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Exciplexes and Electron Transfer Reactions

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Summary. Electronically excited molecules, being better electron donors and acceptors than their ground states, form charge-transfer complexes (exciplexes) which can lead to radical ions. Exciplex emission is widely used to probe polymers and organized media such as membranes and micelles. Exciplexes are also intermediates in photoreactions that lead to unique products. Photochemical electron-transfer processes, which are the basis of silver halide photography and electrophotography, are involved in many reactions of wide scope. Recent studies have led to the discovery of several electron-transfer photooxygenations with a diversity that will probably rival that of singlet oxygen. Both exciplex emission and photochemical electron transfer play important roles in organic photochemistry.

Complexes can be formed in the excited state even when the reactants have no corresponding ground-state interaction. The earliest examples of such complexes are the excited-state dimers of rare gases, which emit energy and return to a dissociated ground state (*1*); and Förster discovered that pyrene forms a dimeric complex in solution that is stable only in the excited state (*2*). Such excited-state dimers, which are called "excimers," have since been encountered in several aromatic hydrocarbons and other organic compounds (*3*).

Both exciton resonance ($^*AA \leftrightarrow AA^*$) and charge-transfer (CT) configurations ($A^+A^- \leftrightarrow A^-A^+$) contribute to the stabilization of the excimer. Complexes in the excited state are not limited to complexes of identical molecules, that is, excimers; they can also be formed between vastly different molecules (*4*). Such mixed complexes, originally called heteroexcimers, are now referred to as "exciplexes."

Typical examples, such as those resulting from interaction of singlet excited pyrene with either *p*-dicyanobenzene (an electron acceptor) or *N*,*N*-dimethylaniline (an electron donor), have strong charge-transfer character. In extreme cases they can be regarded as contact ion pairs. Exciplexes are formed in spite of the absence of ground-state interactions because of the increase of the electron donor and acceptor properties when molecules are electronically excited. For the same reason, excitation in the charge-transfer band of a ground-state electron-donor-acceptor (EDA) complex yields an excited complex that has a stronger binding energy than the ground-state complex.

An excimer or exciplex is best identified by its fluorescence spectrum: a structureless band shifted to longer wavelength from the corresponding monomer emission. The shift is due to stabilization of the complex and to a repulsion energy at the corresponding ground-state configuration (Fig. 1) (*5*). This dissociated ground state is also responsible for the absence of fine structure in the spectrum.

An excimer or exciplex of aromatic molecules usually has a parallel configuration with an interplanar separation of 3 to 4 Å. Excimers have zero dipole moment and consequently show no significant shifts in fluorescence maxima between polar and nonpolar solvents. Charge-transfer exciplexes, however, have high dipole moments, and their emissions are very sensitive to the polarity of the media (*6*). Emissions from such exciplexes also decrease as the polarity increases because of solvent penetration between the components to yield a radical ion pair (*6*). In highly polar solvents (acetonitrile or methanol, for example) the gain of free energy connected with this process is ~20 kJ/mol (*7*). Furthermore, in such polar solvents the formation of CT exciplexes is largely circumvented by the direct formation of radical ion pairs, which can occur while the reactants are 7 Å apart as compared with the 3 to 4 Å required for exciplex formation. Thus weak emissions, if any, are observed from CT exciplexes in highly polar solvents.

Other complexes formed in the excited state could have properties ranging between those of CT exciplexes and excimers. These complexes are formed when there is no marked difference in the donor or acceptor properties of the components. As a result, such complexes have low charge-transfer character and consequently a low dipole moment. Even in strongly polar solvents, these low-CT exciplexes can be formed and emit or lead to products in reasonable quantum yields (*8*), since geminate ion pair formation, being endothermic in these cases, is less competitive.

In fluid media the geminate radical ion pair, formed either directly from the encounter complex or via an exciplex, can dissociate into solvated radical ions. This process competes with back electron transfer; and, being a diffusional reaction, its rate decreases with increas-

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ing viscosity of the medium. In rigid matrices the separation of the charge can be achieved through charge migration from one molecule to another:

$$\mathrm{D}^{\dot{+}}\ldots\mathrm{D}\ldots\mathrm{D}\rightarrow\mathrm{D}\ldots\mathrm{D}^{\dot{+}}\ldots\mathrm{D}\rightarrow\mathrm{D}\ldots\mathrm{D}\ldots\mathrm{D}^{\dot{+}} \qquad (1)$$

or

$$\mathrm{A}^{\dot{-}}\ldots\mathrm{A}\ldots\mathrm{A}\rightarrow\mathrm{A}\ldots\mathrm{A}^{\dot{-}}\ldots\mathrm{A}\rightarrow\mathrm{A}\ldots\mathrm{A}\ldots\mathrm{A}^{\dot{-}} \qquad (2)$$

Photochemical electron-transfer reactions are important in nature (photosynthesis) as well as in many technical applications. Electrophotography (xerography) is based on photoconduction in a charged layer, achieved through photochemical formation of radical ion pairs and subsequent charge migration, as mentioned above. In conventional photography, electron transfer from photoexcited sensitizing dyes, adsorbed on silver halide crystals, reduces silver ions to silver atoms, forming a latent image. Photochemical electron transfer is involved also in photovoltaic and photogalvanic cells. Several initiators for cationic and free-radical photopolymerizations are based on electron-transfer photochemistry. Proton transfer from a radical cation to a radical anion produces a pair of free radicals, either of which can initiate radical polymerization. In addition, electron-transfer reactions have significantly enlarged the scope of organic photochemistry.

The interest in exciplexes and organic photochemical electron-transfer reactions has steadily increased in recent years. There has been significant progress in understanding the phenomena involved and the scope of such reactions.

Exciplexes and Excimers

Fluorescence. As mentioned above, the maximum of an exciplex emission shifts to longer wavelength as the polarity of the medium increases (*6*). This effect can be used as a probe for microenvironments. However, the concurrent decrease in intensity with increasing polarity limits its application to media of moderate polarity.

If the exciplex or the excimer cannot acquire the optimum configuration, a parallel, face-to-face structure with 3 to 4 Å between both components when they are aromatic compounds, then the emission maximum will be shifted to shorter wavelengths, owing to less stabilization of the complex. This was observed in rigid matrices of polymers below their glass-transition temperatures (T_g) (*9*). In addition to this medium-induced restriction on the complex acquiring its optimum configuration, rigid polymeric matrices do not solvate an exciplex as well as fluid solvents of similar structure. This effect causes an additional shift of $\lambda_{\max}$ to shorter wavelengths (*9*).

Temperature also affects exciplexes in a number of ways. Usually a small shift in the emission maximum can be expected from the change of the dielectric constant of the solvent with temperature. However, the observed shifts to shorter wavelengths in exciplex maxima with increasing temperature are more than can be accounted for by the indirect effect of a change in the dielectric constant (*9*).

Temperature also has a profound effect on the ratio of exciplex or excimer emission to that of the monomer (I′/I) (*3*). In the low-temperature range, an increase in temperature lowers the viscosity and hence enhances the rate of diffusion, resulting in greater exciplex or excimer formation. The ratio of exciplex or excimer emission to that of monomer then reaches a maximum, followed by a decrease in I′/I with further increases in temperature. The latter is due to an increase in the rate of dissociation of the exciplex or excimer in relation to its radiative decay. A similar temperature effect has been observed with intramolecular exciplexes and excimers. The increased fluidity of the medium with temperature enhances the rate of configurational changes in these bichromophoric molecules to bring both moieties to the proper alignment for interaction (*10*). Polymers containing excimer-forming substituents such as phenyl, naphthyl, and carbazolyl groups were similarly studied as dilute solutions and in films. Several factors are to be considered in interpreting these data in terms of conformational mobility. For example, the difference between the rates of conformational transition at the middle and rates of conformational transitions at the end of long chains and the possibility for energy migration before excimer emission should be considered (*11*).

In addition to their application in polymer studies, exciplexes and excimers have been used extensively in probing some organized media such as micelles (*12*), microemulsions, synthetic and natural membranes (*13*), and liquid crystals (*14*). The use of bichromophoric, intramolecular excimer-forming molecules such as 1,3-dipyrenylpropane is particularly attractive in these studies because they can be used at very low concentrations ($\leq 10^{-6}M$). Discontinuity in plots of log I′/I as a function of 1/T occurs at the phase-transition temperature for membranes and liquid crystals.

In principle, the absolute value of I′/I at a given temperature could be a measure of fluidity. This, however, is subject to many complications. For example, the change of I′/I with viscosity depends on the chemical nature of the solvents. A monotonic change in I′/I is obtained with hydrocarbon solvents, but the change in I′/I with alcohol solvents, while also monotonic, follows another curve. This structural dependence, combined with the ambiguity in defining the position of the probe in organized media such as vesicles or micelles, where different sites have different viscosities, makes it difficult to select a reliable set of solvents for calibration. There is also evidence that the anisotropic, liquid-crystalline environment of bilayers could affect the conformational equilibrium of molecules such as 1,3-dipyrenylpropane. This medium may also have an orienting effect on the fluorophore. Furthermore, the fluidity in the immediate vicinity of the probe is likely to be altered (*13*) because of perturbations induced by the probe. In summary, these probes are useful in determining phase-transition temperatures and may be useful for comparing the fluidity (and its temperature dependence) of similar systems but not for absolute measurements of fluidity, especially of membranes and related systems.

Cycloaddition reactions. Besides the interesting spectroscopic features of excimers and exciplexes, reactions via such intermediates also have some unique characteristics. These excited-state complexes are important intermediates in many cycloaddition reactions of singlet excited molecules (*15, 16*). Most of these reactions are concerted and yield products that reflect the face-to-face configuration of the intermediates. As a result, the syn dimers or adducts, which might be the thermodynamically least stable products, are usually the predominant products.

The reaction of phenanthrene in its singlet excited state with aryl-substituted olefins gives predominantly the 2+2 cycloadducts in which the aryl group is on the same side of the cyclobutane ring as the phenanthrene moiety, corresponding to the expected configuration of the exciplex (*15, 16*). The stereochemistry of these reactions is different from that of other photochemical 2+2 cycloadditions. Stepwise reactions via molecules in the triplet state or via photogenerated radical cations give predominantly 2+2 cycloadducts in the *anti* configuration,

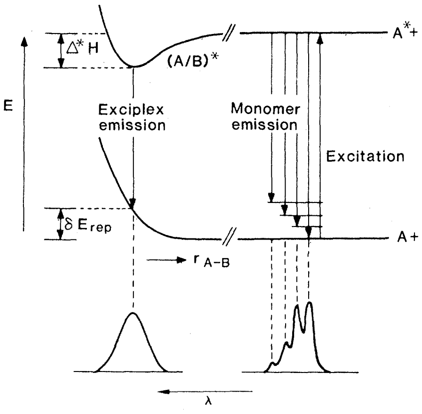

Fig. 1. Energy diagram of an exciplex.

corresponding to head-to-head intermediates. Concerted reactions induced by excitation of ground-state CT complexes resemble those via exciplexes; that is, the products reflect the face-to-face configuration of the intermediates (*16*).

Radical Ions

Energetics. As we said before, molecules in the excited state are easier to reduce and to oxidize than they are in the ground state. Therefore, formation of CT complexes and of radical-ion pairs can result from interactions involving excited states even when there is no binding energy between the reactants in the ground state. Solvents of high dielectric constant solvate radical ions and therefore facilitate their formation. Accordingly, emissions and reactions typical of exciplexes, such as encountered in nonpolar solvents, are often replaced by chemistry of the radical ions when the molecules are irradiated in solvents with high dielectric constants, such as acetonitrile.

The free-energy change for the generation of radical ions in polar solvents can be determined from the equation derived by Weller (*17*):

$$D + A \xrightarrow{h\nu} D^{+\cdot} + A^{-\cdot} \qquad (3)$$

$$\Delta G = (E_{\mathrm{D}}^{\mathrm{ox}} - E_{\mathrm{A}}^{\mathrm{red}}) - E_{\mathrm{excit}} \qquad (4)$$

In Eq. 4, the term for the electrochemical redox potential, in parentheses, represents the energy required for one-electron oxidation of the donor and for one-electron reduction of the acceptor. If this energy is less than the excitation energy (E_{excit}) of the reacting species (donor or acceptor; singlet or triplet, depending on its multiplicity), the reaction will be exothermic (negative ΔG) and usually will proceed at a rate controlled by diffusion. As expected, as radical ion formation becomes increasingly endothermic, the rate constant for quenching excited molecules in polar solvents by bimolecular electron transfer decreases exponentially. At room temperature, when no substantial reorganizational energy is required, an increase in endothermicity by 5.9 kJ/mol decreases the electron-transfer reaction constant by an order of magnitude.

The efficiency of a photochemical electron-transfer process is a function of several factors: (i) the magnitude of the reaction constant, which depends on the free-energy change, as discussed above, and on the intrinsic barrier, which is related to the reorganizational energies associated with the electron transfer; (ii) the lifetime of the excited molecule; and (iii) the concentration of the other reactant. For example, if the lifetime of an excited acceptor is 10 nsec, then a donor that reacts at the diffusion-controlled rate of $10^{10} M^{-1}$ sec^{-1} at a concentration of $0.1M$ would intercept 91 percent of the excited acceptor. In this example, if either the rate constant, the concentration of the donor, or the excited-state lifetime drops by an order of magnitude, then the efficiency of interception will drop to 50 percent.

Fate of the geminate pair. In polar fluid media the geminate pair is likely to be penetrated by the solvent and formed with a spin multiplicity corresponding to that of the precursor excited state. Thus an electron-transfer reaction involving an excited molecule in its singlet state produces a pair in the singlet spin state $^1(A^{-\cdot}/D^{+\cdot})$. Depending on the magnitude of other reactions, hyperfine interaction may be able to elevate the electron spin of the pair to a triplet state $^3(A^{-\cdot}/D^{+\cdot})$ during the lifetime of the pair. Usually, however, other reactions of the geminate pairs dominate (Fig. 2).

The chance of the geminate radical ion pair separating increases with increasing polarity of the medium because of the gain in solvation of the separated radical ions. In addition, the rate of separation of the radical ions, being a diffusional process, is inversely proportional to the medium viscosity. The rate constant for the separation (k_{sep}) of organic, single-charged radical ion pairs in acetonitrile at room temperature seems to be a constant value (*7, 18*) of ~5×10^8 sec^{-1}. In rigid matrices, where molecular diffusion is severely restricted, radical ion pairs are separated by "diffusion" of the charge through migration

$$\begin{aligned}&(A^{-\cdot}\ldots D^{+\cdot}\ldots D\ldots D\ldots \rightarrow\\ &\quad A^{-\cdot}\ldots D\ldots D^{+\cdot}\ldots D\ldots \rightarrow\\ &\quad A^{-\cdot}\ldots D\ldots D\ldots D^{+\cdot}\ldots \qquad (5)\end{aligned}$$

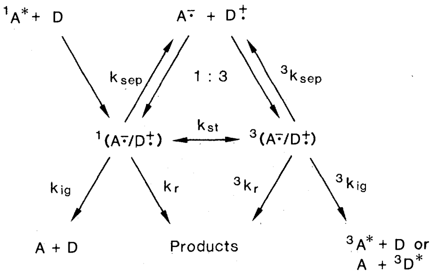

Fig. 2. Reactions of the geminate radical ion pair.

In electrophotography, this process is promoted by the application of an electric field.

The most common reaction of many photogenerated geminate radical ion pairs is back electron transfer (Fig. 2). This reaction depends on the relative alignment of the two unpaired electrons at the moment of back transfer. Pairs in a singlet spin state lead to singlet ground states of the reactants. Since the formation of molecules in their singlet excited state by this process is an endothermic reaction, it is not likely to compete with the other processes. The reaction constant for this process, k_{ig}, depends on several factors and is not well understood. However, in a number of reactions of olefins, acetylenes, and aromatic hydrocarbons induced by di- and tetracyanoanthracene in the singlet state, the quantum yield of the separated radical ions increases from 0.03 to 0.3 as the exothermic character of the back electron transfer increases from 2.1 to 2.8 eV (*19*). On the assumption that the rate of separation of the geminate pair in these reactions (in acetonitrile at room temperature) is 5×10^8 sec^{-1}, this change in quantum yield indicates that the rate constant for electron return decreases from ~2×10^{10} to 10^9 sec^{-1} as the exothermic character increases from 2.1 to 2.8 eV. This behavior is analogous to the rate of radiationless decay, which decreases as the energy gap increases (*20*). Factors other than the size of the energy gap must also play a role. For example, in some systems little change is observed as the energy gap changes, yet in others a large difference in k_{ig} corresponds to a small, irregular change in the energy content of the pair (*7*).

Back electron transfer in radical ion pairs in the triplet state leads to the original reactants, one of which is in its triplet state. This reaction takes place if the energy stored in the radical ion pair exceeds the triplet energy of the donor or the acceptor, otherwise competing reactions are likely to dominate electron transfer.

Radical ion pairs in the triplet state can be obtained from molecules in the singlet state either through spin alignment in the primary pair, as mentioned above, or through the separation of the radical ions followed by recombination (*21*). In the latter process, diffusion-controlled encounters occur with random spin alignment; they lead to 75 percent pairs in the triplet electron spin state and 25 percent in the singlet state. In polar solvents, as a result of the high ratio of k_{sep} to k_{st} and because of the dominance of triplet pair formation in the encounter step, the yield of molecules in the triplet state via this diffusional (also called homogeneous) process is higher than that through the geminate route.

This indirect triplet formation leads to reactions similar to those via conventional triplet-triplet energy transfer (*22*).

Some chemical reactions may occur within the geminate pair. The most common of these reactions is proton transfer from the radical cation to the radical anion, which yields a pair of free radicals that may give homo- or co-coupling products (*19*). More important, a number of excellent initiators for radical polymerization are formed via such photochemical electron transfer followed by proton-transfer reactions (*23*).

Finally, another reactant may intercept the geminate pair by reacting with either of the radical ions, if such a reaction is fast enough to compete with the other processes. These reactions can conceivably yield large quantum yields of products as they compete with the energy-wasting back electron transfer. An interesting feature of such geminate-pair interception is encountered in dimerization reactions. When a donor molecule adds to the donor radical cation while it is still engaged with the acceptor radical anion (path a, Fig. 3), the resultant dimeric radical cation can be reduced to a biradical. Not surprisingly, the product distribution via such a biradical is different from that via the dimeric radical cation formed after separation of the geminate pair (path b, Fig. 3) (*18*).

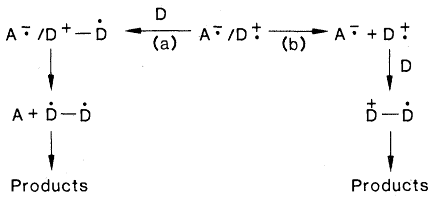

Fig. 3. Possible reaction paths for dimerization involving a geminate ion pair.

Secondary electron transfer. The course of photochemical electron-transfer reactions can be manipulated in a predictable manner through secondary electron-transfer processes. For example, the primary radical cation ($D_p^{\cdot+}$) can react with another electron donor (D_s) to produce the radical cation of the latter.

$$A + D_p \xrightarrow{h\nu} A^{\cdot-} + D_p^{\cdot+} \qquad (6)$$

$$D_p^{\cdot+} + D_s \rightleftharpoons D_p + D_s^{\cdot+} \qquad (7)$$

This reaction will be most efficient if the oxidation potential of D_s is lower than that of D_p. Even if the reaction is isoenergetic or slightly endothermic, it can be efficient if the competing reactions of $D_p^{\cdot+}$ are relatively slow (*19*).

The indirect formation of the radical cation $D_s^{\cdot+}$ and its subsequent reactions could have several advantages. The bypassing of a geminate pair of $D_s^{\cdot+}$ and the acceptor radical anion $A^{\cdot-}$ can prevent undesirable reactions. The proper choice of the primary donor D_p also can lead to higher efficiency for the separation of the geminate pair ($A^{\cdot-}/D_p^{\cdot+}$) than can be achieved from ($A^{\cdot-}/D_s^{\cdot+}$). Higher quantum yields from such reactions are common (*24*).

Secondary electron-transfer reactions are used extensively in kinetic studies. In these experiments D_s is used as a quencher for reactions of $D_p^{\cdot+}$. When D_s has a sufficiently lower oxidation potential than D_p, 0.2 V or more, the reaction constant for the electron transfer reaches the diffusion-controlled rate. Then, from the degree of quenching as a function of D_s concentration, rate constants for reactions of $D_p^{\cdot+}$ are readily obtained (*25*).

The primary radical anion can also be replaced through a secondary electron-transfer reaction ($A_p^{\cdot-} + A_s \rightarrow A_p + A_s^{\cdot-}$). The best known examples of radical anion exchange are where the secondary acceptor (A_s) is molecular oxygen (*26*). Photooxygenation via the radical cation of the donor and the so formed superoxide ion ($O_2^{\cdot-}$) is common.

Radical ion recombination can lead to the triplet state of one of the reactants. Such a process can be enhanced or suppressed by secondary electron transfer based on the triplet energy and redox potential of the secondary donor or acceptor (*19, 22*).

A special case of secondary electron transfer involves the radical cation of the product ($P^{\cdot+}$) and the starting donor (D) in a process that constitutes a chain propagation mechanism

$$D^{\cdot+} \rightarrow\rightarrow P^{\cdot+} \qquad (8)$$

$$P^{\cdot+} + D \rightarrow P + D^{\cdot+} \qquad (9)$$

If the oxidation potential of the product (P) is lower or just slightly higher than that of the reactant (D), the chain propagation step will proceed at the diffusion-controlled rate or a rate a few orders of magnitude lower. This reaction usually competes favorably with electron transfer from $A^{\cdot-}$ to $P^{\cdot+}$ (a chain termination step), because the photostationary concentration of $A^{\cdot-}$ when conventional light sources are used (10^{-8} to $10^{-6}M$) is low compared to the concentration of D (10^{-3} to $1M$).

This type of chain reaction was observed in several isomerizations and rearrangements, in 2+2 cyclodimerizations, and in certain oxygenation reactions (*19*). Products from nucleophilic additions, however, do not undergo chain amplification because the intermediate formed by nucleophilic addition (for example, by an alcohol) deprotonates; the final product is formed in the neutral state. The same is true for the coupling of a radical anion with a radical cation to give a neutral adduct.

Chemical reactions. The chemical reactions of photochemically produced radical ions are diverse (*19*), and they include unimolecular reactions such as rearrangements and geometric or valence isomerizations. Reactions that reflect the radical nature of the intermediates include olefin dimerizations and mixed additions via the radical cation. Other reactions reflect the ionic nature of the intermediates, such as nucleophilic additions to the radical cation and proton transfer to the radical anion. In addition, photochemical electron-transfer reactions carried out in the presence of molecular oxygen give a variety of oxygenation products.

Examples of photoinduced electron-transfer isomerizations are the geometric (*cis-trans*) isomerization (*27*) of olefins and of small-ring compounds such as cyclopropanes and cyclobutanes, and the valence isomerization of quadricyclane to norbornadiene (*28*) and of hexamethyl "Dewar benzene" to hexamethylbenzene (*29*). These reactions proceed either directly, via the radical cation of the reactant, or indirectly, via the triplet state formed by recombination of the radical ion pair. The dimerization of olefins induced by electron transfer can occur via either route, as in the isomerization reactions.

A general mechanism for the direct dimerization via the radical cation is given in Fig. 4 (*30*). The radical cation of the olefin, $D^{\cdot+}$, adds to a neutral molecule, D, to give a dimeric radical cation, D^{+}–$D^{\cdot}$, which cyclizes to $D_2^{\cdot+}$. Electron transfer to $D_2^{\cdot+}$ yields the dimer. In the last step, the electron transferred to $D_2^{\cdot+}$ is likely to be from the monomer, D, which constitutes a chain reaction resulting in high quantum yields.

The head-to-head regiochemistry of the cyclobutane product is readily explained in terms of addition to give the most stable 1,4-radical cation intermediate, D^+–$D^\cdot$. Support for the reversibility of the steps comes from the cleavage of the cyclobutanes that is induced by electron transfer and from their *cis-trans* isomerization.

Mixed additions are analogous to the homodimerizations discussed above. These reactions, in which the radical cation of an olefin or an acetylene ($D^{+\cdot}$) adds to a different, neutral molecule (D'), broaden the scope and potential synthetic utility of electron-transfer sensitization (*25*).

Addition of nucleophiles (*31*), such as water, alcohols, carboxylic acids, or cyanide, to photochemically generated radical cations of olefins or strained-ring compounds is a common reaction. However, it is not a general reaction because the reactivities of such radical cations vary greatly. For example, the addition of methanol to the radical cation of diphenylethylene is almost diffusion controlled; however, the rate constant for its addition to 1,1-dimethylindene is only $\sim 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, and the rate constant for its addition to the methoxy- and dimethylamino-substituted analogs of diphenylethylene, where the positive charge is likely to be much more delocalized, is negligibly small (*32*).

Proton transfer from the radical cation to the radical anion is another important reaction in electron-transfer photochemistry. It plays a major role in the reactions of excited ketones (acceptor) with amines (donor), where electron transfer followed by proton transfer gives a pair of free radicals (*23*). Some of the most efficient initiators for radical polymerization are based on this chemistry. A variety of reactions typical of free radicals, such as coupling and disproportionation, can occur because of proton transfer.

Photosensitized electron-transfer reactions performed in the presence of oxygen may yield oxygenated products. Superoxide, $O_2^{-\cdot}$, can be formed through a secondary electron transfer from the acceptor radical anion to O_2. Addition of $O_2^{-\cdot}$ to the radical cations of olefins predominantly yields ketones; addition to the radical cations of acetylenes, 1,2-diketones; and to the radical cations of dienes, cyclic peroxides (*33*).

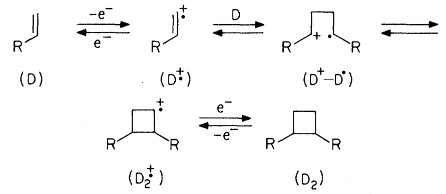

Fig. 4. Mechanism of olefin dimerization via the radical cation.

Several other mechanisms for electron-transfer photooxygenations have been identified. Usually the radical cation of an olefin reacts slowly with molecular oxygen and only if competing reactions can be suppressed. Many of the reactions discussed above yield intermediates that can react efficiently with O_2. These intermediates are free radicals or have a pronounced free-radical character. For example, the radical obtained by nucleophilic addition of an alcohol to an olefin radical cation reacts with O_2, ultimately giving an alkoxy, hydroperoxy derivative of the olefin (*34*). Oxygenation products can also result from addition of oxygen to the radical formed by deprotonation of a radical cation (*35*). 1,4-Radical cations obtained from dimerization of an olefin radical cation or from cleavage of a cyclobutane will react with O_2 to give 1,2-dioxanes if the rate of their cyclization is not too competitive (*19*, *36*).

Singlet oxygen may also be formed by electron transfer from $O_2^{-\cdot}$ to $D^{+\cdot}$ (*37*). Singlet oxygen from such a recombination reacts analogously to that from conventional energy-transfer sensitization.

Electron-transfer oxygenations are being investigated extensively; their diversity may well rival that of the well-studied singlet-oxygen chemistry.

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