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A Pulse Radiolysis Study of the Quenching of Aromatic Carbonyl Triplets by Norbornadienes and Quadricyclenes. The Mechanism of Interconversion

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Abstract: The technique of electron pulse radiolysis has been used to produce aromatic carbonyl triplet states in liquid benzene. Kinetic absorption spectrometry has allowed the determination of the rate constants for quenching of these states by norbornadiene (**1**), quadricyclene (**2**), and their ethoxycarbonyl analogues (**3** and **4**). Analysis of the rate constant data together with quantum yield measurements shows that norbornadienes quench high energy triplets such as that of acetophenone via an energy transfer mechanism and the free triplets of the diene thus produced decay mainly to the corresponding quadricyclene (**2**, ~ 96%, and **4**, ~ 93%). With lower energy triplets the rate constant for quenching decreases as does the proportion of free triplets produced. The balance between energy transfer and decay to ground states then depends on the triplet energy and electron accepting properties of the triplet state involved. Quenching by quadricyclene involves charge transfer stabilization of the encounter complex and subsequent decay to ground states. Although attempted correlation with the function $[^3\Delta E_{0,0} + E(A^-/A)]$ is inconclusive, there is a strong correlation with the quenching of the same triplet states by triethylamine.

Introduction

A classical reaction of organic photochemistry involves the light-induced interconversion of norbornadiene (**1**) and quadricyclene (**2**) and their derivatives. On direct excitation **1** is converted to **2**[2a] whereas triplet sensitization leads to the establishment of a photostationary state between these valence isomers.[2b,3] The strained hydrocarbon **2** has been shown to quench aromatic hydrocarbon fluorescence. It was originally

proposed that this process involved exciplex formation followed by decay to vibrationally excited **2** which was thus thermally converted to **1**.[3] Weller et al. have since found a correlation between rate constants for fluorescence quenching and sensitizer electron affinities, and have proposed the intermediacy of a charge-transfer complex which subsequently collapses to give **1** or **2**.[4]

1, R = H
3, R = COOC$_2$H$_5$

2, R = H
4, R = COOC$_2$H$_5$
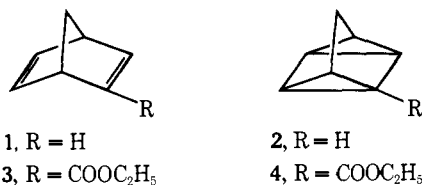
Perhaps the most intriguing situation involves the interconversion of **1** and **2** which is sensitized by the triplet states of aromatic carbonyl compounds. Hammond et al. showed that a photostationary state between **1** and **2** was established, the position of which was apparently dependent on the triplet energy of the sensitizer employed.[2b] This was interpreted in terms of a nonspectroscopic excitation of **2** to either the Franck–Condon triplet of **1** or a biradical produced by cleavage of one of the bonds involved in the interconversion of **1** and **2**. Such proposals presumably stemmed from the fact that a common intermediate for both forward and back reactions would readily accommodate the experimental data. In such a case the different internal energies of **1** and **2** would account for the influence of donor triplet energy on the position of the photostationary state.

In recent years it has become clear that, in many cases where electronic energy transfer would be appreciably endothermic, the primary process leading to quenching of aromatic carbonyl triplets is formation of a triplet exciplex, the stability of which should depend on the electron-donating and -accepting properties of the quencher and excited state, respectively. Based on the pioneering work by Weller et al.[5,6] it has been suggested[7,8] that the relationship between the rate constant for charge-transfer quenching of an aromatic ketone excited state and the relevant physical properties of the reactants may be approximated to the relationship

$$-\log k_{\mathrm{q}} \propto \Delta G_{\mathrm{c}} \sim \mathrm{IP}_{\mathrm{Q}} - [\Delta E_{0,0} + E(\mathrm{A}^-/\mathrm{A})] + C \quad (1)$$
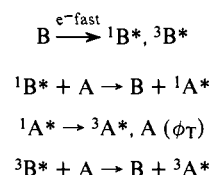
In this expression IP$_{\mathrm{Q}}$ is the quencher ionization potential, $\Delta E_{0,0}$ the electronic energy of the excited state, and $E(\mathrm{A}^-/\mathrm{A})$ the half-wave reduction potential of the ground-state carbonyl compound. It has been suggested that such a relationship should hold for reactions which are endothermic by more than 5 kcal mol^{-1}.

Caldwell et al.,[9-11] Kochevar and Wagner,[12] and more recently Gupta and Hammond[13] have argued persuasively that simple olefins quench aromatic ketone triplets via a triplet exciplex and that decay of this species to ground states can provide a pathway for energy wastage. The exciplex is thought to be stabilized by some degree of charge transfer from the olefin. Kochevar and Wagner have compared the efficiencies for quenching of butyrophenone triplet with olefin ionization potentials. Although a poor correlation was observed, the overall trend was in agreement with their proposals and discrepancies were attributed to differing steric factors.

In connection with our interest in the reactions of olefins with aromatic ketone triplets we have investigated the norbornadiene–quadricyclene system in detail; some preliminary results have been published elsewhere.[14] For comparative purposes we have investigated aspects of the activity of eight carbonyl triplet sensitizers and, in the hope of gaining information concerning the key properties of the norbornadiene/quadricyclene substrates, we have studied **1** and **2** together with their ethoxycarbonyl analogues **3** and **4**.

Experimental Section

1. Determination of Quenching Rate Constants. Electron pulse radiolysis is a technique of great potential for the direct investigation of the reactions of molecular triplet states in fluid solution.[15-17] Energy absorption from a beam of high-energy (several MeV) electrons by an aromatic liquid such as benzene produces significant yields of singlet and triplet states of the matrix.[16] In the presence of additives which can undergo energy transfer reactions with these matrix states the following sequence occurs:

$$\mathrm{B} \xrightarrow{\mathrm{e}^- \text{fast}} {}^1\mathrm{B}^*, {}^3\mathrm{B}^*$$

$${}^1\mathrm{B}^* + \mathrm{A} \rightarrow \mathrm{B} + {}^1\mathrm{A}^*$$

$${}^1\mathrm{A}^* \rightarrow {}^3\mathrm{A}^*, \mathrm{A} \; (\phi_{\mathrm{T}})$$

$${}^3\mathrm{B}^* + \mathrm{A} \rightarrow \mathrm{B} + {}^3\mathrm{A}^*$$

where B and A represent the benzene solvent and energy-accepting solute, respectively. With solutes such as benzophenone and other aromatic ketones where ϕ_{T} is unity and the rate of intersystem crossing is very high, the net result of irradiating a 10^{-2} mol L^{-1} solution of ketone in benzene with, for example, a 50-ns electron pulse is the production of ca. 10^{-5} mol L^{-1} of ketone triplet species whose subsequent decay is governed by the composition of the solution with respect to further additives (e.g., quenching molecules).

Reaction rates have been followed using kinetic absorption spectrometry in which the absorbance at an appropriate wavelength within the triplet–triplet absorption band of the carbonyl compound has been measured as a function of time. Quenching rate constants k_{q} were evaluated by measuring the first-order decay rate constant of the ketone triplet as a function of added quencher, Q, concentration, when the observed value (k') is given by

$$k' = k_{\mathrm{d}} + k_{\mathrm{sq}}[\mathrm{A}] + k_{\mathrm{q}}[\mathrm{Q}]$$

where k_{sq} is the rate constant for self-quenching and k_{d} the rate constant for decay of the triplet in benzene. By varying the ketone concentration in the absence of quencher one can similarly determine k_{sq} and extrapolation to zero concentration gives k_{d}. Concentrations of quencher were kept to less than 10% of that of ketone in order to prevent complications due to direct interaction with the benzene states.

The Christie Hospital and Holt Radium Institute, Manchester, pulse radiolysis facility[18] incorporating a 10-MeV linear electron accelerator and associated nanosecond kinetic spectrometry equipment was used throughout this study.

Solutions were deaerated by prolonged bubbling with argon and measurements were carried out at ambient temperature. Total absorbed doses in the region of 1-5 krad per pulse were used and solutions were replenished after each shot.

2. Quantum Yield Measurements. Reaction and actinometer (benzophenone/benzhydrol in benzene) solutions were irradiated on a merry-go-round in sealed Pyrex tubes which had been degassed ten times by the freeze–thaw method. The incident light consisted of an envelope centered at 313 nm obtained by filtering the light of a 550-W Hanovia medium-pressure mercury arc with a solution of potassium chromate (0.002 M) in 1% aqueous potassium carbonate. All the incident light was absorbed by the aromatic carbonyl compound and conversions were less than 10%. Reaction solutions were analyzed by GLC using *n*-nonane and 2-naphthaldehyde as standards on an Apiezon L column, 6 ft, 12% on Chromosorb A, 70 °C, 10 psi, and a polyethylene glycol adipate column, 3 ft, 4% on Chromosorb G, 100 °C, 10 psi, respectively.

3. Reduction Potential Measurements. The buffer solutions (pH 12.65 in 50% aqueous ethanol) contained carbonyl compound (5 × 10^{-4} mol L^{-1}), acetic, boric, and orthophosphoric acid (each 1.95 × 10^{-2} mol L^{-1}) and KOH (1.03 × 10^{-1} mol L^{-1}). The Tinsley automatic polarograph was calibrated against a standard resistor and correction to a saturated calomel electrode was carried out by determining the voltage correction necessary for the current flowing at the half-wave potential. All solutions were bubbled with nitrogen for 30 min and experiments were carried out under a nitrogen atomosphere.

4. Materials. Benzene (Analar grade) was distilled from phosphorus pentoxide after sulfuric acid–water-bicarbonate treatment. Ethanol was refluxed over magnesium and then distilled. Benzophenone
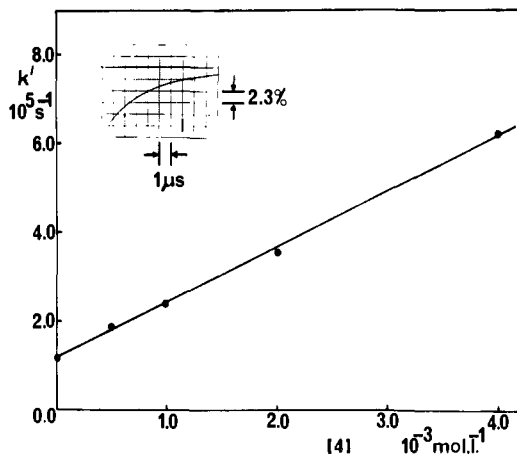
Figure 1. First-order decay constants of benzophenone triplet against concentration of ethoxycarbonylquadricyclene (**4**). Inset: Time dependence of benzophenone triplet decay measured at 525 nm after absorption of a 10-ns electron pulse by liquid benzene containing benzophenone (10^{-2} mol L^{-1}) and ethoxycarbonylquadricyclene (**4**, 10^{-3} mol L^{-1}).

Table I. Rate Constants for Quenching of Triplet Benzophenone in Benzene and Quencher Ionization Potentials

Quencher	k_q, L mol^{-1} s^{-1}	IP, eV
Norbornadiene (**1**)	9.7×10^8	8.69[c]
Quadricyclene (**2**)	8.3×10^8	8.56[c]
Ethoxycarbonylnorbornadiene (**3**)	2.1×10^9	8.87[c]
Ethoxycarbonylquadricyclene (**4**)	1.3×10^8	8.56[c]
Norbornene (**5**)	3.2×10^7	8.95[d]
2-Methylenenorbornane (**6**)	6.2×10^7	9.02[c]
5-Methylenenorborn-2-ene (**7**)	1.4×10^8	8.93[c]
Cyclohexene (**8**)	5.7×10^7 [a]	8.95[a]
2,3-Dimethylbut-2-ene (**9**)	8.95×10^8 [a]	8.30[a]
2-Methylbut-2-ene (**10**)	3.6×10^8 [a]	8.68[a]
3-Methylpent-2-ene (**11**)	2.4×10^8 [b]	8.80[b]
cis-But-2-ene (**12**)	8.0×10^7 [b]	9.13[b]

[a] Reference 12. [b] Reference 7. [c] Reference 24. [d] Reference 25.

(48-49 °C, EtOH), benzil (95-96 °C, EtOH), fluorenone (80-80.5 °C, EtOH/H_2O), and 2-naphthaldehyde (50-51 °C, H_2O) were recrystallized. 2-Acetonaphthone was prepared as described,[19] sublimed, and recrystallized twice (53-54 °C, 30/40 petrol). 1-Acetonaphthone was purified as its picrate and distilled. Triphenylene was zone refined several times.

Norbornadiene and quadricyclene were purified by distillation through a 4-ft steel wool packed column at 19.6 mmHg, still head temperatures 52 (norbornadiene) and 68 °C (quadricyclene). Quadricyclene was prepared by irradiation of acetophenone and norbornadiene in ether.[20] 2-Ethoxycarbonylnorbornadiene and 2-ethoxycarbonylquadricyclene were prepared as described.[21] Other olefins were passed down a column of alumina (neat or in ether) and distilled from sodium.

Results and Discussion

1. Quenching of Benzophenone Triplet by Olefins and Quadricyclenes. Benzophenone has a triplet energy (68.5 kcal mol^{-1})[22] which is significantly lower than that of butyrophenone (72.0)[23] and it is a better electron acceptor (vide infra). It should therefore be a better subject for attempted correlations such as those of Kochevar and Wagner,[12] since the percentage contribution of charge transfer induced decay to the overall quenching process should, if anything, be larger. We have irradiated 10^{-2} mol L^{-1} solutions of benzophenone in benzene and measured the decay of the ketone triplet (λ_{max} 525 nm) as a function of quencher concentration for the compounds **1-4** and a number of olefins. A typical plot of observed first-order rate constant vs. quencher concentration is shown in
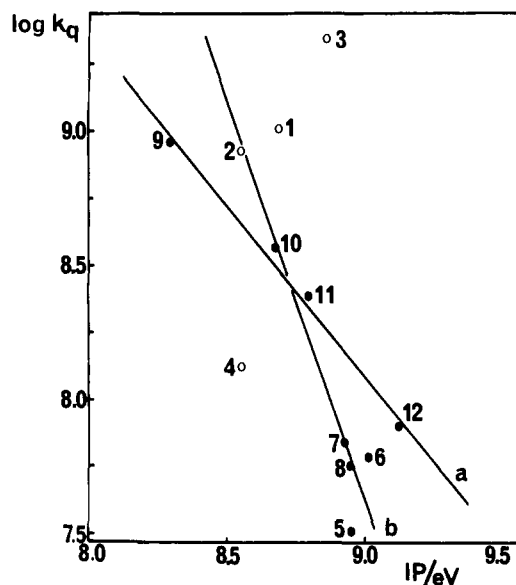

Figure 2. Quenching of benzophenone triplet in benzene: plot of log k_q against ionization potential of quencher. See Table 1 for quencher identity.

Figure 1. Extracted values of k_q are collected in Table I (with some literature values) together with gas-phase vertical ionization potentials of the quenchers employed.

In Figure 2 this data has been used to construct lines (a) and (b) without inclusion of the points for the compounds of immediate interest to us, namely, **1-4**. Line (a) shows the good correlation for the simple acyclic olefins (**9-12**) as also witnessed in the case of butyrophenone triplet.[12] However, the decreasing substitution on going from **9** to **12** would seem bound to lower the apparent sensitivity of the quenching process to the electron-donating capacity of the olefin. Line (b) is obtained by inclusion of the cyclic olefins (**5-8**)[26] and omission of **9** and **12**. We feel that this probably represents more closely the actual quenching sensitivity of olefins of the same steric requirement (were they to exist) to ionization potential. Possibly the correct line lies between (a) and (b)[27] but nevertheless these serve as useful guides for consideration of the quenching efficiencies of compounds **1-4**. On doing this an immediate contrast is apparent. The presence of the ester function markedly increases the quenching rate constant of the norbornadiene whereas the opposite is the case for the quadricyclene.

It is clear from Figure 2 that the ethoxycarbonylnorbornadiene (**3**) is not quenching benzophenone triplet by a predominantly charge-transfer mechanism. A low triplet energy, principally due to the α,β-unsaturated ester function, leads to a rate constant for triplet energy transfer which is only a factor of ~3 down on the optimum experimentally observed values (~6-7 $\times 10^9$ L mol^{-1} s^{-1})[29] for this process in benzene at room temperature. The position of norbornadiene (**1**) itself is somewhat ambiguous. The rate constant is slower than for **3** and a halving of k_q to account for the presence of two double bonds would place it close to line (b) in Figure 2. The fact that benzophenone sensitizes the conversion of both **1** and **3** to **2** and **4**, respectively, suggests that free triplets of **1** are likely to be involved by analogy with **3**. The following evidence indicates the extent to which such triplets are produced.

2. Quantum Yields for Quadricyclene Formation. In Table II are shown the rate constants for quenching of the triplet states of acetophenone, benzophenone, and 2-acetonaphthone by **1** and **3** and the quantum yield for production of the corresponding quadricyclene (ϕ_Q). The quenching rate constants together with the values shown for the self-quenching rate

Table II. Rate Constants and Quantum Yields[a] for Reaction of Norbornadienes with Acetophenone, Benzophenone, and 2-Acetonaphthone Triplets

|	Acetophenone	Benzophenone	2-Acetonaphthone
k_d, s^{-1}	2.5×10^5	1.5×10^5 [b]	8×10^4
k_{sq}, L mol^{-1} s^{-1}	4.6×10^6 [c]	4.0×10^5 [b]	1.0×10^5 [d]
k_q (1), L mol^{-1} s^{-1}	3.9×10^9	9.7×10^8	
k_q (3), L mol^{-1} s^{-1}	5.4×10^9	2.1×10^9	1.1×10^8
ϕ_T [e]	1.0	1.0	0.84
ϕ_Q (1) (ϕ_{max})	0.96 (1.0)	0.54 (1.0)	
ϕ_Q (3) (ϕ_{max})	0.93 (1.0)	0.85 (1.0)	0.80 (0.84)

[a] Determined at 0.1 M diene and 0.1 M ketone in benzene. [b] Reference 30. [c] Reference 31. [d] Reference 32. [e] Reference 33.

constants, k_{sq}, the rate constants for the natural decay of the triplets in benzene, k_d, and intersystem crossing efficiencies, ϕ_T, allow the maximum possible quantum yield for quadricyclene formation, $\phi_{max} = \phi_T k_q$ [quencher]/(k_q [quencher] + k_{sq} [ketone] + k_d), to be calculated. As shown in Table II this is close to unity in all cases for acetophenone and benzophenone.[34]

The rate constants for quenching of acetophenone triplet by **1** and **3** are more or less optimum values[29] and this clearly corresponds to a situation in which the diene triplet states are produced by electronic energy transfer. The slightly faster process for **3** must, at least in part, reflect its lower triplet energy. The quantum yield results indicate that 96% of the norbornadiene triplets and 93% of the corresponding ester triplets decay to the corresponding quadricyclene.

The data for benzophenone are of particular interest since there is a sharp drop in the observed quantum yield for quadricyclene formation (ϕ_Q), and a smaller one for the corresponding ester, compared with the acetophenone-sensitized experiments, although in both cases the quenching rate constants would allow a maximum quantum yield, ϕ_{max}, essentially equal to unity.

There appear to be two possible explanations of this result. Firstly, the lower quantum yield may reflect a change in the quenching mechanism, i.e., a lower percentage of free norbornadiene triplets are produced in the quenching acts. Secondly, the lower triplet energy of benzophenone may allow back transfer of triplet energy from norbornadiene triplet to become a significant process. The latter interpretation demands that at the ketone concentration used to determine quantum yields (0.1 mol L^{-1}) the rate of back transfer of triplet energy to benzophenone is significant with respect to the natural decay of triplet norbornadiene. In this concentration range ϕ_Q should thus vary with ketone concentration. The value of ϕ_Q (1) for benzophenone in Table II was invariant over the range 0.1–0.5 mol L^{-1}. In addition the corresponding rate
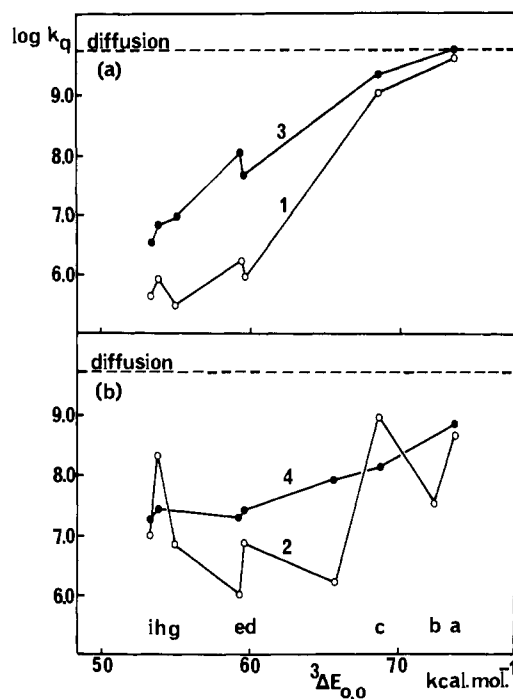
Figure 3. Variation of log k_q with sensitizer triplet energy, (a) for norbornadienes **1** and **3**, (b) for quadricyclenes **2** and **4**. See Table III for sensitizer identity.

constant shown in Table II, k_q (1), determined by pulse radiolysis, was constant within experimental error over the benzophenone concentration range 0.01 (9.7×10^8 L mol^{-1} s^{-1}) to 1.0 mol L^{-1} (9.5×10^8 L mol^{-1} s^{-1}). Reversible energy transfer is therefore excluded.

These results thus clearly indicate that on lowering the triplet energy of the sensitizer from 73.6 to 68.5 kcal mol^{-1} a change in the quenching mechanism takes place. The encounter complex involved in the process decays increasingly via a mechanism which leads to ground state reactants rather than free triplets of the quencher.

3. Effect of Sensitizer Triplet Energy. Pulse radiolysis experiments have been performed in which various ketone sensitizers were employed. Decay rates of the triplets were measured as a function of quencher (**1–4**) concentration and bimolecular quenching rate constants (k_q) were evaluated. Summarized data are presented in Table III.

A comparison has been made of the dependence of log k_q on sensitizer triplet energy for the quenchers **1–4**. This is shown in Figure 3.[35] In the cases of the norbornadienes **1** and **3** an obvious trend is apparent. The greater sensitivity of **3** in the low sensitizer triplet energy region clearly reflects its lower triplet energy with respect to **1**. This is exemplified by 2-ace-

Table III. Rate Constants for Quenching of Aromatic Carbonyl Triplet States by Norbornadienes and Quadricyclenes in Benzene

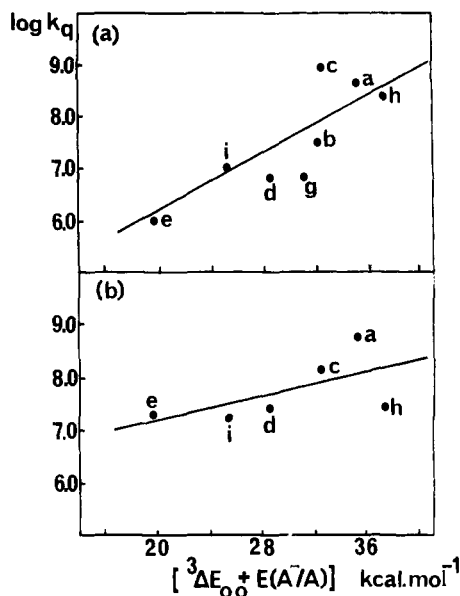|	Quencher			
Carbonyl compd	k_q (1), L mol^{-1} s^{-1}	k_q (2), L mol^{-1} s^{-1}	k_q (3), L mol^{-1} s^{-1}	k_q (4), L mol^{-1} s^{-1}
Acetophenone (**a**)	3.9×10^9	4.3×10^8	5.4×10^9	6.6×10^8
m-Methoxyacetophenone (**b**)		3.0×10^7		
Benzophenone (**c**)	9.7×10^8	8.3×10^8	2.1×10^9	1.3×10^8
2-Naphthaldehyde (**d**)	8.6×10^5	6.9×10^6	4.3×10^7	2.6×10^7
2-Acetonaphthone (**e**)	1.6×10^6	1.0×10^6	1.1×10^8	2.0×10^7
1-Acetonaphthone (**f**)		8.5×10^5		
Biacetyl (**g**)[a]	2.8×10^5	6.7×10^6	9.0×10^6	
Benzil (**h**)	9.2×10^5	1.9×10^8	6.4×10^6	2.7×10^7
Fluorenone (i)	4.6×10^5	1.0×10^7	3.2×10^6	1.7×10^7
Triphenylene (**j**)[a]		1.7×10^6		7.5×10^7

[a] Reference 35.

Figure 4. Plot of log k_q against $[^3\Delta E_{0,0} + E(A^-/A)]$ for quenching of triplets in benzene (a) by quadricyclene (**2**) and (b) by ethoxycarbonyl-quadricyclene (**4**). See Table III for sensitizer identity.

Table IV. Triplet Energies and Half-Wave Reduction Potentials of Carbonyl Compounds

Compd	$^3\Delta E_{0,0}$ kcal mol^{-1}	$-E(A^-/A)$, eV	$[^3\Delta E_{0,0} + E(A^-/A)]$, kcal mol^{-1}
Acetophenone (**a**)	73.6	1.66	35.3
m-Methoxyaceto-phenone (**b**)	72.4	1.74	32.3
Benzophenone (**c**)	68.5	1.55	32.8
2-Naphthaldehyde (**d**)	59.5	1.34	28.6
2-Acetonaphthone (**e**)	59.3	1.72	19.6
Biacetyl (**g**)	54.9	1.03	31.1
Benzil (**h**)	53.7	0.71	37.3
Fluorenone (**i**)	53.3	1.21	25.4

tonaphthone ($^3\Delta E_{0,0} \approx 59.3$ kcal mol^{-1}). The values for ϕ_Q and ϕ_{max} in Table II indicate that 95% of quenchings of this ketone triplet by **3** yield **4**. This is within experimental error of the value of 93% for acetophenone and thus, although the quenching rate constant is one to two orders of magnitude down on the optimum, it involves mainly transfer of electronic energy.

The position of quadricyclene (**2**) in Figure 2 is clearly in agreement with a charge-transfer quenching mechanism. In addition, in contrast to the norbornadienes, introduction of an ester function decreases the rate constant for quenching of benzophenone triplet, a fact which clearly indicates a difference in mechanism. Since **2** and **4** have identical ionization potentials (Table I) it seems probable that the rate constant is lower in the case of **4** because of steric hindrance to complex formation introduced by the ester function. The fact that for acetophenone triplet the quenching rate constant for **4** is slightly higher than for **2** (Table III) suggests that the ester function is playing an additional role in lowering the triplet energy of the quadricyclene as one would expect. These conclusions are borne out by consideration of Figure 3. Whereas quenching by quadricyclene (**2**) appears to be totally unrelated to the sensitizer triplet energy, the corresponding ester (**4**) begins to show a significant dependence at higher triplet energies.

4. Attempted Correlation with the Function $[^3\Delta E_{0,0} + E(A^-/A)]$. In order to confirm our conclusions that quadricyclene is a charge-transfer quencher of aromatic carbonyl triplets we have attempted to employ the approach used by Guttenplan and Cohen[8] for triethylamine, i.e., for the various sensitizers plot log k_q against the function $[^3\Delta E_{0,0} + E(A^-/A)]$ according to eq 1. The literature half-wave reduction potential data on aromatic carbonyl compounds are highly unsatisfactory in that experimental conditions vary considerably and in some cases no confident choice between several published values can be made. We have therefore determined the half-wave reduction potentials of the carbonyl compounds shown in Table IV using a buffered aqueous ethanol solution, pH 12.65 (see Experimental Section). The values obtained together with respective triplet energies and the resultant $[^3\Delta E_{0,0} + E(A^-/A)]$ values are summarized in Table IV. In Figure 4a is shown the plot of log k_q values for quadricyclene
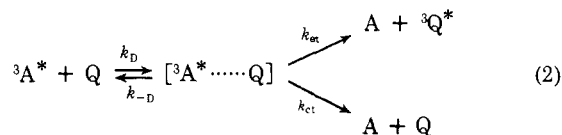
(**2**) against the function $[^3\Delta E_{0,0} + E(A^-/A)]$. The correlation is very poor, the least-squares plot shown having a correlation coefficient of 0.63, which compares very unfavorably with that of 0.98 obtained by Guttenplan and Cohen for triethylamine. The least-squares plot for the ethoxycarbonylquadricyclene (**4**, Figure 4b) shows even less sensitivity to the function under consideration as is to be expected.

We have commented elsewhere on Guttenplan and Cohen's data and indeed our own experiments with triethylamine indicate a poor correlation in benzene.[36] It therefore appears that aromatic carbonyl triplets do not lend themselves to the kind of approach attempted here and for triethylamine, although the quenching process under consideration is of the charge-transfer type.[37] Apart from steric factors and variations in sensitizer electronic configuration a possible cause arises out of consideration of the assumptions underlying the correlation relationship (eq 1).

In the following possible reaction sequence (**2**) k_D and k_{-D} are respectively the rate constants for rapid formation and for

$$^3A^* + Q \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} [^3A^* \cdots \cdots Q] \underset{k_{ct}}{\overset{k_{et}}{\longrightarrow}} \begin{matrix} A + ^3Q^* \\ \\ A + Q \end{matrix} \qquad (2)$$

dissociation of a charge-transfer stabilized complex or exciplex, and k_{el} and k_{cl} the rate constants for formation of energy transfer derived products and for charge-transfer induced decay to ground states from that exciplex, respectively. The overall quenching rate constant, k_q, is given by

$$k_q = \frac{k_D(k_{el} + k_{ct})}{(k_{el} + k_{cl} + k_{-D})} \qquad (3)$$

and with low overall reaction probability, i.e., $k_{-D} > k_{el} + k_{cl}$,

$$k_q = (k_{et} + k_{ct})K_c \qquad (4)$$

where K_c is the equilibrium constant for complex formation.[38] By expressing the free energy of complex formation (ΔG_c) in terms of the individual energy contributions

$$-\Delta G_c = RT \ln K_c = [^3\Delta E_{0,0} + E(A^-/A)] + \text{constant} \quad (5)$$

or

$$\log k_q - \log(k_{et} + k_{ct}) \propto [^3\Delta E_{0,0} + E(A^-/A)] \qquad (6)$$

A linear relationship between log k_q and the sensitizer energy term requires ($k_{el} + k_{cl}$) to be independent of the energy in the complex. That the plots in Figure 4 do not show linear behavior could indicate that the neglect of such an energy dependence is not valid—a not altogether surprising conclusion. The poor correlations are less readily understood if triplet exciplex formation is irreversible as has been proposed for the reaction of
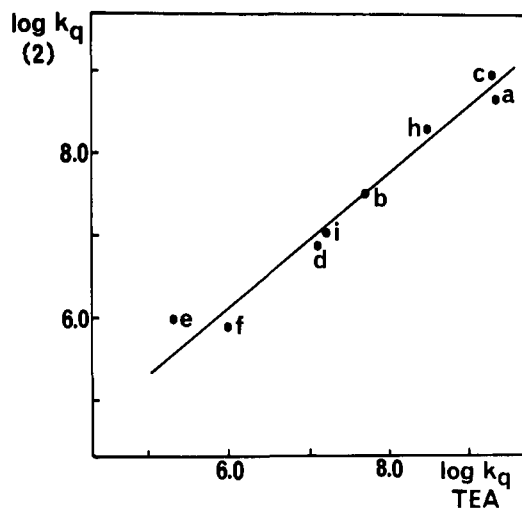
Figure 5. Log-log plot of rate constants for quenching of aromatic carbonyl triplets by quadricyclene (**2**, ordinate) and triethylamine (TEA, abscissa) in benzene. See Table III for sensitizer identity.

triplet benzophenone with but-2-ene and isobutylene.[11]

5. Correlation of Quenching Rate Constants for Quadricyclene with Those of Triethylamine.

In order to obviate the problems associated with a correlation of rate constants with reactant physical properties designed to establish a particular mechanism, a standard procedure is to compare such rate constants with those for a reactant known to react via that mechanism. In a separate study[36] we have, as mentioned, determined the rate constants for quenching of aromatic carbonyl triplets by triethylamine using pulsed nitrogen laser photolysis. In Figure 5 these values for quenching in benzene are plotted as log k_q against log k_q for quadricyclene. An excellent correlation is a clear indication that the two compounds quench aromatic carbonyl triplets via the same mechanism.

Conclusions

The quenching of aromatic carbonyl triplets by norbornadienes may involve either the production of free diene triplets or ground state species. Only high-energy sensitizers lead to efficient quenching to give free triplets, which are the species leading to the corresponding quadricyclene. With lower energy sensitizers the quenching rapidly becomes slower and the balance between free triplet formation and charge-transfer induced quenching depends on the facility with which the sensitizer can act as an electron acceptor. Since optimum rate constants for quenching in benzene are generally about a factor of 2-3 lower than diffusion (cf. ref 29b) we can estimate that, in terms of sequence 2 for the quenching of the high-energy triplet of acetophenone by norbornadiene (**1**, cf. Table II), $k_{-D} \sim k_{el} \gg k_{cl}$. In the case of benzophenone, which has a lower triplet energy but a more favorable reduction potential, $k_{-D} > k_{et} \sim k_{cl}$ and the quantum yield for quadricyclene formation is almost halved (Table II). In the case of the already mentioned quenching of 2-acetonaphthone triplet by the ethoxycarbonylnorbornadiene (**3**, Table II) $k_{-D} \geq k_{et} > k_{cl}$ due to poor electron-accepting properties (cf. Table IV).

Quenching by quadricyclene involves charge-transfer induced decay to ground states. From the known photochemistry[2b,3] these ground states are at least in some instances those of norbornadiene and the sensitizer and their formation must be closely related to the process resulting from reaction of hydrocarbon singlet states with quadricyclene.[4] Presumably the charge-transfer induced decay is facilitated, at least in part, by stabilization of the complex with respect to dissociation. In terms of sequence 2 for quenching by quadricycle $k_{-D} > k_{ct}$

$\gg k_{et}$ and the actual measured rate constant depends on the extent of stabilization of the complex. It would appear that the ethoxycarbonyl analogue (**4**), with a lower triplet energy, can quench high-energy triplets, at least in part, via an energy transfer mechanism, i.e., $k_{-D} > k_{ct} \sim k_{el}$. The fate of the triplet thus produced is unknown. In the case of sensitizers such as acetophenone and benzophenone, with n,π^* triplet states, the charge-transfer stabilized encounter complex must decay, at least in part, to the biradical precursors of the 1:1 adducts which are also formed.[14,39]

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(35) Although this work is specifically concerned with aromatic carbonyl triplet mechanisms, some data available for quenching of biacetyl (g) triplet by **1, 2** and **3** and of triphenylene (j) triplet by **2** and **4** have been included in Table III and Figure 3.
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Base-Catalyzed Oxygenation of *tert*-Butylated Phenols. 1. Regioselectivity in the Base-Catalyzed Oxygenation of *tert*-Butylphenols[1]

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Abstract: In the oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols (**1**) catalyzed by potassium *tert*-butoxide, molecular oxygen is added to the phenolates regioselectively depending on the solvent. In aprotic solvents the para position of the phenolates is oxygenated exclusively, and the resulting *p*-hydroperoxy anion intermediates (**5'**) are converted to the corresponding epoxy-*p*-quinols (**2**). In *tert*-butyl alcohol, the ortho position is oxygenated predominantly, resulting in *o*-hydroperoxy anion intermediates (**16'**) which are converted to epoxy-*o*-quinols (**11**). The oxygenation of 2,6-di-*tert*-butyl-4-methylphenol in *N,N*-dimethylformamide in the presence of a large amount of potassium *tert*-butoxide results in the selective oxidation of the methyl group to give 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde. In the *tert*-butoxide-catalyzed oxygenation of 2,4-di-*tert*-butylphenols (**6**) in aprotic solvents, epoxy-*p*-quinols (**7, 8**) are formed. In *tert*-butyl alcohol epoxy-*o*-quinols (**11**) as well as products (**14, 15**) resulting from ring cleavage are formed. The solvent-dependent regioselectivity may be interpreted in terms of the stability of the peroxy anion intermediates to which the counter cation (K⁺) contributes depending on the solvent.

Base-catalyzed oxygenation of phenols involves oxidation of carbanions generated on the phenolic ring through resonance structures of the phenolate anions. The oxidizability of phenolates depends on their redox potential which, in turn, depends on the nature of the substituents on the aromatic ring. Electron-releasing groups lower the potential which results in an increase of the reactivity, whereas electron-withdrawing groups raise it.[2-5] The oxygenation of phenolates generally leads to a complex reaction mixture resulting from the introduction of oxygen as well as from oxidative coupling of the phenolic ring.[6-8] If, however, *tert*-butyl groups are in the ortho and para positions, a less complex reaction mixture is obtained since no or little oxidative coupling takes place owing to steric hindrance by the bulky *tert*-butyl groups. Base-catalyzed oxygenation of 2,6-di-*tert*-butylphenols in alcoholic alkaline solutions mainly gives 2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienones.[9-14] Semiquinone radicals have been detected in the oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols in aqueous acetone containing potassium hydroxide.[15] Recently, the oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols in diethylamine containing sodium amide has been shown to provide a convenient method for the synthesis of 2,6-di-*tert*-butyl-4-hydroxy-2,5-cyclohexadienones (*p*-quinols).[16]

The present paper deals with the oxygeantion of 2,6- and 2,4-di-*tert*-butylphenols (**1, 6**) catalyzed by potassium *tert*-butoxide. A regioselectivity depending on the solvent used was observed. In aprotic solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (Me₂SO), and hexamethyl phosphoric triamide (HMPT), both phenols are oxygenated exclusively at the para position to give epoxy-*p*-quinols (**2, 7, 8**) in good yields. In *tert*-butyl alcohol, an ortho position is oxygenated predominantly resulting in the formation of epoxy-*o*-quinols (**11**). Both epoxyquinols are formed via hydroperoxy anion intermediates. In the case of 2,4-di-*tert*-butylphenol (**6b**), the hydroperoxy anion intermediate is converted not only to the epoxy-*o*-quinol, but also to products resulting from oxidative ring cleavage. The formation of the epoxy-*p*-quinols

is of particular interest in connection with the biosynthesis of the naturally occurring epoxy-*p*-quinols such as epoxidone (**10**), a fungal metabolite.[17] Interestingly, the use of a large amount of potassium *tert*-butoxide in DMF in the oxygenation of 2,6-di-*tert*-butyl-4-methylphenol (**1d**) leads to the selective oxidation of the methyl group with formation of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**1e**). The regioselective oxygenation of *tert*-butylphenols can be exploited for the synthesis of new compounds.[18-22] This regioselectivity may be interpreted in terms of the stability of the hydroperoxy anion intermediates.

Results

Formation of Epoxy-*p*-quinols. When 4-alkyl-2,6-di-*tert*-butylphenols (**1a–d**, Chart I) and 2,4-di-*tert*-butylphenols (**6a, 6b**, Chart II) are oxygenated (oxygen bubbling at ambient temperature) in aprotic solvents such as DMF, Me₂SO, and

Chart I

R	a	b	c	d	e
	t-Bu	i-Pr	Et	Me	CHO

1820