Activation Parameters in the Photocycloaddition of Phenanthrene to Dimethyl Fumarate

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Abstract: The [2 + 2] direct photocycloaddition of phenanthrene to dimethyl fumarate was studied as a function of temperature in the range 21–65 °C. From temperature dependencies of the quantum yields for the various photoprocesses, activation parameters were derived for the processes originating from the singlet exciplex ^1E. The cycloaddition and internal conversion processes are activated, while intersystem crossing is not. Fluorescence was assumed to be temperature independent. The benzophenone-sensitized reaction is not sensitive to temperature in this range. Cycloaddition enthalpies of activation are found to be larger and entropies of activation less negative for ^1E when compared to previous results for cyanophenanthrene–styrene exciplexes. The difference is attributed to a combination of increased charge transfer and less favorable remote orbital overlap in ^1E.

Introduction

The use of temperature dependency of reaction rate to study the mechanisms of thermal reactions via analysis of activation parameters is ubiquitous. For photochemical reactions, however, it is less common, in part because the relevant elementary rate constants are generally not easy to obtain and in part because temperature sensitivities might have been expected to be rather small in view of the necessarily high reactivities of photochemical intermediates.

Some photochemical reactions which have been studied as a function of temperature have indeed shown quite small energy barriers to reaction, e.g., *trans*-stilbene isomerization[2-4] (1–4 kcal/mol), the addition of alkenes to enones[5] (ca. 1 kcal/mol), and the [4 + 4] cyclodimerization of anthracenes (ca. 1.5 kcal/mol).[6-9] Others are somewhat larger: an intramolecular enone annelation[10] (4.7 kcal/mol), intermolecular hydrogen abstraction of acetophenone[11] (3.3 kcal/mol), and Norrish II reactions of aryl ketones[12,13] (3.5–6.7 kcal/mol) and 4-methyl-2-pentanone[14] (7.9 kcal/mol from the triplet). Structural isomerizations which presumably go through quite strained transition states can have even higher activation energies: the rearrangement of 4,4-diphenylcyclohexenone[15] (10.5 kcal/mol for major product, 11.3 for minor) and the conversion of *o*-xylene to *m*-[16] (7.7 kcal/mol) have been studied.

The role of exciplexes in cycloaddition reactions has become quite clear over the last few years.[17-23] We have undertaken to study a few examples of [2 + 2] cycloadditions involving exciplexes carefully in order to learn as much as possible about the excited-state potential energy surface. The photoreaction of phenanthrene with dimethyl fumarate in benzene[24,25] is an interesting model on two counts. First, the involvement of a singlet exciplex in the reaction has been proven.[19,26] Second, a variety of processes originate from the exciplex, leading to the chance to study several different photochemical and photophysical processes. Elementary rate constants for these processes at room temperature are known.[19] We here report a study of their temperature dependence. Cycloaddition and internal conversion from the singlet exciplex are activated and show substantial negative entropies of activation. Intersystem crossing shows little or no temperature dependence. Fluorescence is assumed to be temperature independent by analogy with related systems. We compare the present activation parameters with those we obtained in a previous study,[27] the addition of cyanophenanthrenes to styrenes, in which the same general features were observed. Differences in the two systems are attributed to a combination of two factors. First, increased charge transfer in the present case stabilizes the exciplex and decreases its (chemical) reactivity. Second, remote orbital overlap in the former, expected to be important in the cycloaddition and internal conversion processes, may lower the energy barrier, but probably at the cost of a more negative $\Delta S^{\ddagger}$.

Experimental Section

Analytical procedures, product structures, and quantum-yield techniques have all been previously reported.[19] For studies at variable temperature, both fluorescence spectra and quantum-yield measurements were taken utilizing the thermostated cell compartment of the Farrand MK-1 spectrofluorometer. Temperatures were measured with an iron–constantan thermocouple and are accurate to ±0.1 °C.

For quantum-yield measurements a quartz plate was placed at an angle of about 45° to the light beam incident on the thermostated cell holder, diverting about 7% of the beam into an insulated 1-cm cuvette. The ratio, *R*, of light entering the sample holder to light entering the cuvette was then determined by ferrioxalate actinometry at ambient temperature before each run. During a run the solution was maintained in the sample holder at the desired temperature (20 → 65 °C) using a Haake circulating bath while the actinometer solution remained at ambient temperature (23–25 °C). In this way the light dose for each sample could be determined from *R* and the actinometer reading.

Results

The photoreaction of phenanthrene (P) with dimethyl fumarate (F)[19] proceeds through both a singlet exciplex (^1E) and a triplet exciplex (^3E), affording as products the two isomeric cyclobutane diester [2 + 2] adducts C and T, an oxetane X arising from addition of the phenanthrene 9,10 bond to an ester carbonyl of F, and isomerization of F to dimethyl maleate (M). A triplet 1,4-biradical ^3SS formed essentially quantitatively from ^3E is the predominant precursor of C and T, although a small amount of T arises as a product of stereospecific collapse of ^1E. Both ^1E and ^3SS are precursors of M. Scheme I summarizes this mechanism.

Quantum Yields. The quantum yields of the various processes are given in Table I for the temperature range 21–64 °C. The concentration of F was 0.2 M, which assures essentially complete scavenging of ^1P by F. Consequently, these values refer to the chemistry of ^1E exclusively. As the temperature increases, the distribution of products at low conversion ($\lesssim 2\%$) changes significantly. Most striking are the increase in oxetane X and the decreases in yield of the cis diester C and the olefin isomer M. As Scheme I shows, X arises purely from ^1E, while C is purely a triplet product. At F = 0.2 M, the yield of M originating from ^1E is much greater than that arising from ^3P or ^3E, and consequently its decrease with increasing temper-

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Table I. Quantum Yields[a] of Photoprocesses Originating in ^{1}E

T, °C	ϕ_F ($\tau_{^1E}$[c])	ϕ_X	ϕ_T	ϕ_C	ϕ_M	ϕ_D[b]
21.0	4.5×10^{-3} (1.2)	0.026	7.0×10^{-3}	3.0×10^{-3}	0.042	0.81
33.8	3.9×10^{-3} (1.04)	0.030	6.2×10^{-3}	2.4×10^{-3}	0.038	0.82
48.8	3.3×10^{-3} (0.88)	0.037	6.0×10^{-3}	1.6×10^{-3}	0.034	0.85
63.5	2.6×10^{-3} (0.69)	0.044	5.7×10^{-3}	1.3×10^{-3}	0.026	0.86

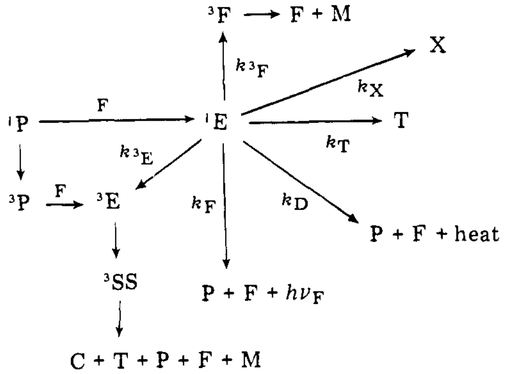
[a] ±5% except as noted. [b] Since ϕ_D is calculated as $1 - \Sigma\phi$(observables), its error is determined by errors in the observables, the sum total of which is a modest fraction of ϕ_D. The ϕ_D error is thus quite modest. We estimate ±1.5%. [c] $\tau_{^1E}(T) = \phi_F(T) \times 1.2 \div 4.5 \times 10^{-3}$. In nanoseconds.

Table II. Fluorescence Quantum Yields and Lifetimes of the Phenanthrene–Fumaronitrile and 9-Cyanophenanthrene–Anisylisobutylene Exciplexes as Functions of Temperature

phenanthrene–fumaronitrile				9-cyanophenanthrene–anisylisobutylene			
T, °C	ϕ_F[a]	τ, ns[b]	k_F, s^{-1}[c]	T, °C	ϕ_F[a]	τ, ns[b]	k_F, s^{-1}[c]
20.4	0.049[d]	18.6	2.6×10^6	23.0	0.14	33.3	4.2×10^6
34.6	0.049[d]	19.3	2.5×10^6	35.6	0.13	28.0	4.6×10^6
49.6	0.049[d]	16.9	2.9×10^6	50.0	0.11	26.2	4.1×10^6
64.6	0.049[d]	16.3	3.0×10^6	64.8	0.088	21.2	4.1×10^6

[a] ±5%. [b] ±1–1.5 ns. [c] Error estimated at ±8%. [d] In the present case, we show that ϕ_F is independent of temperature (±2%) over the range 16–65 °C. The quoted quantum yield is that reported previously.[31]

Scheme I



ature must be explained on the basis of the chemistry of ^{1}E.

Fluorescence quantum yields for ^{1}E decrease as the temperature increases, showing that either k_F varies inversely with temperature or the sum of all rate processes competing with k_F increases with temperature, or both. Direct measurement of $\tau_{^1E}$ as a function of temperature would settle the question, since $k_F = \phi_F/\tau$, but for such short lifetimes (1.2 ns at room temperature) is not feasible.

Fortunately, there is good evidence that radiative lifetimes of exciplexes are essentially constant with temperature.[27-30] Ware has reported that k_F for the 1-naphthonitrile–1,2-dimethylcyclopentene exciplex[28] and for the anthracene–*N*,*N*-dimethylaniline exciplex[29] vary at most slightly with temperature. We have examined exciplexes longer lived than ^{1}E as a function of temperature, measuring both fluorescence yields and lifetimes, and find the same result. Table II presents results for two,[31] the phenanthrene-fumaronitrile exciplex ($\tau_{21\,°C}$ = 19 ns) and the 9-cyanophenanthrene-β-anisylisobutylene exciplex ($\tau_{23\,°C}$ = 33 ns). Here too ϕ_F decreases with temperature, and τ decreases almost in direct proportion, demonstrating that k_F is essentially (±10%) temperature independent in these systems (Table II). The phenanthrene-fumaronitrile exciplex especially is obviously a good model for ^{1}E, and we thus presume that k_F for ^{1}E is also temperature independent. We may thus conclude that *activated alternative processes decrease ϕ_F*.

The knowledge of $\tau_{^1E}$ at room temperature[19] and ϕ_F as a function of temperature permits calculation of $\tau_{^1E}$ as a function of temperature, under the presumption of constant k_F, and thus also calculation of the elementary rate constant k_X (the simplest case among the elementary processes) as a function of temperature, via the simple equation

$$\phi_X(T) = k_X(T)\tau_{^1E}(T)$$

Because other photoproducts of ^{1}E either involve subsequent intermediates (C, T, and M) or are derived from two different pathways, some further manipulation of the results is required. For M, presuming ^{3}F to be the initial product from ^{1}E, the decay ratio of ^{3}F (i.e., its partitioning between M and F) must be known as a function of temperature. From benzophenone-sensitized isomerization at room temperature, we have determined it as 0.50, i.e., 50:50 partitioning between M and F. We have not measured the temperature dependence of our decay ratio directly; however, from a study of the benzophenone-sensitized P–F isomerization and cycloaddition at 65.4 °C, we extrapolate a value of $\phi_{F\to M} = 0.47 \pm 0.03$. The few other studies of the effect of temperature on olefin triplet decay ratios also have shown that it is very slight.[32] We therefore assign $k_{^3F} = 2.0\phi_M/\tau_{^1E}$.

It is necessary to know at least something about the temperature dependence of the triplet pathway to C and T in order to interpret ϕ_C and ϕ_T as a function of temperature. We have studied the temperature dependence of the quantum yields of the benzophenone-sensitized cycloaddition over this temperature range, and find that the total quantum yield $\phi_C + \phi_T$ is nearly temperature invariant. Most importantly, the ratio ϕ_T/ϕ_C is constant within experimental error as 1.85 ± 0.05, over the range 21–63 °C. Since C arises only from ^{3}E, the yield of ^{3}E from ^{1}E can be measured as

$$\phi_{^3E}(T) = \phi_{^3E}(21\ °C)\frac{\phi_C(T)}{\phi_C(21\ °C)}$$

where $\phi_{^3E}$(21 °C) is known.[19] By inspection of Table I, then, it clearly follows that $\phi_{^3E}$ decreases with temperature.

The temperature dependence of ϕ_T is complicated in that T arises by two pathways. The temperature dependence via the ^{3}E route, based on the temperature studies of the benzophenone-sensitized reaction above, is $\phi_T(\text{via } ^3E) = 1.85\phi_C(T)$. This follows, of course, from the constancy of the T/C ratio with temperature. Since the total yield of T is the summation of the yields of the ^{1}E and ^{3}E pathways, the yield via ^{1}E can be determined by subtraction of the ^{3}E derived part from the total, i.e.

$$\phi_T(\text{via } ^1E) = \phi_T - 1.85\phi_C$$

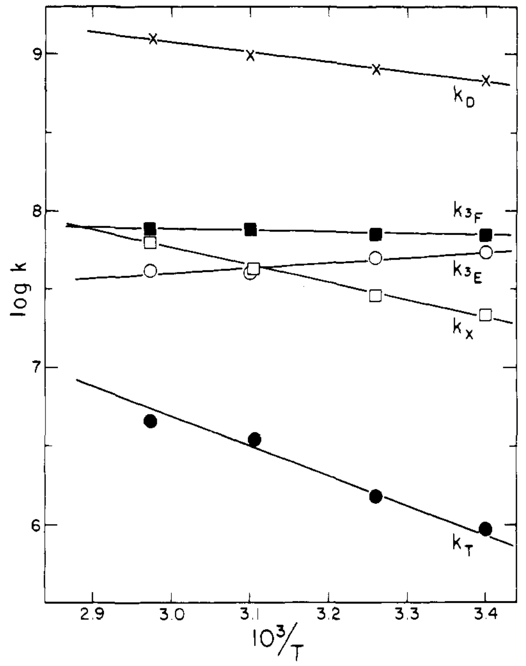


Figure 1. Arrhenius plot for k_D (×), k_{3F} (■), k_{3E} (○), k_X (□), and k_T (●).

The temperature dependence of ϕ_T(via ^{1}E) is the greatest of any exciplex process in this system. The process accounts for only about 15% of total T at 21 °C, but more than 55% at 63.5 °C. The original evidence of Farid[24] from triplet quenching studies that there is a stereospecific singlet component to T formation is strongly supported by our higher temperature results, in which the process is magnified.

Rate Constants and Activation Parameters. As exemplified above for k_X, elementary rate constants for process i originating from ^{1}E can be obtained from the temperature-dependent quantities $\phi_i(T)$ and $\tau_{^1E}(T)$. The analyses above therefore afford k_X, k_{3F}, k_{3E}, and k_T at each temperature (see Scheme I). We take a temperature-independent k_F of[19] 2.5×10^6 s^{-1}. It is then possible to calculate $k_D(T)$, the rate constant for internal conversion of the exciplex, as a function of temperature from the equation

$$k_D(T) = \tau_{^1E}{}^{-1} - \sum_i k_i$$

where all other processes i must be included. All k's are precise to about 10%, except for the 21 °C value for k_T, which is somewhat less precise. The rate constants are given in Table III and displayed graphically as an Arrhenius plot in Figure 1. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ derived from the equations $\Delta H^{\ddagger} = E_a - RT$ and $\Delta S^{\ddagger} = R \ln (hA/ek\langle T\rangle) = 4.60 \log A - 60.95$ are readily derived and are given in Table IV.

Discussion

We have previously reported[27] a study of the temperature dependence of the reactions of substituted 9-cyanophenanthrenes with *trans*-β-methylstyrene and *trans*-anethole. In these cases, based on reaction from the (emissive) exciplex, small activation enthalpies (2-5 kcal/mol) and substantial negative activation entropies (−11 to −16 eu) were observed for cycloaddition, strikingly similar values were observed for internal conversion, and both fluorescence and intersystem crossing from the exciplex were found to be temperature independent. Substituent effects confirmed that the transition states for cycloaddition and internal conversion were certainly similar and quite conceivably identical. The transition state was significantly less polar than the exciplex, a conclusion reached independently for a different system by Lewis and Hoyle.[34] The present system resembles the cyanophenanthrene-styrene one in that the reacting excited chromophore is a phenanthrene, yet differs from it in that the present one represents a much greater difference in the donor-acceptor nature of the reacting partners and a presumably much smaller opportunity for HOMO-HOMO and LUMO-LUMO interactions. It is instructive to compare activation properties in the two systems.

Photophysical Processes from ^{1}E. Fluorescence and Intersystem Crossing in Exciplexes. As discussed above, it now seems likely that fluorescence of exciplexes is nearly a temperature-independent kinetic process, not surprising if it is essentially vertical. The present results reinforce the conclusion, at least for phenanthrenes and alkenes, that intersystem crossing of exciplexes is also negligibly temperature dependent. The ^{1}E → ^{3}E process, k_{3E}, has been recognized clearly in previous work.[24] The present results would suggest a small inverse temperature dependence, but this may be an artifact. The ^{1}E → P + ^{3}F process. k_{3F}, has been postulated[19] without satisfactory supporting evidence as a reasonable hypothesis. We now feel that the absence of an activation energy for k_{3F} is much better in accord with an intersystem crossing mechanism than with conceivable alternatives. If, for example, a 1,4-biradical intermediate were involved in the isomerization, the newly formed bond would require much closer approach of the two partners than is thought to obtain in the stable exciplex geometry,[35] and would thus presumably require activation energy.

The magnitude of the fluorescence rate is quite similar in the two systems. The total intersystem crossing rate, 1.2×10^8 s^{-1}, is somewhat larger (factor of ca. 4) in the present case than in the cyanophenanthrene-styrene one.[27] For the present, it seems best to focus on the rough similarity of the values rather than the small difference. The anthracene-diethylaniline exciplex shows a somewhat smaller k_{isc}, $\sim 3.3 \times 10^6$ s^{-1} at 20 °C,[30] but again nearly of the same order of magnitude; as in our case, the temperature dependence of k_{isc} is small.

We believe that it is justified to conclude that both fluorescence and intersystem crossing in exciplexes are temperature insensitive and structurally insensitive. A good rule of thumb is $k_F \sim 10^6$-10^7 s^{-1}, with considerable documentation,[27-31,40] and $k_{isc} \sim 10^6$-10^8 s^{-1}, with less documentation. Assuming that aromatic exciplexes can be reasonably well represented by a picture of $D^{+\cdot}$ and $A^{-\cdot}$ entities with π systems overlaid, and a roughly constant interplanar spacing, one might expect roughly a structurally insensitive interaction between the two electrons and thus structually insensitive values for k_F and k_{isc}.

Photocycloaddition from ^{1}E. The two photoadducts X and T arise directly from ^{1}E with enthalpies of activation of 4.4 ± 0.65 and 7.3 ± 1.0 kcal/mol, respectively. It is clear that one must introduce energy barriers into the electronic hypersurface between singlet exciplex and cycloadduct, as previously discussed,[27,41] and that the height of each barrier contributes to determining the yield of product to which it leads. The barrier to X is in the range of those for the cyanophenanthrene-styrene exciplexes, but rather toward the higher energy end of the series; the barrier to T is noticeably higher. It is apparent, as mentioned before,[27] that increased CT in an exciplex should increase the activation enthalpy for cycloaddition, and ^{1}E certainly should possess a higher degree of CT than the phenanthrene-styrene cases.[27] We calculate $E_{ox}(D) - E_{red}(A) - E(0,0) = -0.53$ V (−12.2 kcal/mol) for the process ^{1}P + F → $P^{+\cdot}$ + $F^{-\cdot}$, but only −0.28 V (−6.5 kcal/mol) for ^{1}9CP + *t*-An → $9CP^{-\cdot}$ + *t*-$An^{+\cdot}$ (9CP = 9-cyanophenanthrene, *t*-An = *trans*-anethole) from published redox values.[42-44] Also, the possibility of remote orbital overlap in the 9CP· · ·*t*-An

Table III. Rate Constants[a] for Processes Originating from ^{1}E

T, °C	k_T	k_X	$k_{^3E}$	$k_{^3F}$	k_D
21.0	9.16×10^5	2.17×10^7	5.49×10^7	7.0×10^7	6.9×10^8
33.8	1.54×10^6	2.88×10^7	5.07×10^7	7.3×10^7	8.1×10^8
48.8	3.41×10^6	4.20×10^7	3.99×10^7	7.72×10^7	9.7×10^8
63.5	4.62×10^6	6.35×10^7	4.12×10^7	7.50×10^7	1.26×10^9

[a] Calculated as described in text from the quantum yields given in Table I. Units of s^{-1}.

Table IV. Activation Parameters for Processes Originating in ^{1}E

	A, s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal/mol
k_T	6.0×10^{11}	7.9 ± 1	-6.8 ± 3	7.3 ± 1
k_X	1.0×10^{11}	5.0 ± 0.65	-10.3 ± 2	4.4 ± 0.65
$k_{^3E}$	4.0×10^6	-1.5 ± 0.65	-30.6 ± 2[a]	-2.1 ± 0.65[a]
$k_{^3F}$	1.3×10^8	0.4 ± 0.65	-23.6 ± 2[a]	-0.2 ± 0.65[a]
k_D	7.7×10^{10}	2.8 ± 0.45	-10.9 ± 1.5	2.2 ± 0.45

[a] Calculated for comparison purposes only. $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ have no meaning for processes involving transitions between electronic surfaces.

transition state is greater, owing to the more extended conjugation and the especially good match of the orbital coefficients, as we have previously discussed.[17,18]

We have previously pointed out the low reactivity of the phenanthrene-fumaronitrile exciplex toward [2 + 2] cycloadduct formation.[31] This cycloaddition proceeds with very low rate constant ($<5 \times 10^4\ s^{-1}$) from the singlet exciplex, probably owing to high CT in the exciplex. We note that the reduction of fumaronitrile (FN) is substantially less cathodic than that of F: $E_{1/2} = -1.36$ V for fumaronitrile but -1.54 V for diethyl fumarate vs. SCE in either dry or wet DMF.[42] Presumably this stabilizes the P···FN exciplex but affects the less polar cycloaddition transition state much less.

Internal Conversion from ^{1}E. The dominant process originating from ^{1}E (by a factor of 5 over the sum total of isc and a factor of 20 over the sum of k_X and k_T) is internal conversion. It is nearly 300 times the fluorescence rate, in contrast to the cyanophenanthrene-styrene series,[27] in which $k_D \sim$ 1-10 times k_F. One might have expected the difference to result from the introduction of some new purely photophysical internal conversion path. However, k_D is an activated process from ^{1}E, with $\Delta H^{\ddagger} = 2.2 \pm 0.45$ kcal/mol, a fact which seems much better in accord with the previous interpretation[27] of approach over a barrier to a nonpolar pericyclic minimum.

The barrier height for k_D is, however, markedly lower than that for *either* k_X or k_T. It seems necessary to conclude that internal conversion does not simply result from partitioning of two pericyclic minima between adducts X and T and addends P and F, since in that case the 4.5-7 kcal/mol barrier height observed for X and T formation would be expected to obtain. We note, however, that a significant number of other possible geometries (e.g., overlay of the C═C or C═O double bond of F with double bonds of P other than the 9,10) could lead to other pericyclic minima (without the possibility of forming X and T) and thus to different barrier heights. Such a mechanism would be consistent with previous suggestions[38,45,46] that specific geometries are not required for exciplexes in which CT provides the major stabilizing interaction, in that one then might expect a larger range of possible geometries in which decay occurs.

What Follows Exciplex Collapse? Singlet exciplex collapse to adducts and/or addends may occur through pericyclic minima or through a singlet 1,4-biradical. Since the P···F system is not symmetrical (i.e., one ester group must be exo and one endo even in stereospecific collapse to T) there is no necessary requirement that even the pericyclic minimum leading to T be symmetric, i.e., show equal bonding between the reactants at both ends. Simple steric considerations would suggest easier collapse at the carbon bearing the exo ester group. If so, a structure would be reached that is markedly similar to the singlet biradical ^{1}SS, the paired-spin analogue of the triplet biradical ^{3}SS known[19] to be an intermediate in the sensitized cycloaddition, in the process leading to T. There thus is a blend of possibilities, ranging from symmetric concerted collapse through unsymmetric concerted collapse to stepwise collapse.

Unfortunately, the present results do not permit an experimental distinction among these possibilities. The interpretation above of different activation enthalpies based on different pericyclic processes is one adequate explanation of the present results. Another, not unattractive, is collapse through a bona fide singlet biradical which partitions between addends and adducts. On this basis, a difference in apparent activation enthalpies between fragmentation (to P + F) and adduct (X or T) formation may be simply explained by differences in activation energies for scission or closure of the biradical. Representative relative barrier heights are available from cyclic azo compound pyrolyses[47,48] and range from −0.3 to +2 kcal/mol. While these are generally smaller than the differences we observe, the considerable structural difference between these models and our ^{1}SS renders quantitative comparison difficult. We feel that the explanation based on different pericyclic processes is the more likely at present, but we reiterate that the data do not demand it.

Entropies of Activation for k_D, k_T, and k_X. Entropy of activation is often taken to measure the degree of ordering of the system at the transition state. The values obtained for k_D (-10.9 ± 1.5 eu), k_T (-6.8 ± 3 eu), and k_X (-10.3 ± 2 eu) are all markedly negative. As we have pointed out before,[27] this requires that the transition states each be substantially more ordered than the exciplex. Concomitantly, it must then be that *the exciplex itself, ^{1}E, is not very ordered*, a conclusion presaged both by the variety of processes available to it and by previous work.[38,45,46]

The entropies of activation for the processes originating from E are all less negative than the −11 to −16 eu for cycloaddition and decay of the cyanophenanthrene-styrene exciplexes reported previously.[27] It is tempting to suggest that the additional negative entropy in the latter case arises from additional order imposed in the transition state to reach a "perfect sandwich" structure, utilizing remote orbital interactions with the styrene phenyl group as a sort of template to orient the reacting double bonds. We have already discussed the implications of this remote overlap in determining product stereochemistry.[17,18] The present results would suggest that its cost is ca. −5 eu in the previous case.

At first glance it appears anomalous that the cyanophenanthrene-styrene exciplexes, which presumably have the more specific sandwich-like geometry, have the more negative entropies of activation for cycloaddition-internal conversion compared to ^{1}E. One would think that approaching a pericyclic minimum in these cases would require less order, rather than more, since more is already built into the exciplex. We feel that our observations to the contrary underscore the importance of the effects of the remote overlaps at the transition state.

Lack of Temperature Dependence in the Triplet Process. The rate of reaction of ^3P with F has not been studied at elevated temperature. Our results only relate to partitioning of ^3SS among its possible products. They suggest that there is little or no difference in activation enthalpies among the three processes (scission, T formation, and C formation) available to it. As ^3SS appears to be essentially conformationally equilibrated within its lifetime at room temperature, and since the rate-limiting step in product formation appears to be spin inversion,[49,50] there appears to be little opportunity for differential activation. Loutfy and de Mayo[5] and Jones and Ramachandran[10] have previously shown that differences in activation energy between closure and scission for the (triplet) biradicals in enone photoannelation are finite but usually quite small (-2.1 to $+0.27$ kcal/mol), and we would not be able to detect a small difference in our sensitized experiments without more thorough study.

Other Activation Parameters for Photocycloaddition. Our present and previous results constitute the first determinations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in a singlet state cycloaddition system involving an emissive exciplex. Saltiel, Chapman, et al., in their study[51,52] of the addition of stilbene singlet to tetramethylethylene and methylcyclohexene, observed a negative temperature dependence of the phenomenological rate constant for quenching of stilbene singlet and attributed it to the involvement of an exothermically bound but *reversibly formed* exciplex in each case.[53] Inverse temperature dependence indicates a transition state for product formation enthalpically below separated singlet stilbene plus olefin. If $\Delta S^{\ddagger}$ were zero or positive for the exciplex → cycloadduct step, it is therefore hard to see how reversibility could be significant. We accordingly believe that this case also probably would show a significantly negative $\Delta S^{\ddagger}$ if the exciplex were detectable.

Ferguson et al. have conducted a thorough study[6-9] of the temperature dependence of photocyclization of anthracene sandwich pairs, a [4 + 4] photocycloaddition, from 6 K to room temperature. Included are anthracene,[6] linked anthracenes,[7] substituted anthracenes,[8] and anthracenophanes.[9] Excimer fluorescence and photocycloaddition compete. Two points in particular pertain to the present work. First, there appear to be several different geometries for the sandwich pair which lead to excimer fluorescence, and some which lead to cyclodimerization without fluorescence. We feel that these facts are nicely consistent with our ideas that exciplexes generally are not very rigidly structured and that the emissive properties are not particularly related to structural similarity to the pericyclic minimum. Second, the cycloadditions show activation energies of 450–600 cm^{-1} (1.3–1.7 kcal/mol). While these values are considerably lower than ours, they do demonstrate that the excimers are stable potential minima in this case, as the exciplexes are in ours. The existence of energy barriers both to cycloaddition and to reversion of an exciplex or excimer is, we feel, probably the norm rather than the exception.

The present results demonstrate the utility of transition-state theory as applied to [2 + 2] photocycloadditions. Lewis[12] and Zimmerman[15] have previously pointed out that temperature dependencies of excited-state processes in quite different systems are understandable in terms of conventional activation parameters. We continue to encourage wider application of temperature studies in photochemistry.

Our demonstration that, even when the exciplex is reached, further ordering is required to reach the transition state sets limits on the potential for success in the arbitrary [2 + 2] photocycloaddition. The entropy of association of exciplexes falls in the range of -15 to -25 eu. Taking our transition states as typical, it is easy to see that ca. -30 eu (crudely) is necessary to reach the transition state for cycloaddition based on separated reactants. This leads to a preexponential factor $\sim 10^6$ M^{-1} s^{-1}, which should obtain if there is no exciplex intermediate. Given the rather short lifetimes for most excited species, there seems little hope that intermolecular [2 + 2] cycloadditions of any reasonable quantum efficiency can be found in which the enthalpy of the transition state is above that of the separated reactants (including the excitation). If there is a stable exciplex, the preexponential factor for the *bimolecular* process may be higher if formation of the exciplex is at least partly rate limiting.

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References and Notes

(1) Robert A. Welch Foundation Postdoctoral Fellow, 1973–1977. Department of Chemistry, Box 9222, Southern Station, University of Southern Mississippi, Hattiesburg, Miss. 39401.

(2) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 3907 (1968).

(3) R. H. Dyck and D. S. McClure, *J. Chem. Phys.* **36**, 2326 (1962).

(4) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962); **68**, 1153 (1964).

(5) R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977).

(6) J. Ferguson and A. W.-H. Mau, *Mol. Phys.*, **27**, 377 (1974).

(7) J. Ferguson, A. W.-H. Mau, and M. Puza, *Mol. Phys.*, **28**, 1457, 1467 (1974).

(8) J. Ferguson and S. E. H. Miller, *Chem. Phys. Lett.*, **36**, 636 (1975).

(9) J. Ferguson, M. Morita, and M. Puza, *Chem. Phys. Lett.*, **49**, 265 (1977).

(10) G. Jones and B. R. Ramachandran, *J. Photochem.*, **5**, 341 (1976).

(11) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).

(12) F. D. Lewis, R. W. Johnson, and D. R. Kory, *J. Am. Chem. Soc.*, **96**, 6100 (1974).

(13) J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J. Chem. Soc., Chem. Commun.*, 390 (1972).

(14) M. V. Encina, A. Nogales, and E. A. Lissi, *J. Photochem.*, **4**, 75 (1975).

(15) H. E. Zimmerman and W. R. Elser, *J. Am. Chem. Soc.*, **91**, 887 (1969).

(16) R. B. Cundall and J. R. Voss, *Chem. Commun.*, 902 (1968).

(17) R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974).

(18) R. A. Caldwell, N. I, Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *J. Am. Chem. Soc.*, **100**, 2857 (1978).

(19) D. Creed, R. A. Caldwell, and Mary McKenney Ulrich, *J. Am. Chem. Soc.*, **100**, 5831 (1978).

(20) N. C. Yang, D. M. Shold, and B. Kim, *J. Am. Chem. Soc.*, **98**, 6587 (1976); N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *ibid.*, **97**, 5006 (1975); N. C. Yang, D. M. Shold, and J. K. McVey, *ibid.*, **97**, 5004 (1975).

(21) F. D. Lewis and R. H. Hirsch, *J. Am. Chem. Soc.*, **98**, 5914 (1976); F. D. Lewis, R. H. Hirsch, P. M. Roach, and D. E. Johnson, *ibid.*, **98**, 8438 (1976); F. D. Lewis, C. E. Hoyle, and D. E. Johnson, *ibid.*, **97**, 3267 (1975); see especially F. D. Lewis, *Acc. Chem. Res.*, **4**, 152 (1979).

(22) K. Mizuno, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 2993 (1974), and references cited therein.

(23) J. Saltiel and D. Townsend, *J. Am. Chem. Soc.*, **95**, 6140 (1973); J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, *ibid.*, **99**, 884 (1977).

(24) S. Farid, J. C. Doty, and J. L. R. Williams, *J. Chem. Soc., Chem. Commun.*, 711 (1972); S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975).

(25) R. A. Caldwell, *J. Am. Chem. Soc.* **95**, 1690 (1973).

(26) D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, **96**, 7369 (1974).

(27) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **100**, 2905 (1978).

(28) D. V. O'Connor and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4706 (1976).

(29) M.-H. Hui and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4718 (1976).

(30) K. H. Grellmann and U. Suckow, *Chem. Phys. Lett.*, **32**, 250 (1975).

(31) See D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 621 (1976).

(32) The decay ratio for piperylene at -77 °C differs but slightly from the room temperature value; see Loutfy and de Mayo.[5] The quantum yield for isomerization of several *cis*-stilbene derivatives to *trans*- shows but slight temperature dependence from room temperature to ca. -180 °C; see Gegiou, Muszkat, and Fischer.[2] Especially cogent is the case of 4-bromostilbene, in which case intersystem crossing is almost certainly the isomerization mechanism.[2,33]

(33) J. Saltiel, W.-L. Chang, and E. D. Megarity, *J. Am. Chem. Soc.*, **96**, 6521 (1974).

(34) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **99**, 3779 (1977).

(35) Compare the normal C_{sp^3}–C_{sp^3} bonding distance of 1.54 Å with the 3–4-Å spacing thought to be preferred for excited-state complexes.[36-39]

(36) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

(37) H. Braun and Th. Forster, *Ber. Bunsenges. Phys. Chem.*, **70**, 1091 (1966).

(38) G. N. Taylor, E. A. Chandross, and A. H. Scheibel, *J. Am. Chem. Soc.*, **96**, 2693 (1974).

(39) D. F. Eaton and D. A. Pensak, *J. Am. Chem. Soc.*, **100**, 7428 (1978).

(40) See B. Stevens, *Adv. Photochem.*, **8**, 161 (1971), and references cited therein.

(41) See especially J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).
(42) J. P. Petrovich, M. M. Baizer, and M. R. Ort. *J. Electrochem. Soc.*, **116**, 743 (1969).
(43) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-aqueous Systems", Marcel Dekker, New York, 1970.
(44) S.-M. Park and R. A. Caldwell, *J. Electrochem. Soc.*, **124**, 1859 (1977).
(45) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393 (1971).
(46) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).
(47) P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968). We have calculated relative barrier heights from product distributions, assuming that identical singlet 1,4-biradicals are generated in direct photolysis at room temperature and on pyrolysis at 145 °C.
(48) P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976). Again we have calculated relative barrier heights from the temperature dependence of product distributions.
(49) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **99**, 8360 (1977).
(50) R. A. Caldwell and D. Creed, *J. Phys. Chem.*, **82**, 2644 (1978).
(51) O. L. Chapman and R. D. Lura, *J. Am. Chem. Soc.*, **92**, 6352 (1970).
(52) J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *J. Am. Chem. Soc.*, **93**, 2804 (1971).
(53) Others have also noted negative temperature coefficients of cycloaddition: (a) N. C. Yang and D. Shold, *J. Chem. Soc., Chem. Commun.*, 978 (1978); (b) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Lett.*, 667 (1972).

Photoenolization of *o*-Alkyl-Substituted Carbonyl Compounds. Use of Electron Transfer Processes to Characterize Transient Intermediates

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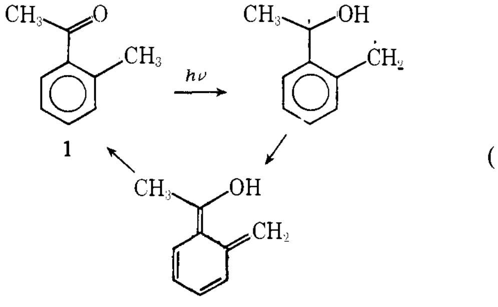
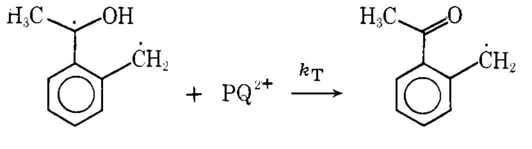
Abstract: Intramolecular hydrogen transfer in photoexcited *o*-methyl-substituted carbonyl compounds leads to the formation of short-lived biradicals which decay to yield unstable enols. The biradicals can be trapped with suitable electron acceptors, and a study of these processes leads to the measurement of biradical lifetimes, quantum yields, and their rates of electron transfer. The combination of these studies with quenching of the process by 1,3-pentadiene leads to the evaluation of the number and lifetime of the triplet state precursors. Ground-state conformation plays an important role in determining the nature and kinetics of triplet state processes. In a typical example, *o*-methylbenzaldehyde, two triplet states are responsible for biradical production; they have lifetimes of 1.1 and 95 ns in wet acetonitrile and account for 58% and 42% of the reaction, respectively. The biradicals are generated with a quantum yield of 0.83, live 1500 ns, and transfer an electron to paraquat dications with a rate constant of $6.2 \times 10^9\ M^{-1}\ s^{-1}$.

The photochemistry of *o*-methylacetophenone and several other *o*-alkyl-substituted carbonyl compounds has been the subject of several studies by steady-state irradiation, as well as flash techniques.[2-15] In general, these studies have led to consistent and reproducible results; nonetheless, the interpretation of those results has been the subject of considerable controversy, reflecting largely the assignment of the same transient signals to different species. Reaction 1 shows a simplified mechanism in the case of *o*-methylacetophenone, **1**.



(1)

When the syn-anti rotational equilibrium in the ground state is taken into consideration, the number of species potentially involved in the reaction includes: two ground states, two singlets, two triplets, two enols, and at least one biradical;[3] further, the biradical can be either described as such or as the triplet state of the enol. During the last few years, several groups have proposed techniques which allow the characterization of some of the species involved in the reaction. For example, Wagner[3] has used the triplet sensitized isomerization of dienes to measure triplet lifetimes and quantum yields of intersystem crossing. Wirz[4] has proposed the use of hexamethylphosphoric acid triamide (HMPA) to characterize the *Z* enols, since this solvent produces a considerable retardation of the reketonization. In a preliminary communication from this laboratory,[11] we proposed the use of electron transfer properties of the biradical in order to measure its lifetime, as well as establish the nature and number of its precursors. For example, reaction 2 shows the reaction with paraquat (1,1′-dimethyl-4,4′-bipyridilium, PQ^{2+}) dications.



$+ PQ^{+}\cdot + H^{+}$ (2)

The intense blue color of the radical ion $PQ^{+}\cdot$ makes it very easy to characterize (λ_{max} 603 nm);[16] if its formation is monitored in time-resolved experiments, the corresponding time profile contains information on the biradical lifetime, τ_B, as well as the rate constant for electron transfer, k_T.

In this paper, we report a study of the photochemistry of **1-6** in wet acetonitrile using the technique described above. We have been able to measure the biradical lifetimes, the quantum yields with which they are produced, Φ_B, their electron donor ability (k_T), the triplet lifetimes, and, when applicable, the syn:anti conformation ratio in the triplet state. Our approach, while indirect, overcomes the problem of transient assignment since, provided the triplet lifetime(s) are short, the only good

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