

ble mercury lines and the 632.8 nm He/Ne laser line (diffracted from rough paper to destroy phase coherence). With this wide slit opening, it was necessary to use Corning colored glass filters in front of the entrance slit in order to reduce background due to scattered and rediffracted light; 2-62 filter for dimol emission and 7-59 filter for formaldehyde emission.

- (15) We have denoted the initially formed addition product of  $O_2(^1\Delta)$  plus ethylene as an *adduct*, and prefer this term to the more constraining terms transition state and activated complex because the latter terms carry implications about the local shape of the potential energy surface. In our earlier study of the reaction of  $O_2(^1\Delta)$  with ethyl vinyl ether (ref 4) we estimated that the initially formed dioxetane adduct had 47 kcal/mol of excess vibrational energy (Figure 2, ref 4) and that the lifetime of this species was less than  $10^{-7}$  s. The present system,  $O_2(^1\Delta)$  plus ethylene has very similar estimated energy levels, and we envision very similar behavior.
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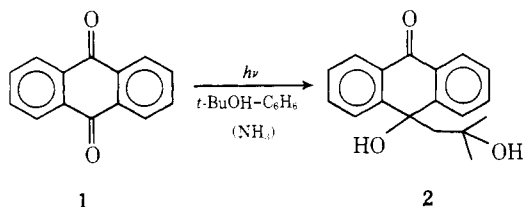
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### Ammonia-Catalyzed Photoaddition of *tert*-Butyl Alcohol to 9,10-Anthraquinone. Electron Transfer Catalysis of a Photochemical Hydrogen Abstraction Reaction<sup>1</sup>

Sir:

We have found that irradiation of 9,10-anthraquinone (**1**) with the reluctant hydrogen donor *tert*-butyl alcohol effects addition of a C-H bond of the alcohol to a carbonyl group of the quinone, and that the photoaddition is strongly promoted by ammonia. Product analyses and kinetic evidence show that ammonia acts as a catalyst by a novel electron-hole transfer process analogous to that reported previously for the nitrobenzene-hydrogen chloride-2-propanol system.<sup>2</sup>

During a survey of systems for aromatic photosubstitution reactions which involve intermediate exciplexes or geminate radicals,<sup>3</sup> we irradiated 1- and 2-chloro-9,10-anthraquinone in *tert*-butyl alcohol-benzene containing aqueous ammonia (0.6 M). The photosubstitution products, 1- and 2-amino-9,10-anthraquinone, were formed in low yields (<10%), but the major product (50-80%) in each case was a 1:1 adduct of the quinone and *tert*-butyl alcohol. Irradiation of **1** ( $4.8 \times 10^{-3}$  M) in *tert*-butyl alcohol-benzene-29% aqueous  $NH_3$  (20:4:1, v/v; 0.6 M  $NH_3$ ) at 45° under  $N_2$  for 75 min using a 450-W Hg lamp (Pyrex filter) caused nearly complete loss of anthraquinone absorbance. The sole product isolated by chromatography on silica gel was 10-hydroxy-10-(2-hydroxy-2-methylpropyl)anthrone (**2**, 74%).



The structure of **2** is based on spectral evidence and elemental analysis.<sup>4</sup> The photoreaction of **1** in *tert*-butyl alcohol-benzene (4:1, v/v) containing no ammonia or water proceeded much less rapidly, giving **2** in 29% yield.<sup>5</sup>

Quantum yields for the disappearance of **1** in various solutions containing *tert*-butyl alcohol are shown in Table I. That for each solution examined, the reaction of **1** and *tert*-butyl alcohol giving **2** occurs cleanly at low photochemical conversions is indicated by our observation for all cases of

Table I. Quantum Yields of the Disappearance of **1** at 313 nm

<b>1</b> , M	Solvent (v/v)	$\Phi^a$
$1.2 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> (93:7)	0.008
$2.5 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> (80:20)	0.0058
$2.5 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> (80:20), 0.6 M $NH_3$	0.10
$2.5 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O (73.6:20:6.4)	0.0044
$2.5 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> -pyridine (75:20:5) <sup>b</sup>	0.005
$2.5 \times 10^{-3}$	<i>t</i> -BuOH-C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O (73.6:20:6.4), 0.97 M $NH_3$	0.16

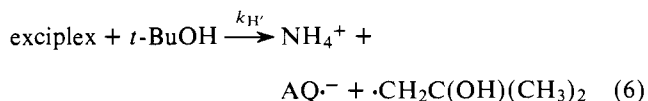
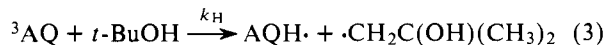
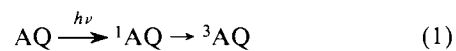
<sup>a</sup> Solutions were degassed to below  $2 \times 10^{-3}$  mm and reactions were carried to ~10% conversion. Disappearance of **1** was monitored at 330 and 335 nm. <sup>b</sup> 0.6 M pyridine.

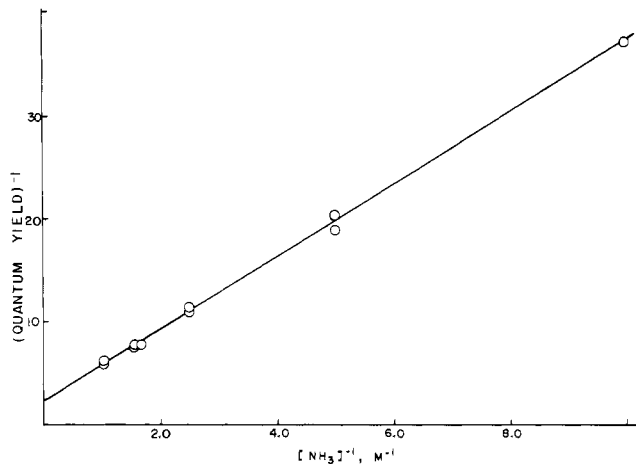
an isosbestic point at 309 nm.<sup>6</sup> The data in Table I show that water, benzene, and pyridine do not enter into the photochemistry, each causing only a slight reduction of the quantum yield attributable to dilution of the *tert*-butyl alcohol. Ammonia, used for convenience in the form of aqueous solutions, causes a striking enhancement of the quantum efficiency. That ammonia, not water nor the combination of ammonia and water, is responsible for this effect is shown by the large enhancement of efficiency caused by dry ammonia (0.6 M) in anhydrous *tert*-butyl alcohol-benzene (Table I).

Because the catalytic effect of ammonia was substantial and appeared novel, the system was an attractive one for mechanistic study. In particular, we wished to know whether ammonia participated in a primary photochemical step, or intervened on the pathway leading to **2** at a secondary stage, by altering the partitioning of an intermediate capable of decay to starting material and to **2**.

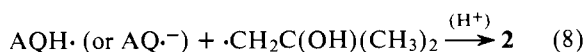
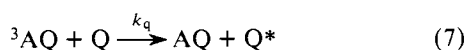
As shown in Figure 1, the plot of  $\Phi^{-1}$  vs.  $[NH_3]^{-1}$  is linear for the photoreaction of anthraquinone ( $2.5 \times 10^{-3}$  M) in *tert*-butyl alcohol-benzene-water (73.6:20:6.4, v/v) containing ammonia (0.1-0.97 M). The extrapolation to infinite ammonia concentration indicates a limiting quantum yield of 0.43. Stern-Volmer plots for quenching by piperylene of the reaction in *tert*-butyl alcohol-benzene and of the reaction in *tert*-butyl alcohol-benzene-water (73.6:20:6.4, v/v) containing 0.64 M ammonia were also obtained.<sup>7</sup> The slopes of these plots, 8810 and 773 (einstein mol<sup>-1</sup>)/M, respectively, provide unequivocal evidence that ammonia participates in the primary photochemistry and that the rate of its interaction with excited anthraquinone is substantially larger than that of *tert*-butyl alcohol under these conditions of concentration.

That water and pyridine have no effect on the photoreaction renders improbable catalytic mechanisms for ammonia based on hydrogen bonding effects or prototropic base catalysis. The mechanism shown below accounts quantitatively for all of our findings on this system.





**Figure 1.** Quantum yield at 313 nm for anthraquinone disappearance in *tert*-butyl alcohol–benzene–water (73.6:20:6.4) containing ammonia.



Following the Stern–Volmer formalism, eq 9 may be derived where  $f$  represents the fraction of exciplex species giving  $\mathbf{2}$ , i.e.,  $f = k_{\text{H}}[t\text{-BuOH}]/(k_{\text{r}} + k_{\text{H}}[t\text{-BuOH}])$ .

$$\frac{1}{\Phi} = \left( \frac{1}{\Phi_{\text{isc}}} \right) \left( \frac{k_{\text{H}}[t\text{-BuOH}] + k_{\text{e}}[\text{NH}_3]}{k_{\text{H}}[t\text{-BuOH}] + fk_{\text{e}}[\text{NH}_3]} + \frac{k_{\text{d}}}{k_{\text{H}}[t\text{-BuOH}] + fk_{\text{e}}[\text{NH}_3]} + \frac{k_{\text{q}}[\text{Q}]}{k_{\text{H}}[t\text{-BuOH}] + fk_{\text{e}}[\text{NH}_3]} \right) \quad (9)$$

For an ammonia concentration of 0.64 M, the value of  $k_{\text{H}}[t\text{-BuOH}]$  is small compared to that of  $k_{\text{e}}[\text{NH}_3]$ , and the expression may be simplified to eq 10.

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{isc}}f} \left( 1 + \frac{k_{\text{d}}}{k_{\text{e}}[\text{NH}_3]} + \frac{k_{\text{q}}[\text{Q}]}{k_{\text{e}}[\text{NH}_3]} \right) \quad (10)$$

Carlson and Hercules have reported<sup>8</sup> that photoexcitation of anthraquinone populates the  ${}^3n,\pi^*$  state with nearly unit efficiency, and that a small fraction ( $10^{-4}$ ) of the excited molecules exists in a  ${}^1n,\pi^*$  state in thermal equilibrium with the triplet. In our system we believe the reactions occur mainly from the triplet since appreciable reaction with ammonia from the singlet would require a rate constant in excess of the diffusion rate constant (*vide infra*). Thus, taking  $\Phi_{\text{isc}} = 1.0$ ,  $f = 0.43$  (from Figure 1), and  $k_{\text{q}}$  equal to the diffusion rate constant,  $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , (calculated from the measured viscosity of the solvent at the reaction temperature,  $31^\circ$ ), we calculate from the Stern–Volmer slope for 0.64 M  $\text{NH}_3$  that  $k_{\text{e}} = 2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . From the Stern–Volmer slope for the reaction in the absence of ammonia and  $k_{\text{q}} = 5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the value of  $k_{\text{H}}$  is  $7.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The values of  $k_{\text{e}}$  and  $k_{\text{H}}$  are reasonable judging from rate constants obtained in analogous systems. Electron transfer from 2-aminobutane to  ${}^3n,\pi^*$  benzophenone is ten times faster than  $k_{\text{e}}$ ,<sup>9</sup> and hydrogen abstraction from *tert*-butyl alcohol by  ${}^3n,\pi^*$  pyruvic acid is four times faster than  $k_{\text{H}}$ .<sup>10</sup>

The evidence leaves obscure an important detail of the reaction path from the exciplex to  $\mathbf{2}$ . Since alkylammonium radicals are very reactive in abstraction of unactivated alkyl hydrogens,<sup>11</sup> we would expect the less stable radical  $\text{H}_3\text{N}^{\cdot+}$  to be reactive toward the C–H bonds of *tert*-butyl alcohol.

Equation 6 shows hydrogen abstraction from the alcohol by the aminium radical of the exciplex. This represents a bimolecular reaction of an exciplex, a reaction type which may be widespread but which has received little attention.<sup>12</sup> Whereas in the nitrobenzene–hydrogen chloride–2-propanol system,<sup>2,13</sup> evidence was obtained which showed that the exciplex  $[\text{PhNO}_2\cdot^-\text{Cl}\cdot]$  participated in bimolecular reactions involving protonation and hydrogen abstraction, with the present evidence we cannot exclude the possibility that exciplex dissociation precedes the hydrogen abstraction.

The evidence for electron transfer in the present system supports the mechanism suggested for photosubstitution by ammonia on 1- and 2-anthraquinone sulfonates,<sup>3</sup> and may be relevant in other instances of nucleophilic aromatic photosubstitution.<sup>14</sup> Research is in progress to determine the scope of electron transfer catalysis of photochemical hydrogen abstractions and to examine with this probe the role of exciplexes in aromatic photosubstitution reactions.

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## References and Notes

- (1) This work was reported at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 10, 1975, Abstract No. ORGN-108.
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- (4) The analytical sample (mp  $146.5\text{--}147.5^\circ$ ), obtained by several recrystallizations from EtOH–H<sub>2</sub>O and benzene–hexane, showed the following characteristics: mass,  $m/e$  (rel intensity) 282 (<1), 264 (13.5), 209 (100), 206 (61), 178 (28), 152 (19), 56 (17), 43 (35); NMR (acetone- $d_6$ )  $\delta$  0.73 (s, 6 H), 2.22 (s, 2 H), 3.77 (s, 1 H), 5.97 (s, 1 H), 7.3–8.15 (m, 8 H); ir (KBr) 3490, 3350  $\text{cm}^{-1}$  (OH str), 1665  $\text{cm}^{-1}$  (C=O str). Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.57; H, 6.43. Found: C, 76.26; H, 6.34.
- (5) We have found that benzophenone undergoes photoreactions analogous to those of  $\mathbf{1}$  which are also made more efficient by  $\text{NH}_3$ .
- (6) The isosbestic point at 309 nm was also observed for each of the preparative photoreactions, but deteriorated at higher conversions for the reaction in (anhydrous) *tert*-butyl alcohol–benzene (4:1). This indicates that the low yield of  $\mathbf{2}$  from the latter reaction may be due to a secondary photoreaction of  $\mathbf{2}$ .
- (7) Reactions were monitored by the loss of anthraquinone absorbance at 335 and 330 nm of diluted, aerated reaction solutions. 9,10-Dihydroxyanthracene ( $\sim 30\%$ ) was formed in the direct reaction, and the anthraquinone anion radical ( $\sim 10\%$ ) was formed with ammonia present. These reverted quantitatively to anthraquinone on aeration, and quantum yields are corrected accordingly. The Stern–Volmer plot for the direct reaction appeared to level off above 0.01 M piperylene; this may stem from some secondary photochemistry of the system or from an unquenched singlet reaction.
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