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Photochemical Cycloadditions via Exciplexes, Excited Complexes, and Radical Ions

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Cycloadditions are among the earliest known reactions in organic photochemistry. Some of the classical examples are the 2 + 2 cyclodimerization of olefins such as coumarin,[1] cinnamic acid,[2] and acenaphthalene;[3] the 4 + 4 cyclodimerization of anthracene;[4] Paternò–Büchi's oxetane formation[5] by 2 + 2 cycloaddition of carbonyl compounds to alkenes; Schönberg's dihydrodioxin formation[6] by 4 + 2 cycloaddition of *o*-quinones to alkenes; and Schenck's epidioxide formation[7] by 2 + 4 cycloaddition in the photosensitized oxygenation of dienes.

Interest in photocycloadditions intensified in the 1960s, when it was discovered that many dimerizations and mixed additions could also be induced by triplet sensitization.[8] A vast number of cyclobutane derivatives became accessible through these reactions. Besides their synthetic value, these reactions constitute the basis for the technically important photo-cross-linking of polymers.[9]

Extensive research on the photophysics of complex formation and electron-transfer processes in the excited state stimulated many investigations of the potential role of such intermediates in photochemical cycloadditions. Indeed, many singlet-excited-state cyclodimerizations were found to proceed via excimers.[10] These studies led also to the discovery of several novel reactions and many mechanisms involved in cycloadditions. Some of the features of these reactions are the subject of this Account.

Before we discuss these reactions, however, we want to emphasize a few points about the nature of complexes in the excited state and the closely related phenomenon of electron transfer.

Excimers, which are dimeric complexes stable only in the excited state, were first discovered by Förster[11] in pyrene and other aromatic hydrocarbons. They can best be identified by their fluorescence, which is structureless and shifted to longer wavelength from the monomer fluorescence. This shift results from the stabilization energy of the excimer and a repulsion energy at the corresponding ground-state configuration.[12] It is generally accepted that excimers have sandwich geometry. Both exciton resonance $({}^*AA \leftrightarrow AA^*)$ and charge-transfer configuration $(A^+A^- \leftrightarrow A^-A^+)$ contribute to the excimer state.[12]

Weller[13] discovered that complexes in the excited state are not limited to dimeric species, i.e., excimers, but can also be formed between vastly different molecules. Such complexes were originally termed heteroexcimers and are now referred to as exciplexes. Here, too, the structureless, long-wavelength-shifted emission from exciplexes offers the best means for their investigation. From the solvent dependence of the exciplex fluorescence maximum, the dipole moment of the exciplex and hence the degree of charge transfer within the complex can be estimated.[14] Temperature-dependence studies[15] of the exciplex-to-monomer fluorescence ratio revealed that these complexes are formed reversibly, with the forward reaction being mostly diffusion controlled. Association enthalpies and entropies are also obtainable from such temperature-dependence studies.[15]

Exciplexes with dominant charge-transfer (CT) character are formed, in spite of the lack of ground-state interaction between their components, because molecules become better donors and acceptors in the excited state than they are in the ground state. Excitation in the CT band of an electron-donor–acceptor (EDA) complex gives an excited complex that has stronger binding energy than in the ground state for the same reasons as with exciplexes. Excitation at wavelengths absorbed by only one of the components results in the formation of a complex in the excited state (an exciplex)

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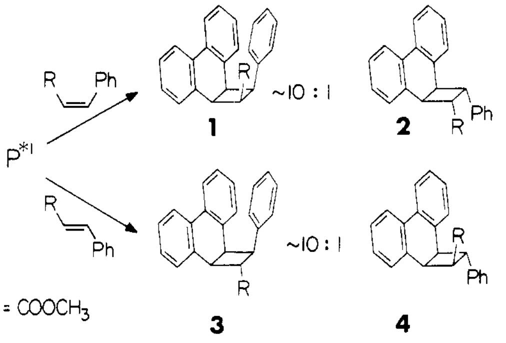
that in several cases was shown to be identical with the complex formed by directly exciting the ground-state complex.[16]

Exciplexes that have only a weak charge-transfer component,[17] i.e., small dipole moment, as well as excimers[18] and mixed excimers[19] can also exist and emit in polar solvents. However, exciplexes with a pronounced CT character and excited complexes tend to dissociate into solvated radical ions in polar solvents.[20] Several cycloadditions, including some dimerizations, occur via radical ions from such photoinduced electron-transfer reactions.

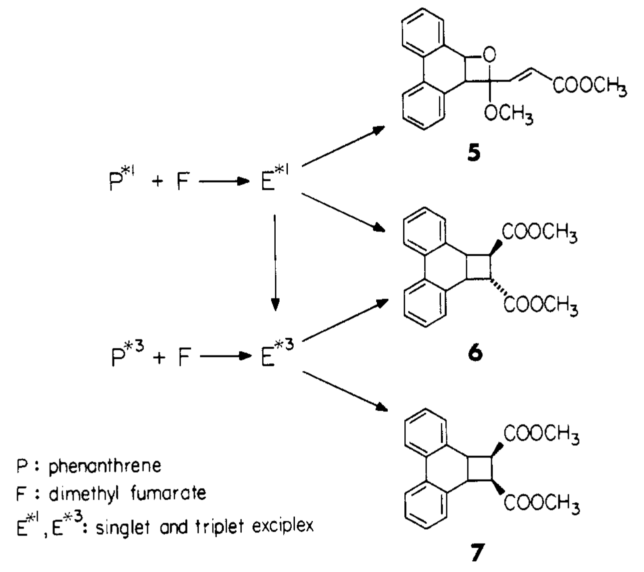
In this article the closely related cycloadditions via exciplexes and excited complexes are contrasted with those via electron transfer.

Exciplexes

Our interest in exciplex chemistry began in 1971 during a study of photochemical reactions of cinnamate esters. We found that irradiation of phenanthrene in the presence of methyl cinnamate led to an efficient mixed cycloaddition.[21] It became clear from the quenching of the phenanthrene fluorescence and the quantum yield of adduct formation as a function of the cinnamate concentration that the 2 + 2 cycloaddition results from the reaction of singlet-excited phenanthrene. As for most singlet, Woodward–Hoffmann-allowed cycloadditions, this reaction is highly stereospecific, i.e., the stereochemistry of the olefin is retained in the adducts. Furthermore, the major products (~ 90%) from the cis and trans olefin are the cyclobutanes with the aryl substituent endo to the phenanthrene moiety (1 and 3, respectively). This relatively high stereoselectivity of the addition, especially that leading to the most sterically hindered endo adduct (1) from the cis isomer, strongly suggests the intermediacy of sandwich exciplexes with strong π orbital overlap between the aromatic moieties of the components. Although no exciplex emission could be detected in these reactions, the structurally related system of pyrene/*trans*-cinnamonitrile, which shows a similar stereoselectivity of addition, showed a weak exciplex emission.[21] Also, in several related reactions of phenanthrene derivatives reported by Caldwell[22] and Pac,[23] exciplex emission was observed.



Scheme I



P : phenanthrene
F : dimethyl fumarate
E^{*1}, E^{*3}: singlet and triplet exciplex

The degree of stereoselectivity seems to depend on the extent of π-orbital overlap in the exciplex. For example, the stereospecific photoaddition of diphenylvinylene carbonate to dienes,[24] which proceeds via exciplex intermediates, has various degrees of stereoselectivity and low regioselectivity. These data suggest[24] that several exciplex minima may be responsible for the different adducts, minima with π-orbital overlap being somewhat more stable. Not surprisingly, the phenyl–alkenyl π-orbital overlap does not seem to contribute as much to the exciplex stabilization as the more extended interaction in the phenyl–phenanthrene systems discussed above.

The next system we studied was that of phenanthrene (P)/dimethyl fumarate (F), which marked the first example where exciplex emission concurred with cycloaddition.[25] In contrast to the reaction with the cinnamate esters, however, the fumarate reaction led to an oxetane derivative (5) in addition to a mixture of trans (6) and cis (7) cyclobutane derivatives. The nonstereospecific formation of the cyclobutane was unexpected because it results from a reaction of singlet-excited phenanthrene (P^{*1}) with the fumarate ester.

Kinetic and quenching studies[25] as well as Caldwell's[26] work on perturbation of this reaction by paramagnetic molecules such as oxygen and nitroxides revealed that, whereas these products were indeed formed via the singlet exciplex (E^{*1}), only the oxetane and small amounts of 6 were directly derived from E^{*1}. The nonstereospecific formation of 6 and 7, which is similar

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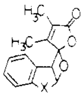
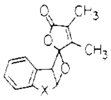
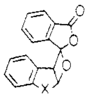
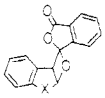
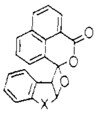
in composition to that from the triplet-sensitized reaction, is preceded by intersystem crossing[27] (isc) of E^{*1}; cf. partial mechanism outlined in Scheme I. This process is also responsible for the accompanying isomerization of fumarate to maleate.[28] Caldwell et al.,[29] using an elegant approach, showed that the *emitting* exciplex is indeed the precursor to the singlet cycloaddition in this and related reactions, since both exciplex emission and cycloaddition are *equally* suppressed by an added quencher that intercepts the singlet exciplex.

Besides the effect of orbital overlap, the polarity of the exciplex appears to play a role in the stereochemistry of cycloaddition. Yang[30] has shown that, in the photoreaction of anthracenes with dienes, less polar exciplexes favor the Woodward–Hoffmann-allowed ${}_{\pi}4_{s} + {}_{\pi}4_{s}$ cycloaddition, whereas polar exciplexes yield the ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ adducts.

Because of the reversibility of exciplex formation, the effect of temperature on cycloadditions has been used to determine whether nonemitting exciplex intermediates are involved. For example, in the reaction of naphthalene with diphenylacetylene, both the quantum yield of photoaddition and the quenching of the naphthalene fluorescence by the acetylene decrease by the same magnitude with increasing temperature.[31] This effect is the result of increased dissociation of the exciplex with increasing temperature. Several other cycloadditions, where exciplex intermediates are likely to be present, showed similar behavior.[32] In addition, it is conceivable that a decrease in stereoselectivity with increasing temperature may be observed in cycloadditions where the exciplex intermediates have poorly defined minima.

Another factor which has a profound effect on exciplexes and the course of their reactions is the solvent polarity. This is well documented in the pioneering work of Weller[20] and Mataga.[14b] With increasing solvent polarity the lifetime of exciplexes with a pronounced CT character decreases, owing to the formation of solvated radical ions. Accordingly, the quantum yield for cycloaddition via polar exciplexes decreases with increasing medium polarity. Other competing reactions via the radical ions eventually replace those via the exciplexes. With exciplexes of low polarity, however, reasonably high quantum yields of cycloaddition could be achieved even in polar solvents.[33]

Table I
Oxetane Products from the CT excitation of 1,1-Dimethylindene/Anhydride Complexes in Nonpolar Solvents

anhydride	oxetane products [X = $C(CH_3)_2$]		
dimethylmaleic	 8	~1:9	 9
phthalic	 10	~1:1	 11
naphthalic	 12		

An intriguing diversion encountered in some cycloaddition reactions is the role of termolecular exciplexes. There is ample spectroscopic evidence that termolecular exciplexes can be formed.[34] Such intermediates were invoked to rationalize the enhanced efficiency of dimerization of anthracene and of 9-phenylanthracene in the presence of dienes.[35] In these reactions it seems that a termolecular exciplex $(A/A/D)^*$ of two anthracene (A) and one diene (D) molecules is more efficient than the excimer $(A/A)^*$ in leading to dimerization. In another example, a termolecular exciplex $(ST/ST/F)^*$, formed by reaction of *trans*-stilbene excimer $(ST/ST)^*$ with dimethyl fumarate (F), was proposed[36] as an intermediate in the formation of an oxetane derivative.

Further work on termolecular exciplexes and the related processes of exciplex substitutions[37] in which one component of an exciplex can be substituted by another

$$(A/B)^* + C \rightarrow (A/C)^* + B$$

will probably unravel other interesting aspects of exciplex chemistry.

Excited Complexes

The general features outlined above for exciplex reactions, such as the stereochemistry of the products, possible intersystem crossing prior to adduct formation, and solvent effects, also hold for the reactions via excited complexes. We found that the role of π-orbital overlap, which, as mentioned above, strongly affects the stereochemistry of cycloadducts via exciplexes, is also dominant in the cycloadditions of excited complexes of anhydrides with benzocyclic olefins.[38]

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(27) Intersystem crossing of exciplexes to triplet excited molecules has been detected by flash photolysis in a number of aromatic hydrocarbon/amine systems; cf.: Orbach, N.; Ottolenghi, M. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975, p 75. Land, E. J.; Richards, J. T.; Thomas, J. K. *J. Phys. Chem.* **1972**, *25*, 3085. Schulten, K.; Staerk, H.; Weller, A.; Werner, H.-J.; Nickel, B. *Z. Phys. Chem.* **1976**, *101*, 371. Nishimura, T.; Nakashima, N.; Mataga, N. *Chem. Phys. Lett.* **1977**, *46*, 334.

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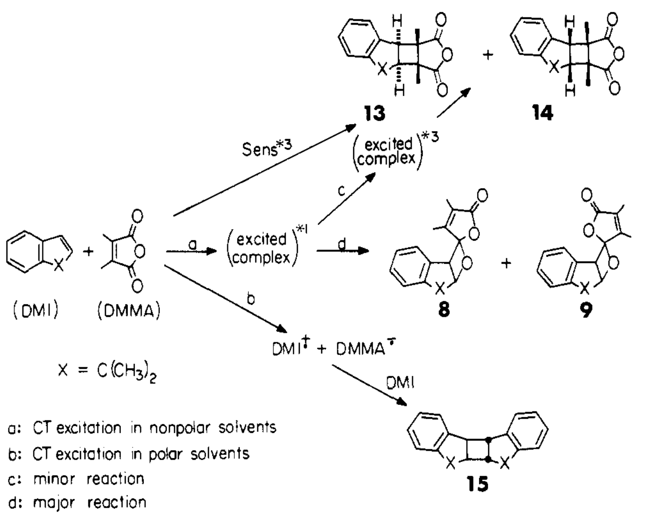
Scheme II

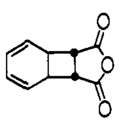


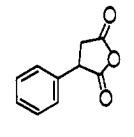
Charge-transfer excitation of dimethylmaleic anhydride (DMMA)/1,1-dimethylindene (DMI) in a nonpolar solvent gives the oxetanes 8 and 9 in ca. 1:9 ratio. On the other hand, phthalic anhydride gives the oxetanes 10 and 11 in ca. 1:1 ratio, and the reaction of naphthalic anhydride gives only the sterically hindered isomer 12 (Table I). These data indicate that, as with exciplexes, increasing the degree of π-orbital interaction in the excited complex will increase the proportion of the product derived from such a complex with a sandwich configuration in spite of the steric hindrance. The energy minimum of the naphthalic anhydride complex is apparently well-defined, resulting in a stereoselective formation of the sterically hindered isomer.

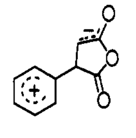
The lack of formation of any oxetanes in the corresponding triplet-sensitized reactions indicates that these products are formed from the singlet excited complex. The triplet-sensitized reactions of DMMA with indenes yield, instead, the cyclobutane addition products[38,39] (Scheme II). Small amounts of these cyclobutane derivatives are also formed in the CT-excited reaction. There is strong evidence that this cyclobutane formation is preceded by isc of the singlet excited complex.[40] The ratio of these cyclobutanes from the CT excitation reaction is the same as that obtained from the triplet-sensitized reaction, and, more important, the dependence of this ratio on the reaction solvent is the same in both the sensitized and unsensitized reactions. It is very unlikely that both the same product ratio and the same solvent dependence would be observed if different intermediates were involved in the two reactions.

For the same arguments mentioned for the exciplex reactions, solvent polarity plays a major role in reactions via excited complexes. CT excitation of dimethylmaleic anhydride/dimethylindene in polar solvents such as acetonitrile gives no mixed adducts (cyclobutanes or oxetanes). Instead, the dimer of dimethylindene is formed, as shown below, via the solvated radical cation.[41] This indicates that in such a polar medium the solvated radical ions are lower in energy than the excited complex.

A similar medium effect could account for the difference in products of CT excitation of the maleic anhydride/benzene complex. In nonpolar media the primary photoproduct is the cycloadduct 16, which in a thermal process leads to a 2:1 adduct.[42,43] In the presence of trifluoroacetic acid (0.8 M), however, instead of the cycloadduct the substitutive addition product 17 is formed.[44] This need not be regarded as an indication that the cycloadduct is formed via a zwitterionic intermediate,[45] 18, which will be intercepted if CF_3COOH is present. It is conceivable that CF_3COOH, especially at high concentrations, can alter the course of reactions of the excited complex by promoting radical ion formation. Protonation of the anhydride radical anion followed by addition to the benzene radical cation can be considered as an alternative route to the zwitterion for the formation of 17.


16


17


18

Radical Ions

In general, the feasibility of producing radical ions in polar solvents via photoinduced electron transfer can be predicted by using the well-known equation derived by Weller.[20a,46]

$$\Delta G = (E_D^{ox} - E_A^{red}) - E_{excit}$$

If the energy stored in the excited species (singlet or triplet, depending on which state is involved) is higher than the energy stored in the radical ion pair (calculated from the oxidation and reduction potentials of the donor and the acceptor, respectively), the electron transfer becomes exothermic and proceeds at a diffusion-controlled rate. Such electron-transfer reactions may be induced by excitation of either the donor or the acceptor or by excitation of a charge-transfer complex. Since the energy content of a radical ion pair solvated by a polar solvent is substantially lower than that in a nonpolar solvent,[20b] photoreactions via separated radical ions are generally observed in polar solvents such as acetonitrile and nitromethane.

As expected, reverse electron transfer can be a dominant factor in the fate of the primary radical ion pair. In addition, secondary electron transfer between either radical ion and another molecule is also possible. For example, a compound with a lower oxidation potential than that of the donor will act as a quencher for the radical cation reactions of the latter. Studying such a

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(39) Metzner, W.; Partale, H.; Krauch, C. H. *Chem. Ber.* **1967**, *100*, 3156.

(40) Intersystem crossing of excited complexes leading to a triplet complex or the triplet of one of its components seems to be a common phenomenon; cf.: Reid, C. *J. Chem. Phys.* **1952**, *20*, 1212. Czekalla, J.; Mager, K. J. *Z. Elektrochem.* **1962**, *66*, 65. Christodouleas, N.; McGlynn, S. P. *J. Chem. Phys.* **1964**, *40*, 166. Eisenthal, K. B. *Ibid.* **1966**, *45*, 1850. Iwata, S.; Tanaka, J.; Nagakura, S. *Ibid.* **1967**, *47*, 2203. Beens, H.; Weller, A.; In "Molecular Luminescence"; Lim, E. C., Ed.; W. A. Benjamin: New York, 1969, p 203. Briegleb, G.; Schuster, H.; Herre, W. *Chem. Phys. Lett.* **1969**, *4*, 53.

(41) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

(42) Angus, H. J. F.; Bryce-Smith, D. *Proc. Chem. Soc. London* **1959**, 326. Bryce-Smith, D.; Hems, M. *J. Chem. Soc.* **1968**, 812.

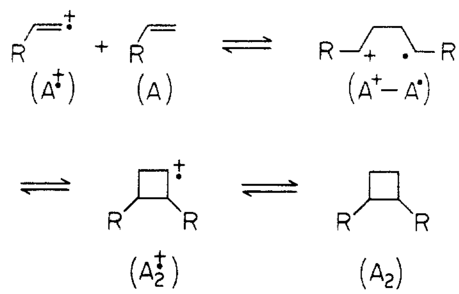
(43) Hartmann, W.; Heine, H.-G.; Schrader, L. *Tetrahedron Lett.* **1974**, 3101.

(44) Bryce-Smith, D.; Deshpande, R.; Gilbert, A.; Grzonka, J. *J. Chem. Soc., Chem. Commun.* **1970**, 561.

(45) Bryce-Smith, D.; Deshpande, R. R.; Gilbert, A. *Tetrahedron Lett.* **1975**, 1627.

(46) Grellman, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 3132.

Scheme III



process is very useful in differentiating among alternative mechanisms as well as in determining reaction kinetics. On the other hand, when the primary radical cation is not a reactive species, this secondary electron-transfer process can generate another radical cation, which leads to cycloaddition products.

A number of cycloadditions are known to proceed via photochemical electron transfer. Most of these reactions involve the radical cation of an olefin or an acetylene, and some of these reactions resemble those via the triplet state, i.e., they yield cyclobutanes by dimerization or mixed addition. In other reactions, the cationic nature of the radical cation is more pronounced, and it undergoes nucleophilic addition. Cycloadditions resulting from the reaction of a radical cation with a radical anion are also encountered. Finally, spectroscopic studies have clearly demonstrated that triplet excited states can be produced by recombination of radical ion pairs, and cycloadditions involving such a mechanism have been observed.

Photocycloadditions via Radical Ions

Only a few examples of photosensitized dimerization of olefins or acetylenes via radical cations are known. These include some enamines,[47] 1,1-diarylethylenes,[48] indenes,[41,49] vinyl ethers,[49-51] styrenes,[52] and phenylacetylene.[21a,53] Contrary to exciplex and excimer reactions, but similar to triplet reactions, dimerizations via radical cations are nonconcerted; i.e., stepwise bond formation produces the thermodynamically more stable exo products derived from the more stable (head-to-head) 1,4-radical cation intermediate.[47c] In the dimerization of indene (IN) the major product of the singlet reaction is the endo head-to-head dimer probably derived from an excimer with overlapping π orbitals.[54] This dimer, however, amounts to only 3% of the products from the triplet-sensitized[54] and electron-transfer-sensitized reactions.[41] In both cases the major product (83% and 97%, respectively) is the less sterically hindered exo head-to-head dimer. Also, the radical cation reaction seems to be more stereoselective than the triplet-sensitized dimerization, as no head-to-tail dimers are obtained in the former reaction whereas the latter gives 14% of these products.

A general mechanism for the cyclodimerization of an olefin (A) via its radical cation ($A^{+}\cdot$) is given in Scheme III.[47c] One feature of this mechanism is that the open-chain ($\cdot A\text{–}A^{+}$) and cyclic ($A_2^{+}\cdot$) butane radical cations may be interconvertible, and examples of one-electron oxidative ring openings of cyclobutanes have been observed.[51,55] In addition, if the oxidation potential of the monomer is lower or only slightly higher than that of the dimer, then a chain reaction can occur. *N*-Vinylcarbazole,[47] phenyl vinyl ether,[49,51] and dimethylindene[49] satisfy this requirement and dimerize via a chain reaction.[56]

Cyclobutanes are not the only products formed by dimerizations via radical cations. 1,1-Diphenylethylene[48] and phenylacetylene[21a,53] give instead 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene and 1-phenylnaphthalene, respectively.

A few examples of addition of the radical cation to a different olefin or acetylene are also known.[49,57-59] The addition of 1,1-dimethylindene (DMI) to phenyl vinyl ether (PVE) to give a cyclobutane product illustrates the reaction kinetics that may be involved in such mixed-addition reactions.[49] This reaction can be sensitized by pyrylium salts or 9,10-dicyanoanthracene (DCA) or it can be induced by charge-transfer (CT) excitation of their electron donor–acceptor (EDA) complexes with anhydrides. In all these cases the radical cations of both olefins are formed, as the oxidation potential of PVE is only slightly higher than that of DMI. The mixed addition, however, occurs only from the reaction of $DMI^{+}\cdot$ with PVE. From quenching kinetics, bimolecular reaction constants for addition of $DMI^{+}\cdot$ to DMI and PVE of 10^6 and 10^8 M^{-1} s^{-1}, respectively, were obtained. The reaction constant for addition of $PVE^{+}\cdot$ to PVE is ca. 6×10^8 M^{-1} s^{-1}, whereas its addition to DMI is much slower than the competing electron transfer, which leads to the lower energy radical cation of DMI. The range of these reaction constants is similar to those encountered in triplet reactions. In both electron transfer and triplet energy transfer, exothermicity by a few kilocalories/mole leads to diffusion-controlled processes (1.5×10^{10} M^{-1} s^{-1} in acetonitrile). Usually, cycloadditions cannot compete favorably with such rates.

Very large reaction constants occasionally measured in triplet cycloadditions are regarded as an indication for triplet excimer or exciplex formation preceding the addition step.[60] The same seems to hold for an electron-transfer reaction in which unusually high reaction

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(47) (a) Carruthers, R. A.; Crellin, R. A.; Ledwith, A. *J. Chem. Soc., Chem. Commun.* **1969**, 252. (b) Crellin, R. A.; Lambert, M. C.; Ledwith, A. *Ibid.* **1970**, 682. (c) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

(48) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

(49) Farid, S.; Hartman, S. E.; Evans, T. R. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975, p 327.

(50) (a) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 2. (b) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Org. Chem.* **1973**, *38*, 3803.

(51) Evans, T. R.; Wake, R. W.; Jaenicke, O. In ref 64, p 345.

(52) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53. Asanuma, T.; Yamamoto, M.; Nishijima, Y. *Ibid.* **1975**, 56. Asanuma, T.; Yamamoto, M.; Nishijima, Y. *Ibid.* **1975**, 608. Asanuma, T.; Gotoh, T.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *Ibid.* **1977**, 485.

(53) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126.

(54) Metzner, W.; Wendish, D. *Liebigs Ann. Chem.* **1969**, *730*, 111.

(55) Beresford, P.; Lambert, M. C.; Ledwith, A. *J. Chem. Soc. C* **1970**, 2508. Helene, C.; Charlier, M. *Photochem. Photobiol.* **1977**, *25*, 429.

(56) In a number of these reactions the presence of catalytic amounts of oxygen increases the quantum yield of dimerization. A possible explanation for this effect is either superoxide replaces the sensitizer radical anion and is partly consumed or oxygen reacts with the sensitizer radical (with pyrylium salts as sensitizers), rendering it a poor electron donor. In either case the reverse electron transfer, which is the termination step, is suppressed.

(57) Mizuno, K.; Kaji, R.; Otsuji, Y. *Chem. Lett.* **1977**, 1027.

(58) Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 594.

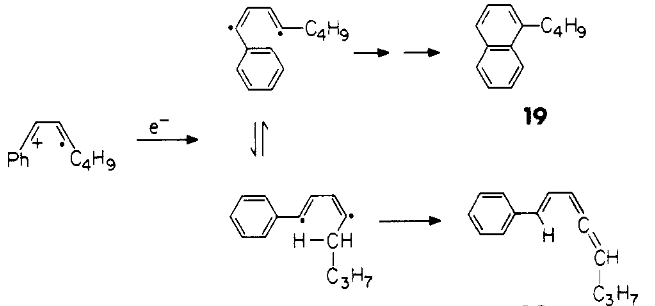
(59) Maroulis, A. J.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1979**, 351. Arnold, D. R.; Borg, R. M.; Albini, A. *Ibid.* **1981**, 138.

(60) Caldwell, R. A. *J. Am. Chem. Soc.* **1979**, *92*, 1439. Kochevar, I. E.; Wagner, P. J. *Ibid.* **1972**, *94*, 3859. Caldwell, R. A. *Ibid.* **1973**, *95*, 1690.

rates were observed. We found that the addition of the radical cation of phenylacetylene ($A^{+\cdot}$) to a molecule of phenylacetylene (A) is preceded by the formation of a complex ($A^{+\cdot}/A$).[61] The presence of this complex and the fact that it is formed at a diffusion-controlled rate were revealed by a study of the quenching kinetics of the electron-transfer-sensitized dimerization of phenylacetylene.

In other cross-additions, 2 + 4 adducts are obtained. These include the additions of indene radical cation to furan[58] and of diphenylethylene radical cation and 2-phenylnorbornene radical cation to isobutene.[59]

In such mixed additions, other reactions occasionally compete with the cyclization. For example, in the cross-addition of phenylacetylene to hexyne, cyclization to **19** is only a minor path competing with rearrangement to an allene product (**20**).[62]

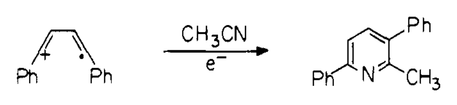


19

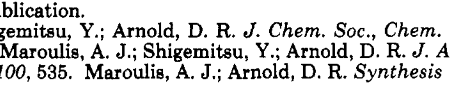
20

Cycloadditions via radical cations can be completely suppressed in the presence of relatively strong nucleophiles such as alcohols and cyanide ions, where anti-Markovnikov adducts are formed. Arnold and collaborators[48,63] extensively studied these nucleophilic additions.

In a few instances, however, nucleophilic cycloadditions are encountered. Evans et al.[51] found that, in the photosensitized electron-transfer reactions of phenyl vinyl ether (PVE) and its dimer, the 1,4-radical cation can be intercepted by acetophenone to give the tetrahydropyran derivative (**21**) or by acetonitrile to give, ultimately, a pyridine derivative. A similar nucleophilic addition occurs in the electron-transfer-sensitized reactions of phenylacetylene, resulting in a cyclotrimerization involving two acetylene and one nitrile molecules[53] to give the pyridine derivative (**22**).



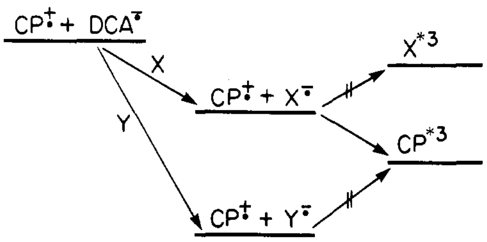
21



22

Reverse electron transfer between radical ion pairs, either in cage or through recombination, leading to the ground state is an unfortunate energy-wasting step responsible for low quantum yields in many electron-transfer reactions. However, spectroscopic studies have clearly demonstrated that recombination of radical ion pairs can also lead to the triplet state of one of the reactants.[46,64] This process can take place when the energy stored in the radical ion pair exceeds the triplet energy of one of the reactants.

Scheme IV



The cyclodimerization of methyl 1,2-diphenylcyclopropene-3-carboxylate (CP) sensitized by 9,10-dicyanoanthracene (DCA) in polar solvents proceeds via the triplet state of the olefin formed by recombination of the sensitizer radical anion ($DCA^{-\cdot}$) and the radical cation of CP ($CP^{+\cdot}$).[65]

$$DCA^{*1} + CP \rightarrow DCA^{-\cdot} + CP^{+\cdot}$$

$$DCA^{-\cdot} + CP^{+\cdot} \rightarrow DCA + CP^{*3}$$

$$CP^{*3} + CP \rightarrow \text{dimer}$$

As expected, the efficiency of formation of CP^{*3} in this reaction is not high, since DCA triplet is also likely to be formed and because the reverse electron transfer produces CP^{*3} in cage with DCA, which acts as a triplet quencher. In agreement with this view, we found that the quantum yield of CP^{*3} could be increased by more than an order of magnitude in the presence of compounds (X) whose reduction potentials are lower (less negative) than DCA but still high enough to produce CP^{*3} and whose triplet energies are higher than CP. Thus, secondary electron transfer will replace $DCA^{-\cdot}$ with $X^{-\cdot}$, and recombination of the new radical ion pair $X^{-\cdot}/CP^{+\cdot}$ will produce CP^{*3} but not X^{*3}. On the basis of the reduction potential of DCA and the triplet energy of CP, the reduction potential of X should be between −0.88 and −0.56 V (vs. SCE). In fact, 1,2,4,5-tetracyanobenzene, 1,4-naphthoquinone, and 2-chloro-9,10-anthraquinone fulfill these requirements and significantly enhance the formation of CP^{*3}.[66] On the other hand, compounds (Y) which have reduction potentials less negative than −0.56 V (vs. SCE), such as benzoquinone and 2,3-dichloronaphthoquinone, quench the triplet formation because recombination of the radical ion pair $Y^{-\cdot}/CP^{+\cdot}$ will lead to the ground-state molecules instead of producing CP^{*3} endothermically[66] (Scheme IV).

In addition to producing the ground states or the triplets of the reactants, recombination of radical ion pairs may yield addition products. One example of such a reaction is encountered in the DCA/CP reactions,

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(61) Mattes, S. L.; Farid, S. Unpublished results.

(62) The formation of the allene derivative was not reported in the preliminary communication, ref 53. Structural proofs will be given in the detailed publication.

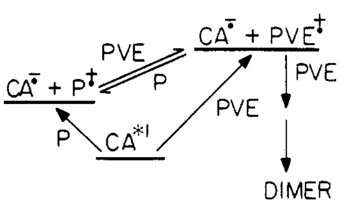
(63) Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. Maroulis, A. J.; Arnold, D. R. *Synthesis* **1979**, 819.

(64) a) Weller, A.; Zachariasse, K. In "Molecular Luminescence"; Lim, E. C., Ed.; W. A. Benjamin: New York, 1969, p 895. (b) Schomberg, H.; Staerk, H.; Weller, A. *Chem. Phys. Lett.* **1973**, *22*, 1.

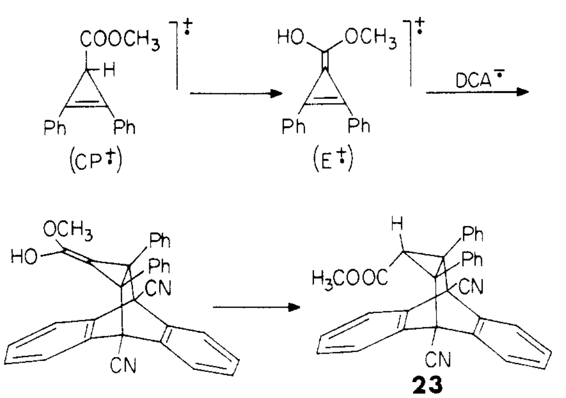
(65) (a) Farid, S.; Brown, K. A. *J. Chem. Soc., Chem. Commun.* **1976**, 564. (b) Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162.

(66) The effect of tetracyanobenzene is reported in ref 65. The quantum-yield enhancement (cosensitization) by some quinones and the quenching by others are from unpublished results.

Scheme V



where an unusually sterically hindered 2 + 4 cycloadduct, 23, was formed from irradiations in polar solvents.[65] The radical cation involved in this reaction is not the primary photoproduct ($CP^{+\cdot}$) but a rearranged intermediate, the enol radical cation, $E^{+\cdot}$. Reketonization of the cycloadduct formed from addition of $E^{+\cdot}$ to $DCA^{-\cdot}$ gives this sterically hindered endo product, 23. It is noteworthy that the exo adduct is formed via an exciplex by irradiation in benzene.



23

In the electron-transfer-sensitized reactions discussed so far, the radical cation of the reactive olefin or acetylene is produced directly through reaction with an excited acceptor or by excitation of its ground-state complex with an acceptor. In some special cases, however, it is desirable or necessary to convert the primary radical cation, through a secondary electron transfer, to another one, which then leads to products. An early example of such a process is the dimerization of phenyl vinyl ether (PVE).[49] With 9-cyanoanthracene (CA) as the sensitizer, electron transfer from PVE to CA^{*1} is very inefficient ($\phi_{\text{dimer}} \sim 10^{-4}$) because it is endothermic. Addition of a cosensitizer such as phenanthrene, durene, or methylnaphthalene increases the quantum yield of dimerization by as much as a factor of 200. Electron transfer from the cosensitizer, e.g., phenanthrene (P), to CA^{*1} is less endothermic and therefore more efficient than from PVE. Then the secondary electron transfer from PVE to $P^{+\cdot}$ will occur, even though it is endothermic, because $P^{+\cdot}$ has a longer lifetime than the singlet-excited sensitizer (Scheme V).

In other photosensitizations involving a secondary electron transfer, the light-absorbing compound is the electron donor. As an example, Pac[67] sensitized the dimerization of indene (IN) by phenanthrene (P) in the presence of *p*-dicyanobenzene (DCB) according to

$$P^{*1} + DCB \rightarrow P^{+\cdot} + DCB^{-\cdot}$$

$$P^{+\cdot} + IN \rightarrow P + IN^{+\cdot}$$

$$IN^{+\cdot} + IN \rightarrow \text{dimers}$$

Photosensitized electron-transfer reactions carried out in the presence of oxygen occasionally yield oxidation products. Some of these reactions proceed via a secondary electron transfer from the sensitizer radical anion to oxygen, producing superoxide, $O_2^{-\cdot}$, which adds to the radical cation of an olefin or acetylene, giving the oxidation products.[68-73] Of interest in the context of this article is that the primary products, in some cases, may be cycloadducts: the dioxetane[68,71,73] or dioxete.[70,72] This mechanism represents only one of several oxygenation pathways that occur via photosensitized electron-transfer reactions.[72,74] The scope and diversity of such reactions seem to be very broad.

Concluding Remarks[75]

Several examples have shown that an extended π-orbital overlap in singlet exciplexes or excited complexes is an important factor contributing to the stability of such sandwich complexes and increasing the stereoselectivity of the addition. The stereochemistry of such adducts reflects the configuration of the complex. Understandably, there are instances with weak interaction between the reactants which result in exciplexes with several less well-defined minima. Ultimately, when the stabilization energy approaches kT, the intermediacy of exciplexes becomes a matter of semantics.

Since intersystem crossing in singlet exciplexes and excited complexes is a common process, "triplet products", which are mostly nonstereospecific, are occasionally encountered in addition to the singlet products.

The mechanisms of photocycloadditions via electron transfer can be quite complex because of the possible involvement of a large number of intermediates, which contributes to the diversity of these reactions. However, these numerous intermediates allow for predictable manipulations of the reactions based on well-understood primary and secondary electron-transfer processes.

The photophysical investigations of exciplexes and electron-transfer processes as well as chemical kinetic studies constitute the most powerful tools in exploring cycloadditions via such intermediates. In addition, CIDNP[76] and ESR[71] can supply valuable mechanistic information. Finally, MO considerations seem to offer a means for predicting the feasibility of singlet cycloadditions.[77]

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(72) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* 1980, 457.

(73) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* 1980, *102*, 6083.

(74) Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* 1980, 4275. Barton, D. H. R.; Haynes, R. K.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Chem. Commun.* 1974, 511. Haynes, R. K. *Aust. J. Chem.* 1978, *31*, 121 and references therein.

(75) For recent reviews on related subjects; cf.: Lablache-Combier, A. *Bull. Soc. Chim. Fr.* 1972, 4791. Davidson, R. S. "Molecular Association", Foster, R., Ed.; Academic Press: London, 1975, p 215. Lewis, F. D. *Acc. Chem. Res.* 1979, *12*, 152. Caldwell, R. A.; Creed, D. *Ibid.* 1980, *13*, 45.

(76) Roth, H. D. "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; D. Reidel: Dordrecht, Holland, 1977, p 39.

(77) Gerhartz, W. R.; Posthusta, R. D.; Michl, J. *J. Am. Chem. Soc.* 1976, *98*, 6427. Michl, J. *Photochem. Photobiol.* 1977, *25*, 141. Caldwell, R. A. *J. Am. Chem. Soc.* 1980, *102*, 4004.