mize solution mixing and unwanted irradiation (even exposure to room illumination for some time can lead to appreciable photoreaction). The quantum yields of protonated product were calculated from the equation below, which includes an approximate correction for the change in the amount of light absorbed by the substrate due to product formation (flux = 6.35 × 10^{-9} eins/cm^2 s at 320 nm). The following symbols were used: D_0, initial optical density of solution; D_t, optical density at time t; D optical density of protonated product after complete conversion; c_{1M}, initial concentration of *N*-alkyl-ANS derivative; v, irradiated volume (see Figure 4); I_0, incident light intensity on area of irradiated volume facing light source; ϵ_{1M}, absorption coefficient for **1M**). All experiments were carried out at 320 nm except for those involving wavelength dependence.

$$\phi_{\mathrm{H}} = \frac{\text{moles of A produced}}{\text{einsteins of light absorbed}}$$

$$= \frac{\dfrac{D_0 - D_t}{D_0 - D_\infty} c_{1M} v}{I_0 \left[1 - e^{-\epsilon_{1M} c_{1M} (1 - 1/2\, D_0 - D_t / D_0 - D_\infty)} \right]}$$

Experiments in 1,2-ethanediol or 1,2-propanediol were carried out in cells in which the exposed area was smaller than the image of the light on the cell (0.2 cm wide × 2 cm high × 1 cm long). Only 0.4 cm^3 of solution was used, and solutions were mixed before absorption spectra were measured. The protonated products were unchanged on further irradiation in glycerol and disappeared extremely slowly in more fluid solvents like 1,2-ethanediol. However, long irradiation of **1** in methanol caused loss of all long wavelength absorption.

Acknowledgment. The support of the United States-Israel Binational Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) Tel-Aviv University; (b) State University of New York at Stony Brook.
(2) (a) C. J. Seliskar and L. Brand, *J. Am. Chem. Soc.*, **93**, 5414 (1971); (b) H. Dodiuk, unpublished results.
(3) (a) E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Ottolenghi, and N. Orbach, *J. Am. Chem. Soc.*, **97**, 2167 (1975); (b) E. M. Kosower and H. Dodiuk, *J. Phys. Chem.*, in press.
(4) E. M. Kosower and H. Dodiuk, *Chem. Phys. Lett.*, **34**, 253 (1975).
(5) R. W. Alder and N. C. Goode, *J. Chem. Soc., Chem. Commun.*, 109 (1976).
(6) E. M. Kosower and H. Dodiuk, *J. Am. Chem. Soc.*, **96**, 6195 (1974).
(7) E. M. Kosower and H. Dodiuk, *Chem. Phys. Lett.*, **26**, 545 (1974).
(8) H. Dodiuk, unpublished results.
(9) M. Ottolenghi and N. Orbach, Hebrew University, unpublished results.
(10) G. E. McDuffie, Jr., and T. A. Litovitz, *J. Chem. Phys.*, **37**, 1699 (1962).
(11) Based on arguments given by M. D. Magee, *J. Chem. Soc., Faraday Trans. 2*, 929 (1974).
(12) R. P. Cory, R. R. Becker, R. Rosenbluth, and I. Isenberg, *J. Am. Chem. Soc.*, **90**, 1643 (1968).
(13) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Laser Photolysis Studies of Duroquinone Triplet State Electron Transfer Reactions

R. Scheerer and M. Grätzel*

Contribution from the Hahn-Meitner-Institut für Kernforschung Berlin GmbH,
Bereich Strahlenchemie, D 1000 Berlin 39, West Germany. Received February 20, 1976

Abstract: A systematic investigation of electron abstraction reactions of triplet duroquinone (DQ^T) has been carried out. A 347.1-nm laser photolysis technique combined with fast conductance measurements and kinetic spectroscopy were used to monitor its reactions with various donor molecules (D). In mixtures of water/ethanol (2:1 v/v) DQ^T abstracts electrons from a variety of substrates such as Fe^{2+}, $Fe(CN)_6^{4-}$, CO_3^{2-}, diphenylamine, and 1,3,5-trimethoxybenzene. Thereby durosemiquinone (DQ^-) and oxidized donor (D^+) is formed. The rate constants for these redox processes are close to the diffusion-controlled limit (10^9–10^{10} $M^{-1}\,s^{-1}$) except for $D = CO_3^{2-}$, where $k = 7 \times 10^7$ $M^{-1}\,s^{-1}$. With all donors conversion of DQ^T into DQ^- was quantitative. DQ^T in the H_2O/EtOH mixture also abstracts electrons from ethanol itself. This quenching reaction occurs at a relatively slow rate and yields only ca. 20% DQ^-. Similarly DQ^T in acetone solution abstracts electrons from the solvent, the pseudo-first-order rate constant being 5×10^4 s^{-1}. However, in *n*-hexane DQ^T disappears predominantly via a bimolecular triplet-triplet annihilation process. Anionic micelles were found to accelerate markedly the electron transfer from Fe^{2+} to DQ^T. These results are discussed in terms of the excited state nature of DQ^T and current theories of electron transfer reactions.

Quinoid compounds undergo a manifold of photochemical reactions which have been dealt with recently in a comprehensive review.[1] Among them processes related to the phototendering of fabrics and photobiological functions of quinones have received particular attention. In this field photochemical pathways leading to reduction of the quinone play a prominent role. In order to establish the basic mechanism of the latter photoreduction process, several investigations with model compounds, in particular duroquinone,[2-7] have been carried out. Durosemiquinone radicals have been identified as intermediates and triplet state duroquinone as their precursor. The conversion of duroquinone triplets into semiquinone radicals is presently believed to occur via hydrogen abstraction from the solvent molecules.

Our current interest in photo redox processes as possible means of light energy utilization has prompted us to inquire into electron abstraction reactions of quinoid compounds. These studies aim at exploring sensitizers suited for photodecomposing water into oxygen. The present paper reports on laser photolysis studies of redox reactions in solutions in which triplet duroquinone acts as an electron acceptor. The strongly oxidizing nature of the triplet state manifests itself through ready occurrence of electron abstractions from diverse substrates such as Fe(II), trimethoxybenzene, ethanol, and acetone. These results will be subject to an analysis based on current theories of electron transfer reactions in liquids.

Experimental Section

Materials. Duroquinone (Aldrich, Europe, >99.9%) was further purified by recrystallization from hexane. Its concentration in solution was maintained at 10^{-3} M throughout the experiments. Sodium lauryl sulfate (Merck, "for tenside investigations") was purified by multiple recrystallization from ethanol/ether mixtures. Acetone (Merck p.a.) was fractionally distilled from dehydrated Na_2SO_4; *n*-hexane (Philips, research grade) was purified by column chromatography. Diphe-

---

* Address correspondence to this author at Ecole Polytechnique, Departement de Chimie-Physique, CH-1007 Lausanne, Switzerland.

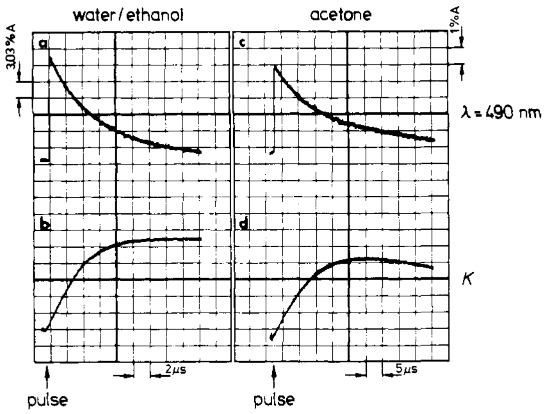


Figure 1. Oscilloscope traces illustrating the changes in absorption at 490 nm and conductance induced by the laser flash in solutions of DQ in H_2O/EtOH and acetone.

nylamine (Merck, pro analysis), 1,3,5-trimethoxybenzene (Aldrich, >99.9%), and ethanol (Merck "absolute", 99.8 and 0.2% water) were used as supplied. Deionized water was distilled from alkaline permanganate and subsequently twice from a quartz still. All other compounds were analytical reagent grade. The samples were deoxygenated by bubbling with highly purified argon.

Apparatus. Laser photolysis experiments were carried out with a frequency doubled, Q-switched Korad K1QP ruby laser. The 347.1-nm pulse had a duration of 15 ns and maximum energy of 100 mJ. Transient species were detected either by fast kinetic spectroscopy[11] or fast dc conductance technique.[12] Suitable cutoff filters were placed in the analyzing light beam to prevent photolysis. Solutions were flowed through a 1 cm^2 quartz cell to obviate interference from product accumulation.

Results

The primary photochemical processes occurring upon absorption of 347.1-nm light by duroquinone are well established. $S_0 \rightarrow S_1$ excitation is followed by intersystem crossing with an efficiency of practically unity. Duroquinone triplets (DQ^T) thus produced have an energy of 2.4 eV above ground state[13] and are characterized by a broad absorption band in the wavelength region between 400 and 500 nm. The shape, fine structure, and extinction coefficient of this band depend strongly on the nature of the solvent.[5,7]

In the following section we shall be concerned with investigations of electron transfer reactions from a donator molecule D to DQ^T for which a general formulation is given by

$$DQ^T + D \rightarrow DQ^- + D^+ \qquad (1)$$

Some experiments will be performed in acidic aqueous solutions where DQ^-, the durosemiquinone anion, is rapidly converted into durosemiquinone (DQH)

$$DQ^- + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} DQH \qquad (2)$$

The dissociation constants of DQH in water and water/ethanol (50% v/v) have been determined as $(8 \pm 2) \times 10^{-6}$ M[14] and 1.2×10^{-6} M,[2] respectively.

The absorption spectra of DQ^- and DQH are also well established (cf. ref 15 and references cited therein), DQ^- and DQH possessing maxima at 440 (ϵ 7600 $M^{-1}\ cm^{-1}$) and 420 nm (ϵ 4700 $M^{-1}\ cm^{-1}$), respectively. The following kinetic investigations of DQ^T electron abstraction reactions were performed at 490 nm, where the triplet has a strong absorption while those of DQ^- and DQH are negligibly small. In several cases the formation of D^+ was observed spectroscopically by monitoring their characteristic absorption in the longer wavelength region. Wherever possible, conductance measurements were carried out to complement and substantiate the optical data.

Duroquinone Triplet Reactions with Solvents. (i) Water/Ethanol. As most of the electron abstraction reactions involving solute donor molecules were investigated in a mixture composed of H_2O/ethanol (2:1 v/v), it seemed appropriate to first ascertain the mechanism of DQ^T deactivation in this medium. Experimental data obtained in such a system are presented in Figure 1. Two oscilloscope traces illustrate both the behavior of optical density at 490 nm and conductance upon illumination of the DQ solution with the laser light. The formation of DQ^T is reflected by the buildup of absorption during the pulse. Subsequently the transient optical density decays via first-order kinetics with a rate constant of $(1.6 \pm 0.2) \times 10^5\ s^{-1}$. As the DQ^T absorption disappears the spectrum of DQ^- develops. This subsequently decays in a second-order reaction, the rate constant being $\simeq 10^8\ M^{-1}\ s^{-1}$.

These optical observations essentially confirm the earlier laser results reported by Kemp and Porter.[7]

Turning now to an examination of the conductivity trace displayed in Figure 1b one notices an increase in the conductance of the solution until a plateau is attained after some 15 μs. The kinetics of the growth are first order and match with those of the 490-nm absorption decay. During the subsequent DQ^- disproportionation reaction, which was followed on a compressed time scale, the conductivity decreases again and finally returns to its initial value.

One interesting feature concerning the detailed mechanism of DQ^- production from DQ^T develops from the conductivity studies. If the reaction proceeded via hydrogen abstraction, that is

$$DQ^T + CH_3CH_2OH \rightarrow DQH\cdot + CH_3\dot{C}HOH \qquad (3)$$

then ions could originate only from two subsequent reactions: first, electron transfer from α-hydroxyethyl radicals to duroquinone,

$$CH_3CHOH + DQ \rightarrow CH_3CHO + DQ^- + H^+ \qquad (4)$$

and second, dissociation of DQH according to eq 2. While at the DQ concentrations employed reaction 4 occurs at a much faster rate than the triplet decay,[16] this is not true for the DQH dissociation. Using $K_2 = 1.2 \times 10^{-6}$ M and as upper limit for the DQ^- protonation rate constant $k_2 \leq 6 \times 10^{10}\ M^{-1}\ s^{-1}$,[17] one derives for k_{-2} a maximum value of $5 \times 10^4\ s^{-1}$, corresponding to a mean DQH lifetime of at least 20 μs. From these considerations a two-step increase of the solution conductance is predicted after the laser pulse. One half of the plateau value should grow concomitantly with the triplet decay, while the remaining fraction should be formed more slowly.

The alternative mechanism to be considered comprises electron abstraction from ethanol:

$$DQ^T + CH_3CH_2OH \rightarrow DQ^- + CH_3CH_2OH^+ \qquad (5)$$

which is followed by immediate proton transfer[18]

$$CH_3CH_2OH^+ + CH_3CH_2OH \rightarrow CH_3CH_2OH_2^+ + CH_3\dot{C}HOH \qquad (6)$$

and reaction 4. In this sequence reaction 5 is rate determining. Hence the conductance increase should conform to the triplet decay.

The experimental results suggest that the latter electron abstraction mechanism is operative in the DQ^T reaction with ethanol. This conclusion is supported further by the evaluation of quantum yields described later.

(ii) **Acetone.** If duroquinone triplets are capable of abstracting electrons from alcohol, it is anticipated that a similar reaction will also occur with other oxygen containing solvent molecules. This possibility was tested by performing laser photolysis experiments with DQ solutions in acetone. The optical and conductivity data displayed in Figures 1c and d

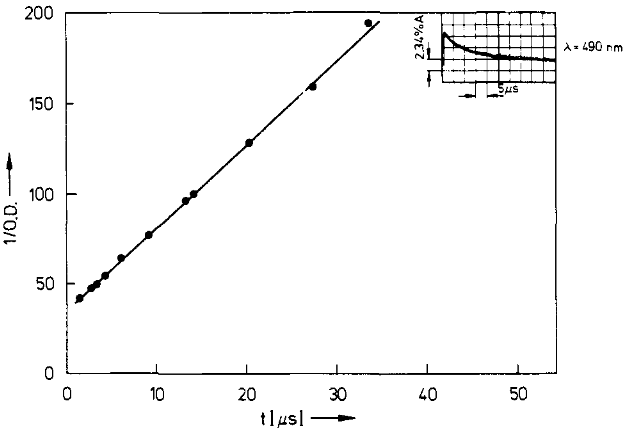


Figure 2. Inserted oscillogram: decay of DQ^T 490-nm absorption in *n*-hexane. Second-order plot of such a decay curve.

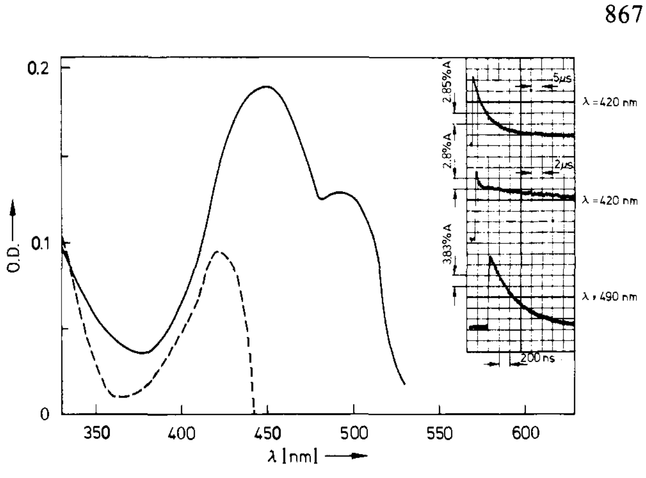


Figure 3. Spectra of transients obtained in the laser photolysis of DQ in $H_2O/EtOH$: (—) end of pulse; (- - -) 2 µs after pulse in the presence of 3×10^{-3} M Fe^{2+}, pH 1. Insert: oscilloscope traces showing (from the top) DQ^T decay and DQH formation in the absence and presence of Fe^{2+}, quenching of DQ triplet by Fe^{2+} at 490 nm.

show close similarity with the alcohol results. Again the triplet absorption at 490 nm decays via first-order kinetics and is accompanied by a simultaneous increase in the conductance of the solution and an appearance of the DQ^- spectrum. These effects are attributed to electron transfer from acetone to duroquinone triplets:

$$DQ^T + CH_3COCH_3 \rightarrow DQ^- + CH_3COCH_3^+ \quad (7)$$

The kinetic evaluation yields a pseudo-first-order rate constant of

$$k_7 = 5 \times 10^4 \, s^{-1}$$

for this process.

Acetone cation radicals are known to absorb in the 600-nm region.[19] Their lifetime is limited to about 3 µs by proton transfer to the solvent.[20]

$$CH_3COCH_3^+ + CH_3COCH_3 \rightarrow H^+_{solv} + CH_3CO\dot{C}H_2 \quad (7a)$$

The relative rates of the consecutive reactions 7 and 7a imply that only a small amount of $CH_3COCH_3^+$ should be present while DQ^T is decaying. This was nevertheless detected by its characteristic absorption in the red, a fact which lends further support to the suggested electron abstraction mechanism.

In contrast to hydroxyethyl radicals, $CH_3CO\dot{C}H_2$ has oxidizing rather than reducing properties. This excludes electron transfer analogous to reaction 4 and makes probable electron abstraction from DQ^- to give back acetone and DQ. Such a process leads to a decrease in the transient conductance, the onset of which is already noticeable in Figure 1d.

(iii) **Hexane.** In view of the results obtained with water/ethanol and acetone solutions it seemed appropriate to reexamine the reactivity of DQ^T toward hydrocarbon solvents. In particular the question had to be clarified whether DQ^T can abstract hydrogen from C–H bonds. For this reason laser experiments were carried out with solutions of duroquinone in hexane. In order to minimize interferences from biphotonic processes the laser intensity was deliberately kept low.

The oscilloscope trace inserted in Figure 2 illustrates the formation and disappearance of 490-nm transient *A*. A notable difference between this curve and the traces shown in Figures 1a and c is the second-order character of the decay kinetics. This was unambiguously established by plotting the reciprocal optical density vs. time for different laser intensities varying by more than a factor of 10. Straight lines were obtained over a time period of several half-lifes. Their slopes varied very little with the laser intensity. A representative example is given in Figure 2. From these results it is concluded that hydrogen transfer from hexane to DQ^T does not occur to any significant extent. Rather it appears that triplets deactivate in the customary bimolecular annihilation process.

$$DQ^T + DQ^T \rightarrow \ldots \text{ ground state duroquinone} \quad (8)$$

Our kinetic evaluation yields:

$$k_8/\epsilon_{490} = (4 \pm 4) \times 10^6 \, s^{-1} \, cm^{-1}$$

Using Land's[5] value for the DQ^T extinction coefficient in cyclohexane, ϵ_{490} 3500 M^{-1} cm, we obtain:

$$k_8 = 1.4 \times 10^{10} \, M^{-1} \, s^{-1}$$

This value is typical for rate constants of triplet–triplet annihilation reactions.[21]

DQ^T Electron Abstraction from Solutes in Water/Ethanol (2:1 v/v). (i) Ferrous Ion in Acidic Solution (pH 1). The relative position of the standard redox potentials of the couples Fe^{2+}/Fe^{3+} (+0.77 V) and DQ^-/DQ (−0.235 V[22]) renders electron transfer from Fe^{2+} to DQ energetically unfavorable by some 1 eV. (This difference may be diminished in a solution of pH 1 by 0.3 V due to protonation of DQ^-.) From energetic considerations triplet duroquinone, on the other hand, should be able to oxidize Fe^{2+}. Figure 3 shows laser photolysis data obtained with Fe^{2+}-duroquinone solutions. Oscilloscope traces are inserted to illustrate the changes in the 490 and 420 nm optical densities induced by the laser flash. It is apparent that the decay of the absorption at 490 nm is accelerated markedly by Fe^{2+} ions, indicating their reaction with duroquinone triplets. The kinetics were found to be pseudo-first-order with respect to Fe^{2+} concentration.

At 420 nm part of the transient *A* disappears concurrently with that at 490 nm and is therefore attributed to DQ^T. After completion of the decay a residual absorption, $A_{420}{}^r$, is left behind, which diminishes slowly by second-order kinetics. This absorption is increased drastically upon addition of ferrous ions to the solution. The enhancement may be expressed quantitatively by the ratio of $A_{420}{}^r$ values observed in the absence and presence of Fe^{2+}. Extrapolation of the second-order decay curves back to the origin yields:

$$A_{420}{}^r (Fe^{2+})/A_{420}{}^r = 2.6$$

Included in Figure 3 are two transitory spectra measured at the end of the laser pulse and after completion of the triplet decay in a DQ/Fe^{2+} solution. The former shows the features of the DQ^T spectrum, while the latter is identical with that of DQH. These data identify DQH as the product of duroquinone triplet reaction with Fe^{2+}. From the observed ratio of $A_{420}{}^r$

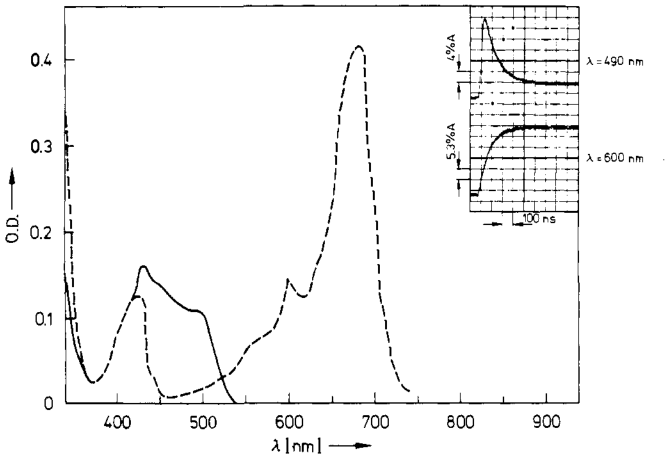


Figure 4. Spectra of transients obtained in the laser photolysis of DQ and diphenylamine (3×10^{-3} M, pH 1) in H_2O/EtOH: (—) end of pulse; (- - -) 600 ns after pulse. Insert: oscilloscope trace showing DQ^T decay at 490 nm and Ph_2NH^+ formation at 600 nm.

values it is then inferred that the yield of DQH is increased 2.6 times in the presence of ferrous ions. These results are interpreted in terms of rapid electron transfer from Fe^{2+} to duroquinone

$$Fe^{2+} + DQ^T \rightarrow Fe^{3+} + DQ^- \qquad (9)$$

and subsequent protonation of DQ^-. The kinetic analysis yields

$$k_9 = 1.3 \times 10^9\ M^{-1}\ s^{-1}$$

(ii) **Diphenylamine.** In Figure 4 laser photolysis results are presented, obtained with acidic solutions of DQ in the presence of diphenylamine. The transitory spectrum recorded immediately after the laser pulse is characteristic for duroquinone triplets. As is noted from the inserted oscillograms, the 490-nm absorption of DQ^T disappears very rapidly. Concurrently one observes in the longer wavelength region a pronounced increase in the optical density. The rate of both events is pseudo-first order with respect to diphenylamine concentration. After completion of the triplet reaction the transitory spectrum has the shape represented by the dashed curve in Figure 4. It is composed of an intense band which peaks around 680 nm and a second maximum at 420 nm. The latter evidently arises from DQH, while the former is readily assigned to diphenylamine cation radicals (Ph_2NH^+), whose spectrum has been reported.[23] The production of DQH and Ph_2NH^+ from duroquinone triplets indicates that its reaction with diphenylamine proceeds through electron abstraction

$$DQ^T + Ph_2NH \rightarrow DQ^- + Ph_2NH^+ \qquad (10)$$

followed by rapid protonation of DQ^-. The rate constant for this process obtained from the kinetic analysis is

$$k_{10} = (3 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$$

An alternative mechanism to be considered comprises hydrogen transfer from Ph_2NH to DQ^T followed by protonation of Ph_2N radicals:

$$\begin{aligned} DQ^T + Ph_2NH &\rightarrow DQH + Ph_2N \\ Ph_2N + H^+ &\rightarrow Ph_2NH^+ \end{aligned} \qquad (11)$$

In order to discriminate between these alternatives laser photolysis experiments with neutral solutions of diphenylamine and duroquinone were performed. The transitory spectra recorded were identical with those obtained in acidic medium, except for the appearance of the DQ^- instead of the DQH absorption band, after completion of the triplet reaction. In addition, conductance investigations were carried out, which are presented in Figure 5. The two lower oscilloscope traces reflecting the changes of the solution conductance induced by the laser pulse are juxtaposed to a 490-nm absorption decay curve. It is readily noted that this decay is associated with a concomitant increase of the conductivity. Such a behavior would be expected if reaction 10 and not the sequence 11 is the pathway of triplet deactivation. The rate constant k_{10} derived from these investigations agrees, within experimental error, with the value obtained in acidic solution.

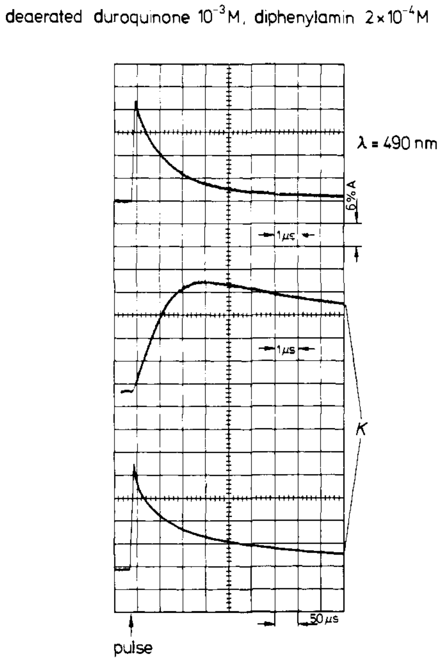


Figure 5. Oscilloscope traces illustrating the changes in absorption at 490 nm and conductance induced by the laser flash in solutions of DQ in H_2O/EtOH containing 2×10^{-4} M diphenylamine.

At longer times the conductance decreases again until it has returned to its initial value. The kinetics follow a second-order rate law. This process reflects annihilation of charged species due to thermal back transfer of electrons from DQ^- to Ph_2NH^+. It documents the reversible nature of a light-driven redox reaction such as eq 10 in a homogeneous medium.

(iii) **1,3,5-Trimethoxybenzene.** Optical and conductance results obtained from the laser photolysis of solutions containing DQ and 1,3,5-trimethoxybenzene (TrMB) are presented in Figure 6. The spectral data resemble closely those observed with diphenylamine as electron donor. The triplet absorption of duroquinone appears at the end of the flash. This decays very rapidly, thereby converting into the spectrum indicated by the dashed line. The latter contains two bands, one being identical with the DQ^- absorption, while the other in the longer wavelength region is assigned to $TrMB^+$ cation radicals. From the inserted oscillograms it may be inferred that the decay of the 490-nm triplet absorption and the formation of the species absorbing at 600 nm occur concurrently. Also an augmentation of conductance after the flash is noted, the increase matching exactly with the time course of the optical events. These effects are explained in terms of electron transfer from TrMB to DQ^T according to the equation:

$$DQ^T + TrMB \rightarrow DQ^- + TrMB^+ \qquad (12)$$

The kinetic evaluation gives a rate constant

$$k_{12} = (3.3 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$$

(iv) **Quantum Yields of Electron Abstraction and Duroquinone Triplet Extinction Coefficient.** The conductance method em-

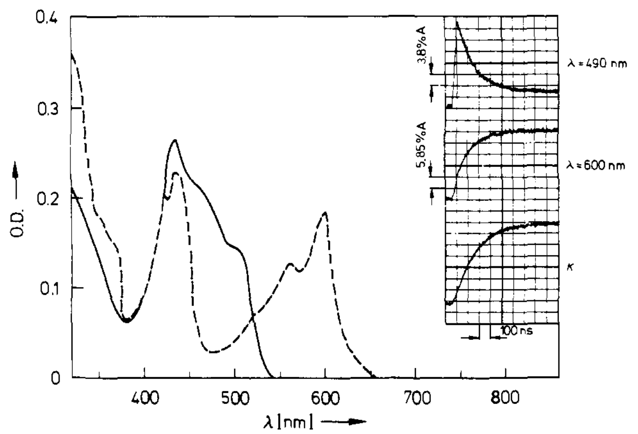


Figure 6. Spectra of transients obtained in the laser photolysis of DQ in H_2O/EtOH in the presence of 3×10^{-3} M trimethoxybenzene: (—) end of pulse; (- - -) 800 ns after pulse. Insert: Decay of DQ^T absorption at 490 nm, formation of $TrMB^+$ absorption at 600 nm, increase in the solution conductance.

ployed above to monitor the time course of DQ^T redox reaction is also suited to the determination of quantum yields. In particular it may be utilized to derive desirable information about the conversion efficiency of DQ^T into DQ^- in H_2O/EtOH solutions alone and in the presence of solutes such as diphenylamine or trimethoxybenzene. A convenient and reliable procedure applied here is to first measure the magnitude of the light-induced conductance change in H_2O/EtOH alone. This is given by the heights of the signal in the plateau region in Figure 1b:

$$h_1 = f(\lambda_{DQ^-} + \lambda_{H^+})C_1$$

where f is a proportionality factor; $\lambda_{DQ^-} + \lambda_{H^+}$, the sum of the equivalent conductances of DQ^- and H^+, is equal to 187 Ω^{-1} cm^2 equiv^{-1} in the H_2O/EtOH mixture (λ_{DQ^-} is assumed to be identical with that of the picrate ion); and C_1 the concentration of DQ^- produced. Note that only one-half of the observed DQ^- is formed directly from the triplet reaction with ethanol. The other arises from a subsequent reaction of hydroxyethyl radicals (eq 4). Second, a solute such as Ph_2NH or TrMB is added to the same solution and the measurement is repeated under elsewise identical conditions. The height of the conductance signal in the plateau region (Figures 4 and 5), where DQ triplets have completed their reaction, is now:

$$h_2 = f(\lambda_{DQ^-} + \lambda_{D^+})C_2$$

where λ_{D^+}, the equivalent conductance of the donor cation radical, is approximately 20 Ω^{-1} cm^2 equiv^{-1} and C_2 is the concentration of DQ^- produced from the triplet reaction with the solute. For the ratio of DQ^- concentrations in the presence and absence of solute one obtains:

$$\frac{C_2}{C_1} = \frac{(\lambda_{H^+} + \lambda_{DQ^-})}{(\lambda_{D^+} + \lambda_{DQ^-})} = \frac{187}{40}\frac{h_2}{h_1} = 4.68\frac{h_2}{h_1}$$

Experimentally one observes $h_2/h_1 = 0.57 \pm 0.03$ and hence $C_2/C_1 = 2.57 \pm 0.12$.

This value agrees within experimental error with the ratio of durosemiquinone yields in the presence and absence of Fe^{2+} ions, which was derived from the optical results. Apparently all three solutes, Fe^{2+}, Ph_2NH, and TrMB cause the same augmentation in durosemiquinone (anion) yield. The amount of DQ^- (DQH) formed in these cases was found to correspond approximately to the number of laser photons absorbed by duroquinone. This shows that in the presence of Fe^{2+}, Ph_2NH, or TrMB, the conversion of DQ^T into DQ^- (DQH) is quantitative and occurs with a quantum yield of practically unity.

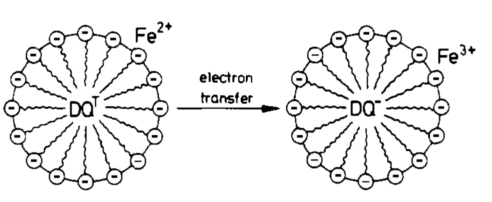


Figure 7. Schematic illustration of an intramicellar electron transfer process from Fe^{2+} to DQ solubilized in anionic micelles.

On this premise an evaluation of the DQ^T extinction coefficient in H_2O/EtOH solution becomes possible. Using the optical data displayed in Figure 3 and ϵ_{420}(DQH) of 4700 M^{-1} cm^{-1} we find

$$\epsilon_{420}(DQ^T)\ (6.6 \pm 0.8) \times 10^3\ M^{-1}\ cm^{-1}$$

Conversely, in H_2O/EtOH solution containing no additive the abstraction of electrons from ethanol is by no means quantitative. The above analysis shows that only 20% of DQ^T is converted into DQ^- under these conditions.

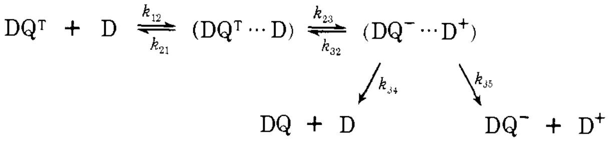
Micellar Solutions of Duroquinone. The behavior of duroquinone triplets in micellar solution of NaLS parallels that observed in H_2O/EtOH. The triplet decays via first-order kinetics ($k = 1.8 \times 10^5$ s^{-1}), thereby producing DQ^- (DQH) with a yield of 15 ± 5%.

The transfer of electrons from ferrous ion to DQ^T was also investigated in the micellar solution. A schematic illustration of the events occurring in such a system is given in Figure 7. Ferrous ions are expected to interact strongly with the negatively charged amphipathic surface of the micelle and hence will be associated with the micellar Stern layer. Duroquinone, on the other hand, is located in the lipoidic interior of the micelle. Hence the intramicellar redox reaction between Fe^{2+} and DQ^T will proceed via electron flux from the donor on the surface across the lipid/water interface to the acceptor inside the micelle. Laser photolysis experiments showed that this process occurs with an extremely rapid rate. The DQ^T lifetime in the presence of Fe^{2+} is only 40 ns, corresponding to a rate constant for the intramicellar electron transfer of 2.5×10^7 s^{-1}. Similar to H_2O/EtOH solutions the conversion of DQ^T into DQ^- in the presence of Fe^{2+} is quantitative in the micellar medium.

Discussion

The intimate mechanism of light-induced redox reactions of the type investigated in this work comprises a sequence of steps which are indicated in Scheme I. Encounter complex formation between duroquinone triplets and the donor is followed by the actual charge transfer event, yielding an ion pair in the solvent cage which either separates into ions or gives ground state DQ and donor via back transfer of electrons. Such a model was used first by Rehm and Weller[24] for the treatment of charge transfer exciplex phenomena and has recently been applied to triplet tris(bipyridine)ruthenium(II)[25] and zinc uroporphyrin[26] redox reactions. When the stationary state approximation is used the observed rate constant for DQ^- formation from DQ^T can be related to the specific rates of the individual steps in Scheme I by:

Scheme I



$$\begin{tikzcd} DQ^T + D \arrow[r, shift left, "k_{12}"] & (DQ^T\cdots D) \arrow[l, shift left, "k_{21}"] \arrow[r, shift left, "k_{23}"] & (DQ^-\cdots D^+) \arrow[l, shift left, "k_{32}"] \arrow[dl, "k_{34}"'] \arrow[d, "k_{35}"] \\ & DQ + D & DQ^- + D^+ \end{tikzcd}$$

$$k_{\text{obsd}} = \frac{k_{12}}{1 + \dfrac{k_{34}}{k_{35}} + \dfrac{k_{21}}{k_{23}}\left(1 + \dfrac{k_{32}}{k_{35}} + \dfrac{k_{34}}{k_{35}}\right)} \tag{13}$$

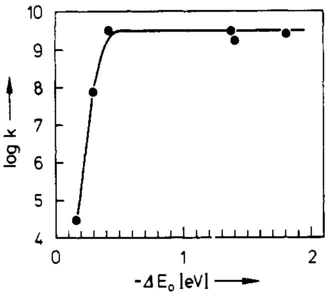


Figure 8. Plot of the logarithm of the specific rate of the electron transfer from various donors to DQ^T in $H_2O/EtOH$ solution against the difference in reduction potential $\Delta E_0 = E_0(DQ^T/DQ^-) - E_0(D^+/D)$.

For most of the donors employed DQ^- formation from triplets was quantitative, implying that $k_{34} \ll k_{35}$. Under these conditions eq 13 reduces to the customary expression

$$k_{\text{obsd}} = \frac{k_{12}}{\frac{k_{21}}{k_{23}}\left(1 + \frac{k_{32}}{k_{35}}\right) + 1} \tag{14}$$

Apparently the rate constant for the photo redox reaction is expected to approach the diffusion-controlled limit ($k_{\text{obsd}} \rightarrow k_{12}$) when $k_{32} \ll k_{35}$ and $k_{21} \ll k_{23}$. Conjectures as to the values of k_{23} and k_{32} can be made on the basis of current theories of electron transfer reaction,[27,28] which express these rate parameters in terms of the Gibbs free energy ΔG_{23}. According to these treatments the above boundary conditions are fulfilled at small negative ΔG_{23} values, where electron transfer should occur at a diffusion-controlled rate. Conversely, when ΔG_{23} approaches zero or even becomes positive, a marked drop in the rate of reaction is predicted. Whether a similar decrease should also occur in a region of large negative ΔG_{23} values is presently a matter of contention.[24,28]

For a comparison of our experimental results with these theoretical predictions it is useful to first consider the reduction potential of the DQ^T/DQ^- couple. This is obtained from the reduction potential of duroquinone by addition of the triplet energy:

$$E_0(DQ^T/DQ^-) = E_0(DQ/DQ^-) + E_T = +2.17 \text{ eV} \tag{15}$$

It should be noted that eq 15 is based on the assumption that triplet and ground state have about the same entropy and geometrical configuration.[29] Accepting this approximation one would expect that donor molecules with reduction potentials at least a few hundred millivolts less positive than 2.17 eV should be rapidly oxidized by DQ^T. Table I lists rate constants for electron abstraction reactions together with $E_0(D^+/D)$ values. Included are data from two inorganic anions $Fe(CN)_6^{4-}$ and CO_3^{2-}, which are also oxidized by DQ^T. In Figure 8 the logarithm of these rate constants is plotted against the difference in the reduction potentials of the DQ^T/DQ^- and D^+/D couples, which is equal to the Gibbs free energy (in eV) of the electron abstraction reaction. With increasing values of $-\Delta E_0$ the rate of reaction accelerates sharply until at $-\Delta E_0 > 0.4$ V the diffusion-controlled limit is reached. From there on k_{obsd} changes little, with ΔE_0 remaining between 10^9 and 10^{10} M^{-1} s^{-1}. These observations agree with previous related studies on excited-state redox reactions and substantiate the expectations from the theoretical treatments of electron transfer processes. The fact that no decrease of log k is noticeable even at ΔE_0 values as negative as -1.8 V seems to favor a free energy-free activation energy relation of the type proposed by Weller,[24] as against the original Marcus expression.[28]

A special case is the DQ^T electron abstraction reactions from alcohol and acetone, which act also as solvents. Here the conversion of DQ^T into DQ^- occurs with the relatively low efficiencies of 20 and 8%, respectively. This behavior may be due to the fact that back transfer of electrons from DQ^- to D^+ in the solvent cage occurs at a rate comparable to that for dissociation into separated ions ($k_{35} \simeq k_{34}$). Alternatively, radiationless triplet deactivation competing with charge transfer quenching could decrease the yield of DQ^- production.

Table I. List of Rate Constants for Electron Transfer from Various Donors to Duroquinone Triplets in $H_2O/EtOH$ (2:1) and the Respective Normal Reduction Potentials (vs. NHE) of the D^+/D Couples

Donor D	$E_0(D^+/D)$	k_2, M^{-2} s^{-1}
$Fe(CN)_6^{4-}$	0.356	2.6×10^9
Fe^{2+}	0.77	1.3×10^9
Diphenylamine	0.78	3×10^9
1,3,5-Trimethoxybenzene	1.73[a]	3.3×10^9
CO_3^{2-}	1.85[b]	7.3×10^7
C_2H_5OH	2.0[c]	2.8×10^4

[a] Measured in acetonitrile.[24] [b] Approximate value, estimated from CO_3^- electron transfer reactions. [c] Considerations on the energies of electron deficient states in liquid ethanol and other solvents can be found in ref. 31.

The lack of hydrogen abstraction of DQ^T from C-H containing solvents such as hexane can be rationalized in terms of the nature of the DQ^T excited state. In a series of elegant experiments with methyl-substituted benzoquinones Kemp and Porter[7] have shown that duroquinone triplets have π,π^* character. Such a state does not possess the electron deficiency at the carbonyl oxygen, which is characteristic for n,π^* carbonyl triplets, and is the reason for their disposition to hydrogen abstraction reactions. As the ionization potential of hexane is too high to allow for electron abstraction, this solvent is inert toward DQ^T and deactivation occurs via a triplet annihilation process.

When DQ is incorporated into anionic micelles, DQ^- is produced from the triplets in a relatively small yield via electron abstraction from the sulfate head groups. In cationic micelles such as trimethyldodecylammonium chloride, where the sulfate group is replaced by a quaternary ammonium group, no DQ^- formation is observed. This excludes the possibility that hydrogen transfer from CH_2 groups of the detergent molecules to DQ^T is responsible for the DQ^- (DQH) production.

The observation of intramicellar electron transfer from Fe^{2+} to DQ^T complements earlier work in which the reverse direction of electron movement, i.e., from a triplet donor inside the micelle to an acceptor on the surface, was investigated.[8,10] Both processes occur at a very rapid rate, which can hardly be accounted for by diffusional encounter complex formation between electron donor and acceptor. A mechanism involving electron tunneling over distances considerably larger than the sum of the reactant radii has been forwarded to explain the earlier results[9] and is suggested to be operative also in the Fe^{2+}/DQ^T reaction.

Similarly, large electron transfer distances have been obtained by Mauzerall and Carapelluci from a study of triplet zinc uroporphyrin redox reactions.[26]

Conclusions

A systematic study of electron abstraction reactions of duroquinone triplets has been undertaken from which a strongly oxidizing character of this excited state can be inferred. The photobiological relevance of the results obtained is evident, since quinoid compounds of similar structure, e.g., ubiquinone and vitamin K, are present in vivo together with electron donors such as Fe^{2+}, iron complexes, and amines. Whether these photo redox reactions are applicable to light energy conversion in particular, exploitation of solar light depends on the successful prevention of thermal back transfer of electrons from DQ^- to D^+. Here micellar systems due to their two-phase character offer some interesting possibilities, which are presently being examined. In particular it seems worthwhile to pursue in more detail the $CO_3{}^{2-}$ oxidation to $CO_3{}^-$ by excited quinones, since $CO_3{}^-$ in its subsequent reactions is known to yield oxygen.[30] Hence in a system containing quinone and carbonate, oxygen evolution from water by visible light becomes feasible. Studies in this direction are now under way.

Acknowledgment. We would like to thank Professor Henglein for many helpful discussions throughout the course of this work. Skillful assistance with the electronics by Dr. G. Beck and technical help by Mrs. H. Pohl are gratefully acknowledged.

References and Notes

(1) J. M. Bruce in "The Chemistry of the Quinoid Compounds", S. Patai, Ed., Wiley, London, 1974, p 465.
(2) N. K. Bridge and G. Porter, *Proc. R. Soc., London, Ser. A*, **244**, 259, 276 (1958).
(3) F. Wilkinson, G. M. Seddon, and K. Tickle, *Ber. Bunsenges. Phys. Chem.*, **72**, 315 (1968).
(4) H. Hermann and G. O. Schenck, *Photochem. Photobiol.*, **8**, 255 (1968).
(5) E. J. Land, *Trans. Faraday Soc.*, **65**, 2815 (1969).
(6) J. Nafisi-Moraghar and F. Wilkinson, *Trans. Faraday Soc.*, **66**, 2257, 2268 (1970).
(7) D. R. Kemp and G. Porter, *Proc. R. Soc. London, Ser. A*, **326**, 117 (1970).
(8) S. A. Alkaitis, G. Beck, and M. Grätzel, *J. Am. Chem. Soc.*, **97**, 5723 (1975).
(9) S. A. Alkaitis, A., Henglein, and M. Grätzel, *Ber. Bunsenges. Phys. Chem.*, **79**, 541 (1975).
(10) S. A. Alkaitis and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 3549 (1976).
(11) G. Beck, J. Kiwi, D. Lindenau, and W. Schnabel, *Eur. Polym. J.*, **10**, 1069 (1974).
(12) G. Beck and J. K. Thomas, *J. Chem. Phys.*, **57**, 3649 (1972).
(13) J. Saltiel and G. S. Hammond,, *J. Am. Chem. Soc.*, **85**, 2515 (1963).
(14) R. L. Willson, *Chem. Commun.*, 1249 (1971).
(15) K. B. Patel and R. L. Willson, *J. Chem. Soc., Faraday Trans. 1*, 814 (1973).
(16) The rate constant k_4 was determined by pulse radiolysis technique as $k_4 = 3.5 \times 10^9\ M^{-1}\ s^{-1}$.
(17) M. Eigen, *Discuss. Faraday Soc.*, **17**, 194 (1954).
(18) G. R. Freeman, *Actions Chim. Biol. Radiat.*, **14**, 73 (1970).
(19) M. A. J. Rodgers, *Trans. Faraday Soc.*, **67**, 1029 (1971).
(20) T. Shida and W. Hamill, *J. Am. Chem. Soc.*, **88**, 3683 (1966); M. S. B. Murton, *ibid.*, **87**, 5313 (1965).
(21) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970.
(22) D. Meisel, Y. Ilan, and G. Czapski, submitted for publication.
(23) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).
(24) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).
(25) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1975).
(26) P. A. Carapellucí and D. Mauzerall, *Ann. N. Y. Acad. Sci.*, **244**, 214 (1975).
(27) V. G. Levich in "Physical Chemistry, an Advanced Treatise", Vol. 9B, H. Eyring, Ed., Academic Press, New York, N.Y., 1970, p 985.
(28) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 155 (1964).
(29) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); A. Weller, *Fast React. Primary Processes Chem. Kinet., Proc., Nobel Symp., 5th, 1967*, 413 (1967).
(30) N. Getoff, *Z. Naturforsch. B*, **17**, 751 (1962).
(31) A. J. Frank, M. Grätzel, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **80**, 595 (1976).

Molecular Design by Cycloaddition Reactions. 30.[1] Photochemical Cycloadditions of Quadricyclane to Aromatic Hydrocarbons and *o*-Quinones. First Example of Photochemical Pericyclic [$4\pi + 2\sigma + 2\sigma$] Addition

Tadashi Sasaki,* Ken Kanematsu, Ichiro Ando, and Osamu Yamashita

Contribution from the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan. *Received April 19, 1976*

Abstract: The photochemical pericyclic [$4\pi + 2\sigma + 2\sigma$] additions of anthracene, acridine, and some 1,2-quinones to quadricyclane were extensively investigated and compared with those of norbornadiene. The structures of these adducts were determined by spectral inspections. The reaction mechanisms for these adducts are discussed in connection with the theory of polar cycloaddition reaction on the basis of configuration interaction analyses.

Many useful examples showing the application of the simple and powerful generalized selection rules for pericyclic reactions have been reported.[2,3] To the best of our knowledge, the photochemical allowed [$4\pi + 2\pi(2\sigma) + 2\pi(2\sigma)$] cycloaddition has no precedent in the chemical literature.

It was of interest to examine the possibility of the mode of [$4\pi + 2\sigma + 2\sigma$] cycloaddition both from a synthetic and a theoretical point of view. Quadricyclane seemed to be a good model for this purpose. By contrast, regio- and stereospecific thermal allowed [$2\pi + 2\sigma + 2\sigma$] cycloaddition reactions[4] and metal-catalyzed [$2\pi + 2\sigma$] cycloaddition reactions of quadricyclane have been investigated.[5] On the other hand, Murov and Hammond[6] have reported that quadricyclane is a very effective quencher of the fluorescence of aromatic hydrocarbons such as anthracene and naphthalene, and suggested that the electronic energy of the aromatic hydrocarbons is efficiently transferred to vibrational energy of quadricyclane followed by isomerization to norbornadiene. Solomon et al.[7] have described that the fluorescence quenching of aromatic hydrocarbons by quadricyclane could proceed via a charge-transfer complex. In spite of these efforts, the possibility of chemical product formation has not been excluded, since Yang et al.[8] and the present authors[9] have shown tht some aromatic hydrocarbons undergo highly efficient photocycloadditions with several cyclic dienes and trienes resulting in chemical product formation through a significant pathway for the decay of the exciplexes.

We have recently communicated the photochemical reaction between aromatic hydrocarbons and quadricyclane.[10] These results are discussed in detail in this paper in comparison with the previous works[7,8] and with further additional data that we have obtained.