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THE EFFECT OF MULTIPLICITY ON REGIOCHEMISTRY OF [2 + 2] PHOTOCYCLOADDITION OF 3,9-DICYANOPHENANTHRENE TO *trans-*β-METHYLSTYRENE[†]

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Summary

The title reaction is known to afford two isomeric [2 + 2] cycloadducts. It is shown that the major adduct isolated under preparative conditions, the head-to-head (HH) isomer, is the exclusive product in the triplet reaction. The singlet reaction affords both HH and its head-to-tail isomer. Rationales are presented based on synchronous (four-center) collapses to adducts from the (emissive) exciplex in the singlet process and non-synchronous collapse in the triplet. A simple method of estimating the exciplex lifetime and the equilibrium constant for its formation from the lifetime of the monomer and the aerated and deaerated Stern–Volmer fluorescence quenching slopes is presented.

1. Introduction

The photocycloaddition of olefins to phenanthrene derivatives has provided important clues to the mechanism of [2 + 2] photocycloaddition reactions generally [1 - 3]. The observation of emissive exciplexes as a common phenomenon has permitted an understanding of the role of exciplexes as photocycloaddition intermediates and of the structural features influencing the exciplex → product step [4]. A particularly interesting question is that of product regiochemistry in exciplex collapse. We have already reported [2] the photocycloadditions of substituted 9-cyanophenanthrene derivatives and styrene derivatives. We found that, while the 3,10-disubstituted cases or 9-cyanophenanthrene itself afforded only head-to-head (HH) adducts, 3-cyano and 3-methoxy substituents caused head-to-tail (HT) products to appear. We now report that, in one case at least, this is a consequence of non-specificity in the *singlet* process; the triplet process is cleanly head-to-head. The inter-

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vention of a substantial yield of HH cycloadduct via a triplet mechanism at least partly explains our lack of success in the previous [2] perturbation molecular orbital rationalization of regiochemistry.

2. Results and discussion

The quantum yields of cycloadduct formation from 3,9-dicyanophenanthrene (3,9-DCP) and *trans-β*-methylstyrene (*t-β*MS) (Fig. 1) were measured as a function of *t-β*MS concentration in outgassed benzene. The fluorescence quenching of 3,9-DCP by *t-β* MS (I^Q/I^0) was studied on the same samples. Figure 2 shows a plot of ϕ_{HH} and ϕ_{HT} *versus* $f_Q = 1 - I^Q/I^0$. The quantity f_Q is the fraction of singlet 3,9-DCP quenched by *t-β*MS and consequently the right-hand intercept of each plot is the quantum yield of the singlet process. The left-hand intercept is the product of the intersystem crossing (ISC) quantum yield of 3,9-DCP and the pure triplet quantum yield. Clearly, HH and HT are formed in comparable amounts from the singlet exciplex; $\phi_{HH}^S = 0.098$ and $\phi_{HT}^S = 0.078$ respectively. The triplet process, however, affords only HH; $\phi_{ISC}\phi_{HH}^T = 0.035$ and $\phi_{ISC}\phi_{HT}^T \approx 0$.

The lack of selectivity in the singlet process is not a consequence of an abnormally unstable reactive singlet exciplex. First, the very observation that the exciplex is long-lived enough to be emissive [2] requires it to be a stable potential minimum. Second, we have determined the equilibrium constant for its formation (about 9 M^{-1}), its lifetime (about 24 ns) and the rate constants for its formation of HH (about 3 × 10^6 s^{-1}) and HT (3.3 × 10^6 s^{-1}) by the analysis outlined in the Appendix. While these values indicate an exciplex that is thermodynamically less stable than the 9-cyanophenanthrene–*trans*-anethole exciplex [5] by a bit more than an order of magnitude, this instability relates to reversion to 3,9-DCP + *t-β*MS only. The rate constants for cycloadduct formation are actually smaller, and the exciplex lifetime longer, compared with the corresponding quantities for the 9-cyanophenanthrene–*trans*-anethole exciplex, which affords only an HH product.

We believe that the lack of regiospecificity is consistent with essentially concerted four-center exciplex collapse processes. The exciplex must be quite reversibly formed in this case (see Appendix) and is therefore able to distribute between HH-like and HT-like geometries. Clearly, in such a case the Curtin–Hammett principle applies and product ratios reflect the relative free energies of the two transition states. The calculations we reported before
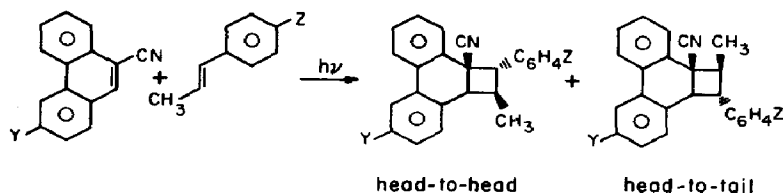

head-to-head   head-to-tail
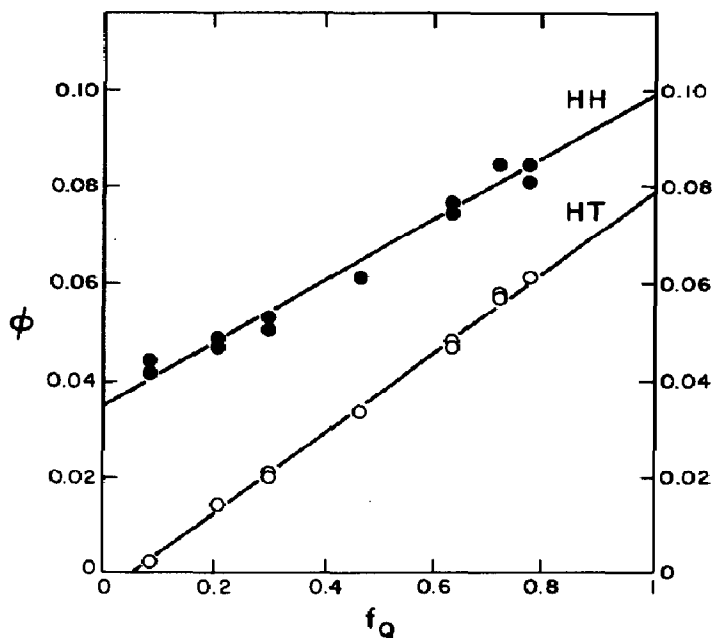
Fig. 1. The reaction scheme.

Fig. 2. Quantum yields of HH (•) and HT (○) as a function of f_Q in benzene at room temperature.

[2] indicated similar perturbation energies in such four-center geometries for HH-like and HT-like exciplexes but showed a preference for HT with 3,9-DCP. These calculations also apply to the four-center transition states. The present analysis shows that the HT/HH ratio directly from the singlet exciplex is close to unity and in fact may even favor HT when the contributions to HH from ISC processes in both [1]3,9-DCP and in the singlet exciplex are considered and subtracted. The regiospecificity in addition of t-βMS to 9-CP [6], however, still cannot be explained by the PMO results.

The high regiospecificity in the triplet reaction is a striking contrast to the result for the singlet reaction. One normally thinks of triplet cycloadditions as leading to multiple products, since the triplet 1,4-biradicals that often intervene are generally capable of stereorandomization [7 - 9]. In several cases, also, triplet photoprocesses are not especially regioselective between HH and HT orientations [7, 8]. Our regiochemical result here probably reflects an unsymmetrical collapse perhaps through a triplet 1,4-biradical or perhaps through a synchronous path. Collapse either to give a 1,4-biradical or through a four-center transition state in which one bond forms well before the others would both suggest that product formation would follow the "most stable 1,4-biradical" maxim. That is, of course, exactly what we observe. Since in none of our cases do we note significant stereorandomization even in triplet processes, we believe that we can rule out freely rotating triplet 1,4-biradicals. The suggestions of Shaik and Epiotis [10] that collapse of triplet exciplexes to cycloadducts may be concerted with spin inversion may apply in the present case, and if so biradicals would

in fact not be present at all. There are, however, other possible explanations for stereoretention, *e.g.* steric hindrance to rotation of the bulky phenyl group, an unusually short-lived triplet 1,4-biradical or a combination of these two factors. We underscore the need for a better understanding of the properties of 1,4-biradicals.

The work of Lewis *et al.* [11] has also demonstrated the value of PMO techniques in predicting regiochemistry in singlet cycloadditions. Interestingly, Lewis and Hirsch [12] have found a similar high regioselectivity in the triplet state [2 + 2] photocycloaddition of diphenylvinylene carbonate to 1,3-dienes which follows the most stable 1,4-biradical prediction. However, in this reaction substantial stereorandomization is observed. Their explanation, that the more hindered (and less stable) biradical is indeed formed but preferentially reverts to addends, can relate to the present results only with a rationalization for our lack of triplet state stereorandomization.

3. Experimental

All compounds have been previously reported [2]. *trans-β*-Methylstyrene (Aldrich, 99+%) was distilled slowly on an annular Teflon spinning band distillation column and filtered through basic alumina immediately prior to use. Samples (3 ml each) were prepared in 13 mm Pyrex ampoules and irradiated as previously described [3] at 366 nm, where only 3,9-DCP absorbs. Ferrioxalate actinometry was employed; the concentration of 3,9-DCP was 10^{-3} M, which necessitated a small (about 10%) correction for incomplete light absorption. Photocycloadditions were analyzed on a μ-Porasil column in a Waters ALC-202 liquid chromatograph, using hexane—chloroform (10:1) as eluting solvent with UV analysis at 254 nm. After each ampoule was opened, 94 μl of $(2.00 \pm 0.01) \times 10^{-2}$ M ethyl *p*-methoxycinnamate was added as internal standard and the solution concentrated to 0.3 ml. Owing to the insolubility of the phenanthrene, each sample was filtered through a 5 μm Teflon filter prior to analysis. Retention volumes under these conditions were 16.3 ml (standard) 25.0 ml (HT), 34.6 ml (3,9-DCP) and 49.4 ml (HH). Known mixtures of HT, HH and the standard were analyzed under identical conditions for calibration. Conversions were kept low (3 - 7% of initial 3,9-DCP) to minimize *trans—cis* isomerization of βMS.

Fluorescence quenching studies were performed on a Farrand MK-1 ratio recording spectrofluorometer. Stern—Volmer slopes and f_Q values reflect a small correction for the contribution of the fluorescence of the exciplex (λ_{max} = 428 nm) at the analyzing wavelength (377 nm).

Acknowledgments

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Appendix

The thermodynamic and kinetic parameters for exciplexes closely related to the present one have already been presented [4, 5]. The thermodynamic data were obtained by relatively tedious analyses of time-resolved nanosecond flash fluorescence spectra. We take the parameters from those studies which seem structurally independent and extrapolate them to the present case. In so doing, we find that the exciplex lifetime and the equilibrium constant for its formation may be easily derived from the Stern–Volmer slopes in degassed benzene ($9.0 \, M^{-1}$) and aerated benzene ($8.7 \, M^{-1}$) with reference to the general scheme below. (M = 3,9-DCP and Q = t-βMS).

$$^1M + Q \underset{k_{MC}}{\overset{k_{CM}}{\rightleftharpoons}} \, ^1(M...Q)$$

$$k_{O_2}^{M}(O_2) \downarrow \quad \tau_M^{-1} \quad k_{O_2}^{C}(O_2) \downarrow \quad \tau_C^{-1}$$

$$M \qquad M + Q, \, ^3(M...Q), \text{ adducts etc.}$$
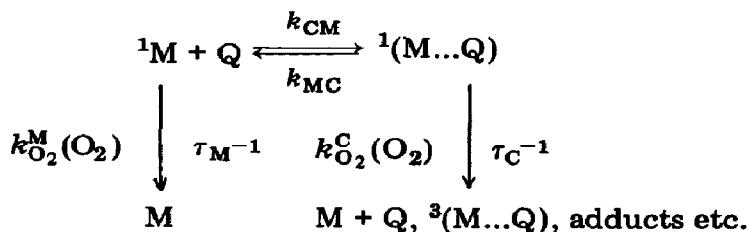
In such reversible systems, it is well known [A1] that $k_{CM}\tau_M$ is not equal to the Stern–Volmer slope S. Instead, eqn. (A1) results:

$$\frac{I_0}{I} = 1 + S(Q) = 1 + \frac{k_{CM}\tau_M^1}{1 + k_{MC}\tau_C^1}(Q) \tag{A1}$$

The values τ_M^1 and τ_C^1 are the lifetimes under a given set of conditions for monomer and exciplex respectively. In degassed benzene, $\tau_M^1 = \tau_M$ and $\tau_C^1 = \tau_C$; in aerated benzene, eqns. (A2) and (A3) result:

$$(\tau_M^1)^{-1} = \tau_M^{-1} + k_{O_2}^M(O_2) \tag{A2}$$

$$(\tau_C^1)^{-1} = \tau_C^{-1} + k_{O_2}^C(O_2) \tag{A3}$$

We have measured the lifetime of ^{13,9}-DCP as 25.6 ± 1 ns in benzene. Values of $k_{O_2}^M(O_2) = 3.7 \times 10^7$ s^{-1} and $k_{O_2}^C(O_2) = 4.2 \times 10^7$ s^{-1} obtain quite closely for other cases we have studied [3, 4] and reflect diffusion-controlled oxygen quenching of the excited singlet species [A2]. We accordingly are confident that they obtain in the present case as well. The two equations relating S to the remaining unknowns k_{CM}, k_{MC} and τ_C^1 in deaerated and aerated solution are insufficient for a complete solution. However, it is generally accepted that k_{CM} will be diffusion controlled, or nearly so [A1], and a reasonable assumption of $k_{CM} = 5 \times 10^9 - 1 \times 10^{10}$ M^{-1} s^{-1} can be made. This value in fact obtains for several very closely related exciplexes [5], and, as shown below, neither τ_C nor $K_{eq} = k_{CM}/k_{MC}$ is very sensitive to the choice of k_{CM}. A value of $k_{MC}\tau_C^1$ can be determined from an assumed k_{CM} using the equation

$$k_{MC}\tau_C^1 = \frac{k_{CM}\tau_M^1}{S} - 1 \tag{A4}$$

for either aerated or degassed solution. The ratio of the two values of $k_{MC}\tau_C^1$ is τ_C/τ_C^{air}, since k_{MC} is the same. Note that eqn. (A3) can be rearranged to

$$\frac{\tau_C}{\tau_C^{air}} = 1 + k_C^{O_2}(O_2)\tau_C = 1 + 4.2 \times 10^7\tau_C \tag{A5}$$

Since the ratio on the left is now known, eqn. (A5) affords τ_C. Substitution of τ_C into the expression for S now affords k_{MC}. Values of τ_C, k_{MC} and K_{eq} calculated from a reasonable range of k_{CM} are given in Table A1. The values diverge significantly below $k_{CM} = 2 \times 10^9$ M^{-1} s^{-1}, but fortunately this is unreasonably low. Assuming a value of $k_{CM} \approx 6.6 \times 10^9$ M^{-1} s^{-1}, the value

TABLE A1

Calculation of various parameters from an assumed k_{CM}

k_{CM} (M^{-1} s^{-1})	τ_C (ns)	k_{MC} (s^{-1})	K_{eq} (M^{-1})
10^{11}	21.1	1.34×10^{10}	7.5
10^{10}	22.5	1.22×10^9	8.2
5×10^9	24.2	5.46×10^8	9.1
2×10^9	31.4	1.49×10^8	13.4
1×10^9	62	2.97×10^7	33.6

for 9-cyanophenanthrene quenched by *trans*-anethole [5], we estimate $\tau_C \approx$ 24 ns and $K_{eq} \approx 9$ M^{-1}.

From τ_C, $k_{HT} = \phi_{HT}^S/\tau_C = 3.25 \times 10^6$ s^{-1}, the rate of collapse of the exciplex to HT, can be calculated directly. Determination of k_{HH} is not straightforward since ISC from the exciplex will afford an alternative path to HH. Assuming that, for internal conversion of the exciplex, $k_D \approx 0.75$ (k_{HH} + k_{HT}), and, for fluorescence of the exciplex, $k_F = 4 \times 10^6$ M^{-1} s^{-1}, as before [4], we calculated k_{ISC} using an iterative procedure. Assuming $k_{HH} = \phi_{HH}^S/\tau_C$ then affords a value of $k_{ISC} = \tau_C^{-1} - (k_D + k_F + k_{HH} + k_{HT})$. The k_{ISC} value, ϕ_{HH}^T and an assumed ϕ_{ISC} for 3,9-DCP of 0.8[†] allow calculation of $\phi(^1$exciplex $\rightarrow$ ^{3}exciplex $\rightarrow$ HH). This value was subtracted from ϕ_{HH}^S to afford a new value of k_{HH} which was iterated to constancy of all parameters. The resultant $k_{ISC} = 2.7 \times 10^7$ s^{-1} is very close to the value observed for related exciplexes [4], which provides an external check. The consequent contribution to ϕ_{HH}^S from singlet exciplex collapse only is

$$\phi(^1\text{exciplex HH}) = \phi_{HH}^S - k_{ISC}\tau_C\left(\frac{\phi_{HH}^T}{\phi_{ISC}^{3,9\text{-DCP}}}\right) = 0.070$$

In view of the assumptions and the somewhat involved calculation, this value is not as precise as a usual straightforwardly measured quantum yield. However, since the correction to ϕ_{HH}^S is only about 30%, and since substantial variations in the assumed parameters cause only small variations ($\tau_C = 15$ ns affords $\phi = 0.071$), we feel that the additional errors are not serious. Accordingly, the conclusion that the singlet exciplex affords HT in a yield equal to or slightly exceeding that of HH is not affected.

Finally, we note that Charlton *et al.* [A2] have reported a somewhat similar but more sophisticated approach to exciplex kinetics in which the input data include the ^{1}M fluorescence lifetimes as a function of (Q).

References to the Appendix

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[†]The ISC yields of 9-cyanophenanthrenes are about 0.8, though we have not made precise determinations [A3]. The arguments in the text are quantitatively slightly sensitive to the exact value but even an error of 20% in the ISC yield would not change our conclusion qualitatively.