in order to quench 10% of the acetone phosphorescence the biacetyl concentration need be only of the order of 10^{-5} M. Since the average emission intensity at 410 nm does not decrease during the period that biacetyl fluctuations are being observed, the acetone can be thought of as a reservoir for the production of biacetyl.[14]

The feedback or autocatalytic step, necessary for oscillations, is not known, although the quenching of acetone by biacetyl might be thought of as feedback. The possible reactions involve both free radicals and hydrogen abstraction from acetone and biacetyl. The acetonitrile probably does not enter into the reaction mechanism, since Porter et al. did not observe any incorporation of deuterium into acetone when acetone was irradiated in CD_3CN.[9]

Data for photolyzed acetone and for photolyzed biacetyl are available both in the gas phase[15,16] and in solution,[8,17-20] but before a mechanism can be proposed with any confidence work must be done to identify the photoproducts, in acetonitrile, after only a small amount of photoreaction.

References and Notes

(1) R. M. Noyes and R. J. Field, *Annu. Rev. Phys. Chem.*, **25**, 95 (1974).
(2) A. T. Winfree, *Sci. Am.*, **230** (6), 82 (1974).
(3) G. Nicolis and J. Portnow, *Chem. Rev.*, **73**, 365 (1973).
(4) H. Degn, *J. Chem. Educ.*, **49**, 302 (1972).
(5) J. Higgins, *Ind. Eng. Chem.*, **59** (5), 19 (1967).
(6) N. J. Turro, H.-C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **95**, 6468 (1973).
(7) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).
(8) D. B. Peterson and G. J. Mains, *J. Am. Chem. Soc.*, 81, 3510 (1959).
(9) G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1462 (1973).
(10) N. J. Turro, "Molecular Photochemistry", W.A. Benjamin, New York, N.Y., 1965, pp 115–119.
(11) D. I. Schuster, G. C. Barile, and K. Liu, *J. Am. Chem. Soc.*, **97**, 4441 (1975).
(12) A. Nitzan and J. Ross, *J. Chem. Phys.*, **59**, 241 (1973).
(13) A. Nitzan, P. Ortoleva, and J. Ross, *J. Chem. Phys.*, **60**, 3134 (1974).
(14) As pointed out by one of the referees, the system does not have to be "open" in the sense of taking reactants from a reservoir. Reference 12 contains an example of a model system in which light and heat flow replace mass flow.
(15) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).
(16) J. Heicklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 81, 3858 (1959).
(17) B. M. Monroe, *Adv. Photochem.*, 8, 77 (1971).
(18) W. G. Bentrude and K. R. Darnall, *Chem. Commun.*, 810 (1968).
(19) S. A. Greenberg and L. S. Forster, *J. Am. Chem. Soc.*, **83**, 4339 (1961).
(20) T. Bérces in "Comprehensive Chemical Kinetics", Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N.Y., 1972, pp 234–380.

Thomas L. Nemzek, J. E. Guillet*
Department of Chemistry, University of Toronto
Toronto, Ontario, Canada M5S 1A1

Received August 28, 1975

Gas Phase Dioxetane Chemistry. Formaldehyde (A → X) Chemiluminescence from the Reaction of $O_2(^1\Delta_g)$ with Ethylene

Sir:

The reactions of $O_2(^1\Delta_g)$ with olefins have been studied extensively in recent years.[1,2] Various substituted monoolefins which are incapable of undergoing the "ene" reaction (yielding an allylic hydroperoxide) have been shown to produce 1,2-dioxetanes or their expected fragmentation products, upon reaction with $O_2(^1\Delta_g)$.[1e-g,2] It has recently been noted that,[3] "the reaction of singlet oxygen with ethylene, although not yet experimentally observed, is of special interest because it provides the simplest example of a 1,2-cycloaddition of oxygen with no competing side reactions." We report the observation of formaldehyde (A $^1A_2 \to$ X $^1A_1$) chemiluminescence from the gas phase reaction of ethylene with $O_2(^1\Delta)$. No other product emissions were observed, and the formaldehyde emission intensity was found to have a first-order dependence on the concentrations of both $O_2(^1\Delta)$ and ethylene.

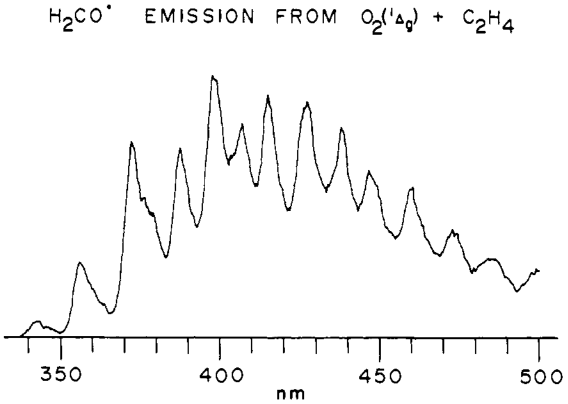


Figure 1. Formaldehyde (A–X) emission spectrum from the reaction of $O_2(^1\Delta_g)$ with ethylene. Experimental conditions: P_{total} = 4 Torr, T = 650 K, $[C_2H_4] \approx [O_2(^1\Delta_g)] \approx 2 \times 10^{15}$ molecules/cm^3; spectrometer conditions: spectral slit width = 2 nm, grating of 2360 lines/mm and blazed at 300 nm, peak intensity ≈500 counts/s, scan speed = 12.5 nm/min, time constant = 3 s.

We have previously observed formaldehyde chemiluminescence from the gas phase reactions of $O_2(^1\Delta)$ with methyl, ethyl, and *n*-butyl vinyl ethers.[4,5] Both previous and present experiments were performed at pressures of 1–10 Torr and reactor residence times of <0.5 s, conditions which minimize the effects of quenching and energy transfer processes hence allowing the observation of chemiluminescence from the primary excited products.

The experimental techniques and apparatus used for this work were the same as previously described,[4] with the following minor changes. Radiation emitted from a heated Pyrex flow reactor of 30 cm path length (viewed axially) was focused through a quartz window into a ¼ m f/3.5 grating spectrometer. The detector was an S-5 photomultiplier operated at −78 °C, and single photon counting was used, as before.

The chemiluminescence spectrum shown in Figure 1 consists solely of formaldehyde (A $^1A_2 \to$ X $^1A_1$) emission, and is very similar to formaldehyde emission spectra previously observed in this laboratory.[4-6] The small hot band peaking at 343 nm is relatively ca. three times more intense than previously observed for the vinyl ether reactions. The most satisfactory assignment for this band is the vibrational transition 4_0^3 within the electronic ($^1A_2 \to {}^1A_1$) transition[7,8] (ν_4 is the out-of-plane bending vibration). Excitation in ν_4' which has B_1 symmetry, allows the electronically forbidden ($^1A_2 \to {}^1A_1$) transition to become vibronically allowed and to borrow intensity from the electronically allowed (B $^1B_2 \to$ X $^1A_1$) Rydberg transition.[8] Furthermore, it is to be expected that the initially formed excited product arising from dioxetane fragmentation will have excitation in ν_4'. This is because a rapid fragmentation (see discussion below) will be governed by essentially Franck-Condon considerations[9] and the principal difference between the geometry of the free H_2CO^* ($^1A_2$) and the H_2CO group in dioxetane is in the out-of-plane bending angle.[8,12]

While the observation of formaldehyde emission in the reaction of ethylene with $O_2(^1\Delta)$ is convincing evidence for the presence of the unobserved (directly) dioxetane adduct,[15] further support for our mechanism comes from the first-order test plots shown in Figure 2. The data for Figure 2 were obtained by monitoring the oxygen dimol emission at

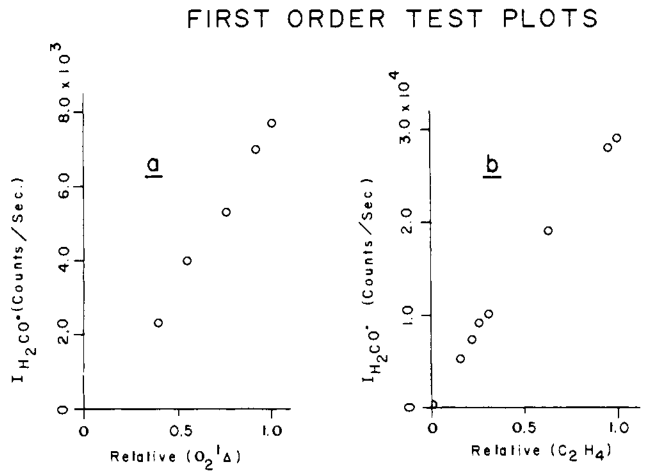


Figure 2. First-order test plots for the reaction of $O_2(^1\Delta_g)$ with ethylene at P_{total} = 4 Torr (nominal), T = 605 K. (a) Dependence of H_2CO^* emission intensity on relative $[O_2(^1\Delta_g)]$ at constant $[C_2H_4]$ = 3.1×10^{15} molecules/cm^3. Relative $[O_2(^1\Delta_g)] = 1.0$ corresponds to 2.3×10^{15} molecules/cm^3. Variation of $[O_2(^1\Delta_g)]$ was accomplished by variation of the microwave discharge power. (b) dependence of H_2CO^* emission intensity, normalized for $[O_2(^1\Delta_g)]$, upon $[C_2H_4]$. Relative $[C_2H_4] = 1.0$ corresponds to 1.6×10^{16} molecules/cm^3. Variation of $[C_2H_4]$ was accomplished with a calibrated metering system. For a, relative error of each point is ca. 10% and is more severe at low power levels where it is difficult to maintain a stable discharge. For 2b, relative error is ca. 5%.

634 nm with an effective spectral slit width of 25 nm, and the formaldehyde (A → X) emission at 405 nm with a 25-nm spectral slit width.[14] The dimol emission intensity (due to the cooperative transition $2O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g) + h\nu$ (634 nm)) was assumed to be proportional to the square of the $O_2(^1\Delta)$ concentration,[10] and the ethylene concentration was calculated from the measured ethylene flow and total flow. This experiment was performed at several temperatures with the same result.

The temperature dependence of the formaldehyde emission was measured over the range T = 500-650 K. The individual intensity readings were normalized for the concentrations of each reactant where the requisite concentrations were determined as described above, and the activation energy was found to be 21.0 ± 1.3 kcal/mol. Given the thermochemistry of the overall reaction

$$C_2H_4 + O_2(^1\Delta_g) \rightarrow 2H_2CO \qquad \Delta H = -90.5 \text{ kcal/mol}$$

and the observed activation barrier, we estimate that the initially formed dioxetane lies ca. 112 kcal/mol above the ground state products. The heat of formation of 1,2-dioxetane has been estimated[11] and places the ground state vibrationally cold dioxetane 55 kcal/mol above the ground state products. Thus there are ca. 57 kcal/mol of excess vibrational energy in the initially formed dioxetane and 31 kcal/mol in excess of the threshold for formation of the products,[15] $H_2CO^* + H_2CO$ ($E(H_2CO^*\ ^1A_2)$ = 81 kcal/mol). This is very similar to the thermochemistry of the ethyl vinyl ether plus $O_2(^1\Delta)$ system.[4]

In our previous studies of the reactions of $O_2(^1\Delta)$ with vinyl ethers, we showed experimental evidence in support of a two-step mechanism involving formation of a vibrationally excited (chemically activated) dioxetane followed by rapid fragmentation, giving the products H_2CO^* plus HCOOR, on a time scale faster than the mean time between collisions which was ca. 10^{-7} s.[4,5] The lifetime of the dioxetane formed from the ethylene reaction should be even less than for the ethyl vinyl ether reaction because in the latter case, there are more molecular vibrations to share the excess energy, thus decreasing the probability of concentrating this energy in the reaction coordinate. The experimental observation of a greater population in the formaldehyde hot band in the case of ethylene supports this view.

The observation that the H_2CO^* chemiluminescence intensity has a first-order dependence on both $O_2(^1\Delta)$ and ethylene concentrations proves that the transition state for the process which is rate limiting enroute to H_2CO^* ($^1A_2$) is a 1:1 adduct of $O_2(^1\Delta)$ and ethylene.[15] This fact, together with the lack of alternative reactive paths for $O_2(^1\Delta)$ plus ethylene provide compelling evidence that the transition state preceding the formation of H_2CO^* ($^1A_2$) is dioxetane. We believe that the two transition states, mentioned above, are the same, namely, vibrationally excited dioxetane.

These experiments provide a highly significant addition to the field of dioxetane chemistry because they establish that (a) it is not necessary that an olefin be substituted in order that a dioxetane be formed from reaction with $O_2(^1\Delta)$, and (b) the simplest 1,2-dioxetane[13] has at least a transient existence in the gas phase.

References and Notes

(1) See the following and references therein: (a) R. D. Ashford and E. A. Ogryzlo, *J. Am. Chem. Soc.*, **97**, 3604 (1975); (b) R. E. Hule and J. T. Herron, *Int. J. Chem. Kinet.*, **5**, 197 (1973); (c) "International Conference on Singlet Molecular Oxygen and Its Role in Environmental Sciences", Oct 15, 1970; published by, *Ann. N.Y. Acad. Sci.*, **171**, 1–302 (1970); (d) Proceedings of the International Oxidation Symposium, San Francisco, Calif., Aug 28–Sept 1, 1967, published in *Adv. Chem. Ser.*, **No. 77**, 78–169 (1970); (e) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (f) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); (g) W. Adam, *Chem.-Ztg.*, **99**, 142 (1975).

(2) (a) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. Y. Acad. Sci.*, **171**, 79 (1970); (b) D. R. Kearns, *J. Am. Chem. Soc.*, **91**, 6554 (1969); (c) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972); (d) P. D. Bartlett and M. S. Ho, *J. Am. Chem. Soc.*, **96**, 627 (1974).

(3) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975).

(4) D. J. Bogan, R. S. Sheinson, R. G. Gann, and F. W. Williams, *J. Am. Chem. Soc.*, **97**, 2560 (1975).

(5) (a) D. J. Bogan, R. S. Sheinson, and F. W. Williams, paper F-9, VIII International Conference on Photochemistry, Edmonton, Canada, Aug 8, 1975; an abstract including spectra will be published in *J. Photochem.*; (b) D. J. Bogan, R. S. Sheinson, and F. W. Williams, Code 6180, Naval Research Laboratory, Wash., D.C. 20375, to be submitted for publication; (c) the spectrum, published in ref 4, was obtained with a different photomultiplier and grating than the spectrum shown as Figure 1. The spectra of ref 5a are directly comparable to Figure 1.

(6) R. S. Sheinson and F. W. Williams, *Combust. Flame*, **21**, 221 (1973).

(7) The formaldehyde (A $^1A_2 \rightarrow$ X $^1A_1$) transition is complicated by inversion doubling in the nonplanar upper state. The upper state levels having odd v in ν_4' represent the upper components of the inversion doubled manifold and have $^1B_2$ vibronic symmetry, while the even v in ν_4' levels represent the lower components and have $^1A_2$ vibronic symmetry (see ref 8 for discussion). Therefore the transition 4_0^1 within $^1A_2 \rightarrow {}^1A_1$ originates from the *ground* vibrational state of the $^1B_2$ vibronic manifold and the transition 4_0^3 originates from the *first excited* vibrational state of the $^1B_2$ vibronic manifold. Thus our assignment of the 343-nm hot hand is physically reasonable. The $^1A_2$ (4_0^3) $\rightarrow$ $^1A_1$ transition lies at 343.22 nm (ref 8b). Other possible assignments are $^1A_2$ ($4_0^0\ 2_0^1$) $\rightarrow$ $^1A_1$ and $^1A_2$ ($4_1^0\ 2_0^2$) $\rightarrow$ $^1A_1$ which were observed by J. R. Henderson and M. Muramoto, *J. Chem. Phys.*, **43**, 1215 (1965), at 340.51 and 340.65 nm, respectively. We believe that the latter two assignments are implausible, based upon inspection of the band shape and position, and we assign the hot band transition to $^1A_2$ (4_0^3) $\rightarrow$ $^1A_1$, exclusively.

(8) (a) G. W. King, "Spectroscopy and Molecular Structure", Holt, Rinehart and Winston, New York, N.Y., 1964, pp 424–431; (b) D. C. Moule and A. D. Walsh, *Chem. Rev.*, **75**, 67 (1975). (c) The out-of-plane angle of formaldehyde $^1A_2$ is 33.6° (Table XI, ref 8b) and the out-of-plane angle of the tetrahedral carbon is 54.7°. The precise geometry of the H_2CO group in dioxetane is not known; however, a CNDO/2 minimum energy geometry gives the out-of-plane angle as 65° (G. Barnett, *Can. J. Chem.*, **52**, 3837 (1974)).

(9) (a) M. J. Berry, *Chem. Phys. Lett.*, **29**, 329 (1974); (b) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969).

(10) L. W. Bader and E. A. Ogryzlo, *Discuss. Faraday Soc.*, **37**, 46 (1964).

(11) H. E. O'Neal and W. H. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 1970.

(12) A more detailed discussion of the reaction dynamics, as deduced from reactant and product vibronic states, will be published, see (a) Y. N. Chiu, *J. Chem. Phys.*, in press; (b) Y. N. Chiu, D. J. Bogan, and R. S. Sheinson, to be submitted.

(13) To our knowledge, no attempts to synthesize 1,2-dioxetane, either successful or unsuccessful, have been reported in the open literature.

(14) The ¼ m spectrometer has removable knife type slits and for these experiments they were removed, leaving a geometrical slit opening of 11 mm. The spectral slit widths were then determined by scanning the visi-

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.

(16) National Research Council Resident Research Associate.

Denis J. Bogan,*[16] Ronald S. Sheinson, Frederick W. Williams

Chemical Dynamics Branch, Code 6180
Naval Research Laboratory
Washington, D.C. 20375

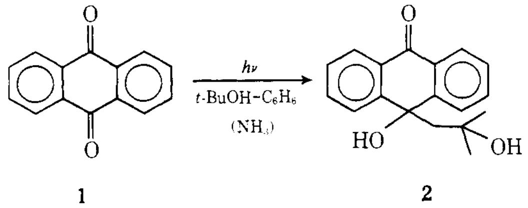
Received October 3, 1975

Ammonia-Catalyzed Photoaddition of *tert*-Butyl Alcohol to 9,10-Anthraquinone. Electron Transfer Catalysis of a Photochemical Hydrogen Abstraction Reaction[1]

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.[2]

During a survey of systems for aromatic photosubstitution reactions which involve intermediate exciplexes or geminate radicals,[3] 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** (4.8×10^{-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%).



1 2

The structure of **2** is based on spectral evidence and elemental analysis.[4] 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.[5]

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 an isosbestic point at 309 nm.[6] 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).

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

1, M	Solvent (v/v)	Φ^a
1.2×10^{-3}	t-BuOH–C_6H_6 (93:7)	0.008
2.5×10^{-3}	t-BuOH–C_6H_6 (80:20)	0.0058
2.5×10^{-3}	t-BuOH–C_6H_6 (80:20), 0.6 M NH_3	0.10
2.5×10^{-3}	t-BuOH–C_6H_6–H_2O (73.6:20:6.4)	0.0044
2.5×10^{-3}	t-BuOH–C_6H_6–pyridine (75:20:5)[b]	0.005
2.5×10^{-3}	t-BuOH–C_6H_6–H_2O (73.6:20:6.4), 0.97 M NH_3	0.16

[a] Solutions were degassed to below 2×10^{-3} mm and reactions were carried to ~10% conversion. Disappearance of **1** was monitored at 330 and 335 nm. [b] 0.6 M pyridine.

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 Φ^{-1} vs. $[NH_3]^{-1}$ is linear for the photoreaction of anthraquinone (2.5×10^{-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.[7] The slopes of these plots, 8810 and 773 (einstein mol^{-1})/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.

$$\mathrm{AQ} \xrightarrow{h\nu} {}^1\mathrm{AQ} \rightarrow {}^3\mathrm{AQ} \qquad (1)$$

$$^3\mathrm{AQ} \xrightarrow{k_d} \mathrm{AQ} \qquad (2)$$

$$^3\mathrm{AQ} + t\text{-BuOH} \xrightarrow{k_H} \mathrm{AQH}\cdot + \cdot\mathrm{CH_2C(OH)(CH_3)_2} \qquad (3)$$

$$^3\mathrm{AQ} + \mathrm{NH_3} \xrightarrow{k_e} [\mathrm{AQ}\cdot^- \ \mathrm{NH_3}\cdot^+] \text{ (exciplex)} \qquad (4)$$

$$\text{exciplex} \xrightarrow{k_r} \mathrm{AQ} + \mathrm{NH_3} \qquad (5)$$

$$\text{exciplex} + t\text{-BuOH} \xrightarrow{k_{H'}} \mathrm{NH_4}^+ + \mathrm{AQ}\cdot^- + \cdot\mathrm{CH_2C(OH)(CH_3)_2} \qquad (6)$$