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Lifetimes and Energies of the Relaxed Triplet States of Cyclopentadiene and Tetramethylbutadiene. A Pulse Radiolysis and Pulsed Laser Study

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Abstract: The triplet states of cyclopentadiene and tetramethylbutadiene have been produced in benzene by pulse radiolysis. Energy-transfer experiments have established natural lifetimes of 1.7 μs and 73 ns, respectively. The observation of triplet energy transfer equilibria with pulse radiolysis and pulsed laser photolysis has established a relaxed triplet energy for cyclopentadiene of 58.0 ± 0.2 kcal mol^{-1}, which shows that relaxation from the Franck–Condon state is negligible. An approximate "available" triplet energy of 42 kcal mol^{-1} for the relaxed tetramethylbutadiene triplet has been determined. The rate constant data for energy transfer obtained by using both pulse radiolysis and pulsed laser photolysis appear totally consistent with vertical energy transfer processes only.

1. Introduction

A major area of organic photochemistry concerns the reactivity of the triplet states of both conjugated and nonconjugated olefins which have been produced via triplet energy transfer from a suitable donor molecule. In general the donor triplet states, usually of aromatic carbonyl compounds or aromatic hydrocarbons, have been well characterised in terms of electronic energy and lifetime from phosphorescence spectra and time-resolved absorption or emission spectroscopy, respectively. In contrast, olefin triplet states do not phosphoresce and triplet–triplet absorption spectra have not been observed.[1] Singlet–triplet absorption spectra measured at high oxygen pressures,[2-4] and more recently gas-phase electron-impact spectroscopy,[5] do yield spectroscopic triplet energies. However, the flexibility of the σ framework, in conjunction with unfavorable π-electron interactions introduced by excitation to the Franck–Condon π,π^* state, will result in relaxation to an equilibrium state which may be appreciably different in terms of geometry and vertical triplet energy to the Franck–Condon triplet. The classic case of such behavior is that of ethylene for which the S_0 and T_1 potential-energy surfaces either cross or are very close together at an angle of twist about the C–C axis of approximately 90°.[6] For such relaxed triplets fast intersystem crossing to vibrationally and torisonally excited S_0 takes place followed by relaxation to equilibrium S_0 which, in appropriately substituted ethylenes, may be geometrically isomeric or identical with the initially excited species. That such processes are rapid is demonstrated by the fact that energy-transfer effects from olefins such as 2-butene have never been observed.[7] However, if a simple π bond is accommodated within a rigid σ framework, which severely restricts the twisting tendency within T_1, the relaxed species would be expected to have both a triplet lifetime longer than that witnessed for simple olefins and a significant vertical triplet energy. We have recently used the pulse radiolysis technique to show this to be true for norbornene, the relaxed triplet of which, in benzene, has a lifetime of 250 ns and an "available" triplet energy of ~57 kcal mol^{-1}, probably at least 15 kcal mol^{-1} less than that of the Franck–Condon triplet.[8]

In the case of 1,3-dienes molecular orbital considerations indicate that relaxation of the lowest triplet state should involve twisting about a terminal C–C bond of the π system to give the orthogonal methyl-allyl biradical structure. The calculated extent of stabilization varies between 5 and 40 kcal mol^{-1}[9] and as far as we are aware the vertical energy difference between the relaxed diene triplet and the ground-state potential-energy surface has not been estimated. Thus whether or not the S_0 and T_1 surfaces are likely to cross, as in the case of simple olefins, is unknown and the effect of relaxation on diene triplet lifetimes remains a matter for speculation. In addition, although a considerable body of data exists concerning the triplet-sensitized dimerization and geometrical isomerization of 1,3-dienes,[10-15] the only triplet lifetimes to be estimated are those of isoprene in benzene, values as different as ≥5 μs[10f,12] and ≥12.5 ns[11c] being quoted, and of cyclohexa-1,3-diene in benzene for which a value of ≥20 μs has been proposed.[11d] We have therefore addressed ourselves to the problem of determining lifetimes and energies of 1,3-diene triplets. Ideally we wished to (a) establish both the Franck–Condon and relaxed triplet energies in solution by witnessing time-resolved triplet energy transfer both to and from the dienes using donors and acceptors of appropriate triplet energies and (b) determine the relaxed triplet lifetimes from the experiments involving energy transfer to a suitable acceptor.

One would anticipate that for cyclopentadiene (CPD) relaxation by twisting about a terminal C–C bond of the π system will be severely restricted and therefore that it should possess a relaxed triplet state of higher energy and longer lifetime than an acyclic diene triplet. We have therefore concentrated our initial efforts

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(1) We exclude extended polyenes such as β-carotene from this discussion. They, of course, show intense triplet–triplet absorption in an accessible spectral region.

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on CPD and compared its triplet energy accepting properties and triplet lifetime with those of a simple acyclic diene, namely, 2,5-dimethylhexa-2,4-diene (tetramethylbutadiene, TMB). We have used a series of aromatic hydrocarbons plus β-carotene, which exhibit intense triplet–triplet absorption spectra, as the donor/acceptor monitors (M) and our experimental approach is outlined below.

2. Determination of Rate Parameters

2.1. Pulse Radiolysis. Electron pulse radiolysis is a technique of great value in the direct investigation of molecular triplet states in fluid solution.[8,16] Energy absorption from a 10 or 20 ns pulse of high-energy electrons (several MeV) by an aromatic liquid such as benzene (B) produces significant yields of short-lived bound excited states of the matrix molecules[16b] according to eq 1. After

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

the pulse these species decay via the normal photophysical channels or can in the presence of suitable additive molecules pass on their electronic excitation energy. Since the rate of this transfer is purely concentration dependent for exothermic processes a solute of concentration 100-fold higher than other additives will be essentially exclusively excited. The short lifetimes of ${}^1\mathrm{B}^*$ and ${}^3\mathrm{B}^*$ in liquid benzene, 12[17] and 3 ns, respectively,[7] and the short lifetime of the singlet state of the acceptor molecule mean that the formation of the triplet state of the latter will be complete within 50 ns. Its subsequent lifetime is governed by the composition of the solution with respect to further low-concentration additives.

High Monitor–Low Diene Concentrations. For pulse radiolysis of benzene containing a monitor M (10^{-1}–10^{-2} mol L^{-1}) and a diene D ($\sim 10^{-4}$ mol L^{-1}) where triplet energy transfer from M to D is appreciably exothermic the processes to be taken into account are those summarized in eq 2–6. Such low diene concentrations

$${}^1\mathrm{B}^* + \mathrm{M} \rightarrow \mathrm{B} + {}^1\mathrm{M}^* \tag{2}$$

$${}^1\mathrm{M}^* \rightarrow {}^3\mathrm{M}^*, \mathrm{M} \tag{3}$$

$${}^3\mathrm{B}^* + \mathrm{M} \rightarrow \mathrm{B} + {}^3\mathrm{M}^* \tag{4}$$

$${}^3\mathrm{M}^* \xrightarrow{k_\mathrm{M}} \mathrm{M} \tag{5}$$

$${}^3\mathrm{M}^* + \mathrm{D} \xrightarrow{k_\mathrm{MD}} \mathrm{M} + {}^3\mathrm{D}^* \tag{6}$$

will significantly quench ${}^3\mathrm{M}^*$ without competing for the benzene excited states. One may then observe the decay of ${}^3\mathrm{M}^*$ according to eq 7. The corresponding first-order decay constant, k', is given by eq 8 and plots of k' vs. [D] allow determination of k_M and k_MD.[18]

$$\frac{-\mathrm{d}[{}^3\mathrm{M}^*]}{\mathrm{d}t} = (k_\mathrm{M} + k_\mathrm{MD}[\mathrm{D}])[{}^3\mathrm{M}^*] \tag{7}$$

$$k' = k_\mathrm{M} + k_\mathrm{MD}[\mathrm{D}] \tag{8}$$

High Diene–Low Monitor Concentrations. For reversal of the diene and monitor concentrations in a situation where triplet energy transfer from D to M is appreciably exothermic, and the ${}^3\mathrm{D}^*$ lifetime is long enough, the important processes are those summarized by eq 9–14. These take into account (a) the known

$${}^1\mathrm{B}^* + \mathrm{D} \rightarrow \text{loss of } {}^1\mathrm{B}^* \tag{9}$$

$${}^1\mathrm{D}^* \rightarrow \mathrm{D} \tag{10}$$

$${}^3\mathrm{B}^* + \mathrm{D} \rightarrow \mathrm{B} + {}^3\mathrm{D}^* \tag{11}$$

$${}^3\mathrm{D}^* \xrightarrow{k_\mathrm{D}} \mathrm{D} \tag{12}$$

$${}^3\mathrm{D}^* + \mathrm{M} \xrightarrow{k_\mathrm{DM}} \mathrm{D} + {}^3\mathrm{M}^* \tag{13}$$

$${}^3\mathrm{D}^* + \mathrm{D} \xrightarrow{k_\mathrm{DD}} \mathrm{D}_2 \tag{14}$$

fact that dienes quench benzene and substituted benzene singlets[19] (eq 9), (b) the fact that intersystem crossing will be unimportant for ${}^1\mathrm{D}^*$, unimolecular decay giving only ground state (eq 10), and (c) the known triplet-sensitized dimerization of dienes already referred to[10] (eq 14). Assuming the relatively long-lived diene triplet, slow grow-in of ${}^3\mathrm{M}^*$ should be observed via eq 13, the first-order rate constant for grow-in, k', being defined by eq 15. Plots of k' vs. [M] at constant [D] and of k' vs. [D] at constant [M] would then allow determination of k_DM, k_DD, and k_D.

$$k' = k_\mathrm{D} + k_\mathrm{DD}[\mathrm{D}] + k_\mathrm{DM}[\mathrm{M}] \tag{15}$$

2.2. Pulsed Laser Photolysis. In situations where it is necessary to monitor the decay of a monitor triplet state in the presence of high concentrations of a poor quencher, the direct excitation of quencher by the benzene states may become a problem in pulse radiolysis, particularly if reverse energy transfer is possible (vide infra). Thus for such situations we have employed pulsed nitrogen laser excitaton of the monitor at 337 nm, the dienes being transparent at this wavelength. Rate constants were determined according to eq 8.

2.3. Reversible Energy Transfer. As the triplet-energy difference between donor and acceptor decreases to about 3 kcal mol^{-1} back-transfer may become quite efficient; i.e., the relationships of eq 8 and 15 may no longer hold due to competition between steps 6 and 13. Whether this is the case depends on (a) the rate of the energy-transfer steps relative to triplet-state decays, (b) the relative values of donor and acceptor triplet lifetimes, and (c) whether donor concentrations allow back-transfer to compete with acceptor triplet decay.[20b,21] For the case of CPD, the triplet state of which may not relax to a significant extent, reverse transfer requires serious consideration.

3. Experimental Section

3.1. Pulse Radiolysis. Experiments were performed at the Christie Hopsital and Holt Radium Institute, Manchester, using the Vickers 10-MeV linear accelerator with pulse widths of either 10 or 20 ns. Kinetic absorption spectrometry measurements were made with the apparatus described by Keene and Hodgson.[22] The time dependencies of monitor triplet–triplet absorptions were displayed as CRO traces of voltage waveforms at the anode of an EMI 9783R photomultiplier coupled to a 56 Ω load resistance, minimum rise time 5 ns. Irradiations were carried out at room temperature. Solutions were deaerated by prolonged argon bubbling and those containing β-carotene were prepared and used with the exclusion of ambient light.

3.2. Pulsed Laser Photolysis. Experiments were performed with a Lamda Physik I MW nitrogen laser, pulse width 2.5 ns, wavelength 337 nm, at right angles to a pulsed xenon analyzing lamp and Hilger-Watt monochromator. The time dependencies of monitor triplet–triplet absorptions were displayed, via a Tektronix 7912 Transient Digitizer, as CRO traces of voltage waveforms at the anode of an EMI 9781 photomultiplier coupled to a 50 Ω load resistance, minimum rise time 1 ns. Monitor solutions were such as to give an optical density at 337 nm of $\sim$0.7 and were dearated by prolonged nitrogen bubbling. Experiments were performed at room temperature.

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(17) In neat benzene at room temperature ${}^1\mathrm{B}^*$ is the excimer ${}^1\mathrm{E}_\mathrm{u}$ state; this does not affect the energy-transfer scheme.

(18) Self-quenching which is relatively unimportant for aromatic hydrocarbon triplets has not been separated from k_M since we are only interested in k_MD.

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Table I. Rate Constants (L mol^{-1} s^{-1})[a] for Triplet Energy Transfer in Benzene between Monitors (M) and 1,3-Dienes (CPD and TMB)

monitor (λ, nm)	E_T, kcal mol^{-1}	M → CPD	CPD → M	M → TMB	TMB → M
biphenyl (370)	65.7[b]	2.0×10^{10}		5.4×10^9	
naphthalene (420)	60.9[b]	3.0×10^9	2.0×10^7 [g]	3.2×10^9	
chrysene (570)	56.6[b]	3.2×10^8 [f,g]	3.0×10^9	1.4×10^9 [f]	
fluoranthene (415)	54.2[b]	3.0×10^7 [f,g]	5.9×10^9	1.8×10^8 [f]	
pyrene (415)	48.2[c]	$<5.0 \times 10^4$ [f]	7.6×10^9	4.0×10^5 [f]	
anthracene (425)	42.7[d]	$<5.0 \times 10^4$ [f]	9.8×10^9	$<3.0 \times 10^4$ [f]	2.8×10^9
β-carotene (520–550)	<23.0[e]	*h*	1.4×10^{10}	*h*	8.0×10^9

[a] Determined by pulse radiolysis unless otherwise stated. [b] Reference 24, hydrocarbon glass at 77 K. [c] Reference 25, EPA glass at 77 K. [d] Reference 26, EPA glass at 77 K. [e] Reference 27. [f] Determined by pulsed laser excitation at 337 nm. [g] Calculated from equilibrium constant (section 4.3). [h] Reference 28.

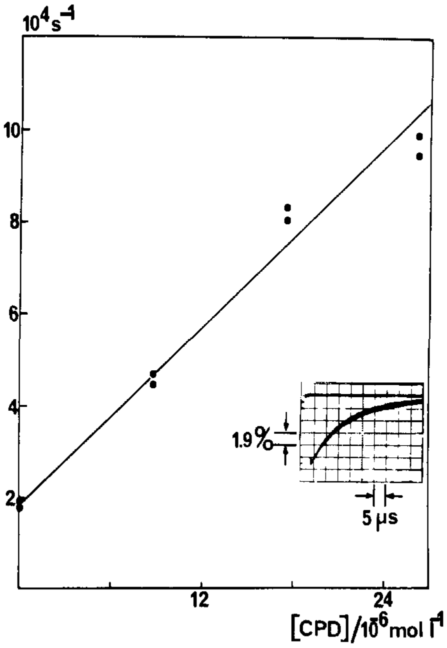

Figure 1. First-order constants for naphthalene triplet decay against CPD concentration. Inset: Time dependence of naphthalene triplet decay monitored at 420 nm after absorption of a 20 ns electron pulse by liquid benzene containing naphthalene (10^{-3} mol L^{-1}) and CPD (1.75×10^{-5} mol L^{-1}).

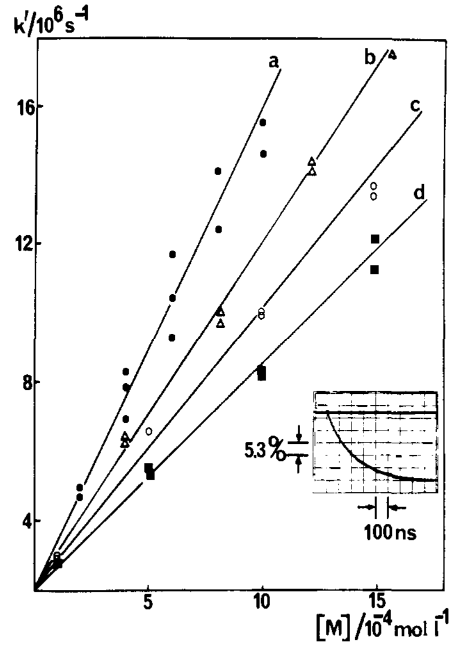

Figure 2. First-order constants for monitor triplet formation vs. monitor concentration: (a) β-carotene, (b) anthracene, (c) pyrene, and (d) fluoranthene. Inset: Time dependence of β-carotene triplet formation monitored at 550 nm after absorption of a 20 ns electron pulse by liquid benzene containing CPD (10^{-1} mol L^{-1}) and β-carotene (2×10^{-4} mol L^{-1}).

3.3. Materials. Benzene (Analar) was distilled from phosphorus pentoxide after sulfuric acid, water, bicarbonate, and water treatment. Biphenyl ($MeOH-H_2O$), chrysene (C_6H_6), fluoranthene (EtOH), pyrene (EtOH) and β-carotene (C_6H_6–MeOH) were recrystallized. Naphthalene and anthracene (BDH scintillation grade) were used as received. Cyclopentadiene was prepared immediately before use by thermal decomposition of the dimer (Koch-Light) over iron filings. Tetramethylbutadiene (Aldrich) was distilled from lithium aluminum hydride before use.

4. Results and Discussion

In the light of the considerations discussed in section 2 we have been able to determine the rate constants for triplet energy transfer between the monitor hydrocarbons plus β-carotene and CPD and TMB. The results are summarized in Table I.[23]

4.1. Initial Excitation of Monitor in Presence of Cyclopentadiene. Pulse radiolysis of benzene solutions of biphenyl (10^{-2} mol L^{-1}) containing various CPD concentrations ($<10^{-4}$ mol L^{-1}) allowed straightforward determination of the rate constant for energy transfer according to eq 8. The same was true for naphthalene although the problem of reverse energy transfer (section 4.3) required use of a lower monitor concentration (10^{-3} mol L^{-1}) (Figure 1). For monitors with lower triplet energies, chrysene and below, the relatively high CPD concentrations required made monitor excitation by laser a better technique.[28] In the cases of chrysene and fluoranthene reverse energy transfer prevented direct determination of the rate constants, which were obtained from the equilibrium constant for energy transfer (section 4.3).

4.2. Initial Excitation of Cyclopentadiene in Presence of Monitor. Pulse radiolysis of benzene solutions of CPD (10^{-1} mol L^{-1}) containing monitor (10^{-3} mol L^{-1}) resulted in no significant monitor fluorescence but an excellent "slow" grow-in of monitor triplet absorption for fluoranthene and the lower triplet energy monitors as exemplified in Figure 2. Plots of *k'* vs. [M] according to eq 15 gave rate constants for triplet energy transfer to monitor from CPD and a common intercept (Figure 2) corresponding to a $^3CPD^*$ lifetime of 500 ns in the presence of CPD (10^{-1} mol L^{-1}). A plot of *k'* vs. [CPD] at constant pyrene concentration (Figure 3) allowed determination of the rate constant for the known reaction between $^3CPD^*$ and CPD[30] (eq 14), $k_{DD} = 1.4 \times 10^7$

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[23] It is recognized that rate constants for quenching of monitor triplets by diene which are very much less than optimum may reflect processes other than energy transfer.

[24] S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, Inc., New York, 1973.

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[28] ^{1}β-carotene* does not intersystem cross[29] and hence laser excitation was not a viable technique for this monitor.

[29] T. G. Truscott, E. J. Land, and A. Sykes, *Photochem. Photobiol.*, **17**, 43 (1973).

[30] It is not known whether k_{DD} contains a contribution from reactions which do not lead to dimer, classical self-quenching for instance.

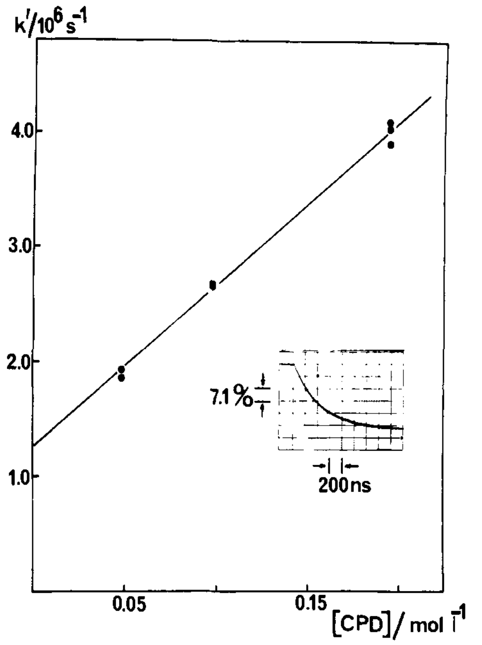

Figure 3. First-order constants for pyrene triplet formation vs. CPD concentration. Inset: Time dependence of pyrene triplet formation monitored at 415 nm after absorption of a 20 ns electron pulse by liquid benzene containing CPD (1.46×10^{-1} mol L^{-1}) and pyrene (10^{-4} mol L^{-1}).

L mol^{-1} s^{-1}, and therefore the rate constant for natural decay of $^3CPD^*$ in benzene, $k_D = 6.0 \times 10^5$ s^{-1}. This corresponds to a lifetime of 1.7 μs.

In the corresponding experiments no triplet grow-in was observed for biphenyl or naphthalene. Although energy transfer is reversible for the latter (section 4.3) the lack of triplet observation simply reflects the high rate constant for the reverse reaction and the high CPD concentration. A similar situation holds for chrysene but its lower triplet energy allowed observation of a small amount of triplet formation from which an approximate rate constant of 3.0×10^9 L mol^{-1} s^{-1} was determined.

4.3. Reversible Triplet Energy Transfer between CPD and the Monitors Naphthalene, Chrysene, and Fluoranthene. There has been considerable discussion concerning the relationship between the optimum observed rate constants for triplet energy transfer in solution and calculated rate constants for diffusion based on the Debye equation.[31,32] In particular, optimum values for benzene solutions are reported[31,33] to be ~5×10^9 L mol^{-1} s^{-1} compared with a diffusion rate constant of 1.55×10^{10} L mol^{-1} s^{-1}. Consideration of Table I shows that those rate constants for triplet energy transfer involving CPD as donor or acceptor, which are fast, increase from the normal optimum value up to the diffusion-controlled value as exothermicity increases. The reasons for this may be connected with (a) the size and geometry of CPD and (b) the nature of the monitors selected. Whatever the explanation, it is at least clear from Table I that the quenching of naphthalene triplet (60.9 kcal mol^{-1}) by CPD and of $^3CPD^*$ by fluoranthene (54.2 kcal mol^{-1}) are efficient processes and this places the triplet energy of the relaxed $^3CPD^*$ between those of naphthalene and fluoranthene. Thus, since reverse energy transfer may be important for triplet-energy differences between donor and acceptor of below 3-4 kcal mol^{-1},[20] it was clearly necessary to consider the possibility of such energy transfer between CPD and the monitors naphthalene, chrysene, and fluoranthene.[34]

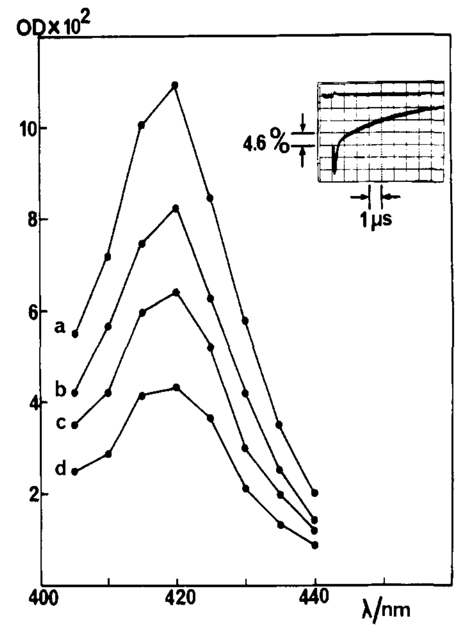

Figure 4. Transient absorption spectra (a) 0.25, (b) 0.55, (c) 1.5 and (d) 3.5 μs after absorption of a 20 ns electron pulse by liquid benzene containing naphthalene (10^{-1} mol L^{-1}) and CPD (10^{-3} mol L^{-1}). Inset: Time dependence of naphthalene triplet decay monitored at 420 nm.

Table II. Equilibrium Data for Reversible Triplet Energy Transfer

reactants[a]	K	ΔE_T, kcal mol^{-1}	E_T (CPD)
naphthalene ⇄ CPD[b]	148 ± 37	−2.9 ± 0.15	58.0 ± 0.15
chrysene ⇄ CPD[c]	0.11 ± 0.03	1.3 ± 0.15	57.9 ± 0.15
chrysene ⇄ naphthalene[c]	(7.7 ± 2.0) × 10^{-4}	4.2 ±0.15	

[a] See Table I for E_T values. [b] Determined by naphthalene excitation using pulse radiolysis. [c] Determined by pulsed laser excitation of chrysene at 337 nm.

It is possible to observe an equilibrium between triplet states, e.g., eq 16, if the energy-transfer processes are fast relative to the

$$^3M^* + CPD \rightleftarrows M + {}^3CPD^* \qquad (16)$$

decay of those states. Such equilibria have been observed in the case of eosin and anthracene[36] and for pairs of aromatic hydrocarbons.[37] For a true equilibrium the free-energy change, ΔG_T, may be assumed to equal the difference in energies between the two triplets, ΔE_T. Thus eq 17 should hold[20b,37]

$$-\Delta E_T = 2.303RT \log K \qquad (17)$$

where $K = [M][^3CPD^*][^3M^*]^{-1}[CPD]^{-1}$ and we have been able to demonstrate the rapid establishment of such an equilibrium for energy transfer between CPD and the three monitors mentioned by suitable adjustment of monitor and diene concentrations.

Pulse radiolysis of benzene solutions of naphthalene (10^{-1} mol L^{-1}) containing CPD ($5-25 \times 10^{-4}$ mol L^{-1}) showed rapid exponential decay of naphthalene triplet to an equilibrium position dependent on CPD concentration (Figure 4) followed by a slow bleeding of this equilbrium. As shown, the spectrum of the absorbing species was the same before and after equilibration. By assuming that a negligible amount of triplet states are lost to decay before the equilibrium is established, i.e., naphthalene triplets lost equals cyclopentadiene triplets formed, an equilibrium constant of 148 ± 37 was determined. This corresponds to a ΔE_T value of −2.9 ± 0.15 kcal mol^{-1} and to a rate constant for reverse transfer, K_{DM}, of 2.0×10^7 L mol^{-1} s^{-1}. Similar experiments have

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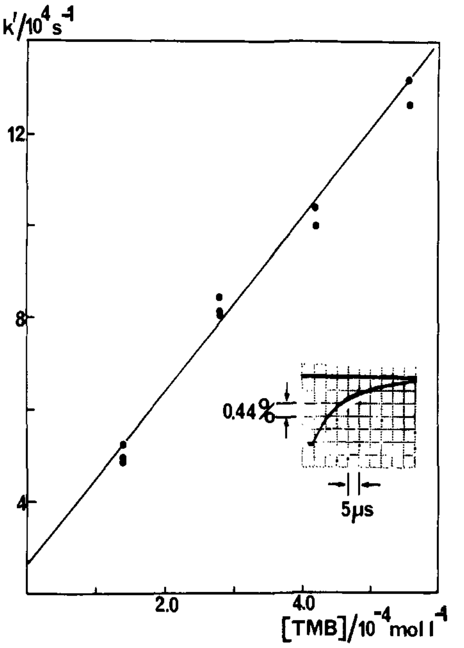

Figure 5. First-order constant for fluoranthene triplet decay vs. TMB concentration. Inset: Time dependence of fluoranthene triplet decay monitored at 415 nm after absorption of a 2.5 ns laser pulse (337 nm) by fluoranthene (10^{-4} mol L^{-1}) in benzene containing TMB (2.8×10^{-4} mol L^{-1}).

been performed for chrysene (10^{-3} mol L^{-1}) and CPD ($1-12 \times 10^{-3}$ mol L^{-1}) using laser excitation of the former. This gave an equilibrium constant of 0.11 ± 0.03 corresponding to a ΔE_T value of 1.3 ± 0.15 kcal mol^{-1}. These ΔE_T values for naphthalene/CPD and chrysene/CPD give ΔE_T for naphthalene/chrysene as 4.2 ± 0.3 kcal mol^{-1} in excellent agreement with the difference in phosphorescence $\Delta E_{0,0}$ values for nonpolar solvents of 4.3 kcal mol^{-1}. A further check on the accuracy of our data was obtained by witnessing the establishment of the triplet equilibrium after laser excitation at 337 nm of chrysene (5×10^{-4} mol L^{-1}) in the presence of napthalene (5×10^{-1} mol L^{-1}). This again gave a ΔE_T value of −4.2 kcal mol^{-1}.[38]

On the basis of the equilibrium data summarized in Table II we conclude that the equilibrium triplet energy of ^{3}CPD* is 58.0 ± 0.2 kcal mol^{-1}.[39] The singlet–triplet absorption spectrum of CPD gives a $\Delta E_{0,0}$ value of 58.3 kcal mol^{-1} [2] and clearly relaxation of ^{3}CPD* is not significant.

4.4. Initial Excitation of Monitor in Presence of Tetramethylbutadiene. As described in section 4.1 for CPD a combination of pulse radiolysis and laser photolysis was used to determine the rate constants, k_{MD}, for quenching of monitor triplets by TMB (cf. Figure 5). Hammond et al. had carried out similar experiments much earlier as part of a flash photolysis study.[40] Our data are in broad agreement in that, as shown in Table I, rate constants become significantly less than the optimum around the napthalene triplet energy level (~60 kcal mol^{-1}). This is in accord with the singlet–triplet absorption spectra of predominantly s-trans dienes which yield $\Delta E_{0,0}$ values of 59–60 kcal mol^{-1}.[2] However, of particular significance is our finding that TMB does not quench anthracene triplet. The value of $<3.0 \times 10^4$ L mol^{-1} s^{-1} quoted in Table I, which simply reflects the detection limit of our experiments,[41] is smaller by a factor of 2000 than that of 7.0×10^7 L mol^{-1} s^{-1} [40] which was claimed to support the proposal of "nonvertical" transfer of triplet energy from anthracene and other low-energy sensitizers to 1,3-dienes.[10f] In no case were we able to demonstrate reverse triplet energy transfer between a monitor and TMB. This would appear to indicate significant relaxation of ^{3}TMB* and/or a much shorter lifetime relative to ^{3}CPD*.

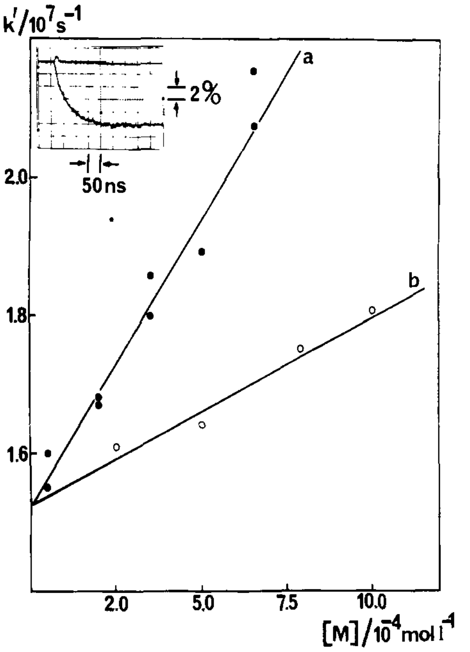

Figure 6. First-order constants for monitor triplet formation vs. monitor concentration: (a) β-carotene, (b) anthracene. Inset: Time dependence of β-carotene triplet formation monitored at 555 nm after absorption of a 20 ns electron pulse by liquid benzene containing TMB (1.7×10^{-1} mol L^{-1}) and β-carotene (5×10^{-4} mol L^{-1}).

4.5. Initial Excitation of Tetramethylbutadiene in Presence of Monitor. Pulse radiolysis of benzene solutions of TMB (5×10^{-1} mol L^{-1}) and monitor (10^{-3} mol L^{-1}) resulted in "slow" exponential grow-in of monitor triplet only in the cases of the low-energy acceptors anthracene and β-carotene (Figure 6). The triplet formation clearly corresponded to energy transfer from a species shorter lived than ^{3}CPD* and k' vs. [M] plots according to eq 15 gave the rate constants, k_{DM}, for energy transfer (Table I) and a common intercept corresponding to a ^{3}TMB* lifetime of 65 ns in the presence of TMB (5×10^{-1} mol L^{-1}) (Figure 6). Experiments with β-carotene (1.1×10^{-4} mol L^{-1}) as monitor at various TMB concentrations ($2-9 \times 10^{-1}$ mol L^{-1}) yielded the rate constant for reaction of ^{3}TMB* with TMB, $k_{DD} = 3.5 \times 10^6$ L mol^{-1} s^{-1}, a factor of 4 down on the value for CPD. The natural lifetime of ^{3}TMB* in benezene is therefore 73 ns.

The rate constant for triplet energy transfer from ^{3}TMB* to β-carotene (Table I) is fast, corresponding to an exothermic process. In the case of anthracene the rate constant is a factor of 3 down and a consideration of the values in Table I suggests that this process is in the isoenergetic region. We therefore place the "available" triplet energy of ^{3}TMB* at about 42 kcal mol^{-1}. If triplet energy transfer between anthracene and acyclic dienes and vice versa were "nonvertical" as has been suggested[10f] the rate constant for transfer of energy from anthracene to TMB should also be in the $1-5 \times 10^9$ L mol^{-1} s^{-1} region. The determined value of $<3.0 \times 10^4$ L mol^{-1} s^{-1}, which if anything is lower than that for CPD which must be essentially vertical, together with values for even higher energy monitors, is clearly not in agreement with such a situation.[42,43] If, as we suggest, the transfer of triplet energy

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[38] A value of −4.0 ± 0.2 kcal mol^{-1} has already been reported for such an experiment.[37]

[39] Laser excitation of fluoranthene (1.4×10^{-4} mol L^{-1}) in the presence of CPD (5.0×10^{-2} mol L^{-1}) showed the anticipated fast decay of fluoranthene triplet to an equilibrium situation. However, the accuracy of the equilibrium constant determination was affected by fluoranthene fluorescence at the monitoring wavelength (415 nm). The value of ΔE_T obtained was 3.1 kcal mol^{-1} which is to be compared with a difference of 3.7–3.8 kcal mol^{-1} between the phosphorescence $\Delta E_{0,0}$ values for fluoranthene (54.2 kcal mol^{-1}) and the equilibrium triplet energy of CPD (Table II).

[40] A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966).

[41] The first-order constant, k', for decay of anthracene triplet after laser excitation at 337 nm of anthracene (2×10^{-4} mol L^{-1}) in benzene was 1.4×10^4 s^{-1}. This was unaffected by the presence of TMB (0.15 mol L^{-1}) in repeated experiments. The limiting value for k_{MD} quoted in Table I is based on a generous error of ±15% in the reproducibility of our k' values.

from diene to monitor is vertical, the estimated "available" triplet energy of 42 kcal mol^{-1} for the relaxed ^{3}TMB* represents the energy gap between the latter and the corresponding vibrationally and torsionally excited S_0. The energy gain due to the twisting of the planar triplet can therefore not be estimated.

5. Conclusions

An application of the pulse radiolysis technique has allowed the first direct determinations of conjugated diene triplet lifetimes. The triplet state of cyclopentadiene has a natural lifetime of 1.7 μs in benzene. The establishment of energy-transfer equilibria between this triplet state and those of naphthalene and chrysene has yielded an accurate equilibrium triplet energy of 58.0 ± 0.2 kcal mol^{-1}, just below the singlet–triplet $\Delta E_{0,0}$ value of 58.3 kcal mol^{-1}. Thus, as might be anticipated on the basis of steric constraint, relaxation of the Franck–Condon triplet in solution is negligible. In contrast the triplet state of tetramethylbutadiene has a much shorter natural lifetime of 73 ns which presumably reflects the much greater degree of relaxation. In the absence of observation of energy-transfer equilibria it has only been possible to place its "available" triplet energy at approximately 42 kcal mol^{-1}. The energy transfer rate constant data for both dienes appear totally consistent with the participation of vertical processes only.

Work on related systems is in progress.[44]

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(42) As pointed out by a referee the above data are also inconsistent with the proposed quantum chain process for cis-trans isomerization of 1,3-dienes.[11c]

(43) The rate constants for quenching of pyrene, fluoranthene, and chrysene triplets by TMB appear to be somewhat larger than those for CPD. On the assumption that this is significant we have considered the possibility that it reflects a contribution from a low population of the s-cis form of TMB. This could have a significantly lower (~6–7 kcal mol^{-1}) Franck–Condon triplet energy, that of cyclohexa-1,3-diene being reported as 53.5[2] and 52.5[3] kcal mol^{-1}. However, steric interactions may well make the s-cis population totally insignificant and, as a referee has pointed out, some degree of nonverticality in the quenching process could account for this result.

(44) Since the submission of this manuscript we have observed what are almost certainly the triplet–triplet absorption spectra of CPD (λ_{max} 300 nm) and TMB (λ_{max} 290 nm) by pulse radiolysis of benzene solutions of these dienes. The lifetime of the CPD transient (1.6 μs, extrapolated to zero CPD concentration) compares well with that of ^{3}CPD* (1.7 μs) determined from the energy-transfer experiments. In the case of TMB the transient absorption is much weaker. This, coupled with the faster decay, has made kinetic analysis more difficult. An approximate lifetime of 50 ns (at 10^{-1} mol L^{-1} TMB) is to be compared with that for ^{3}TMB* of 71 ns calculated from the energy-transfer experiments.

Aryloxenium Ions. Generation from *N*-(Aryloxy)pyridinium Tetrafluoroborates and Reaction with Anisole and Benzonitrile[1]

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Nissanke L. Dassanayake, Mutiah N. Inbasekaran, and Shiego Kato

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Abstract: *N*-(Aryloxy)pyridinium tetrafluoroborates (**4**) decompose thermally at 180–200 °C in anisole and benzonitrile to form products of intermolecular C–O–C and C–C bond formation. With anisole, diphenyl ethers (**5**) and hydroxybiphenyls (**6**) are formed; with benzonitrile, the main product is a benzoxazole (**14**). A homolytic process was ruled out by showing that none of these products were formed when perbenzoyl *p*-nitrophenyl carbonate (**18**) was decomposed in these solvents. The main products in this case were those of homolytic phenylation (and benzoyloxylation with anisole). A concerted S_N2-type heterolytic process was ruled out by showing that the nature of the substituent in the pyridine ring had no effect on the isomer ratios of **5** and **6** in the thermolysis of **4** (X = *p*-NO_2) in anisole. The results are explained in terms of a unimolecular heterolysis of **4** to give the pyridine and an aryloxenium ion **2** which now attacks solvent molecules. When an electron-withdrawing substituent is present in **2**, more C–O–C than C–C products are formed with anisole. When it is absent only products of C–C bond formation are found. PhO^+ is apparently electrophilic enough to attack anisole and give the four possible hydroxymethoxybiphenyls (**10**–**13**).

In recent years there has been considerable interest in the chemistry of phenoxenium ions,[3] particularly in connection with phenol oxidation in general[4b,5,6a,c,10,12] and biosynthetic-type oxidative coupling reactions in particular.[4a,10,11] The fact that oxenium ions are isoelectronic with carbenes and nitrenes adds

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(1) For preliminary communications on some of this work, see: (a) Abramovitch, R. A.; Inbasekaran, M.; Kato, S. *J. Am. Chem. Soc.* **1973**, *95*, 5428; (b) Abramovitch, R. A.; Alvernhe, G.; Inbasekaran, M. N. *Tetrahedron Lett.* **1977**, 1113.

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(3) A variety of names have been used to describe the species ArO^+: phenoxonium ions,[4] phenoxylium ions,[5] aryloxy cations,[6] phenonium ions,[7] and aryloxenium ion.[7a,8,9] Of these, phenonium ion is quite unacceptable since it refers to a totally different, well-documented species. The "oxonium" ion terminology should be reserved for trisubstituted positively charged oxygen species R_3O^+. By analogy with positvely charged divalent nitrogen and trivalent carbon intermediates, a positively charged monovalent oxygen intermediate should have a name ending in "-enium", hence oxenium.

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