

Exciplex Intermediates in [2 + 2] Photocycloadditions

RICHARD A. CALDWELL*

Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080

DAVID CREED*

Department of Chemistry, The University of Southern Mississippi, Hattiesburg, Mississippi 39401

Received August 16, 1979

In the subjects which we propose to investigate, our inquiries should be directed, not to what others have thought, nor to what we ourselves conjecture, but to what we can clearly and perspicuously behold and with certainty deduce; for knowledge is not won in any other way.

Rene Descartes (1596-1650)

Photocycloadditions and cyclodimerizations have been known since the early days of organic photochemistry. Reactions such as the Paterno-Büchi reaction¹ and photoannulation of cyclohexenones² with simple olefins afford numerous examples of compounds accessible at best with difficulty by other routes. The formation of α -truxillic vs. β -truxinic acid from different crystal modifications of cinnamic acid is a landmark of our knowledge of the chemistry of the organic solid state.³ The dimerization of pyrimidine residues such as thymine is one of the principal reactions responsible for UV inactivation in vivo of genetic material.⁴

For a number of years, we have studied the mechanisms of such reactions, both to model bimolecular photochemical events generally and to understand the factors which affect reactivity in photocycloaddition.

Exciplexes. As the synthetic potential of photocycloadditions was under study by organic chemists, an apparently unrelated development was occurring in the laboratories of several physical chemists. The work of Forster,⁵ Weller,⁶ and Birks⁷ was clearly establishing the photophysics of photoassociation. Long wavelength emissions at high concentrations of pyrene and other arenes were ascribed to *excimers*, and corresponding *exciplexes* were reported as a result of diffusive quenching of excited arenes by amines, especially arylamines.⁸ These species were shown to be formed reversibly but with essentially diffusion-controlled rate constants, and, as evidenced by temperature-dependence studies,^{6,8} were bound with heats of association a few (5-10) kilocalories/mole exothermic. Entropies

of association were ca. -20 eu, as expected for bimolecular association. Radiative lifetimes were remarkably structure independent, all⁸⁻¹¹ being within an order of magnitude of 3×10^{-7} s. The red shift of the structureless emission of the exciplex or excimer relative to excited monomers was due both to the enthalpy of association and to ground-state repulsion of the closely held chromophores as sketched in Figure 1.

The polar nature of exciplexes was revealed by the red shifts of their emission maxima in solvents of increasing polarity and by the tendency of exciplex-forming systems to give radical ions or radical ion related chemistry in highly polar solvents at the expense of the emission.^{12,13} Weller's classic empirical analysis of exciplex association^{6b} in terms of excitation energies and redox properties of the partners, eq 1, provides a good guide to the tendency of any photochemical system to undergo exciplex formation. In this model stabilization is quantitatively accounted for by one-electron transfer from excited donor to acceptor (or from donor to excited acceptor). For this process in hydrocarbon solvents:

$$\Delta H^\circ = \Delta E_{0,0} - [E_{1/2}^{\text{ox}}(\text{D}) - E_{1/2}^{\text{red}}(\text{A}) + 0.13 \text{ V}] \quad (1)$$

The Dilemma. In the fifties and sixties, organic chemistry was deluged with a series of proposed new reaction intermediates, and in fairness one must admit that the evidence was not always unambiguous. The most notorious was the nonclassical carbonium ion. Others included π complexes in electrophilic additions and charge-transfer complexes between Diels-Alder addends. Lively debates were stimulated regarding the existence, nature, and relevance of the intermediates in the reactions in question.

(1) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968); see E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909).

(2) P. DeMayo, *Acc. Chem. Res.*, **4**, 41 (1971).

(3) G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971); see also A. W. K. de Jong, *Ber. Dtsch. Chem. Ges.*, **56**, 818 (1923).

(4) J. G. Burr, *Adv. Photochem.*, **6**, 193 (1968).

(5) T. Forster and K. Kasper, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 275 (1954); T. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 33 (1969).

(6) (a) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963); (b) H. Knibbe, D. Rehm, and A. Weller, *ibid.*, **73**, 839 (1969).

(7) J. B. Birks, D. J. Dyson, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **275**, 575 (1963).

(8) See B. Stevens, *Adv. Photochem.*, **8**, 161 (1971), for a useful review.

(9) (a) N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967); (b) Y. Shirota, I. Tsushi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **47**, 991 (1974).

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

(11) Other more recent values compare well; cf. D. V. O'Connor and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4706 (1976); M. H. Hui and W. R. Ware, *ibid.*, **98**, 4718 (1976).

(12) Cf. A. Weller in "Fast Reactions and Primary Processes in Chemical Kinetics", S. Claesson, Ed., Wiley-Interscience, New York, 1967, p 413.

(13) H. Knibbe, K. Rollig, F. P. Schafer, and A. Weller, *J. Phys. Chem.*, **47**, 1184 (1967).

Richard A. Caldwell was born in 1940 at Huntington, West Virginia. He received his Bachelor's degree from M.I.T. and his Ph.D. from The University of California at Berkeley. Following 6 years on the Cornell faculty, he joined the University of Texas at Dallas in 1971 where he is now Professor of Chemistry. His interests in organic photochemical mechanisms and photophysics have recently been broadened by a sabbatical year at the IBM San Jose Research Laboratories and now include photoelectrochemistry, some aspects of polymer photochemistry, and low-temperature photochemistry and spectroscopy.

David Creed was born in Colchester, England, in 1943. He received the B.Sc., M.Sc., and Ph.D. degrees from the University of Manchester and after postdoctoral experiences too numerous to relate on both sides of the Atlantic, joined the faculty of the University of Southern Mississippi in 1977. His current research interests are in reaction mechanisms in photochemistry and the application of photochemical electron-transfer reactions to solar energy conversion.

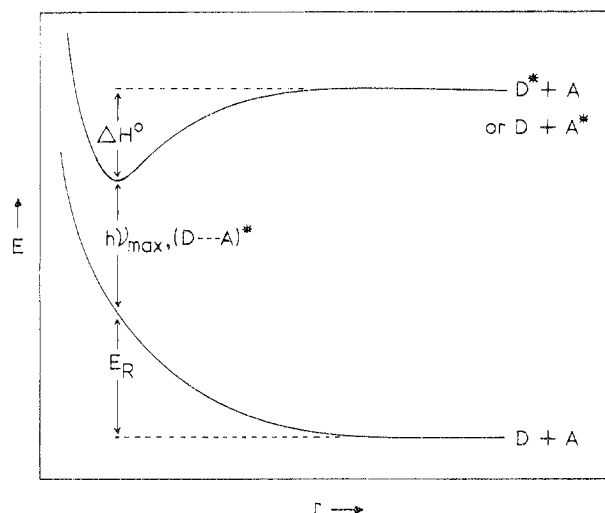


Figure 1. Potential energy vs. intermolecular separation for ground- and excited-state association of D and A. ΔH° is the exciplex association enthalpy, $h\nu_{\max}$ is the energy corresponding to the exciplex emission maximum, and E_R is the ground-state repulsion energy.

In 1964, Corey¹⁴ suggested the intermediacy of both an "oriented π complex" and 1,4-biradical intermediates in enone photoannulation, the former to rationalize regiochemistry and intermolecular selectivity, the latter to rationalize stereorandomization. Others followed suit, proposing exciplexes, or at least some sort of complex of the excited state, to explain other diverse results. For example, Hammond et al.,¹⁵ in an early study of arene fluorescence quenching by dienes and especially by quadricyclene, suggested exciplex formation as the quenching mechanism despite the failure to observe exciplex emission. Not surprisingly, photo-physicists and spectroscopists were skeptical. An exciplex intermediate which did not luminesce? How could one claim its presence? Each of the present authors remembers meetings in the early seventies at which organic chemists' suggestions of exciplex intermediates met with responses for which derision seemed a more appropriate description than skepticism.

Yet it was undeniable that *something* was needed. Chapman and Lura^{16,17} had demonstrated inverse temperature dependence in the photoaddition of stilbene to tetramethylethylene, showing that a bound species was involved. The photodimerization of anthracene was *enhanced* in the presence of diethylaniline¹⁸ or dienes,¹⁹ both quenchers of anthracene singlet, and the former in particular was well-known to form an exciplex. McCullough²⁰ saw evidence for interception of some dipolar bimolecular complex of naphthalene and acrylonitrile in protic solvents. Our own isotope effect studies^{21,22} of the Paterno-Büchi reaction of diaryl ke-

tones with simple alkenes revealed the presence of a complex with charge-transfer character formed prior to a 1,4-biradical. The singlet-state photodimers of 9-cyanophenanthrene,²³ acenaphthylene,²⁴ and coumarin²⁵ all had the endo structure which was sterically disfavored but which was what was expected from the maximum overlap structure of an excimer intermediate. A structure-reactivity relationship in the triplet-state reaction of substituted phenanthrenes with dimethyl fumarate, the nonstereospecificity of which required a 1,4-biradical, suggested yet again the formation of a charge-transfer complex prior to the biradical.²⁶ The inefficiency of several photoreactions could be better accounted for by partitioning of an intermediate exciplex (or congener) than by quite separate pathways for reaction and decay.²⁷

Clearly, this array of evidence was impossible to ignore;²⁸ yet it failed to define what the species was (were?) or to allow any very clear generalizations that were predictively useful. The maximum overlap dimers from singlet reactions were often accompanied by minimum overlap exo dimers^{24,25} from triplet reactions or else exo dimers^{23d} were formed in triplet reactions in related systems. The sequence triplet reactant + olefins \rightarrow "CT complex" \rightarrow triplet 1,4-biradical \rightarrow photoproducts increasingly appeared,^{2,14,21,23,26} yet the intermediacy of CT complexes was obviously at best an imperfect description for the symmetric dimerizations.

In 1972 Farid, Doty, and Williams²⁹ published an observation of an exciplex-like emission accompanying the photoaddition of phenanthrene to dimethyl fumarate. Studying the same reaction in 1971 but unfortunately were too timid to publish it. We learned later that Pac and Sakurai at Osaka were also observing exciplex emissions in parallel with bimolecular photoreactions.³⁰ The knowledge that exciplex-like emissions sometimes accompanied cycloadditions fueled our interest further, but an obvious dilemma existed. Innumerable photocycloadditions were known but almost never were exciplex or excimer emissions observed. Conversely, systems where bona fide excimer or exciplex emission was observed were generally photochemically unreactive. Did excited-state complex formation occur on the way to product or was it just an energy-wasting but stereoscopically observable dead end?

(22) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973).

(23) (a) H. Bouas-Laurent, R. Lapouyade, A. Castellan, A. Nourmamode, and E. A. Chandross, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 39 (1976); see also (b) R. Galante, R. Lapouyade, A. Castellan, J. P. Morand, and H. Bouas-Laurent, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **277**, 837 (1973); however, see (c) G. Sugowdz, P. F. Collin, and W. H. F. Sasse, *Tetrahedron Lett.*, 3483 (1969), for an exo adduct of another phenanthrene.

(24) D. O. Cowan and R. L. E. Drisko, *J. Am. Chem. Soc.*, **92**, 6281, 6286 (1970); I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

(25) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971), and references therein.

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

(27) R. A. Caldwell and R. P. Gajewski, *J. Am. Chem. Soc.*, **93**, 532 (1971); J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970); D. Valentine, Jr., and G. S. Hammond, *ibid.*, **94**, 3449 (1972).

(28) An excellent review including much or all of the early evidence is by R. S. Davidson in "Molecular Association", R. Foster, Ed., Academic Press, London, 1975, p 215.

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

(30) T. Sugihara, C. Pac, and H. Sakurai, *Chem. Lett.*, 667 (1972); K. Mizuno, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 2993 (1974).

(14) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

(15) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

(16) O. L. Chapman and R. D. Lura, *J. Am. Chem. Soc.*, **92**, 6352 (1970).

(17) J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *J. Am. Chem. Soc.*, **93**, 2804 (1971).

(18) (a) N. C. Yang, D. Shold, unpublished; quoted in (b) J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. C. Finson, *J. Am. Chem. Soc.*, **99**, 884 (1977).

(19) J. Saltiel and D. E. Townsend, *J. Am. Chem. Soc.*, **95**, 6140 (1973).

(20) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974), and references therein.

(21) R. A. Caldwell, *J. Am. Chem. Soc.*, **92**, 1439 (1970).

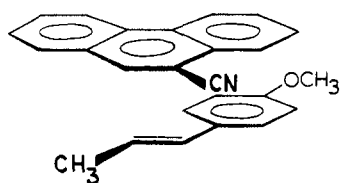


Figure 2. A maximum orbital overlap "sandwich" model for the 9CP...*t*-An exciplex.

In 1972 and 1973 we formulated the dilemma more precisely and began to attack it systematically.

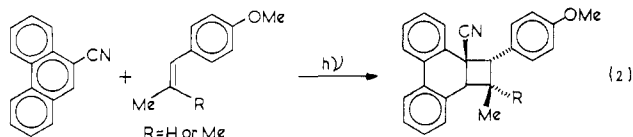
(1) Are exciplexes present in [2 + 2] cycloaddition systems, and if so how do their properties compare to the properties of the ones observed by the photophysicists?

(2) If present, are exciplexes in fact on the reaction coordinate for cycloaddition or are they diversions of the starting excited species?

(3) More generally, what is the nature of the first excited singlet adiabatic hypersurface relevant to [2 + 2] photocycloaddition?

Resolution of the Dilemma. Exciplex Quenching

We had been studying³¹ the photoadditions in benzene of 9-cyanophenanthrene (9CP) to *trans*- β -methylstyrene (β MS), the anethole isomers (*t*-An and *c*-An), and 1-anisyl-2-methylpropene (pBA). Reaction 2 ap-



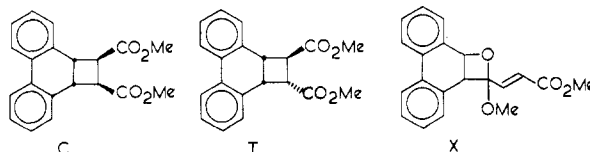
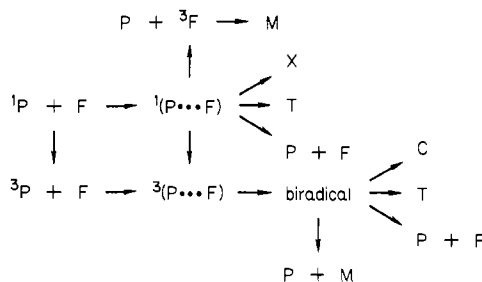
peared to afford only the more hindered *endo*-phenyl adducts and to give only retention in the olefin even with *c*-An for which *endo* addition required two *endo* substituents. We were gratified to note that all the reactions except the one with β -MS exhibited exciplex-like emissions (that reaction, we later³² found out, shows exciplex emission very weakly at -40°C), and we could therefore tackle the question of intermediacy of the exciplex in the reaction.

If a compound could be found which selectively quenched the exciplex, without substantially quenching the initial excited state, the question of intermediacy could be resolved. This proved to be the case. We thought that an exciplex stabilized by CT interactions ought to be susceptible to further CT perturbation. We initially showed that the phenanthrene-fumaronitrile exciplex could be quenched by 2,3-dimethyl-2-butene, a donor which did not significantly quench phenanthrene fluorescence. Donors were quite ineffective in the case of 9-cyanophenanthrene-anethole; however, good electron acceptors quenched the exciplex fluorescence without significantly quenching the fluorescence of 9CP itself. In the 9CP-*t*-An system, quenching of photocycloaddition quantitatively paralleled exciplex fluorescence quenching, rigorously demonstrating the intermediacy of the exciplex.³¹ The product structures suggested that they arose from stereospecific collapse of the maximum overlap, "sandwich" exciplex of Figure 2.

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

(32) R. A. Caldwell and T. S. Maw, unpublished results; T. S. Maw, M.S. Thesis, The University of Texas at Dallas, Dec 1977.

Scheme I



We returned to the reaction of phenanthrene (P) with dimethyl fumarate (F) because Farid's original contention²⁴ of exciplex emission had been questioned.³³ Repeating our original work, we indeed found the *cis*-*exo* (C) and *trans* (T) cyclobutane adducts, the oxetane (X) reported by Farid, and isomerization of F to dimethyl maleate (M). All were quenched by electron donors, and these observations could be nicely correlated with quenching of the exciplex emission.^{34,35} Only partial quenching of C and T formation was observed since a substantial part of cyclobutane formation arises from intersystem crossing of ¹P prior to exciplex formation. Nevertheless, Scheme I, the complicated kinetic scheme, a synthesis of our and Farid's earlier studies, was vindicated.

Reactive and Unreactive Exciplexes. The role of exciplexes was now established in the phenanthrene-olefin singlet-state cycloadditions. Furthermore, increasing numbers of photoaddition reactions were being reported³⁶⁻⁴⁴ in which concomitant excimer or exciplex emissions were observed. The original contentions of exciplex intermediacy in organic photoreactions which showed no exciplex emission seemed much more likely to be correct. We therefore next turned our attention to the relationship between the "reactive" exciplexes we were observing and the "unreactive" exciplexes well-known to photophysicists. The introduction describes several properties of "unreactive" exciplexes, and we set out to measure as many of these properties as we could for our "reactive" exciplexes.

We first observed^{31,45} that emission from our phenanthrene-styrene exciplexes showed the same sort of

(33) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **12**, 765 (1973).

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

(35) D. Creed, R. A. Caldwell, and M. M. Ulrich, *J. Am. Chem. Soc.*, **100**, 5831 (1978).

(36) N. C. Yang, D. M. Shold, J. K. McVey, *J. Am. Chem. Soc.*, **97**, 5004 (1975).

(37) N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *J. Am. Chem. Soc.*, **97**, 5006 (1975).

(38) N. C. Yang, D. M. Shold, and B. Kim, *J. Am. Chem. Soc.*, **98**, 6587 (1976).

(39) E. A. Chandross and A. H. Scheibel, *J. Am. Chem. Soc.*, **95**, 611, 1671 (1973).

(40) F. D. Lewis and R. H. Hirsch, *J. Am. Chem. Soc.*, **98**, 5914 (1976).

(41) F. D. Lewis, R. H. Hirsch, P. M. Roach, and D. E. Johnson, *J. Am. Chem. Soc.*, **98**, 8438 (1976).

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

(43) J. J. McCullough, R. C. Miller, D. Fang, and W.-S. Wu, *J. Am. Chem. Soc.*, **97**, 5942 (1975).

(44) F. C. DeSchryver et al., *Pure Appl. Chem.*, **49**, 237 (1977).

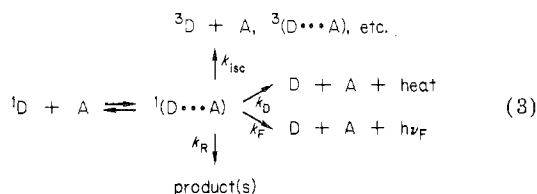
(45) R. A. Caldwell, N. I. Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *J. Am. Chem. Soc.*, **100**, 2857 (1978).

solvent dependence as did that from arene-amine exciplexes. The emission increased sharply in wavelength as solvent polarity increased and was undetectable in solvents of higher polarity than acetone. We also noted⁴⁶ that, in methanol, the photoreaction of 9-cyanophenanthrene and *trans*-anethole afforded only small amounts of cycloadduct as part of a complex mixture of electron-transfer-derived products. These results point to the inherently polar nature of the bimolecular interaction, as observed for "normal" exciplexes.

Through the use of nanosecond time-resolved spectrofluorimetry and with the collaboration of Professor L. A. Melton and Dr. P. H. Wine, we were able⁴⁷ to analyze the kinetics of formation and decay of several phenanthrene-styrene type reactive exciplexes as well as some unreactive model cases. We quickly learned that exciplex formation was reversible; emission from the phenanthrene persisted long after quenching by the styrene was complete and tracked the exciplex fluorescence decay. It proved possible to analyze the results in considerable detail and to obtain equilibrium constants for exciplex formation, exciplex lifetimes, and (after fluorescence quantum yield measurements) exciplex radiative lifetimes. Rates of formation were essentially diffusion controlled. Enthalpies of the exciplex formation⁴⁷ were roughly in the range predicted by the Weller relationship,^{6b} eq 1; cf. -7.3 kcal/mol vs. -4.0 kcal/mol calculated⁴⁸ for ${}^1(9\text{CP}\cdots t\text{-An})$ and -7.4 kcal/mol vs. -6.3 kcal/mol calculated for ${}^1(9\text{CP}\cdots \text{pBA})$. For the latter, we measured the entropy of association and found a normal value of -13 eu. Clearly, the thermodynamic behavior of our reactive exciplexes is almost identical with that of the known, unreactive ones previously examined.^{6b}

Even more importantly, the radiative lifetimes of the reactive exciplexes ($k_F \sim 2-4 \times 10^6 \text{ s}^{-1}$ in general)^{35,47,49} closely matched those that we and others⁶⁻¹¹ determined for the unreactive ones. This observation points to the similarity of electronic structures in the two series. The conclusion seems inescapable that, in the phenanthrene-styrene series at least, and probably in other series of reactions in which exciplex emission and chemical reaction occur together, the first step is formation of an exciplex with *all* the properties expected from study of nonreactive models.

Why are exciplex emissions still the exception in organic photoreactions? We certainly must exclude triplet photoprocesses from our expectations since fluid solution phosphorescence is seldom observed. Even for singlet reactions, the following analysis shows that only special cases will be expected to show simultaneous emission and reaction. Consider eq 3:



(46) R. A. Caldwell and L. Smith, unpublished.

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

(48) Redox parameters in acetonitrile: S.-M. Park and R. A. Caldwell, *J. Electrochem. Soc.*, **124**, 1859 (1977).

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

In the limit of low reversibility, attainable either by very high $[\text{A}]$ or by structural or temperature variations, the lifetime τ_{C} of the exciplex will be given by (4). If k_{F}

$$\tau_{\text{C}} = (k_{\text{F}} + k_{\text{isc}} + k_{\text{R}} + k_{\text{D}})^{-1} \quad (4)$$

$\sim 10^6-10^7 \text{ s}^{-1}$ and $k_{\text{isc}} \sim 10^7-10^8 \text{ s}^{-1}$, as seems to be usual, it is easy to see that $k_{\text{R}} \lesssim 10^5 \text{ s}^{-1}$ will lead to an apparently "unreactive" exciplex and $k_{\text{R}} \gtrsim 10^9 \text{ s}^{-1}$ will lead to so great a dominance of photochemistry over photophysics that emission will be essentially noncompetitive. For simultaneous emission and reaction to be observed, the range of k_{R} values is limited. We simply conclude that it is common for organic bimolecular singlet photoreactions to proceed with nanosecond or shorter relaxation times once the exciplex is reached. The photochemically allowed nature (in the Woodward-Hoffmann sense), at least for $[2+2]$ and $[4+4]$ cycloadditions and cyclodimerizations, renders this conclusion perhaps unremarkable.

Adiabatic and Diabatic Processes on the $[2+2]$ Excited Singlet Hypersurface

With the role of exciplexes in $[2+2]$ photocycloadditions and the similarity of reactive and nonreactive exciplexes clear, we have attempted more recently to understand the four possible exit channels from the excited $[2+2]$ hypersurface via the exciplex, especially of course the ones leading to products.

The Diabatic Processes. The fluorescence and intersystem crossing processes appear to be rather straightforward. A fluorescence rate of ca. $3 \times 10^6 \text{ s}^{-1}$ and an intersystem crossing rate of ca. $3 \times 10^7 \text{ s}^{-1}$ are pervasive in this series.^{35,49} The rates are temperature independent,^{49,50} do not depend very much on substituent or even rather gross reactant variations, are similar to literature values⁷⁻¹¹ for unreactive exciplexes, and thus have all the hallmarks of "normal" processes. Little can be predicted about the magnitude of either. Since one-center integrals probably dominate spin-orbit coupling, locally excited configurations of the exciplex (cf. *a* and *b* of (5)) may play an important role.⁵¹ In-

$$\psi_{1(\text{DA})} = a\psi_{1\text{D},\text{A}} + b\psi_{1\text{D},\text{A}} + c\psi_{\text{D}^+\text{A}^-} + d\psi_{\text{D}^-\text{A}^+} \quad (5)$$

creased polarity of the exciplex (high *c* or *d*, low *a* and *b*) may inhibit intersystem crossing, and efficient isc in one or the other component may enhance it. We note that even very short-lived exciplexes can still undergo intersystem crossing,³⁵ e.g., ${}^1(\text{P}\cdots\text{F})$, $\tau_{\text{C}} \sim 1.2 \text{ ns}$ with $k_{\text{isc}} = 1.2 \times 10^8 \text{ s}^{-1}$. The lowest singlet of F is n,π^* ; perhaps El Sayed's rules⁵² are relevant. The ${}^1(9\text{CP}\cdots\beta\text{MS})$ exciplex, for which τ_{C} is surely $< 1 \text{ ns}$,³² still affords some 30% intersystem crossing at room temperature⁵³ and thus $k_{\text{isc}} > 3 \times 10^8 \text{ s}^{-1}$. In this case, unusually efficient SO coupling in one of the locally excited configurations seems unlikely. Clearly, further study will be rewarding.

The Adiabatic Processes. Both cycloadduct formation (k_{R}) and internal conversion (k_{D}) show very pronounced dependences on exciplex component structure and on temperature.^{49,50} Both are activated, with $\Delta H^{\ddagger} \sim 2-7 \text{ kcal/mol}$ and with substantial negative

(50) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **101**, 6960 (1979).

(51) C. P. Keijzers, J. Duran, and D. Haarer, *J. Chem. Phys.*, **69**, 3563 (1978).

(52) M. A. ElSayed, *J. Chem. Phys.*, **38**, 2834 (1963); **36**, 573 (1962); **41**, 2464 (1964).

(53) (a) By taking $2\phi_{\text{isc}}$ for βMS as ϕ_{isc} for the exciplex;^{49,50} (b) R. A. Caldwell, D. Creed, and T. S. Maw, *J. Am. Chem. Soc.*, **101**, 1293 (1979).

Table I
Rate Constants and Activation Parameters for Cycloadduct Formation and Internal Conversion of Exciplexes^a

exciplex ^b	k_R^C , s ⁻¹	ΔH_R^\ddagger , kcal/mol	ΔS_R^\ddagger , eu	k_D^C , s ⁻¹	ΔH_D^\ddagger , kcal/mol	ΔS_D^\ddagger , eu
¹ (3-MeO-10-CP... <i>t</i> -An)	2.8×10^8	2.7	-11	2.1×10^8	2.1	-13
¹ (9CP... <i>t</i> -An)	4.2×10^7	2.2	-16	3.2×10^7	3.0	-14
¹ (3,10-CN,P... <i>t</i> -An)	4.6×10^6	4.2	-14	4.4×10^6	2.2	-20
¹ (9CP...pBA)	5.6×10^5	4.8	-16			
¹ (P...F) → T	9×10^5	7.3	-7			
				7×10^8	2.2	-11
¹ (P...F) → X	2.2×10^7	4.4	-10			

^a From ref 49 and 50. ^b MeO = methoxy, CN = cyano, P = phenanthrene; other symbols explained in text. ^c 21–23 °C.

entropies of activation, typically -10 to -17 eu. Table I summarizes selected rate constants and activation parameters. They are quite revealing about the nature of both processes.

Most striking is the general similarity of the two in the substituted cyanophenanthrene-styrene series. The magnitudes of the rate constants k_R and k_D vary by as much as 500-fold, yet their ratio is nearly constant! The entropies of activation correspond to the conversion of a rather loose exciplex (for which others^{54–58} have evidence) to a rather tight transition state, quite in line with other values for unimolecular thermal reorganizations. For these reasons, we feel that both k_R and k_D are best represented as adiabatic, at least through a transition state immediately following the exciplex. A surface-hopping (diabatic) process could only fortuitously give a sensible ΔS^\ddagger .

Variation with substituent similarly can be reasonably interpreted by familiar ground-state polar and steric substituent effects and judicious consideration of the energy surface suggested by Michl⁵⁹ for [2 + 2] photocycloaddition. The exciplex is a polar "pause point" on the way to products, and must pass over a transition state at the crossing of the polar S surface and the relatively nonpolar D (doubly excited) surface of Figure 3. Since D is nonpolar, the transition state is necessarily less polar than the exciplex, and the decrease in rate of cycloadduct formation with increasing ability of the exciplex to stabilize charge separation (Table I) thus also necessarily follows. A study of solvent effects by Lewis for other exciplexes has afforded the same conclusion.⁶⁰ The increased steric hindrance in the ¹(9CP...pBA) case due to the *endo*-methyl must also be a retarding effect on k_R .

Since exciplexes appear now to be common (perhaps universal) photocycloaddition intermediates, the decrease in reaction rate constant with increase in exciplex stability is an apparent paradox which requires more careful consideration of the importance of the exciplex to the overall reaction. We feel that exciplexes can exert a favorable effect on cycloaddition reactions in two ways. Most important is the prior association of the reacting chromophores with consequent overcoming of a substantial fraction of the ΔS^\ddagger of the bimolecular

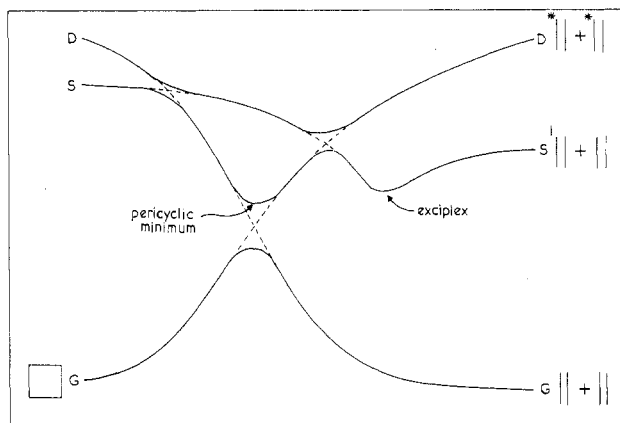


Figure 3. Schematic energy surface (after Michl⁵⁹) for [2 + 2] cycloadditions.

process. Second, exciplex formation may bias the system toward cycloaddition and away from competing chemical processes. In the present case, for example, dimerization of the phenanthrene can be a serious competing process when the phenanthrene-olefin exciplex is relatively unstable, i.e., highly reversible.

The Pericyclic Minimum. Another Entry. The next frontier for those interested in photocycloadditions is clearly the pericyclic minimum in S_1 of Figure 3. Michl's proposed surfaces⁵⁹ depict this as a second "pause point" and the one from which diabatic conversion to the ground surface results. The nearly 50:50 partitioning between k_R and k_D we observe fits very well with the idea of a vertical drop to a flat top of the ground surface in the vicinity of the pericyclic minimum. However, there is no independent experimental evidence for a pericyclic minimum of finite lifetime in S_1 at present. We have attempted to obtain evidence, if not for the nature and lifetime of the species at the pericyclic minimum, at least for common intermediates in cycloadditions and cycloreversions consistent with such species.

Our work with the ¹(9CP...*t*-An) and ¹(P...F) exciplexes, especially determination of k_R and k_D , provided an understanding of the forward process. We noted that both the ¹(9CP...*t*-An) adduct and T, the trans adduct from ¹(P...F), afforded efficient and nearly stereospecific fragmentation upon irradiation. Only weak fluorescence ascribable to the adduct was observed for the latter, and none for the former. Consequently, we suspected that, whatever the next "pause point" in cycloreversions was, it was reached essentially quantitatively. A test of whether the pause points were the same in both directions was then immediately apparent, since the fraction $k_R/(k_R + k_D)$ of exciplex leading to adduct and the fraction $k_D/(k_R + k_D)$ of adduct frag-

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

(55) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393 (1971).

(56) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).

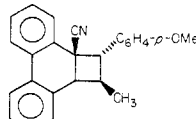
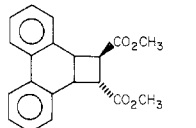
(57) R. S. Davidson, *J. Chem. Soc. Chem. Commun.*, 827 (1976).

(58) J. J. McCullough, private communication.

(59) W. Gerhartz, R. D. Poshusta, and J. Michl, *J. Am. Chem. Soc.*, **98**, 6427 (1976); J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

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

Table II
Comparison of Adduct Photofragmentation Quantum Yields with Photocycloaddition Quantum Yields

adduct	Φ_{addends}^a	k_R^b		sum
		$k_R + k_D$		
	0.38, ^c 0.39 ^d	0.57		0.96
	0.98, ^c 1.00 ^d	1.3×10^{-3}		0.99

^a Fragmentation at 295 nm. ^b From Table I, for adduct formation from corresponding addends. ^c Phenanthrene. ^d Olefin.

menting to addends could now be compared. They would be required to sum to unity if a common intermediate existed and (as we knew) no other chemistry occurred.

The results⁶¹ (Table II) certainly support the idea of a common intermediate, which we believe (but cannot yet prove) is the species at the pericyclic minimum. Others⁶² have noted similar outcomes in dimerization of compounds related to anthracene (cf. especially the work of Jones^{62c}), and indeed the [4 + 4] surface is expected to behave in similar fashion. We cannot yet rule out the possibility of separate one-bond processes leading to the same singlet 1,4-biradical.

Active pursuit of the pericyclic minimum and an understanding of the dynamics of systems passing through it are now major challenges for experimentalists interested in excited-state cycloaddition hypersurfaces.

Challenges for the Future

The role of exciplexes in [2 + 2] photocycloaddition systems is now established beyond doubt, and exciplex quenching is generally well understood. However, detailed understanding of factors leading to exciplex or excimer collapse to products has hardly emerged. How to predict heights of energy barriers and determine the properties of surfaces near critical points (maxima and minima) are the real keys to the prediction of success or failure of *any* chemical reaction, including photocycloadditions.

We have recently⁶³ used the Michl model to correlate known photocycloaddition and photodimerization reactivities. If the D-S energy gap at infinite reactant separation and the behavior of each as the reactants approach are both known, the D-S crossing and thus the cycloaddition transition state will be located. It proves possible to make reasonable zeroth-order estimates of reactivity easily, and thus also to predict the

outcome in untried cases. High singlet energy in the excited reactant, low triplet energies for both, and high frontier orbital densities appear to presage high reactivity. Tests of these predictions are now under way. The second critical feature, partitioning at the pericyclic minimum, seems less amenable to simple prediction, yet may also significantly affect quantum yields of photo-reaction.

The studies we have made of triplet-state photocycloadditions^{22,26,53b} suffer from our inability to observe triplet reactive exciplexes by emission. Our work, and that of others generally, is suggestive but we believe not definitive on the points we have here touched on for singlets. While we suspect that there will be, *mutatis mutandis*, a general similarity to singlet exciplexes,^{53b} confirmation must await observation in key examples.

Our work on exciplex quenching has convinced us that an enormous body of termolecular photophysics and photochemistry lies fallow. Stable, emissive excited termolecular complexes, which we have named exciplexes, have been detected by others,^{10,64-67} generally under either forcing conditions of high concentration,^{64a} low temperature,¹⁰ or surpassing what must be a substantial termolecular entropy problem via incorporation of two of the chromophores in a polymer chain⁶⁷ or via their linking by alkyl chains.⁶⁶ Chemical reactions now ascribable to termolecular processes include enhanced cycloadditions,^{18,19} electron-transfer reactions,³⁸ and in some cases the formation of adducts that do not form via bimolecular routes.^{68,69} While the separation of charge in chloroplasts during photosynthesis presumably follows a different mechanism in detail,⁷⁰ the necessity for polymolecularity is clear and is obviously at least indirectly relevant to our termolecular CT quenching.⁷¹ Future work may reveal a significant and fascinating set of useful and practical ramifications of termolecular processes.

This work could not have been done without the efforts of the co-workers listed in the references, efforts we greatly appreciate. We are grateful for financial support by the Robert A. Welch Foundation (Grant AT-532) and the National Science Foundation. While our colleagues who have provided stimulation and encouragement are too numerous to list, Professor F. D. Lewis and Dr. C. E. Hoyle deserve our thanks for a number of stimulating discussions and for the sharing of results prior to publication.

(64) (a) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); (b) E. A. Chandross and H. T. Thomas, *ibid.*, **9**, 397 (1971); (c) G. S. Beddard, S. E. Carlin, and C. Lewis, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1894 (1975).

(65) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *J. Am. Chem. Soc.*, **97**, 5688 (1975).

(66) T. Mimura and M. Itoh, *J. Am. Chem. Soc.*, **98**, 1095 (1976); see also T. Mimura and M. Itoh, *Bull. Chem. Soc. Jpn.*, **50**, 1739 (1977), and T. Okamoto, M. Itoh, T. Ohta, and T. Oramto, *ibid.*, **50**, 1665 (1977); R. A. Beechcroft, R. S. Davidson, and T. D. Whelan, *J. Chem. Soc., Chem. Commun.*, 911 (1978).

(67) C. E. Hoyle and J. E. Guillet, *Macromolecules*, **11**, 221 (1978).

(68) R. O. Campbell and R. S. H. Liu, *Chem. Commun.*, 1191 (1970).

(69) F. D. Lewis, *Acc. Chem. Res.*, **12**, 152 (1979); see also F. D. Lewis and D. E. Johnson, *J. Am. Chem. Soc.*, **100**, 983 (1978).

(70) For leading references to the possible role of chlorophyll aggregates in photosynthesis, see S. G. Boxer and R. R. Bucks, *J. Am. Chem. Soc.*, **101**, 1883 (1979); A. Warshel, *ibid.*, **101**, 744 (1979); N. Periasamy and H. Linschitz, *ibid.*, **101**, 1056 (1979); F. K. Fong, A. J. Hoff, and F. A. Brinkman, *ibid.*, **100**, 619 (1978).

(71) R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wine, *J. Am. Chem. Soc.*, in press.

(61) R. A. Caldwell and N. Giau, unpublished.

(62) (a) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **11**, 313 (1972) (anthracenophane); (b) W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, and A. A. Lamola, *Appl. Opt.*, **11**, 533 (1972) (acridizinium ion); (c) W. R. Bergmark, G. Jones, T. Reinhardt, and A. M. Halpern, *J. Am. Chem. Soc.*, **100**, 6665 (1978).

(63) R. A. Caldwell, *J. Am. Chem. Soc.*, submitted for publication.