Section

Materials. All materials were purchased from Aldrich unless otherwise noted. 3-Nitroanisole (**1**) and 3-nitrophenol were recrystallized from methanol−water mixtures. Phenol (Fisher) was vacuum sublimed. Cyclohexadienes were distilled before use. Cumyl alcohol, trifluoroethanol, methylviologen, and sorbic acid (2,6-hexadienonic acid, Sigma) were used as received. Solvents for spectroscopy (Aldrich, BDH, or Rathburn) were of the highest quality commercially available and were used as received. High performance liquid chromatography (HPLC) mobile phase solvents (Rathburn, HPLC grade) were filtered and degassed before use. Conductivity water was prepared by passing distilled water through a Lab-Ion L2 system. Oxygen-free nitrogen was used for sample degassing. Inorganic salts (Merck, BDH, Fisher) were used as received.

Steady-State Photolysis: Rate Determination. Samples typically contained ca. 2×10^{-4} M **1** in aqueous pH 12 KCl/NaOH buffer[7] or mixtures of buffer and methanol. pH values were monitored with a Radiometer PHM80 pH meter. Approximately 3 mL samples were placed in Pyrex test tubes. The tubes were sealed with rubber septa and degassed by bubbling with oxygen-free nitrogen. Photolyses were performed in a Rayonet photochemical chamber reactor (RPR-100, Southern New England Ultraviolet Co.) equipped with a Rayonet merry-go-round (RMA-500) and operating with RPR-3500 Å, 21 W lamps.

Formation of 3-nitrophenolate (**2**) as a function of irradiation time was followed by monitoring the phenolate absorption at 420 nm, a wavelength where **1** does not absorb. Absorption values were converted to concentrations using an absorption coefficient of 900 M^{-1} cm^{-1} for **2**.[6] From these data the initial rate of phenolate formation (d[3-nitrophenolate]/d*t*) could be determined. Absorption measurements were made on a Per-

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kin-Elmer Lambda 3B instrument or a Hewlett-Packard 8451 diode array spectrometer.

Product formation was also followed by analytical HPLC. HPLC was carried out on an LDC Analytical HPLC instrument fitted with a ConstaMetric 3200 pump and a SpectroMonitor 3200 detector operating at 270 nm. Separations were achieved on an 11 cm silica column fitted with a 10 mm silica guard column. The mobile phase used was 15 vol % ethyl acetate in hexane and a typical flow rate was 1.0 mL/min.

GC-MS measurements were made with a Fisons MD800 system. The GC column was a 30 m J&W DB5 with a 0.32 mm i.d. and 25 μm films. The MS used simple ion detection and TIC integration.

After photolysis, samples for HPLC and GC-MS analysis were neutralized with dilute HCl. The aqueous phase was extracted several times into ether, the ether evaporated, and the residue redissolved in a small volume of ether. This was then injected onto the HPLC or GC column and eluted. HPLC and GC-MS peaks for photolyzed samples were compared to authentic samples for identification.

Laser Flash Photolysis Measurements. For triplet spectra, lifetime measurements, and quenching studies a concentration of ca. 3×10^{-4} M **1** was used. The samples were irradiated in 7×7 mm^2 Suprasil quartz cuvettes with pulses (355 nm, ≈10 ns, ≤30 mJ/pulse) from a frequency tripled Surelite Nd:YAG laser. Transient decays were averages of 5−10 laser shots with monitoring at 400 nm or other suitable wavelengths. Transient absorption spectra were constructed from decay traces monitored at different wavelengths. In all cases transient absorption was captured with a Tektronix 2440 transient digitizer and transferred to a Power Macintosh computer. The computer controlled the experiments and provided suitable processing facilities through use of home-developed programs written in the LabVIEW-3.1 environment from National Instruments. Further details on similar laser systems have been provided elsewhere.[8,9]

In the absence of hydroxide the samples were found to be rather stable as judged by comparison of pre- and post-laser absorption spectra. In the presence of hydroxide (pH 11.5 phosphate buffer[7]) significant photoconversion was observed so that it was necessary to flow the samples using homemade 7×7 mm^2 Suprasil flow cells. In either case degassing was achieved by bubbling with oxygen-free nitrogen. In the flow systems the nitrogen was passed through a reservoir attached to the photolysis cell with Teflon tubing. pH 11.5 rather than 12 was used in the transient studies so that the **1** triplet lifetime would not be so short as to be difficult to measure.

Results

Steady-State Behavior of the 3-Nitroanisole System. 3-Nitroanisole exhibits two absorption bands at about 270 and 326 nm in polar solvents.[10] Upon photolysis of 3-nitroanisole in pH 12 buffer (excitation centered at 350 nm) there is a reduction in intensity of the **1** bands, and three new bands are observed at 254, 280, and 410 nm. These are due to formation of 3-nitrophenolate.[1,11] The initial rate of **2** formation (d[3-nitrophenolate]/dt) could be determined from plots of the concentration of **2** (based on its absorbance at 420 nm) formed as a function of irradiation time. Two such plots are shown in Figure 1 for 0.5% and 10% methanol by volume. The plots curve at long irradiation times as a result of depletion of starting material and absorption of the exciting radiation by the phenolate. The rates are calculated from the linear portion of the curves. Clearly, the rate of phenolate formation is surpressed by methanol, in agreement with earlier reports.[4−6]

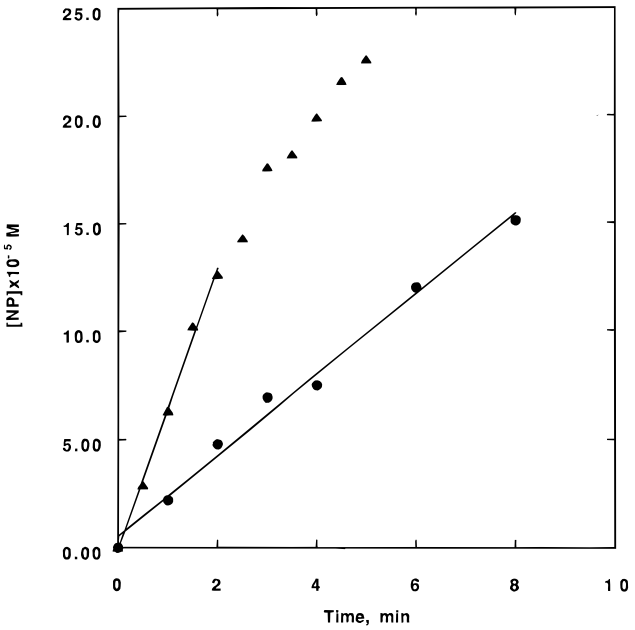

Figure 1. Concentration of 3-nitrophenolate as a function of steady-state irradiation time. 0.2 mM 3-Nitroanisole in pH 12 buffer containing (a) 0.5% methanol (triangles), (b) 10% methanol (circles). Detection wavelength = 420 nm.

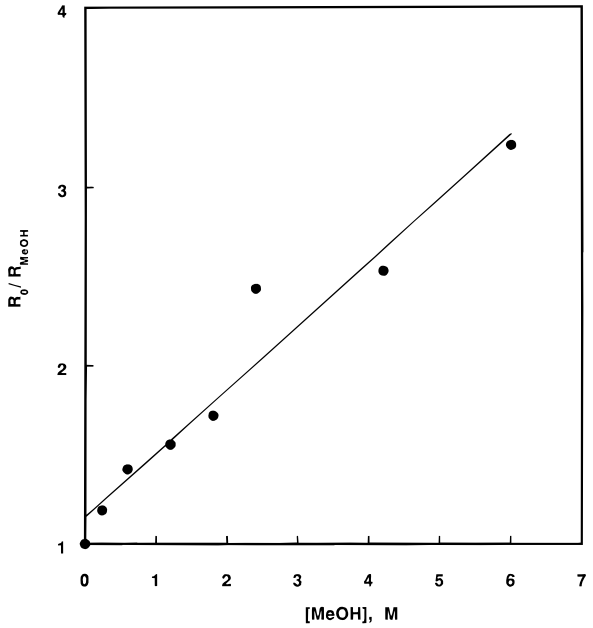

Figure 2. Stern−Volmer plot showing quenching of 3-nitrophenolate formation by methanol in pH 12 buffer. Based on steady-state measurements. *R* refers to rate of appearance of 3-nitrophenolate.

Figure 2 is a Stern−Volmer plot showing the influence of methanol on the formation rate of phenolate. The plot is linear with a slope of 0.36 ± 0.03 M^{-1}. Over this range of added methanol the measured pH (pH meter) of the buffer−methanol mixtures showed only slight variations (<0.1 pH units).

No reaction occurs without hydroxide. Under these conditions absorption spectra and HPLC indicate that only starting material is present after 10 min photolysis. This is true both in water and in water containing 10% methanol by volume. When **1** is photolyzed at pH 12, HPLC shows the presence of **1** (eluting at 1.8 min) and **2** (eluting at 3.5 min), as expected. However, when the photolysis is carried out in alkaline solution with 7%

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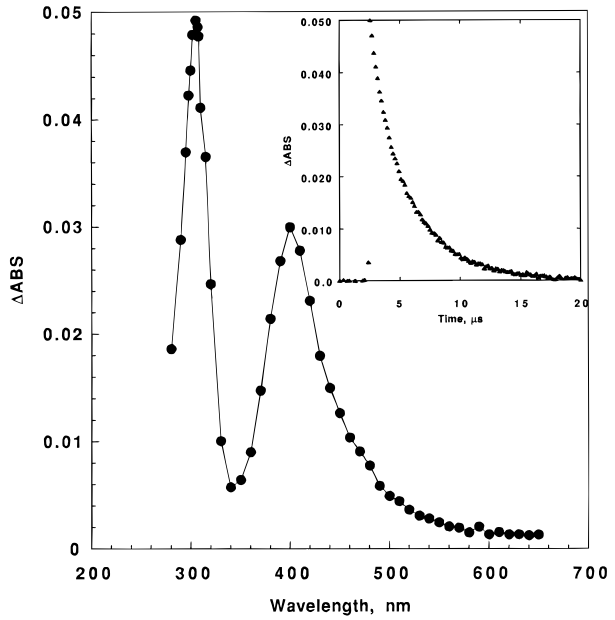

Figure 3. Triplet absorption spectrum of **1** recorded in water 1 μs after excitation of a 0.3 mM solution by 355 nm laser pulses. The insert shows a typical decay trace recorded at 400 nm.

methanol by volume an additional, very small peak is observed eluting at about 1.4 min. When an unphotolyzed sample of **1** in pH 12 buffer containing 7% methanol is treated by the extraction procedure outlined above and then injected into the HPLC, no such peak is observed. This is also the case when methanol alone is injected into the HPLC. Prolonged irradiation (30 min) of 3-nitrophenol in pH 12 buffer containing 10% methanol did not generate this additional peak in the HPLC. Evidently the peak at 1.4 min is due to some interaction of excited 3-nitroanisole and methanol in basic aqueous solution.

It should be emphasized that this peak corresponds to a trace product representing no more than 1% of the total material. Attempts to further identify this trace substance via GC-MS were unsuccessful.

Similar irradiation experiments were carried out using 15% 2-propanol or 5% *tert*-butyl alcohol instead of methanol. In these systems no reduction in the rate of product formation was observed, and no species other than **1** and **2** were detected in HPLC.

Transient Spectrum and Lifetime of the 3-Nitroanisole Triplet. Laser excitation of dilute solutions of **1** in water with 355 nm pulses results in formation of a transient species with the spectrum shown in Figure 3. This transient, which forms within the laser pulse duration, exhibits two absorption bands, an intense band at 307 nm and a weaker band at 400 nm. The spectrum exactly matches that assigned previously to the triplet state of 3-nitroanisole in water.[12]

In water the triplet decays via pseudo-first-order kinetics, with a 3 to 4 μs lifetime; the signal returns back to the preexcitation baseline level following triplet decay (Figure 3, insert). A residual signal following triplet decay had been reported previously.[12] The spectrum of this residual showed a weak absorbance near 420 nm and a strongly rising absorbance below 340 nm. This residual was also observed in some of our early experiments but could be eliminated by repetitive recrystallization of the nitroanisole.

Table 1. Triplet 1 Lifetime in Various Solvents (λ_{mon} = 400 nm)

solvent	τ_T, ns
CF_3CH_2OH	8000
H_2O	3500
H_2O, pH 12	156
CH_3OH	760
2-propanol	70
tert-butyl alcohol	50
CH_3CN[a]	30

[a] CH_3CN was not dried.

The lifetime of the 3-nitroanisole triplet state depends strongly on the solvent. It varies from about 8 μs in trifluoroethanol (TFE) down to about 30 ns in acetonitrile (Table 1). Attempts to observe the triplet in cyclohexane proved futile.

This variation in lifetime is due to the influence of hydrogen bonding on the triplet state.[13] In hydrogen bonding solvents the lowest energy triplet of **1** is believed to be a $\pi\pi^*$ charge transfer state with the π^* electron strongly localized on the nitro group.[13] It has been reported that strong hydrogen bonding of the nitro group inhibits certain bending vibrations which facilitate rapid triplet decay in non-hydrogen bonding solvents. The triplet lifetime of **1** in cyclohexane is thus expected to be in the subnanosecond regime.[13]

The large difference between the triplet **1** lifetimes in methanol and 2-propanol is surprising. One possible explanation is that 2-propanol, a good hydrogen-donor,[14] photoreduces triplet **1**. This seems unlikely as we detected no permanent change in sample absorbance when **1** was photolyzed in neat 2-propanol. In addition, the transient spectrum of **1** observed in 2-propanol was that of triplet **1** at all times after the laser pulse. The fact that triplet **1** is also short-lived in *tert*-butyl alcohol, a much poorer hydrogen donor than 2-propanol,[14] also argues against photoreduction as the source of the short triplet lifetime in these solvents.

The triplet lifetime of **1** is determined by the strength of the hydrogen bond to it.[13] The hydroxyl group of *tert*-butyl alcohol is sterically hindered enough that it cannot form a particularly strong hydrogen bond with triplet **1**. This results in a short triplet lifetime. A similar situation likely pertains for 2-propanol as solvent.

For our purposes it is sufficient to note that the triplet lifetime changes little over the range of alcohol concentrations used in the steady-state experiments (0 to 6 M methanol, 0 to 2 M 2-propanol, 0 to 0.6 M *tert*-butyl alcohol). This is illustrated in Figure 4 which shows how the triplet decay rate varies as a function of water concentration in water:methanol mixtures. A 6 M aqueous solution of methanol corresponds to a water concentration of about 44 M. Clearly there is no significant difference in triplet decay rate between pure water and 44 M water. Similar results were obtained with mixtures of water and 2-propanol or *tert*-butyl alcohol.

Whatever its cause, the short lifetime of triplet **1** in neat propanol and *tert*-butyl alcohol has no consequences for triplet behavior in dilute alcohol solutions at pH 12. Under these conditions the triplet lifetime is determined by the hydroxide concentration.

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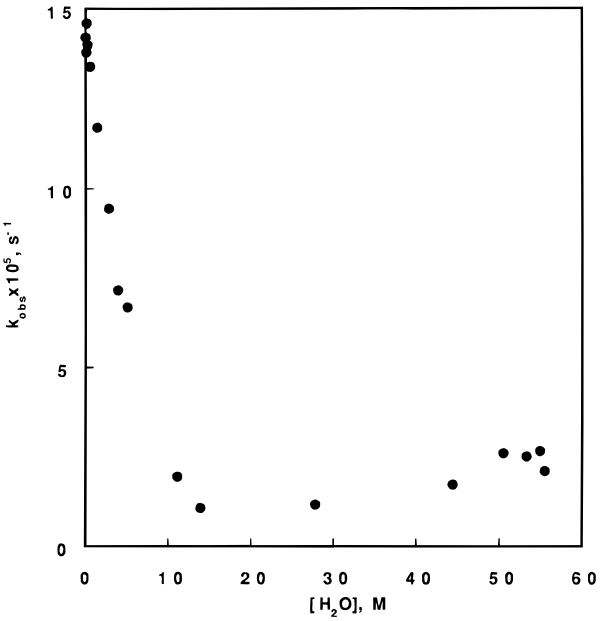

Figure 4. Dependence of 3-nitroanisole triplet decay rate, k_{obs}, on water concentration in mixtures of water and methanol. The anisole concentration was 0.3 mM and the triplet decay monitored at 400 nm.

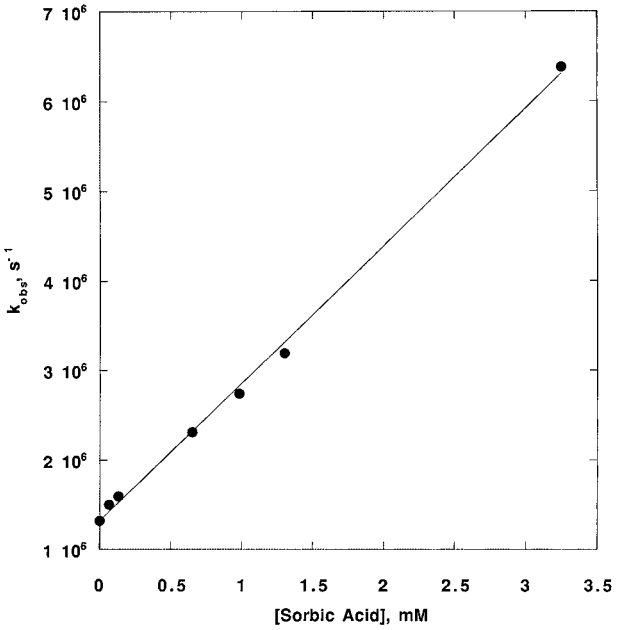

Figure 5. Stern−Volmer plot of sorbic acid quenching of triplet **1** in methanol. The triplet decay was monitored at 400 nm. [**1**] = 0.3 mM.

Table 2. Rate Constants for Quenching of Triplet 1 by Various Substrates

solvent	quencher	k_q, $\times 10^8$ M^{-1} s^{-1}
water	O_2	30
water	sorbic acid	7.5
methanol	sorbic acid	15
1:1 MeOH:H_2O	1,3-cyclohexadiene	16.3
methanol	1,3-cyclohexadiene	50
water	phenol	36.9
water, pH 11.5	phenolate	49.7
1:1 MeOH:H_2O	1,4-cyclohexadiene	1.5
methanol	1,4-cyclohexadiene	1.8
water	MV^{2+}	0.2
water	OH^-	4.1
water	CN^-	1.8
water	NO_2^-	51.3
water, pH 11.5	methanol	0.02[a]
water, pH 11.5	methanol	0.03[b]

[a] By laser flash photolysis. [b] By Stern−Volmer analysis of product yield (3-nitrophenolate formation).

Quenching of the 3-Nitroanisole Triplet. Quenching data are summarized in Table 2. Unless otherwise noted the rate constants were determined by monitoring the triplet decay rate constant, k_{obs}, at 400 nm as a function of quencher concentration and fitting the decay rates to the expression

$$k_{obs} = k_o + k_q[Q]$$

k_o is the triplet decay rate constant in the absence of added quencher, Q, and k_q is the bimolecular rate constant for the quenching process. Figure 5 shows a typical quenching plot.

Oxygen, sorbic acid, and 1,3-cyclohexadiene can be considered to be energy transfer quenchers,[15,16] and in each case they quench **1** without product formation.

Methylviologen (MV^{2+}) is a well-known electron acceptor.[17] It reacts rapidly with triplets to yield the radical cations of methylviologen and of the sensitizer. Based on the monitoring of the triplet decay at 460 nm, MV^{2+} reacts only slowly with **1**. Nonetheless, the absorption spectrum of the $MV^{+\bullet}$ radical cation, with bands at 390 and 600 nm, was readily observed following **1** triplet decay. Further, the $MV^{+\bullet}$ radical cation grew in as the triplet decayed, monitoring at 600 nm. The rate of growth of the $MV^{+\bullet}$ signal matched the rate of triplet decay. Thus we conclude that MV^{2+} quenching is due to electron transfer and that the **1** triplet is at best a poor electron donor. We were unable to observe evidence for the radical cation of **1**, but this is probably due to spectral overlap. The **1** radical cation is expected to have a strong band below 400 nm and only a weak band near 500 nm.[18]

1,4-Cyclohexadiene and phenol are expected to quench triplet **1** via hydrogen abstraction.[19−21] In the latter case this should lead to formation of the readily detectable phenoxy radical.[19] In the former case the quenching process is expected to yield the 1,4-cyclohexadienyl radical. Both of these radicals have distinct spectra.[19,22,23]

Quenching by 1,4-cyclohexadiene occurs in methanol and methanol:water with a rate constant close to 2×10^8 M^{-1} s^{-1} (Table 2). The quenching process leads to formation of a new transient which grows in as the triplet decays (monitoring near 300 nm), is long-lived (half-life ca. 40 μs), and decays via second-order kinetics. The spectrum of this transient is shown in Figure 6 and is consistent with the known spectrum of the 1,4-cyclohexadienyl radical.[21,23] The insert shows the initial decay of the triplet followed by the growth of the radical. The

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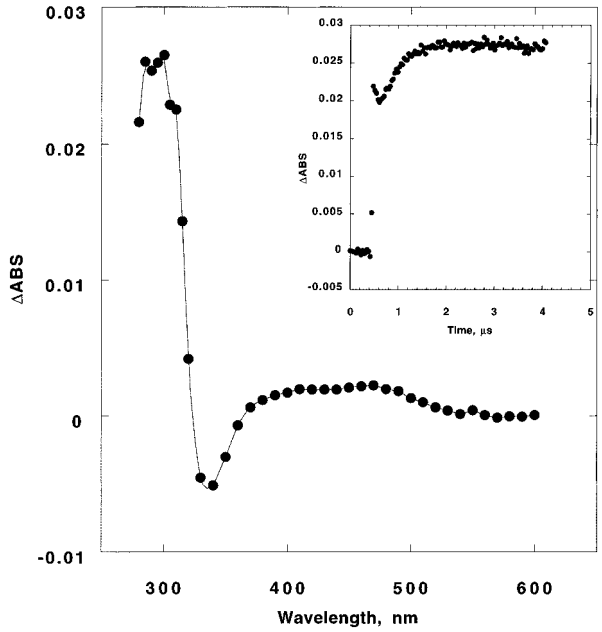

Figure 6. Transient spectrum recorded following 355 nm excitation of 0.3 mM **1** in methanol in the presence of 53 mM 1,4-cyclohexadiene. The spectrum was recorded 3 μs after the laser pulse. The inset shows the initial decay of triplet **1** followed by a growth monitored at 300 nm. The spectrum is probably a mixture of the cyclohexadienyl radical and the neutral **1H**$^{\bullet}$ radical.

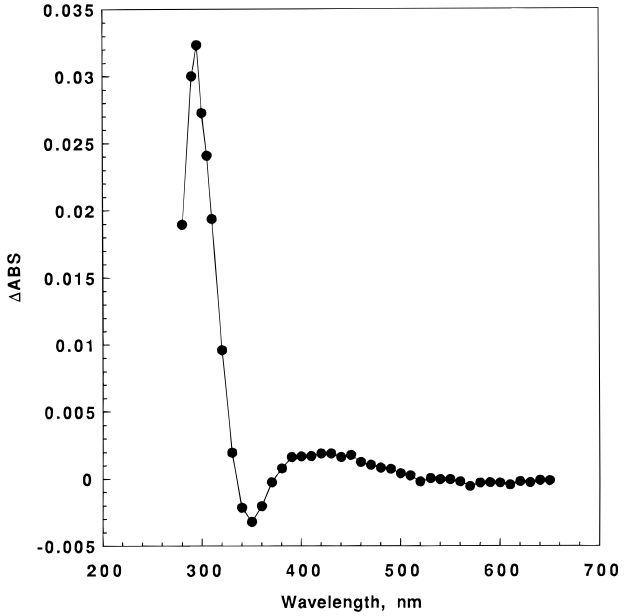

Figure 7. Transient spectrum of the **1** radical anion recorded 56 μs after excitation of an aqueous solution containing 0.3 mM **1** and 20 mM $NaNO_2$.

negative signal near 340 nm occurs because the absorbance of ground state **1** is larger in this wavelength range than that of the transients; as a result bleaching is observed.

There is no conclusive evidence for the formation of the neutral radical, **1H**$^{\bullet}$, expected as a product in the photoreduction of **1** by 1,4-cyclohexadiene. The corresponding neutral radical formed in the photoreduction of 3,5-dinitroanisole has a strong absorption band below 400 nm and a very weak band in the 400 to 500 nm range.[18] Corresponding bands of **1H**$^{\bullet}$ may overlap with the spectrum of the 1,4-cyclohexadienyl radical since the latter has only weak absorptions in the visible region.[21,23] This may also account for the unusually broad UV band in the spectrum of Figure 6.

Phenol quenches triplet **1** at close to the diffusion controlled rate in unbuffered water (pH ca. 6.5 in the presence of 1.5 mM phenol). In this case the rate constant was obtained by monitoring triplet decay at 460 nm, a wavelength where the phenoxy radical does not absorb.[19,22] After triplet decay a typical phenoxy radical spectrum [19,22] was observed, exhibiting sharp peaks at 380 and 400 nm and a stronger absorbance rising to the UV. Phenol was also used as a quencher under basic (pH 11.5) conditions. At this pH the phenol should be completely in the phenolate form ($pK_a = 9.9$ for phenol.[24]) The diffusion-controlled quenching process (monitored at 460 nm) lead to observation of the phenoxy radical spectrum as well as to a weak absorbance extending out to near 500 nm.

The rapid quenching of triplet **1** by $NaNO_2$ lead to formation of a new transient which decayed via second-order kinetics (half-life ca. 100 μs). The spectrum of the new transient is shown in Figure 7. It closely matches that reported for the radical anion of 3,5-dinitroanisole.[18]

It appears that no value for the standard redox potential of **1** in water has been reported due to the irreversibility of single electron reduction of nitrobenzenes in this solvent.[25] Values reported for *m*-methyl, *m*-chloro, and *m*-amino nitrobenzene in aqueous surfactant solutions cover a narrow range between −0.4 and −0.47 V vs NHE[26] (based on the relationship $V_{NHE} = V_{SCE} + 0.24V$[27]). If we assume that the redox potential for **1** will be roughly similar and take the redox potential for the $NO_2^-/NO_2^{\bullet}$ couple in water as 1.03 V vs NHE[28] and the **1** triplet energy as 59.8 kcal/mol,[29] we can apply the Rehm−Weller equation[30] to this system. Assuming the Coulombic term is zero, we find that the electron transfer from nitrite to triplet **1** is strongly exergonic with $\Delta G° < -26$ kcal/mol. Such a large negative value is consistent with a diffusion controlled electron-transfer process. We thus suggest that nitrite quenching of triplet **1** proceeds via an electron-transfer mechanism leading to formation of the **1** radical anion. The fact that the nitro group is so electron deficient may explain why oxygen did not quench the radical anion signal in these experiments.

When hydroxide is present, aqueous solutions of **1** undergo irreversible photoreaction. Transient absorption measured under these conditions shows a residual absorption following decay of the triplet. The spectrum of the residual is shown in Figure 8. A similar spectrum is observed when methanol is present. The shape of this residual spectrum suggests that the long-lived species in basic medium is the photoproduct, 3-nitrophenolate, and is in agreement with previous work.[12]

The location of the short wavelength band of the nitrophenolate spectrum (Figure 8) is slightly different than is observed in a UV−vis spectrophotometer (vide

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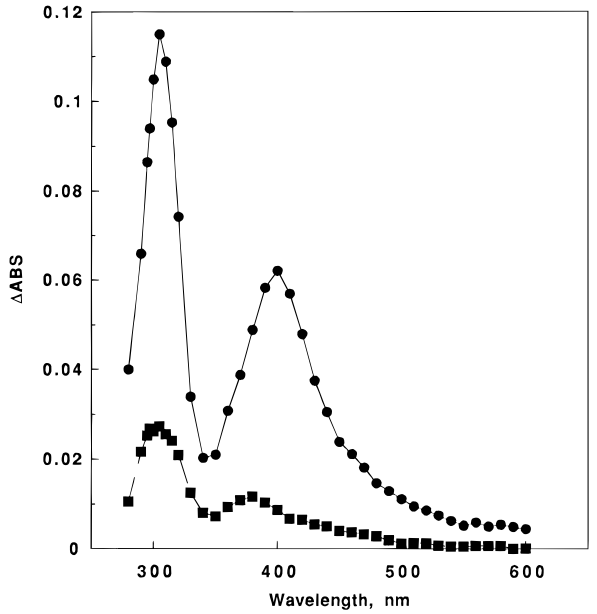

Figure 8. Transient spectra recorded 360 ns (circles) and 7 μs (squares) after 355 nm excitation of 0.4 mM **1** aqueous solution containing 10% methanol and 2.5 mM NaOH.

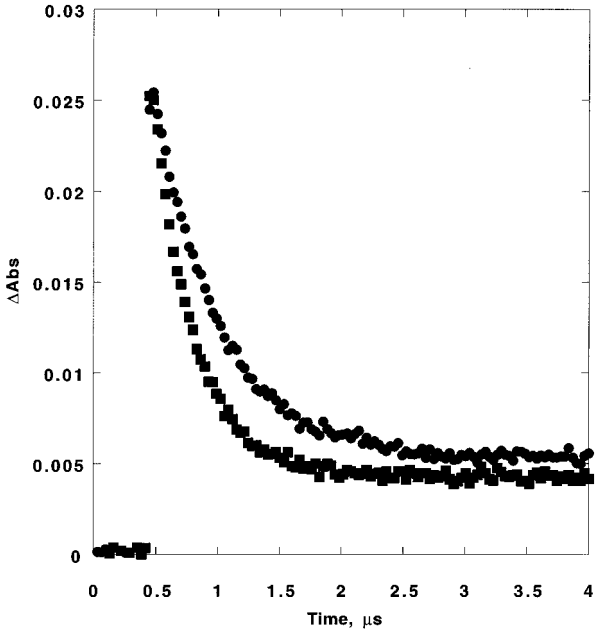

Figure 9. Transient decay traces recorded at 400 nm following 355 nm excitation of 0.3 mM **1** in pH 11.5 phosphate buffer with 0 M (circles) and 5 M (squares) methanol added.

supra). This simply reflects that the spectra of Figure 8 are difference spectra. There is significant spectral overlap between the nitrophenolate and the ground-state absorption spectrum of its precursor, 3-nitroanisole, at and below 300 nm which results in slight distortion of the difference spectrum.

The cyanide anion is also known to act as a nucleophile in the photosubstitution of triplet **1**.[1] The rate constant for triplet quenching by cyanide is included in Table 2 simply by way of comparison with that for hydroxide quenching.

At pH 12 methanol quenches the triplet state of 3-nitroanisole as shown in Figure 9. The rate constant for quenching is $k_{MeOH} = 1.8 \pm 0.1 \times 10^6\ M^{-1}\ s^{-1}$. In the absence of hydroxide the alcohol does not quench triplet anisole at methanol concentrations up to ca. 6 M (see Figure 4).

Under basic conditions, methanol inhibits the formation of 3-nitrophenolate and also quenches the triplet of 3-nitroanisole. The reduction in phenolate formation rate as a function of methanol concentration yields a Stern–Volmer constant $K_{SV} = 0.36 \pm 0.03\ M^{-1}$. In the absence of methanol the lifetime measured for the triplet anisole at pH 12 is 156 ns. The quotient of K_{SV} and the triplet lifetime yields, the rate constant for methanol quenching of the excited-state responsible for the formation of the phenolate; in this case $(2.6 \pm 0.2) \times 10^6\ M^{-1}\ s^{-1}$. This is in reasonable agreement with the directly measured value for methanol quenching of triplet 3-nitroanisole, $k_{MeOH} = (1.8 \pm 0.1) \times 10^6\ M^{-1}\ s^{-1}$. We conclude that methanol inhibits phenolate formation because it quenches triplet 3-nitroanisole at pH 12.

Discussion

The rate constant for oxygen quenching of triplet **1** is near diffusion controlled as expected.[14] By contrast, sorbic acid quenching in water is rather slow. The triplet energies of 2,4-hexadienes are near 60 kcal/mol[15,16] while the reported triplet energy for **1** is 59.8 kcal/mol.[29] The energy transfer from triplet **1** to sorbic acid will be essentially thermoneutral and is thus expected to be significantly below the diffusion limit.[16] The rate constant for this quenching process increases in methanol. This might reflect a destabilization of triplet **1** in this less hydrogen bonding solvent[13] and/or it may simply reflect the fact that diffusion is faster in methanol than water. The results with 1,3-cyclohexadiene ($E_T = 52.3$ kcal/mol[15]) suggest that the increase in rate constant for quenching in methanol is due to an increased rate of diffusion in that solvent, as energy transfer from **1** to 1,3-cyclohexadiene should be rather exothermic in both methanol and water rich solvents.

The transient spectrum shown in Figure 6 supports hydrogen abstraction as the mechanism for quenching of triplet **1** by 1,4-cyclohexadiene. The similarity of the rate constants for the reaction in methanol and in water: methanol indicate that the extent of hydrogen bonding does not strongly influence the ability of **1** to abstract hydrogen.

At first glance the phenol results seem straightforward evidence for direct hydrogen abstraction from phenol by triplet **1**. However, it is interesting to compare the rate constant observed here with that for phenol quenching of ketone triplets in hydrogen bonding solvents.[19] For example, phenol quenches benzophenone triplet with a rate constant of $1.3 \times 10^9\ M^{-1}\ s^{-1}$ in benzene. This is reduced to only 8.0×10^7 in wet acetonitrile.[19] This reduction has been attributed to hydrogen bonding of the phenolic hydroxyl group. Clearly this is not a factor in the interaction of triplet **1** and phenol. Most likely, the initial interaction here involves electron or charge transfer.

Quenching of aromatic ketone triplets by phenolate is a well-known process[31] and proceeds via an electron-transfer mechanism to yield the phenoxy radical and the ketone radical anion. In the case of triplet **1** the phenoxy radical is observed. It decays via complicated kinetics which include a major second-order component and a residual signal at long delay times. In addition to the sharp bands near 380 and 400 nm a weak absorption extending to about 500 nm is observed. We attribute this

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to the **1** radical anion. The spectrum of the 3,5-dinitroanisole radical anion shows a band centered near 400−410 nm and extending to slightly greater than 500 nm.[18]

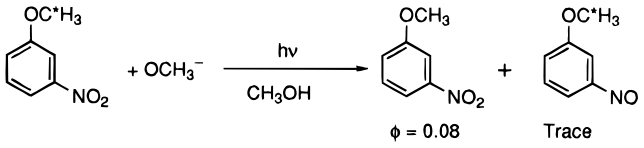
Nitrite quenching seems to lead to formation of the **1** radical anion (Figure 7). Clearly the band in the 400 to 500 nm region is consistent with that observed in the phenolate quenching of triplet **1**.

The question arises as to the nature of the quenching process between methanol and the triplet anisole. One possibility is that methanol simply lowers the hydroxide concentration by dilution. This would tend to lengthen the lifetime, not shorten it. In addition, no reduction in rate of product formation was observed when *tert*-butyl alcohol and 2-propanol were used. Also, this would not explain the formation of the material with the 1.4 min elution time observed in HPLC.

Another possibility is that addition of methanol increases the solution concentration of dissolved oxygen. Great pains were taken to ensure degassing was as complete as possible in all experiments. Further, this effect should also be active if 2-propanol or *tert*-butyl alcohol are added. As indicated previously, neither of these had any effect on the rate of triplet decay at pH 12.

Additional possible interactions of methanol with triplet **1** in basic solution which might lead to an increase in the triplet decay rate are hydrogen abstraction by the triplet from the alcohol or changes in the triplet lifetime due to changes in the hydrogen bonding power of the solvent as methanol is added. Neither of these effects will play a role here as indicated by the results presented in Figure 4.

A likely interaction of methanol with triplet anisole is photoreduction leading to nitroso formation. Photoreduction of nitrobenzenes occurs in 50% aqueous methanol with rather high chemical yields when hydroxide is present but is very inefficient in its absence.[32,33] Photoreduction is also rather efficient in neat alcohols when alkoxide ions are present.[32,33] Furthermore, the following process, where the star refers to isotopically labeled carbon, has been reported to occur with a rate constant of 3.4×10^9 M^{-1} s^{-1}. The products were determined at 0.25 M methoxide.[3,12]



A process like this would be compatible with the data reported here. Small amounts of methoxide formed in the very basic buffer solution would be available as triplet state quenchers leading ultimately to photoreduction products. Yields would be relatively small because of the low methanol concentration (≤6 M) and therefore low (potential) methoxide concentration. For example, on the basis of the Henderson−Hasslebach equation

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{methoxide}]}{[\text{methanol}]}$$

we can estimate the concentration of methoxide in equilibrium with, for example, 4.94 M (the second largest value used in the steady-state experiments) methanol at pH 12. Taking 15.5 as the pK_a of methanol[34] we find that [methoxide] is 1.6 mM. This means that the [OH^-] will remain essentially constant at 0.01 M. That is the main reaction channel will be photohydroxylation. Even so some methoxide does form and it will quench the nitroanisole triplet. The rate constant for hydroxide quenching of triplet 3-nitroanisole is $(4.1 \pm 0.3) \times 10^8$ M^{-1} s^{-1} (Table 2) but for methoxide quenching in methanol it is $k_{\text{methoxide}} = 3.4 \times 10^9$ M^{-1} s^{-1}.[12] Assuming the latter to be solvent independent, we can predict the value of k_{obs}, the rate of triplet decay, at pH 12 and 4.94 M methanol compared to its value at pH 12 without methanol. That is we can estimate the contribution of methoxide to the observed rate of triplet decay. We use the Stern−Volmer expression

$$k_{\text{obs}} = k_o + k_{\text{methoxide}}[\text{methoxide}]$$

where k_o is the rate of triplet decay at pH 12 in the absence of methanol. Its value is 1/156 ns $= 6.4 \times 10^6$ s^{-1}. So the predicted value of k_{obs} at 4.94 M methanol, which corresponds to 1.6 mM methoxide, is 1.18×10^7 s^{-1}. The experimentally obtained value for the same solution is 1.20×10^7 s^{-1}. Thus it seems reasonable to conclude that the observed triplet quenching in strongly basic aqueous solution and the reduction in rate of formation of the nitrophenolate both arise because small amounts of methoxide form, providing an alternate decay channel for the anisole triplet. Methoxide quenching is a reactive process which ultimately leads to stable products as indicated in the literature[32,33] and as observed in our HPLC study. This view also explains why we see no effect of *tert*-butyl alcohol or 2-propanol on the rate of product formation and why no additional products are detected during HPLC of the 2-propanol system. These alcohols are simply too weak acids to form significant yields of their corresponding alkoxides in aqueous solution, even at pH 12. In support of this we note that pK_a for *tert*-butyl alcohol is 19.[24]

The case of TFE is special in this context. Clearly this alcohol is more acidic than methanol, and yet it has no influence on the decay of triplet **1** in basic solution. We explain this by noting that the same feature that makes TFE quite acidic, i.e., the triflurometyl group, also make its alkoxide a poor nucleophile. Simply stated, the negative charge on the TFE anion is stabilized by the triflurometyl group and is thus not particularly reactive.

In conclusion we suggest that the influence of methanol on the rate of the alkaline photolysis of 3-nitroanisole arises from this alcohol's nature as a weak, but not too weak, acid.

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