

is not unusual when ab initio calculations which do not include d orbitals and configuration interaction are used.^{8b}

Conclusion

Both theoretically calculated and experimental results^{9,10} indicate that the rate of proton exchange in α -methyl- β -hydroxyacrolein is one order of magnitude smaller than that of β -hydroxyacrolein.^{6,9} This difference is due to the strong coupling that exists between the proton exchange and the rotation of the methyl group. The strong coupling is due to the fact that the proton will exchange only when the conformation of the methyl group leads to a symmetric double minimum profile. The same effect was proposed to explain the rate of proton transfer between methoxide and methyl alcohol and methyl alcohol and methyloxonium ion.⁵

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- (16) The effective mass was calculated as the ratio of the component along the reaction coordinate g_{jj} of the kinetic energy tensor to the metric g_{jj} .¹² The average values for $(\partial x_j / \partial \xi)^2$ were calculated from the initial and intermediate structures after elimination of translational and rotational displacements.

A Predictor of Reactivity in Allowed Photodimerizations and Photocycloadditions

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Abstract: A paradigm for prediction of reactivity in allowed, [2 + 2] and [4 + 4] singlet-state photodimerizations and photocycloadditions is developed and compared to results obtained from the literature. Favorable features for high reactivity are high singlet energy, low triplet energy, and high frontier orbital density at reacting positions. The quantitative algorithm $\gamma(r_c) = (E_T^A + E_T^B - E_S^A)/c^2$ is derived, where $\gamma(r_c)$ is the resonance integral for end-on interaction of carbon 2p orbitals at distance r_c , E_T^A and E_T^B are triplet energies of reactants A and B, E_S^A is the singlet energy of the excited reactant A, and c^2 is the sum of HOMO and LUMO orbital coefficient products over reacting positions. The algorithm correlates a substantial body of known photoreactivities with considerable success.

Despite the large number of allowed, [2 + 2] and [4 + 4] singlet-state photocycloadditions and photodimerizations reported in the last 15 years,¹ a simple paradigm for predicting reactivity has not hitherto emerged. Some theoretical treatments have offered elegant but qualitative analyses based on state correlation diagrams; cf. especially the analysis of the $H_2 + H_2$ reaction by Michl and co-workers.² Others³ have emphasized PMO techniques,^{3a} frontier orbitals,^{3b} or configuration interaction analysis.^{3c} The Michl model has been useful both to others^{4,5} and to us⁶ in rationalizing certain aspects of photocycloaddition reactivity. Further tests of the model would increase our confidence in its utility and, if quantitative, might lead to a generally useful structure-reactivity relationship.

The analysis below suggests and tests a paradigm based on the Michl model which places [2 + 2] and [4 + 4] singlet-state photodimerizations and photocycloadditions on a common scale. Favorable features for high reactivity are high singlet energy, low triplet energy, and high frontier orbital density at reacting positions. An easily applied algorithm allows concrete predictions of reactivity.

The Model

The feature of allowed photocycloadditions key to the present analysis is the correlation of a doubly excited configuration D of addends with the ground state $G^{2,6}$ of the adduct. The crossing of this correlation line with the S-S line essentially locates the transition state for the reaction (Figure 1). Note that the point at which crossing occurs would be determined if the D-S gap at infinite separation ΔE_∞ and the behavior of the two correlation lines up to the crossing point were known.

The D-S gap ΔE_∞ is usually known precisely! The D state in this region in fact corresponds to overall singlet coupling of the HOMO-LUMO (i.e., L_a) triplets of the reacting partners.² For common chromophores, this is nearly always the lowest triplet, for which triplet energies are generally available. The S state corresponds to excitation of the reactant of lower excitation energy. For reactants A and B, then, with $E_S^A < E_S^B$, ΔE_∞ may be expressed as

$$\Delta E_\infty = E_T^A + E_T^B - E_S^A \quad (1)$$

As reaction proceeds, the D state drops extremely rapidly as a result of the interchromophoric interaction. The initial

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Table I. Parameters for Arenes, Alkenes, and Dimerizations

compd	E_S^a	E_T^a	c^2	$\gamma(r_c)^a$	results ⁱ
anthracene	75.6	42.6	1.55 ^b	6.2	+
stilbene	85.3	49	1.55 ^c	8.2	+
tetracene	60.7	29.4	1.16 ^b	-1.7	+
1,3-cyclohexadiene	91.3 ^d	53	2.88 ^b	5.1	0
styrene	99.3	62	1.98 ^c	7.4	+
1,2-benzanthracene	74.7	47.1	2.04 ^c	12.1	+
simple alkenes	124 ^e	78 ^e	1.42 ^b	13.7	+ ^j
acenaphthylene	61.1	43-47	4.04 ^c	16	+
naphthalene	90.9	60.9	1.45 ^c	17-23	+
			1.41 ^b	21.9	±
			0.98 ^c	31.7	-
phenylacetylene	101.4	72	2.04 ^{c,f}	20.9	0
tolan	89.9	62.5	1.55 ^{c,g}	22.7	0
9-cyanophenanthrene	80.3	58.1	1.41 ^{c,h}	25.4	±
pyrene	77.0	48.3	0.72 ^c	27.2	-
phenanthrene	82.4	61.7	1.41 ^c	29.1	-
chrysene	79.4	57.1	0.79 ^c	44.1	-

^a In kcal/mol. ^b [4 + 4]. ^c [2 + 2]. ^d Longest wavelength at which photochemistry has been reported; cf. Y. L. Bahurel, D. J. McGregor, T. L. Penner, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 637 (1972). ^e For tetramethylethylene. ^f For styrene. ^g For stilbene. ^h For phenanthrene. ⁱ +, dimerization reported; ±, dimerization reported, but is slow or requires substituents; -, dimerization not reported; 0, other chemistry occurs. ^j A. Castellán, R. Lapouyade, and H. Bouas-Laurent, *Bull. Soc. Chim. Fr.*, 201 (1976).

slope of the D → G correlation line can be estimated from a perturbation model for the interaction of the two triplet states. For dimerizations, assuming only HOMO-HOMO and LUMO-LUMO interactions, eq 2 results, where ΔE_p is the interaction energy of the two HOMO-LUMO triplets, c^2 is defined by eq 3 in terms of tabulated⁷ Hückel coefficients for the reactants at the reacting positions 1 and 2 of the addends A and B, and $\gamma(r)$ is the resonance integral for end-on interaction of carbon 2p orbitals at distance r . The choice of Hückel coefficients corresponding to the parent π system was made deliberately to simplify calculations.

$$\Delta E_p(r) = c^2 \gamma(r) \quad (2)$$

$$c^2 = 2(AC_1^{\text{HOMO}}BC_1^{\text{HOMO}} + AC_2^{\text{HOMO}}BC_2^{\text{HOMO}}) + 2(AC_1^{\text{LUMO}}BC_1^{\text{LUMO}} + AC_2^{\text{LUMO}}BC_2^{\text{LUMO}}) \quad (3)$$

Figure 1 depicts the S-S correlation line as rising gently as the addends approach. This should be typical, since the adduct will generally have a higher singlet energy than the excited addend. I assume that this rise is at least roughly independent of addend. Note that early crossings, with large r_c and low $\gamma(r_c)$, will correspond to low barriers and thus high reactivity. Late crossings imply low reactivity. Earliness or lateness of crossing may conveniently be defined with respect to the line $E = E_S^A$ instead of the S-S line (Figure 1), since in that case the crossing condition is simply $\Delta E_p(r_c) = \Delta E_\infty$. This condition allows combination of eq 1 and 2 into the equation

$$\gamma(r_c) = (E_T^A + E_T^B - E_S^A)/c^2 \quad (4)$$

Equation 4 shows qualitatively that $\gamma(r_c)$ will be smallest when triplet energies are low, E_S^A is high, and the HOMO and LUMO coefficients at reacting positions are high. Since the parameters on the right are readily available, eq 4 can be tested quantitatively as a predictor of relative reactivity.

Results

Table I presents parameters for a series of arenes and alkenes and $\gamma(r_c)$ for their photodimerizations. For $\gamma(r_c) \lesssim 20$ kcal/mol, dimerizations are quite facile. Stilbene and anthracene, with relatively low E_T and high E_S values, show very low values of $\gamma(r_c)$ and dimerize readily. Diffusion-controlled self-quenching is observed for each with minimal excimer emission at room temperatures.⁸ Other cases also show low values. Tetracene⁹ and simple alkenes¹⁰ are also known to dimerize, the latter despite exceedingly short singlet life-

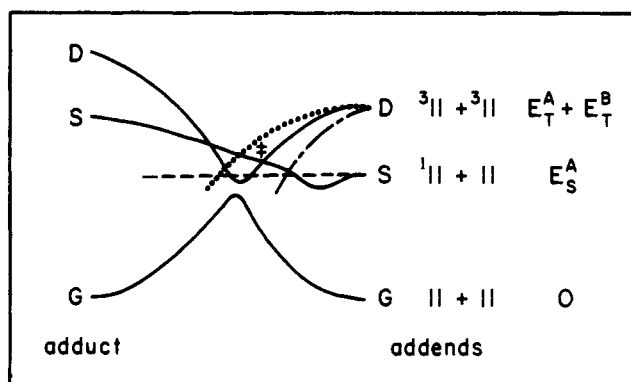


Figure 1. Correlation diagram (schematic) showing the crossing (±) which determined the transition state, an earlier crossing (---), a later crossing (.....), and the line $E = E_S^A$ (---). The G-D and D-G crossing is shown as avoided, and a weak excimer (exciplex) minimum is depicted.

times.^{10c} Styrenes dimerize, albeit by a complexity of mechanisms.¹¹ However, 1,3-cyclohexadiene dimerizes to a mixture of products,¹² apparently via ground-state complexes, without forming the [4 + 4] product favored by the HOMO coefficients. Note that the present criterion is an enabling one. The predicted dimerization may be supplanted by more rapid processes. Also, partitioning from the pericyclic minimum^{2,6} may occasionally favor internal conversion by large margins and thus impede reaction.

In the range of $\gamma(r_c)$ ca. 20–25 kcal/mol, reactivity appears to be moderate. Dimerization may occur but is either substantially slower than diffusion controlled or requires the presence of substituents to facilitate dimerization. Thus, naphthalene dimerization is unreported, though the dimerization of substituted naphthalenes¹³ and internal addition in 1,3-bis(α -naphthyl)propane¹⁴ are known. Dimerization of 9-cyanophenanthrene occurs,¹⁵ albeit with rather low rate constant (self-quenching is inefficient¹⁶), and contrasts to the total failure of phenanthrene itself. The ca. 4 kcal/mol higher triplet energy of phenanthrene is responsible for its markedly larger $\gamma(r_c)$. Acenaphthylene dimerization¹⁷ is probably at the low (reactive) end of the moderate reactivity range. Tolan falls in this range but affords rather unusual bimolecular photochemistry.¹⁸

Arenes with $\gamma(r_c) \gtrsim 25$ kcal/mol have not been reported to dimerize; cf. phenanthrene, pyrene, and chrysene. Of these,

Table II. Successful Cycloadditions. Comparison of Results with Prediction from $\gamma(r_c)$

system	$\gamma(r_c)^a$	result ^e	ref
anthracene-CHD ^b	6.4	$k_Q \sim 3 \times 10^9$	f, g
naphthalene-CHD ^b	11.4	$k_Q \sim 2.5 \times 10^9$	g, h
anthracene-DMHD ^c	13.3	$k_Q \sim 2 \times 10^9$; exciplex	f, i
stilbene-dienes	14.9	$k_Q \sim 2 \times 10^9$ to 1×10^{10}	j
stilbene-TME ^d	16.7	$k \sim 1 \times 10^9$ (25 °C)	k
9-cyanophenanthrene-stilbene	18.2	$k \sim 4 \times 10^9$ (no exciplex)	l
9-cyanophenanthrene-DMHD ^c	21.9	$k \sim 3.5 \times 10^9$ (exciplex)	m
9-cyanophenanthrene- <i>trans</i> - β -methylstyrene	22.8	$k \sim 5 \times 10^7$	n
9-cyanophenanthrene-TME ^d	23.4	$k \sim 3 \times 10^7$	m
naphthoitriles-TME ^d	24.8	$k \sim 3 \times 10^7$ (no exciplex; β) $k \sim 10^9$ (exciplex; α)	o
9-cyanophenanthrene- <i>cis</i> - β -methylstyrene	26.3	no reaction	n
9-cyanophenanthrene-4,4'-dimethoxytolan	27.4	addition (no kinetics)	p
naphthalene-tolan	28	long irradiation time	q
phenanthrene-tolan	28.6	even longer irradiation time	r

^a kcal/mol. ^b 1,3-Cyclohexadiene. ^c 2,5-Dimethyl-2,4-hexadiene. ^d Tetramethylethylene. ^e Rate constants calculated as bimolecular, $M^{-1} s^{-1}$, based on data in reference given. ^f N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *J. Am. Chem. Soc.*, **97**, 5006 (1975). ^g L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969). ^h N. C. Yang, J. Libman, and M. Savitzky, *J. Am. Chem. Soc.*, **94**, 9226, 9228 (1972). ⁱ N. C. Yang, D. Shold, and J. K. McVey, *ibid.*, **97**, 5004 (1975). ^j F. D. Lewis and C. E. Hoyle, *ibid.*, **99**, 3779 (1977). ^k J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *ibid.*, **93**, 2804 (1971). ^l R. A. Caldwell and P. E. Hansen, unpublished. ^m K. Mizuno, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 2993 (1974). ⁿ R. A. Caldwell, N. I. Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *ibid.*, **100**, 2857 (1978). ^o J. J. McCullough, R. C. Miller, D. Fung, and W.-S. Wu, *ibid.*, **97**, 5942 (1975). ^p R. A. Caldwell and C.-D. Ho, unpublished. ^q W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron Lett.*, 3373 (1965); 1689 (1968). ^r G. Sugowdz, P. J. Collin, and W. H. F. Sasse, *ibid.*, 3843 (1969).

the most likely candidate for success is pyrene. However, the well-known pyrene excimer is a stable minimum in the S surface, decreasing the S energy by ca. 10 kcal/mol.¹⁹ We have previously shown⁶ that stabilization of an exciplex can substantially decrease the rate of its forming cycloadduct. Cases in which stable excimers form should similarly be less reactive than otherwise would be expected.

The $\gamma(r_c) \leq 25$ kcal/mol criterion also appears to apply to some photocycloadditions. Table II presents results for representative cases. Note that for $\gamma(r_c) \leq 22$ kcal/mol reactions proceed with rate constants approaching diffusion controlled. This range includes [4 + 4] reactions of anthracene and [2 + 2] reactions of stilbene, the success of which now seems due to relatively high E_S and low E_T for both; cf. also their facile dimerizations. Several cases in the 22–27 kcal/mol range are known, but the rate constants are rather lower. The additions of tolan to naphthalene and phenanthrene are qualitatively slow, as predicted, but quantitative data are lacking. Some unreported cases for which a low $\gamma(r_c)$ obtains are the reactions of styrene with simple alkenes²⁰ (14.9), pyrene with stilbene (19.2), and phenanthrene [2 + 2] with 1,3-cyclohexadiene (19.8). Others surely exist.

Yang²¹ has very recently reported the additions of 1,3-cyclohexadiene to dibenz[*a,c*]anthracene and dibenz[*a,h*]anthracene and has offered a rationalization, based on local symmetry, for an efficient [4 + 4] process in the former case but not in the latter. I calculate $\gamma(r_c) = 16.8$ and 22.8 kcal/mol, respectively, quite in accord with the observed relative reactivities. The value of 22.8 would, however, suggest a borderline situation in the latter rather than a failure. Interestingly, an allowed, [2 + 2] adduct forms slowly as a minor product from dibenz[*a,h*]anthracene, exactly as the calculated $\gamma(r_c) = 27.1$ would suggest.

The present treatment offers insight into some otherwise perplexing reactions we have attempted over the years. In several examples of quenching of phenanthrenes by stilbenes, very efficient formation of cycloadduct occurs with exciplex fluorescence absent or else very weak in comparison to either the corresponding tolan or the corresponding styrenes.²² This now seems due to low E_T^B and thus high reactivity in reactions involving stilbene. I suggest that the exciplexes form but proceed extremely rapidly to adducts. Dimethyl acetylenedicarboxylate fails to add to phenanthrene,²² while dimethyl fumarate adds (though inefficiently²³), interpretable as a consequence of the higher E_T that results in general²⁴ for alkynes when compared to the corresponding alkene. The unreactivity of *cis*- β -methylstyrene as an addend for 9-cyanophenanthrene, earlier a puzzle in our work,²⁵ now follows from a calculated $\gamma(r_c) = 26.3$.

Discussion. Scope and Limitations

For the most part, eq 4 successfully segregates photocycloadditions into three categories: highly reactive ($\gamma(r_c) \leq 20$ kcal/mol), moderately reactive ($20 \leq \gamma(r_c) \leq 25$), and unreactive ($\gamma(r_c) \geq 25$). In view of the assumptions necessarily made about the S-S correlation line, no more quantitative outcome should be expected. The outcome provides further evidence for the validity of the Michl model as a description of photocycloadditions. The avoidance of computational complexities renders eq 4 attractive from a practical chemist's point of view.

Equation 4 is only intended to rank-order barrier heights to crossing from S_1 of excited reactant A into the pericyclic minimum. I reiterate that, as such, it should be considered an *enabling* criterion. While its apparent overall success suggests that this barrier height may be the dominant consideration, other factors may also affect rates and quantum yields of photocycloadditions and photodimerizations. These factors, and some other limitations of the present treatment, are discussed below.

The systems discussed comprise a substantial fraction of the known singlet-state photocycloadditions. I have, however, specifically omitted cases in which substantial charge transfer is expected. Such cases, though certainly important, give rise to several difficulties. First, eq 4 assumes degenerate perturbation theory, which obviously cannot be applied if there are serious orbital energy mismatches. There surely will be polar contributions to the cycloaddition transition state which cannot yet be treated. Finally, with heteroatoms a significant part of the chromophore, simple Hückel coefficients will probably be inapplicable. I chose to include a number of cyanoarenes because they comprise an important fraction of the literature. Apparently, one cyano group causes little or no difficulty within the present level of accuracy.

Additionally, the role of excimers and exciplexes is outside the scope of eq 4. Excited state complex formation generally will impede cycloaddition in an energy sense by lowering the S surface, as discussed for the pyrene excimer. The chief advantage of exciplex formation will be entropic.²⁶ Excimer (exciplex) chemistry, and therefore cycloaddition quantum yields, may be dominated by alternative processes. While, for

example, radiative rates seem reasonably predictable, inter-system crossing rates may vary substantially and are more difficult to predict.²⁶ High rates for competing decay processes will cause inefficient cycloaddition.

Partitioning in radiationless decay to S_0 , and any subsequent partitioning on the S_0 surface, will also be important determinants of cycloaddition quantum yield. These are also outside the scope of the present treatment, and their study will be rewarding.

A referee has suggested that the barrier may be higher for cycloaddends in which the lowest singlet is of the L_b type relative to the L_a type. This is reasonable, since the D state arises from interaction of L_a states. In fact high reactivity from molecules with L_a lowest singlets will usually follow from eq 4. Since 1L_a - 3L_a splittings are generally large, a low ΔE_∞ is a very likely consequence of an L_a lowest singlet. Of the L_a examples in Tables I and II (cf. alkenes, stilbene, anthracene, and tetracene), high reactivity is predicted and also observed. A critical experiment to test the point that 1L_a states are intrinsically more reactive than 1L_b states is therefore difficult to devise.

We are continuing to test eq 4 by searching for new photocycloadditions which are predicted to be successful, and we are simultaneously considering modifications to incorporate charge-transfer effects and excited complex formation.

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Influence of Starting Conformations on Intramolecular Exciplex Formation in ω -Phenyl- α -*N,N*-dimethylaminoalkanes

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Abstract: The intramolecular complex formation of ω -phenyl- α -*N,N*-dimethylaminoalkanes in isopentane was investigated using stationary and nonstationary techniques. Analysis of the decay curves indicates that ground-state starting conformations influence the rate of complex formation. In deviation of the classical kinetic scheme for inter- and intramolecular exciplex and excimer formation, the emission of the locally excited state contains a slow-decaying component whose lifetime is longer than that of the exciplex. This slow-decaying emission is attributed to molecules in which the C-N bond has a conformation unfavorable for exciplex formation.

Introduction

Up to now it has been assumed that intramolecular exciplex and excimer formation²⁻⁴ follows the same kinetic scheme as

the intermolecular processes.⁵ The adopted scheme could be presented as shown in Scheme I. The ratio of the quantum yields for emission from the exciplex, ϕ_E , and from the locally