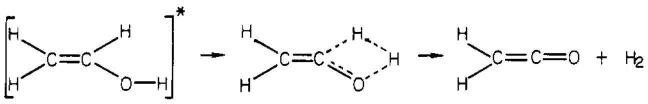
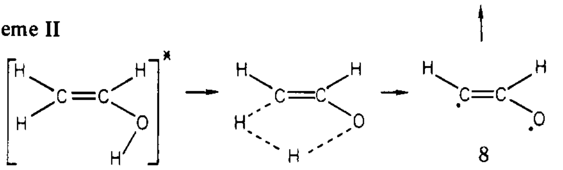
Scheme I



Scheme II



8

C_2H_4/O_3 samples in argon matrices. Concerted four- and three-center elimination of H_2 from vinyl alcohol (Scheme I) and **4**, respectively, would provide a low-energy pathway for decomposition. Elimination of H_2 from excited vinyl alcohol in the syn conformation **1** would also lead to ketene, via the intermediate **8** that may be responsible for the same product in $O + C_2H_2$ reactions (Scheme II). The lack of C_2H_2 photoproduct in irradiated C_2H_4/O_3 samples however favors α rather than β elimination of H_2 from vinyl alcohol.

The distribution of products in the C_2H_4/O system cannot distinguish between the intermediates **4** and **5**. If these intermediates are an important source of ketene, however, the biradical **4** would probably be favored. It is difficult to predict the pathway for the complex **5** to decompose to ketene involving, as it does, elimination of two hydrogen atoms from the same carbon atom. The study of the formation of ketene in this and other systems is being continued in an attempt to elucidate details of this mechanism.

Conclusion

The photolysis of O_3 in argon matrices containing ethene leads to the formation of acetaldehyde, ethylene oxide, ketene, and vinyl alcohol as primary products. There is some evidence for the participation of excited $O(^1D)$ atoms, in addition to $O(^3P)$, which may increase the relative yields of vinyl alcohol via H-atom abstraction or insertion mechanisms. Ketene is considered to be formed primarily by H_2 elimination from either vinyl alcohol or the initial addition product, a biradical, although the decomposition or arrangement of "hot" acetaldehyde and ethylene oxide cannot be ruled out.

The vibrational spectrum of vinyl alcohol exhibits several characteristics of alkyl vinyl ethers. Fermi resonance between the overtone of the out-of-plane CH_2 wag and the C=C stretch is relieved on ^{13}C or deuterium enrichment. Evidence for slight π character in the C-OH bond is found in the torsional frequency of the OH group which lies between that for saturated alcohols and carboxylic acids. Extensive interaction between the C-O stretch and in-plane COH and CH′ deformations leads to reduced ^{18}O and ^{13}C shifts and a large deuterium shift for the former vibrational mode. Finally the similarity between the infrared spectra of vinyl alcohol and the vinyl halides and ethers does not reflect the observed instability of vinyl alcohol. That samples can be kept at room temperature suggests that vinyl alcohol is indeed a stable if reactive molecule.

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Role of Higher Triplet States in the Anthracene-Sensitized Photoisomerization of Stilbene and 2,4-Hexadiene[1]

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Abstract: Irradiation of benzene solutions of anthracene (A) in the presence of varying amounts of *trans,trans*-2,4-hexadiene (tt) leads to trans → cis photoisomerization of the diene. Ratios of tc/cc are close to those expected for a high triplet energy donor. The anthracene-sensitized diene photoisomerization is not quenched significantly by *cis*-stilbene, though pronounced c → t stilbene photoisomerization is observed. Conversely, the diene quenches the anthracene-sensitized *cis*-stilbene photoisomerization. In air-saturated solutions where the lowest triplet of anthracene, $^3A^*$, is quenched by oxygen and is thus unavailable for interactions with the diene, diene photoisomerization to tc is slightly enhanced, as are tc/cc ratios. The upper limit for the rate constant of $^3A^*$ quenching in benzene by tt, determined by flash-kinetic spectroscopy at room temperature, is $1.2_5 \times 10^3\ M^{-1}\ s^{-1}$. When reported values for the interaction of A excited singlets, $^1A^*$, with the diene and A are used, kinetic analysis of the isomerization quantum yields leads to the conclusion that triplet excitation transfer to the diene is almost exclusively from a higher A triplet, $^3A^{**}$, while $^3A^*$ is responsible for stilbene photoisomerization. The data require that formation of the two triplets from $^1A^*$ be mainly sequential: $^1A^* \rightarrow {}^3A^{**} \rightarrow {}^3A^*$. The estimated effective lifetime of $^3A^{**}$ is ~30 ps. The effect of oxygen on the formation of cc suggests that quenching of $^1A^*$ by oxygen leads in part to adiabatic formation of $^3A^{**}$. This pathway may account for the inefficiency in singlet oxygen formation associated with $^1A^*$ quenching.

It is well established that the chemical response of acceptor molecules in triplet-sensitized photoreactions often depends on the energy of the triplet state of the donor (sensitizer) that transfers the excitation.[2] Commonly, the active state is the lowest triplet state of the donor, T_1, but in a series of elegant papers, Liu and co-workers showed that when anthracenes are employed as sensitizers, triplet-triplet energy transfer from a higher triplet state, T_2, becomes the dominant sensitization process.[3] At one stroke these experiments explained why product ratios from the acceptor molecules were consistent with excitation transfer from a high

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[1] (a) Supported by National Science Foundation Grants GP-24265 and CHE 80-26701. (b) Taken in part from the M.Sc. Thesis of D. E. Townsend, Florida State University, 1972.

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Table I. Anthracene-Sensitized *trans,trans*-2,4-Hexadiene Photoisomerization Quantum Yields[a]

	degassed[b]		stilbene[c]		air[b,d]	
$[\mathrm{tt}]_0$, M	$\phi_{\mathrm{tt}\to\mathrm{tc}} \times 10^2$	$\phi_{\mathrm{tt}\to\mathrm{cc}} \times 10^2$	$\phi_{\mathrm{tt}\to\mathrm{tc}} \times 10^2$	$\phi_{\mathrm{tt}\to\mathrm{cc}} \times 10^2$	$\phi_{\mathrm{tt}\to\mathrm{tc}} \times 10^2$	$\phi_{\mathrm{tt}\to\mathrm{cc}} \times 10^2$
0.065_4	0.70	0.17_6			0.7_5	0.13
0.078_5			0.70_5	0.21_7		
0.087_2	0.89	0.25_2			0.8_9	0.21
0.130_8	1.37	0.41	1.17	0.33_0	1.2_8	0.34
0.174_4	1.65	0.49	1.87	0.41_4	1.8_2	0.36
0.263	2.95	0.79	2.4_8	0.72_8	2.9_3	0.6_9
0.43_6	4.2_8	1.13	3.5_9	1.05	5.2_3	1.1_5
0.61_6	4.8_8	1.12	4.0_0	1.2_0	5.6_8	1.1_5
0.87_2	4.5_7	1.3_6	3.6_9	1.5_9	5.2_1	1.1_8
1.30_8	5.0_2	1.1_3	3.2_5	1.5_3	4.9_4	1.0_1
$(\mathrm{tc/cc})_{\mathrm{ave}}$:	3.8 ± 0.3		3.2 ± 0.5		4.6 ± 0.5	

[a] Ranges of corrected conversions: tt → tc, 0.078–0.60%; tt → cc, 0.024–0.14%; reproducibility for duplicate GLC analyses was always better than 5%; actinometer: 0.050 M benzophenone, 0.300 M *cis*-1,3-pentadiene, 8.15% corrected conversion. [b] $[\mathrm{A}]_0 = 8.3 \times 10^{-3}$ M. [c] $[\mathrm{A}]_0 = 6.6_4 \times 10^{-3}$ M, $[\mathrm{c\text{-}St}]_0 = 1.00 \times 10^{-2}$ M. [d] Adjusted for small diene loss, see text.

triplet energy donor (in several anthracenes T_2 is 68–74 kcal/mol and T_1 is 40–42.5 kcal/mol relative to S_0) and appeared to eliminate the need of postulating highly endothermic nonvertical[2,4] triplet excitation transfer from T_1. Ample spectroscopic evidence for the existence of a higher triplet in anthracenes, nearly isoergic with S_1, and formed upon intersystem crossing from the latter, was available then[5] and has been growing since.[6] The case for T_2 sensitization is especially strong for a series of rigid acceptors having relatively high lowest triplet excitation energies, $62 \leq E_T \leq 69$ kcal/mol.[3] Not only are these energies too high to be reached by excitation transfer from T_1 (40–42.5 kcal/mol) but the rigidity of these systems renders highly improbable the existence of relaxed triplet states with significantly different geometries that might be attained by nonvertical excitation transfer from T_1. The T_1 states of anthracenes were shown to be ineffective as sensitizers by employing them in the presence of a second sensitizer having E_T intermediate between T_1 and T_2 but well below the triplet energy of the acceptor. Less convincing results were obtained by using flexible acceptors such as the 1,3-pentadienes[3d] and the stilbenes,[3c,e] whose lower lying triplets (*s-cis*-diene ~52 kcal/mol, stilbene ~49 kcal/mol)[2b] might more readily be reached by endothermic triplet energy transfer from T_1. Such transfer, though inefficient, need only compete with the enormously slower decay rate of T_1. In addition, only qualitative data were presented for anthracene itself, whose lowest triplet, being some 2 kcal/mol higher in energy content than those of the substituted anthracenes, should have the best chance of sensitizing reactions in these olefins.

The following describes a study that fills the gap with respect to the parent anthracene and resolves the ambiguities mentioned above. It concerns the anthracene-sensitized trans → cis photoisomerization of *trans,trans*-2,4-hexadiene, tt, in the absence and presence of *cis*-stilbene and oxygen. This diene was selected because of the striking difference in the decay fractions of its s-trans and s-cis triplets.[7]

Results

Photoreaction Quantum Yields. Hexadiene photoisomerization quantum yields to the trans,cis (tc) and cis,cis (cc) isomers determined as a function of diene concentration in degassed (with and without 1.00×10^{-2} M *cis*-stilbene) and air-saturated benzene are listed in Table I. Irradiations were carried out in a Moses merry-go-round apparatus[8] at 30.0 ± 0.1 °C using 366-nm light. The benzophenone-sensitized isomerization of *cis*-1,3-pentadiene was used for actinometry.[9] Anthracene loss and anthracene/hexadiene 1:1 adduct yields were measured by GLC for the degassed samples using stilbene as internal standard; diene loss was measured by GLC for a few solutions using methylcyclohexane as internal standard. Results from these measurements are reported in the Experimental Section. Due to the low diene isomerization quantum yields, a long irradiation period was employed (1.32×10^{-4} einstein per ampule, 22 h) and anthracene consumption was substantial (up to 75% at the highest diene concentrations). Since, on the other hand, *cis*-stilbene photoisomerization is relatively efficient, the irradiation period employed to obtain the data in Table I led to large conversions to *trans*-stilbene (13–52%) in the samples containing 1.00×10^{-2} M *cis*-stilbene. *cis*-Stilbene photoisomerization quantum yields were therefore obtained by irradiating duplicate solutions for a shorter time period (5.23×10^{-6} einstein per ampule, 1 h), Table II. All conversions were corrected for back reaction and isomer contamination at zero time.[9a,10,11]

Table II. Anthracene-Sensitized *cis*-Stilbene Photoisomerization Quantum Yields[a]

$[\mathrm{tt}]_0$, M	$\phi_{\mathrm{c}\to\mathrm{t}}$	$[\mathrm{tt}]$, M	$\phi_{\mathrm{c}\to\mathrm{t}}$
0	0.22_8	0.174_4	0.19_8
0.043_6	0.21_9	0.26_3	0.18_4
0.061_6	0.21_8	0.43_6	0.16_2
0.078_5	0.21_4	0.61_6	0.13_9
0.087_2	0.20_9	0.87_2	0.11_6
0.130_8	0.19_8	1.74_4	0.062

[a] Solutions as described in Table I; corrected conversions ranged from 1.08% to 3.87% t; actinometer: 0.050 M benzophenone, 0.100 M *cis*-1,3-pentadiene, 0.97% conversion.

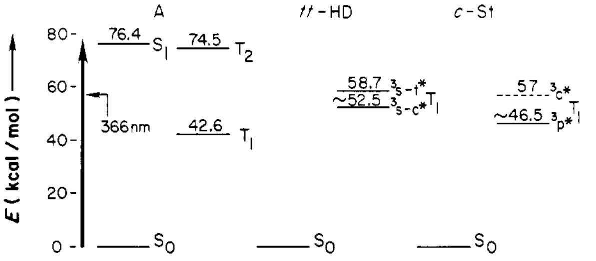

Figure 1. Donor–acceptor-state diagram.

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Table III. Rate Constants for Anthracene T_1 Quenching[a]

quencher	[Q], M	$k_d \times 10^{-2}$,[b] s^{-1}	$k_{dq} \times 10^{-2}$,[c] s^{-1}	$k_q \times 10^{-5}$, M^{-1} s^{-1}
tt-2,4-Hexadiene	0.42	1.15 ± 0.09	6.54 ± 0.30	0.013 ± 0.002
	0.42	11.4 ± 0.8	16.7 ± 1.0	0.012 ± 0.001
cis-Stilbene	$6.0_5 \times 10^{-3}$	1.43 ± 0.04	24.9 ± 1.3	3.88 ± 0.20

[a] [A] = 1.00×10^{-5} M in benzene, ~22 °C. [b] First-order rate constant before admission of quencher. [c] As in *b* after quencher was added (break-seal).

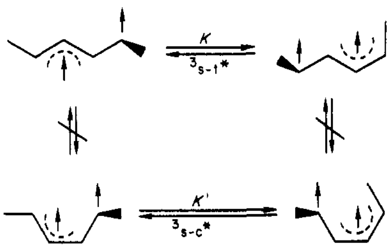
Spectroscopic Measurements. Rate constants for quenching of anthracene T_1, $^3A^*$, by tt and c-St in benzene were determined by kinetic flash spectroscopy as previously described.[13] The anthracene transient was monitored at 423 nm. First-order-decay rate constants were separated from second-order contributions to the decay, and the resulting quenching constants are reported in Table III. In the course of the flash kinetic measurements, 1.13% of the stilbene quencher isomerized to the trans isomer (GLC).

Discussion

Excitation energies of acceptor and donor states lying below the energy of the exciting light (366 nm, 78 kcal/mol) are shown in Figure 1. Absorption ($S_0 \rightarrow S_1$, $T_1 \rightarrow T_2$) and emission ($S_0 \leftarrow S_1$, $S_0 \leftarrow T_1$, $T_1 \leftarrow T_2$) spectra narrowly define anthracene energies.[5,6] A third triplet, T_3, in the vicinity of S_1 and T_2 may also play a role in intersystem crossing from S_1.[6,14] The $S_0 \rightarrow T_1$ spectroscopic transition of 2,4-hexadiene is assigned to the s-trans conformer, and the energy of the minor s-cis (skewed)[15] conformer is estimated by using 1,3-cyclohexadiene as a model.[2b,16] These energies are consistent with changes in diene adduct and isomer distributions with sensitizer triplet energy.[2,7,17] The triplet energy of stilbene is estimated relative to the ground state of the cis isomer and refers to the relaxed twisted conformer, $^3p^*$.[2,18] A dashed line above it shows the energy obtained from the origin of the $S_0 \rightarrow T_1$ absorption spectrum of *cis*-stilbene.[19] This energy is associated with Franck–Condon-allowed vertical excitation of the cis isomer to a cisoid triplet state, $^3c^*$.[2,18] Not shown are the two lowest singlet states of oxygen, the lowest of which, $^1\Delta_g$, 22.5 kcal/mol, forms when oxygen quenches triplets and, when energetically feasible, excited singlet states of aromatic hydrocarbons.[20] Clearly, the only transition promoted directly by 366-nm light is the $S_0 \rightarrow S_1$ transition in anthracene.

In dilute solutions at room temperature, $^1A^*$ undergoes intersystem crossing, $\phi_{is} = 0.72 \pm 0.02$,[21] and fluorescence, $\phi_{fm} = 0.27 \pm 0.02$.[22] At the high anthracene and diene concentrations employed in this work, dimerization via singlet excimers, $^1(AA)^*$,[23] and cycloadditions via singlet exciplexes, $^1(AD)^*$,[24] are efficient competing processes. These reactions have been studied thoroughly in this and other laboratories, and our most recent work[25] concerning each will be published separately. They impact the use of anthracene as a donor of triplet excitation by rendering ϕ_{is} a function of [^1A] and [^1D] and by causing rapid depletion of [^1A]. In this study these impacts were minimized by measuring [^1A] at the end of the irradiation period, thus ensuring that sufficient ^1A remained to absorb >95% of the incident radiation and by using average ^1A concentrations, $[^1A]_{ave}$, and known rate constants[23,24] to correct ϕ_{is}.

Scheme I. Dynamic Behavior of 2,4-Hexadiene Triplets



Diene Photoisomerization. The behavior of 2,4-hexadiene triplets has been inferred from the effects of sensitizer triplet excitation energy[7] and temperature[26] on their decay fractions. In fluid solution at 30 °C, sets of noninterconverting *s-trans-* and *s-cis-*2,4-hexadiene triplets, $^3s\text{-}t^*$ and $^3s\text{-}c^*$, respectively, assume relaxed allylmethylene geometries that, within each set, have fully equilibrated *cis-* and *trans-*allyl moieties, Scheme I. High triplet excitation energy donors, $E_T > 60$ kcal/mol, provide entry almost exclusively into the s-trans set of diene triplets. In each s-trans triplet the allylic moiety retains its stereochemistry, but the twisted ends upon intersystem crossing give cis and trans double bonds with equal probability. The deviation of the overall decay process from the random distribution of 1:2:1 (eq 1) is attributed to a

$$^3s\text{-}t^* \rightarrow 0.31tt + 0.50tc + 0.19cc \qquad (1)$$

smaller than unity equilibrium constant K in Scheme I;[26] e.g., for benzophenone $E_T = 68$ kcal/mol, starting from tt, (tc/cc) = 2.8 ± 0.1. Lower excitation energy donors excite larger fractions of the lower energy $^3s\text{-}c^*$, which, owing to steric hindrance, does not decay to the cc isomer (eq 2)[7] and is reflected in much higher

$$^3s\text{-}c^* \rightarrow 0.70tt + 0.30tc \qquad (2)$$

tc/cc ratios; e.g., for pyrene $E_T = 48$ kcal/mol, (tc/cc) = 17. Consideration of the triplet energies in Figure 1 suggests that if T_1 anthracene, $^3A^*$, can transfer triplet excitation to the diene

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at all, it will excite s-cis conformers exclusively, while T_2, ${}^3A^{**}$, should give predominantly s-trans triplets. It follows that the tt → cc quantum yields should provide a quantitative measure of T_2 participation, whereas deviations of tc/cc ratios from the high-energy-sensitizer value should reveal the relative importance of T_1 and T_2 involvement in photoisomerization. *Low concentrations* of additional quenchers such as *cis*-stilbene or O_2, unable to compete for the short-lived T_2 state, are expected to become involved mainly in T_1 deactivation.

In degassed solutions the tc/cc ratios in Table I deviate only slightly from the ratio expected from the decay of ^{3}s-t* (eq 1), confirming Liu's conclusion[3] that anthracene sensitizes diene reactions by excitation transfer from T_2. Furthermore, a minor T_1 component in the isomerization appears to be diminished by the presence of 10^{-2} M *cis*-stilbene, leading to tc/cc = 3.2 ± 0.5, nearly indistinguishable from the value obtained with benzophenone. Accordingly, tt → cc quantum yields for degassed solutions, including or excluding *cis*-stilbene, should be accounted for by eq 1 together with eq 3–9. As indicated above, quenching

$$ {}^1A \xrightarrow{h\nu} {}^1A^* \qquad (3) $$

$$ {}^1A^* \xrightarrow{k_{fm}} {}^1A + h\nu \qquad (4) $$

$$ {}^1A^* \xrightarrow{k_{is}} \alpha\,{}^3A^{**} + (1-\alpha)\,{}^3A^* \qquad (5) $$

$$ {}^1A^* + {}^1A \xrightarrow{k_e} {}^1(AA)^* \qquad (6) $$

$$ {}^1A^* + {}^1D \xrightarrow{k_e'} {}^1(AD)^* \qquad (7) $$

$$ {}^3A^{**} \xrightarrow{k_{td}'} {}^3A^* \qquad (8) $$

$$ {}^3A^{**} + {}^1D \xrightarrow{k_{qD}'} {}^1A + {}^3\text{s-t}^* \qquad (9) $$

of ${}^3A^{**}$ by *cis*-stilbene, c-St, does not significantly deplete ${}^3A^{**}$ at the low concentration employed and is not included. Also omitted are (1) formation of ${}^1(AA)^*$ via triplet–triplet annihilation of ${}^3A^*$, because this pathway is not important at the low incident radiation intensities and relatively high anthracene concentrations employed,[25,27] (2) the quantum chain process for photoisomerization that has been proposed to occur by triplet-excitation-hopping from diene to diene but at higher diene concentrations than used here,[28] and (3) the very inefficient addition of diene triplets to tt.[28] If intersystem crossing from S_1 proceeded exclusively via T_2[5] (or even T_3)[6,14] as has been proposed, then α = 1 in eq 5. Application of the steady-state approximation to all excited species gives

$$ \frac{\phi_{is}(D,A)}{\phi_{tt\to cc}} = \frac{1}{\alpha\beta}\left(1 + \frac{1}{k_{qD}'\tau_t'[{}^1D]}\right) \qquad (10) $$

as the relationship between $\phi_{tt\to cc}$ and $[{}^1D]$, where β = 0.19 ± 0.01 is the decay fraction of ^{3}s-t* to cc (eq 1), k_{qD}' is the rate constant for eq 9, τ_t' is the effective lifetime of ${}^3A^{**}$ $(1/k_{td}')$, and $\phi_{is}(D,A)$ is the overall intersystem crossing quantum yield of ${}^1A^*$ at specific ${}^1A$ and ${}^1D$ concentrations,

$$ \phi_{is}(D,A) = k_{is}\tau_m/(1 + k_e\tau_m[{}^1A] + k_e'\tau_m[{}^1D]) \qquad (11) $$

In eq 11, τ_m is the lifetime of ${}^1A^*$, $(k_{fm} + k_{is})^{-1}$, and the rate constants are defined in eq 4–7. Values of $\phi_{is}(D,A)$ were calculated by using $k_{is}\tau_m$ = 0.73 (see above), $k_e\tau_m$ = 40 M^{-1},[23,25] $k_e'\tau_m$ = 0.57,[24b,c] the initial diene concentration $[tt]_0$, and the average anthracene concentration (see Experimental Section for final [A]).

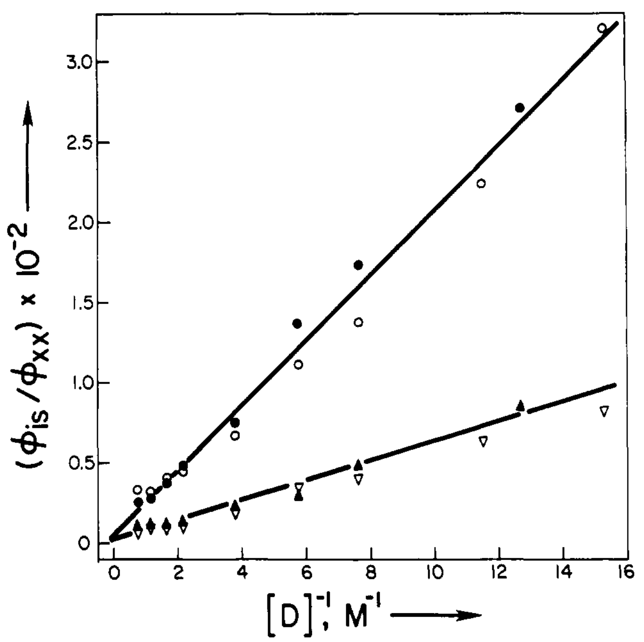

Figure 2. Diene concentration dependence of diene isomerization quantum yields in degassed solutions: (○) $\phi_{tt\to cc}$, (▽) $\phi_{tt\to tc}$, (●) $\phi_{tt\to cc}$ with 10^{-2} M c-St, (▲) $\phi_{tt\to tc}$ with 10^{-2} M c-St.

The values $\phi_{is}(D,A)/\phi_{tt\to cc}$ for degassed solutions show no consistent change when *cis*-stilbene is included in the solutions. They are considered to be unaffected by *cis*-stilbene within the experimental uncertainty for determining the very low conversions to the cc isomer. The plot of the tt → cc quantum yields, Figure 2, adheres nicely to eq 10 (correlation coefficient r^2 = 0.985). The intercept of the line through all the points gives $\alpha\beta$ = 0.19 and β = 0.19 ± 0.01,[29] eq 1 gives α = 1.0, which is, possibly fortuitously, identical with the proposed value of unity; suffice it to say that some minor leakage directly to ${}^3A^*$ cannot be excluded. The intercept to slope ratio gives $k_{qD}'\tau_t'$ = 0.26 M^{-1} from which the effective lifetime of T_2 τ_t' = 27 ps can be calculated, assuming that exothermic triplet excitation transfer from T_2 to the diene is diffusion controlled, k_{qD}' = 9.6 × 10^9 M^{-1} s^{-1}.[13,27] The tt → tc quantum yields are also plotted according to eq 10 in Figure 2. Since larger conversions to tc are involved, these values are somewhat more accurate. It can be seen that with a single exception the values for solutions excluding *cis*-stilbene fall consistently below those obtained in its presence. The best line through the points for the stilbene experiment is in fact very close to that predicted for pure ^{3}s-t* decay, and diene excitation exclusively via T_2 excitation transfer: $\alpha\gamma$ = 0.50 from the intercept (compare with γ = 0.50 in eq 1; perhaps coincidentally α = 1.0 is again inferred) and k_{qD}' τ_t' = 0.32 M^{-1} from the intercept/slope ratio, r^2 = 0.975. Nonetheless, the $\phi_{tt\to tc}$ values and the tc/cc ratios do suggest the functioning of a *minor* T_1 pathway to diene photoisomerization which is quenched somewhat by *cis*-stilbene. This point will be considered further in a separate section.

Effect of Oxygen. The quenching of S_1 and T_1 states of anthracene by O_2 has been studied thoroughly (for a review of the literature see ref 20). The quenching of S_1 though very rapid[30] is inefficient owing to S_1's short lifetime. It gives T_1 with unit efficiency[31] and O_2 ${}^1\Delta_g$ with an efficiency of 0.46.[20] In air saturated-benzene, $k_{qs}{}^{ox}\tau_m[O_2]$ = 0.19.[23,30] Though the quenching of T_1 anthracene is slower by a factor of ~9 (spin-statistical

$$ {}^1A^* + O_2\,{}^3\Sigma \xrightarrow{k_{qs}^{ox}} {}^3A^* + 0.46O_2\,{}^1\Delta + 0.54O_2\,{}^3\Sigma \qquad (12) $$

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(27) Saltiel, J.; Marchand, G. R.; Smothers, W. R.; Stout, S. A.; Charlton, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 7159.

(28) Saltiel, J.; Townsend, D. E.; Sykes, A. *J. Am. Chem. Soc.* **1973**, *95*, 5968.

(29) For benzophenone, $\phi_{tt\to cc}$ = 0.18,[28] so the $\alpha\beta$ value is a little high; however, the experimental uncertainty in the intercept is large.

(30) (a) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612. (b) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 709.

(31) Potashnik, R.; Goldschmidt, C. R.; Ottolenghi, M. *Chem. Phys. Lett.* **1971**, *9*, 424.

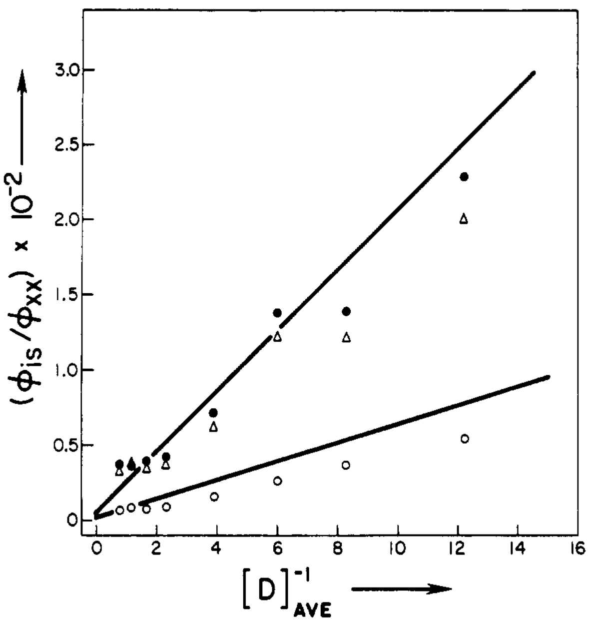

Figure 3. Diene concentration dependence of diene isomerization quantum yields in air-saturated solutions: (●) $\phi_{tt\to cc}$ and (○) $\phi_{tt\to tc}$ by using eq 16 for ϕ_{is}; (△) $\phi_{tt\to cc}$ by using eq 14 for ϕ_{is}; lines are taken from Figure 2.

factor),[20,30,32] it is the only significant T_1 quenching process in the air-saturated solutions since T_1 is very long-lived even in the presence of the diene (see below). This process gives $O_2\ ^1\Delta_g$ with unit efficiency[20]

$$^3A^* + O_2\ ^3\Sigma \xrightarrow{k_{qt}^{ox}} {}^1A + O_2\ ^1\Delta \tag{13}$$

Dienes are good substrates for $O_2\ ^1\Delta_g$, probably accounting for observed diene depletion[33] (up to 15% at the lowest diene concentration, see Experimental Section). However, diene photooxidation does not seem to deplete O_2, since the loss of anthracene is identical in paired irradiations of ampules open to the air and ampules through which air is bubbled throughout the course of the irradiation.

The inefficiency in $O_2\ ^1\Delta_g$ formation in eq 12 has been interpreted[20,34] in terms of a reencounter quenching of $O_2\ ^1\Delta_g$ by anthracene T_1. If so, the effect of oxygen on T_2 formation would be given by

$$\phi_{is}(D,A,O_2) = k_{is}\tau_m/(1 + k_e\tau_m[^1A] + k_e'\tau_m[^1D] + k_{qs}^{ox}\tau_m[O_2]) \tag{14}$$

which replaces eq 11. However, since T_2 is nearly isoergic with S_1, the inefficiency in $O_2\ ^1\Delta_g$ formation could reflect a competing

$$^1A^* + O_2\ ^3\Sigma \xrightarrow{0.54k_{qs}^{ox}} {}^3A^{**} + O_2\ ^3\Sigma \tag{15a}$$

$$^1A^* + O_2\ ^3\Sigma \xrightarrow{0.46k_{qs}^{ox}} {}^3A^* + O_2\ ^1\Delta \tag{15b}$$

process in which oxygen adiabatically converts S_1 to T_2.[35] Equation 14 would then be modified to

$$\phi_{is}(D,A,O_2) = \left(\frac{k_{is}\tau_m + 0.54k_{qs}^{ox}\tau_m[O_2]}{1 + k_e\tau_m[^1A] + k_e'\tau_m[^1D] + k_{qs}^{ox}\tau_m[O_2]}\right) \tag{16}$$

which predicts a smaller oxygen effect on T_2 formation.

Figure 3 shows a plot of the $\phi_{tt\to cc}$ values for air-saturated solutions using both eq 14 and 16 to calculate ϕ_{is}. The lines drawn in Figure 3 are taken from Figure 2. The points obtained by using eq 16 are generally in better agreement with the results from the degassed solutions, but the differences from the points obtained by using eq 14 are too small and the scatter in the data too large to allow a clear preference for the quenching mechanism in eq 15. What is certain is that $\phi_{tt\to cc}$ is not measurably affected when oxygen quenching completely eliminates T_1 excitation transfer as a viable possibility. *T_2 excitation transfer is confirmed as the sole pathway leading to cc.*

Seemingly in contradiction with the above reasoning is the observation that the presence of O_2 increases tc/cc ratios somewhat. Either there must be other mechanism(s) leading to tc so that the deviation of the tc/cc ratio from ~2.8 cannot be taken strictly as a measure of T_1 participation in the isomerization process or oxygen opens an entry to the T_1 photoisomerization pathway not involving bimolecular T_1/diene encounters.[37] This dilemma will be revisited below.

Stilbene Photoisomerization. The absence of a *cis*-stilbene effect on $\phi_{tt\to cc}$ shows clearly that T_2 excitation transfer to *cis*-stilbene need not be considered at the low *cis*-stilbene concentration employed. This is consistent with the low T_2 lifetime estimated above (~30 ps). The large c → t stilbene quantum yields, Table II, must therefore be a consequence of T_1 sensitization. Since T_1 formation appears to be primarily sequential, the presence of the diene should diminish $\phi_{c\to t}$ by quenching S_1, T_2, and possibly T_1. While a satisfactory qualitative interpretation of the results in Table II is thus accomplished readily, a quantitative interpretation is much less straightforward. In the following, the minimum number of steps that must be included in order to account for $\phi_{c\to t}$ dependence on substrate concentrations are considered in turn.

We begin with the quenching of $^3A^*$ by the two olefins

$$^3A^* + {}^1D \xrightarrow{k_{qD}} {}^3(AD)^* \tag{17}$$

$$^3A^* + {}^1c\text{-}St \xrightarrow{k_{qS}} {}^1A + {}^3p^* \tag{18}$$

As will be shown in the next section, $^3A^*$ quenching by ^1D, to the extent that it occurs, does not involve triplet excitation transfer as a significant process. For this reason the interaction is shown as leading to a triplet exciplex (eq 17), though it is recognized that other interactions such as biradical formation or impurity quenching cannot be excluded. An early flash-spectroscopic kinetic determination of the rate constant for $^3A^*$ quenching by 2,5-dimethyl-2,4-hexadiene resulting in $k_{qD} \simeq 7 \times 10^7\ M^{-1}\ s^{-1}$[38] was shown to be in error by a recent study that established an upper limit of $k_{qD} \leq 3 \times 10^4\ M^{-1}\ s^{-1}$ for the same diene.[39] Our observations, Table III, set an even lower limit, $k_{qD} \leq 1.2_5 \times 10^3\ M^{-1}\ s^{-1}$, for the $^3A^*$/tt interaction. This value is regarded as an upper limit because though reproduced in two independent experiments, it is so small that it may be dominated by efficient quenching by tiny impurity levels adventitiously present in the diene.

Our rate constant for $^3A^*$ quenching by c-St, $k_{qS} = 3.9 \times 10^5\ M^{-1}\ s^{-1}$, Table III, is about a factor of 5 larger than an earlier flash-spectroscopic kinetic determination also in benzene, $k_{qS} = 7.6 \times 10^4\ M^{-1}\ s^{-1}$.[40] A careful systematic study of the temperature dependence of k_{qS} has been carried out in toluene.[41] The activation parameters obtained give k_{qS} values of $2.0 \times 10^5\ M^{-1}\ s^{-1}$ and $2.4 \times 10^5\ M^{-1}\ s^{-1}$ at 23 °C (spectroscopic measurements) and 30 °C (photochemical measurements), respectively.[41] In view of the similarity of the solvents, the latter value is probably the most

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(32) Algar, B. E.; Stevens, B. *J. Phys. Chem.* **1970**, *74*, 3029.

(33) (a) Kondo, K.; Matsumoto, M. *J. Chem. Soc., Chem. Commun.* **1972**, 1332. (b) Hasty, N. M.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380.

(34) (a) Stevens, B.; Small, R. D., Jr. *Chem. Phys. Lett.* **1979**, *61*, 233. (b) Stevens, B. *J. Phys. Chem.* **1981**, *85*, 3555.

(35) This would be another example of spin-exchange quenching.[36]

(36) (a) Saltiel, J.; Thomas, B. *Chem. Phys. Lett.* **1976**, *37*, 147. (b) Görner, H.; Eaker, D. W.; Saltiel, J. *J. Am. Chem. Soc.* **1981**, *103*, 7164.

(37) For abnormally high $\phi_{tt\to ct}$ values not involving triplet states, see: (a) Hyndman, H. L.; Monroe, B. M.; Hammond, G. S. *J. Am. Chem. Soc.* **1969**, *91*, 2852. (b) Saltiel, J.; Metts, L.; Wrighton, M. *Ibid.* **1969**, *91*, 5684.

(38) Fry, A. J.; Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4781.

(39) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1981**, *103*, 4553.

(40) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.

(41) Saltiel, J.; Charlton, J. L.; Mueller, W. B. *J. Am. Chem. Soc.* **1979**, *101*, 1347.

reliable for use in accounting for our photochemical observations.

Next we consider the decay of the lowest anthracene and stilbene triplets

$$^3\mathrm{A}^* \xrightarrow{k_{\mathrm{td}}} {}^1\mathrm{A} \tag{19}$$

$$^3\mathrm{A}^* + {}^1\mathrm{A} \xrightarrow{k_{\mathrm{sq}}} 2\ {}^1\mathrm{A} \tag{20}$$

$$^3\mathrm{p}^* \overset{K_{\mathrm{pt}}}{\rightleftharpoons} {}^3\mathrm{t}^* \tag{21}$$

$$^3\mathrm{p}^* \xrightarrow{k_{\mathrm{dp}}} \delta\,{}^1\mathrm{t\text{-}St} + (1 - \delta)\,{}^1\mathrm{c\text{-}St} \tag{22}$$

$$^3\mathrm{t}^* + {}^1\mathrm{A} \xrightarrow{k_{\mathrm{tA}}} {}^1\mathrm{t\text{-}St} + {}^3\mathrm{A}^* \tag{23}$$

The smallest unimolecular decay rate constants measured for ^{3}A* at room temperature in dilute anthracene solutions, [^{1}A] $\leq 5 \times 10^{-5}$ M, are 50–100 s^{-1}.[42] Self-quenching via triplet excimer formation has been proposed to account for the dependence of the first-order decay constant on [^{1}A].[43d] However, serious doubt has been cast on this interpretation,[42d] and the larger rate constants[43] have been attributed generally to quenching by adventitious impurities (including oxygen) present in either the solvents or the anthracene.[42] Transient kinetics have not been reported for the high anthracene experiments employed in the photochemical experiments.[44] Whatever the origin of the "self-quenching" event, such a step (eq 20) $k_{\mathrm{sq}} \simeq 3 \times 10^5$ M^{-1} s^{-1} is necessary in accounting for the anthracene concentration dependence of (1) $\phi_{\mathrm{c\to t}}$ in the absence of diene[45] and (2) the triplet–triplet annihilation component of anthracene dimerization.[25]

The behavior of stilbene triplets (eq 21–23) is well characterized by steady-state[2,10,18] and transient measurements.[46] The calculation of the equilibrium constant $K_{\mathrm{pt}} \simeq 11$ at 30 °C in benzene[36b,46,47] is based on the well-founded assumption that k_{tA} is diffusion controlled when the acceptor is azulene.[13,36b,48] Steady-state[3c,e] and transient observations[49] show that excitation transfer from ^{3}t* to anthracenes is at least as efficient as to azulene. In eq 22, $k_{\mathrm{dp}} = 1.8 \times 10^7$ s^{-1} [46] and $\delta = 0.41$.[10] The possible conversion of ^{3}p* to ^{3}t* within the initial encounter cage of eq 18 followed by back excitation transfer (eq 23) before diffusive separation of the donor–acceptor pair has been proposed,[2b,3c,e,50] but in cases involving stilbene and aromatic hydrocarbons in nonviscous solvents, it appears to be at best of minor consequence.[2b,3c,4b] When operative, its effect is to give an apparent δ value somewhat higher than the natural decay ratio of eq 22.

Application of the steady-state approximation to all excited species in eq 3–9 and 17–23 gives the following complex relationship between $\phi_{\mathrm{c\to t}}$ and substrate concentrations:

$$\phi_{\mathrm{is}}/\phi_{\mathrm{c\to t}} = 1/f_{\mathrm{T_1}} \left(\frac{1 + k_{\mathrm{qS}}\tau_{\mathrm{t}}[^1\mathrm{c\text{-}St}] + K_{\mathrm{A}}[^1\mathrm{A}] + (1 + K_{\mathrm{A}}[^1\mathrm{A}])k_{\mathrm{qD}}\tau_{\mathrm{t}}[^1\mathrm{D}]}{k_{\mathrm{qS}}\tau_{\mathrm{t}}[^1\mathrm{c\text{-}St}](\delta + K_{\mathrm{A}}[^1\mathrm{A}])} \right) \tag{24}$$

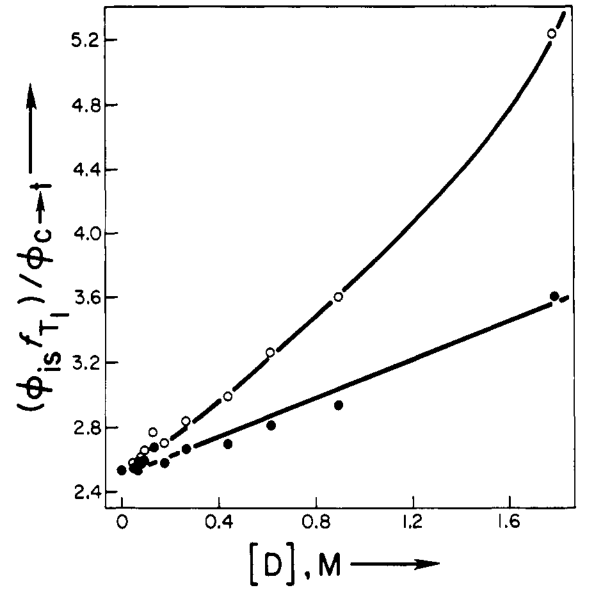


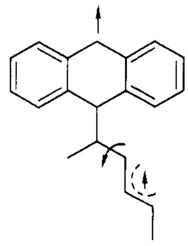
Figure 4. Diene concentration dependence of *cis*-stilbene isomerization quantum yields: (○) with $f_{\mathrm{T_1}} = 1$, (●) with $f_{\mathrm{T_1}}$ from eq 25.

where ϕ_{is} is defined by eq 11, $\tau_{\mathrm{t}} = (k_{\mathrm{td}} + k_{\mathrm{sq}}[^1\mathrm{A}])^{-1}$ is the lifetime of ^{3}A* at a specified [^{1}A], $K_{\mathrm{A}} = k_{\mathrm{tA}}/K_{\mathrm{tp}}k_{\mathrm{dp}}$, and $f_{\mathrm{T_1}}$ is the fraction of ^{1}A* that, following intersystem crossing, reach T$_1$

$$f_{\mathrm{T_1}} = \frac{1 + (1 - \alpha)k_{\mathrm{qD}}'\tau_{\mathrm{t}}'[^1\mathrm{D}]}{1 + k_{\mathrm{qD}}'\tau_{\mathrm{t}}'[^1\mathrm{D}]} \tag{25}$$

Since α is close to unity, a quadratic dependence of $\phi_{\mathrm{is}}/\phi_{\mathrm{c\to t}}$ on [^{1}D] is expected at constant [^{1}A] and [^{1}c-St]. Indeed, the plot of $\phi_{\mathrm{is}}/\phi_{\mathrm{c\to t}}$ vs. [^{1}D], Figure 4, shows pronounced upward curvature. With use of $k_{\mathrm{qD}}'\tau_{\mathrm{t}}' = 0.26$ M^{-1} and $\alpha = 1.0$ (see above), $f_{\mathrm{T_1}}$ was calculated at each diene concentration and a plot of $(\phi_{\mathrm{is}}f_{\mathrm{T_1}})/\phi_{\mathrm{c\to t}}$ vs. [^{1}D] is also given in Figure 4: intercept 2.52; slope 0.585; $r^2 = 0.965$. The slope/intercept ratio of this plot together with $K_{\mathrm{A}} = 60$ M^{-1} [3c,e] and the other rate constants given above predicts $k_{\mathrm{qD}} = 9 \times 10^2$ M^{-1} s^{-1}, which is in satisfactory agreement with the values obtained from the ^{3}A* transient decay, Table III. The magnitude of $\phi_{\mathrm{c\to t}}$ and its dependence on [^{1}D], though very complex, is completely predictable from independently determined rate constants assuming *only T$_1$ excitation transfer to cis-stilbene*.[51]

T$_1$ Diene Photoisomerization Pathway. We have established above that the diene (or some unknown impurity contained in it) is an inefficient quencher of ^{3}A* and tentatively have formulated the quenching step as triplet exciplex formation (eq 17), $k_{\mathrm{qD}} \simeq 1.2 \times 10^3$ M^{-1} s^{-1}.[52] That the diene itself is involved, at least in part, in the quenching process is suggested by observed tc/cc ratios somewhat larger than expected if excitation transfer to the diene were exclusively from T$_2$. Enhanced $\phi_{\mathrm{tt\to tc}}$ values could reflect either some s-cis-diene triplet formation by selective excitation



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(42) (a) Linschitz, H.; Steel, C.; Bell, J. A. *J. Phys. Chem.* **1962**, *66*, 2574. (b) Jackson, G.; Livingston, R. *J. Chem. Phys.* **1961**, *35*, 2182. (c) Livingston, R.; Ware, W. R. *Ibid.* **1963**, *39*, 2593. (d) Grellmann, K. H.; Scholz, H.-G. *Chem. Phys. Lett.* **1979**, *62*, 64.

(43) (a) Porter, G.; Wright, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1958**, *705*, 2593. (b) *Discuss. Faraday Soc.* **1959**, *27*, 18; (c) *Ibid.* **1959**, *27*, 94. (d) Langelaar, J.; Jansen, G.; Rettschnick, R. P. H.; Hoytink, G. J. *Chem. Phys. Lett.* **1971**, *12*, 86.

(44) Such research is in progress in our laboratory: Marchand, G.; Dabestani, R.; Saltiel, J.

(45) Saltiel, J.; Townsend, D. E.; Chang, D. W.-L.; Mitchener, J. C., unpublished results.

(46) See, especially: Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.

(47) The somewhat larger K_{pt} and k_{dp} values given here are based on $k_{\mathrm{tA}} = k_{\mathrm{dif}} = 9.6 \times 10^9$ M^{-1} s^{-1} by using triplet indeno[2,1-*a*]indene as a model for *trans*-stilbene.[13,48]

(48) Saltiel, J.; Chang, D. W.-L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559.

(49) Dainton, F.; Robinson, E. A.; Salmon, G. A. *J. Phys. Chem.* **1972**, *76*, 3897.

(50) Mercer-Smith, J. A.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 2620.

(51) Initial results concerning the dependence of $\phi_{\mathrm{c\to t}}$ on [^{1}A] and [^{1}c-St] or [^{1}t-St] are consistent with this conclusion. They will be published in connection with self-quenching of ^{3}A*, eq 20.[44] Saltiel, J.; Mitchener, J. C.; Townsend, D. E.; Chang, D. W.-L., unpublished results.

(52) For evidence of triplet exciplex formation between ^{3}A* and ethyl iodide, see: Tamargo, M. C.; Cowan, D. O. *J. Am. Chem. Soc.* **1982**, *104*, 1107.

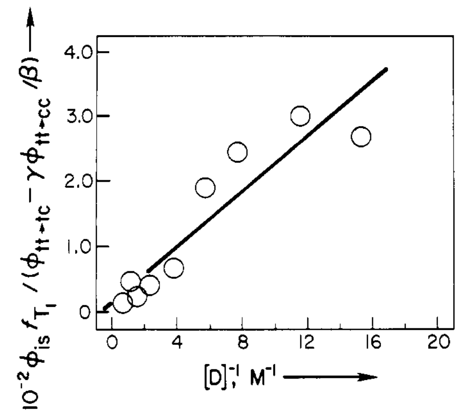

Figure 5. T_1 diene photoisomerization pathway for degassed solutions.

transfer from T_1 to the diene or T_1 addition to the diene to give a triplet biradical that might revert, in part to the diene and ^{1}A. The latter pathway would also not give cc since the allyl moiety is expected to maintain its stereochemistry;[28] a precedent for such biradical formation is the addition of benz[*a*]anthracene triplets to 1,3-pentadienes.[53] Avoiding a choice between these mechanisms, enhanced tc formation can be represented as a consequence of triplet exciplex decay,

$$^3(\mathrm{AD})^* \xrightarrow{k_{de}} {}^1\mathrm{A} + \epsilon\mathrm{tc} + (1 - \epsilon)\mathrm{tt} \qquad (26)$$

The dependence of $\phi_{tt\to tc}$ on $[^1\mathrm{D}]$ is then described by

$$\frac{\phi_{tt\to tc}}{\phi_{is}(\mathrm{D,A})} = \left(\frac{\alpha\gamma k_{qD}'\tau_t'[^1\mathrm{D}]}{1 + k_{qD}'\tau_t'[^1\mathrm{D}]}\right) + \left(\frac{f_{T_1}\epsilon k_{qD}\tau_t[^1\mathrm{D}]}{1 + k_{qD}\tau_t[^1\mathrm{D}] + k_{qS}\tau_t[^1\text{c-St}] + k_{qt}^{\mathrm{ox}}\tau_t[\mathrm{O}_2]}\right) \qquad (27)$$

where the first term gives the T_2 contribution (compare with eq 10) and the second term gives the T_1 contribution to tc formation. For degassed solutions, $k_{qt}^{\mathrm{ox}}\tau_t[\mathrm{O}_2] = 0$, combining eq 27 with eq 10 and rearranging gives

$$\phi_{is}(\mathrm{D,A})f_{T_1}/(\phi_{tt\to tc} - (\gamma\phi_{tt\to cc}/\beta)) = \frac{1}{\epsilon}\left(1 + \frac{1 + k_{qs}\tau_t[^1\text{c-St}]}{k_{qD}\tau_t[^1\mathrm{D}]}\right) \qquad (28)$$

Though the isomerization quantum yields are not sufficiently accurate to allow definitive application of eq 28, the values obtained for degassed solutions are in qualitative agreement with this relationship. A plot of the data in the absence of stilbene is shown in Figure 5: intercept = 16.1, slope = 21.0 M, $r^2 = 0.849$. The intercept gives $\epsilon \simeq 0.06$, and the intercept/slope ratio gives $k_{qD}\tau_t = 0.77$ M^{-1}. Since ^{1}A losses are substantial (see Experimental Section), τ_t, the lifetime of ^{3}A*, is really not a constant (recall that τ_t includes self-quenching). With average $[^1\mathrm{A}]$, the rate constants from the previous section give $k_{qD}\tau_t = 0.5$–0.7 M^{-1}, in satisfactory agreement with the value obtained from Figure 5. If all $^3\mathrm{A}^*/^1\mathrm{D}$ quenching events gave s-cis triplets, $\epsilon = 0.30$ would be expected (eq 2), so that a lower value of $\epsilon \simeq 0.06$ from Figure 5 could be accommodated by s-cis triplets only if no more than about one-fifth of the quenching events involved triplet excitation transfer to s-cis ground-state conformations. We draw no firm conclusion, however, since ϵ is very poorly defined in Figure 5. According to Figure 1, such a transfer process, if vertical, should be ~10 kcal/mol endoergic. A k_{qD} value of $\sim 1 \times 10^3$ M^{-1} s^{-1} would be consistent with this energy gap if the Arrhenius *A* factor for excitation transfer were $\sim 3 \times 10^{11}$ M^{-1} s^{-1} (note that only ~6% of the diene molecules are present in the s-cis conformation at 30 °C[15a]). Empirically, a value of $A \simeq 10^{10}$ M^{-1} s^{-1} accounts for the dependence of endoergic triplet excitation transfer rate constants on donor–acceptor triplet excitation energy differences.[40,54] It seems prudent to leave the question of the details of T_1 diene isomerization pathway open at this time.

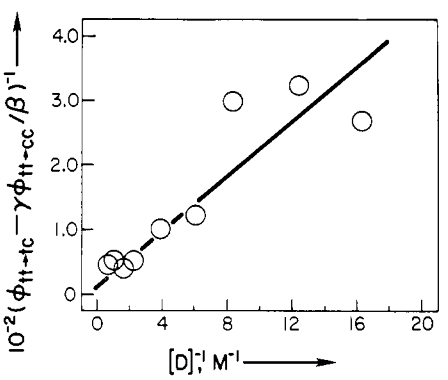

Figure 6. T_1 diene photoisomerization pathway for air-saturated solutions.

The decrease in tc/cc ratios in the presence of *cis*-stilbene is in qualitative agreement with eq 27 because of the predicted decrease of the T_1 term. Since $k_{qt}^{\mathrm{ox}}[\mathrm{O}_2] \sim 5 \times 10^6$ s^{-1},[30] the T_1 term should decrease to nearly zero in the presence of air. However, instead of dropping to ~2.8, tc/cc ratios for air-saturated solutions increase to ~4.6. Clearly, the mechanism considered thus far cannot account for this change. A clue to the explanation of this discrepancy may be provided by concomitant pronounced decreases in the quantum yields for anthracene loss[24b] and 1:1 A/tt adduct formation,[25] which have been attributed to oxygen quenching of a long-lived singlet exciplex.[24b,c,25] This process could provide direct entry into the triplet exciplex or any other intermediate involved in the T_1 isomerization pathway. The

$$^1(\mathrm{AD})^* + \mathrm{O}_2\ {}^3\Sigma \xrightarrow{k_{qe}^{\mathrm{ox}}} {}^3(\mathrm{AD})^* + \mathrm{O}_2\ {}^3\Sigma \qquad (29)$$

contribution to the tc isomer from this pathway can again be expressed as $(\phi_{tt\to tc} - (\gamma\phi_{tt\to cc}/\beta))$, which is related to substrate concentrations by

$$(\phi_{tt\to tc} - (\gamma\phi_{tt\to cc}/\beta))^{-1} = \left(\frac{1 + k_{qe}^{\mathrm{ox}}\tau_e'[\mathrm{O}_2]}{\epsilon k_{qe}^{\mathrm{ox}}\tau_e'[\mathrm{O}_2]}\right)\left(1 + \frac{1 + k_e\tau_m[^1\mathrm{A}] + k_{qs}^{\mathrm{ox}}\tau_m[\mathrm{O}_2]}{k_e'\tau_m[^1\mathrm{D}]}\right) \qquad (30)$$

where k_{qe}^{ox} is defined in eq 29 and τ_e' is the lifetime of the singlet exciplex in the absence of oxygen. Again, the isomerization quantum yields are not sufficiently accurate to allow quantitative treatment using eq 30; however, they are in qualitative agreement with this relationship, Figure 6. The line drawn in Figure 6 is the best straight line through the points having the expected intercept/slope ratio of 0.40 M^{-1}. The intercept of ~8 obtained in this way suggests that ϵ is about two or three times larger than the approximate value obtained above. Although no firm conclusions can be drawn, it should be recognized that oxygen quenching could involve an intermediate other than the exciplex.

Lifetime of T_2. The method used above to obtain $\tau_t' \simeq 30$ ps is essentially that applied earlier by Liu and co-workers to estimate T_2 lifetimes for several substituted anthracenes. Since Liu's estimates are generally about an order of magnitude larger (200–560 ps)[3f,55] than our value for anthracene, a critical evaluation of the method and its application is in order.

Quantum yields, ϕ_p, for T_2-anthracene-sensitized reactions are described by expressions analogous to eq 10,

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(55) Using the data in Table III of ref 3f, we are not able to reproduce the intercepts and lifetimes given in Table I. Least-square analyses of these data give intercept/slope ratios corresponding to τ_t' values of 17, 196, 118, and 73 ps for 9,10-dibromoanthracene, 9,10-dichloroanthracene, 9-phenylanthracene, and 9,10-diphenylanthracene, respectively ($k_q' = 8.5 \times 10^9$ M^{-1} s^{-1} was assumed for k_{dif} in benzene at 25 °C;[13] Liu used $k_q' = 6.2 \times 10^9$ M^{-1} s^{-1} from ref 40).

$$\frac{1}{\phi_p} = \frac{1}{\alpha\phi_{is}\beta}\left(1 + \frac{1}{k_q'\tau_t'[S]}\right) \qquad (31)$$

where $\alpha\phi_{is}$ is the $S_1 \rightarrow T_2$ intersystem-crossing yield and β is the efficiency with which the triplet state of the substrate, S, gives product P. In the earlier work, $1/\phi_p$ was plotted vs. $1/[S]$, $k_q'\tau_t'$ estimated from intercept/slope ratios, and τ_t' values obtained by assuming k_q' to be diffusion limited.[3] Two conditions were assumed to be fulfilled: (1) that there is no contribution from T_1 sensitization pathways to ϕ_p and (2) that ϕ_{is} is independent of substrate and anthracene concentration. It was, in part, to fulfill the latter condition and avoid competing anthracene dimerization that meso-substituted anthracenes were employed.[3] Unfortunately, since quantum yields for T_2-sensitized reactions are generally small, the intercepts of such plots are usually ill-defined. Apparently, for that reason in the latter work T_2 lifetimes were somehow based solely on the slopes of the plots (see Table I, ref 3f).[55]

The problems can be illustrated by considering results for the most thoroughly studied anthracene, 9,10-dibromoanthracene, DBA. Equation 31 was quantitatively applied to quantum yields for the DBA-sensitized photoisomerizations of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (**1**), *cis*-1,3-pentadiene, and *trans*-1,3-pentadiene[3c] and qualitatively to the photoisomerization of endodicyclopentadienone, EDP, and the photodimerization of cyclohexadiene.[3f] DBA fluorescence was shown to be quenched by cyclohexadiene[3f] but not by **1**. It was assumed not to be quenched by the pentadienes[3c] and EDP.[3f] Least-squares fit of the quantum yields for **1** (Table II, ref 3c) to eq 31 gives a negative intercept of −3.89. For the pentadienes, the reported intercepts are 5.98 (t → c) and 5.51 (c → t).[3c] Of course, the negative intercept has no physical meaning (a value of 1 was used instead in ref 3c), while the pentadiene intercepts suggest either significant inefficiency in T_2 formation from S_1 (i.e., $\alpha \simeq 0.3$) or some S_1 quenching by the dienes. Since recent work demonstrates convincingly that $T_2 \leftarrow S_1$ is the dominant intersystem crossing pathway in DBA (i.e., $\alpha = 1.0$),[56] more reliable estimates of $k_q'\tau_t'$ can probably be obtained by fixing the intercepts in eq 31 using known or estimated values of ϕ_{is} and β. Assuming $\phi_{is} = 1 - \phi_f$, values of $\phi_{is} = 0.78$ and 0.91_4 are calculated for benzene and *n*-hexane, respectively.[57] Setting $\alpha = 1.0$[56] and $\beta = 1.0$,[3c] 0.55[9] and 0.45[9] for **1**, *cis*- and *trans*-pentadiene, respectively, expected intercepts for the three substrates in the same order are 1.09, 2.33, and 2.84. Fixing the intercepts of the plots to these values, gives $k_q'\tau_t'$ values of 2.2, 0.58, and 0.49 M^{-1} (same substrate order) from which $\tau_t' = 110$ ps (*n*-hexane) and 68, 58 ps (benzene) can be obtained by using $k_q' = k_{dif} = 2.0 \times 10^{10}$ and 8.5×10^9 M^{-1} s^{-1} for *n*-hexane and benzene, respectively.[13] As indicated above, a T_1 photoisomerization pathway was excluded for **1** but not for the dienes.[3c] If s-cis conformations play a role in such a pathway, it should be least likely to interfere in the case of *cis*-1,3-pentadiene,[7] suggesting that the 68-ps lifetime is the more reliable value for benzene.

Though the above T_2-lifetime estimates for DBA are substantially lower than those in ref 3c, they are still a factor of 2–4 larger than our value for anthracene. A longer T_2 lifetime for DBA would not be surprising since it may explain in part the much larger $T_n \rightarrow T_1$ (n = 3 or 2) DBA fluorescence quantum yield; 1.0×10^{-6} for DBA vs. 5×10^{-8} for A in methylcyclohexane.[6] The question[6] of the source of the heavy-atom effect on $T_n \rightarrow T_1$ fluorescence and τ_t' remains. It seems likely that the answer must include the opening of the $T_n \rightarrow S_1$ channel by heavy-atom substitution. Ample evidence for reverse intersystem crossing in DBA has been obtained from its use as a luminescence enhancer in chemiluminescent reactions which give mainly excited triplet products.[58] The consequence of reversibility in intersystem crossing

$${}^1A^* \overset{K_{is}}{\rightleftharpoons} {}^3A^{**} \qquad (32)$$

on the decay kinetics is the coupling of the lifetime of $T_{2(n)}$ to that of the longer lived S_1 state; hence the larger apparent τ_t' and the larger $T_n \rightarrow T_1$ fluorescence quantum yield for DBA. For the case of fast equilibration relative to decay to lower energy states, the intercept/slope ratios discussed above give $k_q'K_{is}/k_{fm}$, so that $\tau_t' = K_{is}/k_{fm}$; the larger τ_t' then would reflect $K_{is} < 1.0$.[56] Since K_{is} for DBA is expected to be smaller in benzene than in *n*-hexane,[56] this analysis predicts the solvent effect on the effective lifetime of T_2 that was inferred above from Liu's data. The important point here is that the heavy-atom effect can lead to larger effective T_2 lifetimes without requiring changes in rate constants for internal conversions between states of the same multiplicity, e.g., k_{td}'.

Summary

Competitive quenching experiments have allowed separation of T_2 and T_1 contributions in anthracene-sensitized olefin photoisomerizations. Anthracene sensitizes 1,3-diene photoisomerization primarily from the T_2 state and stilbene photoisomerization (at concentrations normally employed for sensitized reactions) almost exclusively from the T_1 state. These findings confirm Liu's proposal that triplet excitation transfer from T_2 of anthracenes is an important process[3] but show that caution must be applied in neglecting T_1 contributions with specific acceptors (e.g., ref 3c,e). The method employed to estimate the lifetime of T_2 of anthracenes[3] (~30 ps for A) was critically examined and Liu's results with DBA reevaluated. It was suggested that the longer effective lifetime of T_2 in DBA and its larger triplet–triplet fluorescence quantum yield[6] are related in part to heavy-atom-induced coupling of T_2 decay with S_1 decay. This reasoning casts doubt on long T_2 lifetimes[3f] inferred for anthracenes lacking heavy-atom substituents.

Much more tentative conclusions concern the effects of oxygen on anthracene-sensitized diene photoisomerization. Two viable proposals are (1) that quenching of S_1 of A by oxygen is in part adiabatic leading to T_2 formation and (2) that quenching of the singlet A/tt exciplex by oxygen provides entry into the T_1 photoisomerization pathway.

Experimental Section

Materials. Anthracene (Eastman, blue-violet fluorescent) was zone-refined, 78 passes, on a Zone-Melter Model 2, Sloan-McGowan Co.; the middle cut was used. Benzophenone (Aldrich) was recrystallized three times from *n*-pentane and sublimed. *trans,trans*-2,4-Hexadiene and *cis*-pentadiene (Columbia) were bulb-to-bulb distilled immediately prior to use; isomeric impurity levels were 0.23% *cis,trans*-2,4-hexadiene and 0.07% *trans*-pentadiene, 0.50% cyclopentene, respectively (GLC). *cis*-Stilbene was prepared by pyrene-sensitized photoisomerization of *trans*-stilbene (K & K) in benzene.[2a] After irradiation (450-W Hanovia mercury lamp, Uranyl glass filter), the solution contained 91% *cis*-stilbene. Pure *cis*-stilbene was obtained by alumina (Baker, reagent) chromatography with *n*-pentane eluent (<0.01% trans, GLC). Pyrene (K & K) was chromatographed twice on alumina with *n*-pentane eluent and recrystallized from ethanol. Benzene (Fischer, Spectranalized) was used without purification except in the flash-kinetic experiments for which it was passed through an alumina column immediately before use.

Irradiation Procedures. Quantum yields were determined on a merry-go-round apparatus (13-mm o.d. tubes, 3-mL aliquots) immersed in a 30 °C water bath and equipped with Corning filters CS 7-37 and CS 0-52 for isolation of the 366-nm lines of a 200-W medium-pressure Hanovia mercury lamp. Five freeze–pump–thaw cycles to $<10^{-5}$ torr were employed for degassing. Duplicate samples were irradiated first open to the air and second with compressed air bubbling through the solution during the course of the irradiation in order to test for oxygen depletion in air-saturated solutions. A collimated light beam from a Schoeffield 150-W Xenon lamp was employed and passed through a high-intensity Bausch and Lomb monochromator set at 366 nm. An-

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(58) For recent results and key references, see: Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7272; *Ibid.* **1980**, *102*, 7279. See also: Kobayashi, S.; Kukuchi, K.; Kokubun, H. *Chem. Phys.* **1978**, *27*, 399.

Table IV. Anthracene Loss and Adduct Yield[a]

$[tt]_0$, M	degassed f_{-A} obsd	degassed f_{-A} calcd[b]	degassed f_{Ad} obsd	stilbene f_{-A} obsd	stilbene f_{-A} calcd[b]	stilbene f_{Ad} obsd	f_t[c]
0.065_4	0.50	0.45	0.019				
0.087_2	0.60	0.52	0.034				
0.130_8	0.66	0.54	0.040	0.74	0.58	0.029	0.35
0.174_4	0.74	0.58	0.047	0.84	0.65	0.070	0.52
0.26_3	0.84	0.65	0.10_5	0.92	0.66	0.080	0.48
0.43_6	0.96_7	0.66	0.21_7	0.98	0.72	0.20	0.47
0.61_6				0.97_9	0.73	0.27	0.41
0.87_2	0.97_1	0.73	0.31	0.97_2	0.67	0.24	0.22
1.30_8	0.97_5	0.70	0.31	0.97_3	0.68	0.30	0.19

[a] Same samples as in Table I. [b] Calculated actual loss using eq 33. [c] Fraction of *trans*-stilbene not corrected for back reaction.

thracene conversions were in the 10.1–18.3% range (UV analyses) and were not affected by bubbling air through the solutions. Diene concentrations checked were 0, 0.0876, 0.876, and 1.74 M; $[A]_0$ was 8.3×10^{-3} M throughout.

Analytical Procedures. GLC conditions for isomeric composition determinations of the hexadienes,[28] the pentadienes,[28] and the stilbenes[10] have been described previously. Diene loss to other reactions was checked at low diene concentrations by using methylcyclohexane as internal standard; GLC conditions have been described.[28] Losses were 3.0% and 15% at $[tt]_0 = 0.065$ M and 4.0% and 9.4% at $[tt]_0 = 0.174$ M for degassed and air-saturated solutions, respectively. Diene loss was taken into account in calculating isomerization quantum yields for air-saturated solutions and neglected for degassed solutions. Following the irradiation, solution absorbances were measured directly in the ampules (Cary 14 spectrophotometer), and it was determined that sufficient anthracene remained to absorb at least 95% of the incident radiation; $\epsilon = 2.7 \times 10^3$ M^{-1} cm^{-1}. GLC analyses for diene isomer composition were carried out immediately upon opening the ampules to the air. The solutions were then concentrated and analyzed for anthracene loss f_{-A}^{obsd}, 1:1 adduct, f_{Ad}^{obsd}, and, when applicable, stilbene isomerization, f_t, ($^1/_8$ in. × 3.5 ft column packed with 5% Apiezon M on Chromosorb W; column and injector temperatures were 170 °C to avoid splitting anthracene dimer). Stilbene was used as internal standard, Table IV. Anthracene concentrations determined by GLC were corrected for anthracene loss, f_{-A}, due to (at that time unknown) thermal addition of anthracene to the major 1:1 adduct,[24d] which is extensive during sample preparation,[25]

$$f_{-A} = f_{-A}^{obsd} - [f_{-A}^{obsd} - (1 + a)f_{Ad}^{obsd}]/(2 + a) \qquad (33)$$

where *a* is the independently determined ratio of anthracene loss contributions due to dimerization and adduct formation in the absence of the thermal reaction.[25] Anthracene loss in the presence of air was obtained by adjusting the values for degassed solutions with the ratio of anthracene loss quantum yields for degassed and air-saturated solutions.[25]

Flash-Kinetic Measurements. The apparatus and procedure used for these measurements have been described.[13]

Registry No. Anthracene, 120-12-7; (*E,E*)-2,4-hexadiene, 5194-51-4; (*E,Z*)-2,4-hexadiene, 5194-50-3; (*Z,Z*)-2,4-hexadiene, 6108-61-8; (*Z*)-stilbene, 645-49-8; (*E*)-stilbene, 103-30-0; oxygen, 7782-44-7.

Carbon-13 and Proton Two-Dimensional NMR Study of the *Ormosia* Alkaloids Panamine, Ormosanine, and Ormosinine

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Abstract: Three different types of two-dimensional NMR spectroscopy have been used to study the *Ormosia* alkaloids panamine, ormosanine, and ormosinine. By assigning the proton and carbon-13 NMR spectra of panamine and ormosanine, it has proved possible to establish the previously unknown structure of ormosinine as a molecule of panamine linked at C21 to C22 of ormosanine.

Introduction

Although *Ormosia* alkaloids do not have commercial utility in modern pharmacology, recent biological screening studies[1,2] suggesting sedative, hypnotic, and analgesic properties prompted our medicinal and structural examination of some of the substances in the series. The *Ormosia* alkaloids[3] ($C_{20}H_{31-35}N_3$) are pentacyclic and hexacyclic molecules that do not contain any functional groups other than the three basic ring nitrogen atoms. Because of this unusual molecular arrangement, prior to our current NMR study, detailed mapping of these compounds was limited to X-ray diffraction[5] and total synthesis.[3,6] This was how the structures of panamine $C_{20}H_{33}N_3$ (I) and ormosanine $C_{20}H_{35}N_3$ (II) were established[3,56]. However the identity of the dimer ormosinine[3,4] (III) remained in doubt; it shows a parent ion $C_{40}H_{66}N_6^+$ in its mass spectrum and sublimes to pure panamine. This paper elucidates the structure of ormosinine (III) and develops a methodology suitable for determining the structure of other *Ormosia* alkaloids. Proton and carbon-13 NMR spectroscopy is used together with the newly developed techniques of two-dimensional

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