Photoionization Processes in Organic Solids and Fluids

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The utilization of electromagnetic stimuli at the molecular level is of great practical significance. In many organisms, the photon transduction which occurs in the eye serves as a primary source of information about the surroundings. Nonphysiological photon transducers vary in nature from photographic films to image intensifiers.

In many naturally occurring photoprocesses and in some photodevices, no charge separation is necessary for response to the light stimulus. However, the absorption of a quantum of light often leads indirectly through a sequence of short-lived excited states or directly by electron ejection to the separation of oppositely charged particles. The charge separation may be manifested as a voltage rise, as a current rise, or as production of oxidant and reductant and their ensuing reactions.

In this Account, the term photoionization will be used to encompass charge separation resulting from photostimuli. However, those ionizations which result because an excited state is a stronger or weaker acid than the ground state are not included. The liberation of free mobile charge will be viewed as a triggering action which may initiate further chemical reaction or which may initiate a sequence of events resulting in no permanent chemical alterations.

Development of a latent image and the solar bleaching of dyes are examples of permanent chemical changes initiated by a photoionizing trigger event. Electron emission from a photocathode, excitation of an electron from valence band to conduction band in photoconducting materials, and charging of barrier layer interfaces are examples of nonreactive photoionization.

The specific topics of this Account are a few photoionizations in which mobile charges are liberated in crystals of aromatic hydrocarbons or in common fluids used as spectroscopic solvents. The ionizations discussed are initiated by light absorbed in the visible to near-ultraviolet region not exceeding 5.9 eV (2100 Å) in photon energy. Most of the ionizations discussed are excited with photons of less than 3.6-eV energy, and some of the processes require multiphoton absorption for their initiation. Attention will be given to the modes of excitation and to the yields of separated charge which may result. The ionization phenomena, whether occurring in solids or liquids, have many kinetic features in common but differ in the modes of energy transport to the reaction center and in the modes of charge transport away from the reaction center. Most of the reactions discussed are very fast, being limited by excitation diffusivity, molecular diffusivity, or charge mobility. In dielectric media of low mobile charge content the photoreleased charge can be detected with great sensitivity through measurement of transient photocurrents of nanosecond and longer duration.

Electron Ejection in Gas Phase

A brief outline concerning photoionization in the gas phase is useful for perspective and for illustrating notation. Among the simplest photoionizations is electron ejection from an isolated molecule (eq 1). $^1M_0$

$$^1M_0 + h\nu_1 \longrightarrow {}^2M_0^+ (E_i) + e^- (E_e) \quad (1)$$

represents a molecule in its ground electronic state of unit spin multiplicity. If the product ion is in its lowest vibrational and electronic state, $E_i = 0$. If also the ejected electron has no kinetic energy relative to the ion–electron center of mass, $E_e = 0$, and the energy of transition is called the first ionization potential, IP. For singlet molecular ground states the ionic species is of necessity a doublet, $^2M_0^+$.

First ionization potentials often are 6 eV (2000 Å) and larger, and as a result direct photoelectron ejection is of little consequence in condensed organic media except within the small absorption depth near the surface of solids and fluids or as produced by penetrating high-energy radiation such as X-rays and γ rays.

Electron ejection by light with $h\nu_1 <$ IP is possible. One possibility is a tandem two-photon process represented in eq 2 and 3. M* is an excited state of M

$$^1M_0 + h\nu_1 \longrightarrow M^* (E_*, \tau) \quad (2)$$

$$M^* + h\nu_2 \longrightarrow {}^2M^- (E_i) + e^- (E_e) \quad (3)$$

with lifetime τ and energy E_*. The energy criterion for electron ejection is $h\nu_1 + h\nu_2 \geq$ IP. If, prior to the arrival of $h\nu_2$, M* undergoes energy loss but remains in some electronically excited state, then the energy criterion for electron ejection is $h\nu_1 + h\nu_2 \geq (E_* - \Delta E) + h\nu_2 \geq$ IP, in which ΔE is the amount of energy lost. M* in eq 3 then represents the relaxed excited state. In condensed phases the ionization potential requirement is reduced from that required under vacuum by an amount of order $[e^2/r][(\kappa - 1)/\kappa]$, in which r is the average radii of charged products and κ the optical dielectric constant.

Biphotonic excitations such as reactions 2 and 3 are intrinsically less probable than are monophotonic excitations. Thus, if biphotonic ionization is to be a significant source of free charge, there is required larger photon fluxes than for monophotonic processes or there is required long intermediate lifetime in order to permit accumulation of excited intermediate population.

Charge Separation Resulting from One Excited State in Fluids, Solids, and Interfaces

A number of monophotonic ionizations involve the reactions of an electronically excited molecule with an unexcited molecule to form an excited complex or involve the excitation of an already existing complex. In either case, if the resulting excited complex possesses sufficient charge-transfer character, then under suitable conditions of solvent dielectric constant the excited complex may dissociate into a pair of ions having strong oxidizing and reducing ability. The dissociation of excited complex into ions is in competition with light emission and with other means of decay. The reaction scheme given in eq 4, 5, and 6 is a minimum frame for description of the steps leading to charge separation in fluids.

$$^1M_0 + h\nu_1 \longrightarrow {}^1M_1(\tau_s) \quad (4)$$

$$^1M_1 + {}^1N_0 \longrightarrow {}^1(M^{\pm}N^{\mp})^* \quad (5)$$

$$^1(M^{\pm}N^{\mp})^* \longrightarrow M^{\pm} + N^{\mp} \quad (6)$$

An excited singlet state such as $^1M_1$ may decay by fluorescence and/or by nonradiative processes. If the ionization processes are to be competitive with all channels of $^1M_1$ decay, then the concentration of unexcited reaction partner, $^1N_0$, must be large enough to allow molecular diffusive motion to form an electronically excited double molecule, $^1(M^{\pm}N^{\mp})^*$, during the lifetime of $^1M_1$. The specific rate of process 5 is diffusion limited, and in many fluids of order $k \simeq 10^{10}$ M^{-1} sec^{-1}. Therefore a competitive concentration of unexcited reactant is $[^1N_0] = (k\tau_s)^{-1} \simeq 10^{-2}$ M.

The investigations of Weller and coworkers[1] have illustrated the energy limitations required for these type processes as well as demonstrated many of the kinetic details involved. Weller's results were primarily obtained from measurement of photon emission intensity and wavelength structure of $^1M_1$ and $^1(M^{\pm}N^{\mp})^*$, from determination of the functional dependence of the emissions upon the concentrations of M and N, and obtained from the dependence of the emissions on medium dielectric constant. The essential results are: (1) the fluorescence of $^1M_1$ is quenched by N; (2) the excited complex always emits to the red of $^1M_1$; (3) the excited complex emission is strongest in media of low dielectric constant and decreases as dielectric constant increases; (4) the optical absorption of the product radical ions $M^{\pm}$ or $N^{\mp}$ have been obtained. Examples are obtained with M and N selected from aromatic hydrocarbons and anilines as well as other reaction pairs.[1]

Either M or N may be the electron donor or acceptor independent of which molecule has been excited. The acceptor will be that member of the pair for which (IP + EA) is greatest. IP is the ionization potential and EA is the electron affinity of the ground-state molecule. M and N may be the same molecule.[2] Whether M and N are the same or different, the nondissipated photon energy is stored in the ions of large oxidizing and reducing ability which are set free.

The formation of ground-state charge-transfer complex is widely recognized.[3] The charge-transfer char-

$$^1M_0 + {}^1N_0 \longrightarrow {}^1(M^{\pm}N^{\mp})_0 \quad (7)$$

acter of a complex, $^1(M^{\pm}N^{\mp})_0$, may be too small to permit significant dissociation into ions in any medium, even those of large dielectric constant; however, the charge-transfer character of an excited state of the

$$^1(M^{\pm}N^{\mp})_0 + h\nu_1 \longrightarrow {}^1(M^{\pm}N^{\mp})^* \quad (8)$$

complex may be larger and permit dissociation into ions or permit transfer of charge to still a different acceptor. Ilten and Calvin[4] have shown the excited state of a preformed complex between tetrahydrofuran and tetracyanoethylene to cause ion release. Perhaps such a preformed complex between flavin and chlorophyll molecules in special locations within the subcellular structure form the photobleachable P700 in green plants.[5] Photoenergy utilization by preformed complexes may be more efficient than formation of the excited complex from $^1M_1$ because the channels for $^1M_1$ decay are bypassed.

Preformed complexes in interfacial regions have been shown to be effective in enhancing charge injection into solids. Excitation of the charge-transfer complex formed at the interface between aqueous I_3^- and single-crystal anthracene is an example.[6] In this case the molecular crystal is the donor, but the cation radical does not form as a free charged particle. In its place a hole is injected into the valence band of the crystal. Such holes have relatively large mobilities ($\mu_{hole} \simeq 1$ cm^2 V^{-1} sec^{-1}; $\mu_{pos\ ion} \simeq 10^{-4}$ cm^2 V^{-1} sec^{-1}) and in the presence of electric fields currents may be passed through the crystal. Hole injection from one crystal face must be accompanied by hole discharge at the opposite face. It has been speculated that hole discharge at an aqueous–anthracene interface may lead to O_2 evolution;[6] however, this failed to be the case at least with anthracene. Hole discharge at the anthracene–aqueous face resulted in O_2 consumption and anthraquinone formation.[7] Alkali metal–mercury amalgam electrodes in contact with molecular crystals of the aromatic hydrocarbon variety form ground-state charge-transfer complexes which can be photodissociated with injection of electrons into conduction bands of the crystals.[8]

(1) A. Weller in "Fifth Nobel Symposium—Fast Reactions and Primary Processes in Chemical Kinetics," Interscience, New York, N. Y., 1967.

(2) If M and N are the same, then the excited complex has little electronic contribution to its dipole moment; however, its charge-transfer character may be quite large.

(3) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Göttingen, 1961; R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969.

(4) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

(5) J. H. Wang, *Accounts Chem. Res.*, **3**, 90 (1970).

(6) M. Pope and H. Kallman, "Symposium on Electrical Conductivity in Organic Solids," Interscience, New York, N. Y., 1958; M. Pope, H. Kallmann, A. Chen, and P. Gordon, *J. Chem. Phys.*, **36**, 2486 (1962).

(7) R. C. Jarnagin, J. Gilliland, Jr., J. S. Kim, and M. Silver, *ibid.*, **39**, 573 (1963).

(8) A. Many, J. Levinson, and I. Teucher, *Mol. Cryst.*, **5**, 273 (1969).

The factors controlling the formation of ground-state or of excited complex at interfaces or in homogeneous fluids are similar; however, factors controlling dissociation of the excited complex are quite different. In fluids the role of dielectric constant is paramount. Within the bulk of solids or at solid interfaces the electronic structure of the solid controls the energy of the valence bands and conduction bands and determines the injection characteristics. In addition to band considerations the charge injection into a solid is strongly limited by formation of space charge within the crystal.

Charge Separation Resulting from Two Excited States in Fluids and Solids

Several biphotonic ionizations have been examined in both solids and fluids. The transient products of these ionizations could initiate reactions leading to permanent chemical changes. Free electron–hole pairs have been liberated as a result of the bimolecular collision of a pair of singlet excitons in crystalline anthracene[9a] and naphthalene.[9b] Since the excitons are the products of single photon absorption, then the free charge generation is a biphotonic process. In eq 9a, $^1M_1$ is the mobile singlet excitation. Collisions destroying the singlets occur with a specific rate of

$$^1M_1 + {}^1M_1 \longrightarrow X^* \quad (9a)$$

$$X^* \longrightarrow e^- \text{ (conduction band)} + h^+ \text{ (valence band)} \quad (9b)$$

about $2 \times 10^{13}\ M^{-1}\ \text{sec}^{-1}$ and $1 \times 10^{12}\ M^{-1}\ \text{sec}^{-1}$ in anthracene[9c] and naphthalene,[9b] respectively. A fraction, η, of these interactions result in free charge separation. The specific rate for free charge generation has been estimated as $2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ (anthracene[9a,b]) and $1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ (naphthalene[9c]), so that $\eta \leq 10^{-4}$ and includes the probability for process 9b as well as other charge escape factors.

In the special case of crystalline anthracene the diffusivity of singlet exciton allows the excitation to sample lattice sites in a volume whose radius is of order 1000 Å during its lifetime of about 10 nsec. The exciton diffusivity and lifetime is strongly dependent on crystal perfection. In noncrystalline media the excitation may be transported by a Förster[10] mechanism which does not depend on lattice periodicity. The excited encounter complex X* has been interpreted as two excited singlets on adjacent lattice sites.[11] The special geometry imposed by the crystal is not a necessary condition for interaction; in fact, other intermolecular conformations may be more favorable for charge separation and result in larger values of η. Although the encounter complex X* has not been observed by emission it is analogous in concept to $^1(M^{\mp}N^{\mp})_1$ which has been observed in some situations.[1]

Other examples of bimolecular interaction between excited states are provided by encounter of a pair of triplet-state excitations which allow the formation of an excited complex. Such a complex has been recognized to lead to an excited singlet state of one of the members of the encounter pair and results in a lingering fluorescence from solids, liquids, and gases which ultimately decays with a characteristic time comparable to the triplet lifetime.[12] The triplet–triplet encounter complex may also lead to ion formation, as demonstrated by the rise of a photocurrent following an impulsive excitation. The rise time of the photocurrent was comparable to the triplet lifetime and could be used to estimate triplet lifetime[13] because the triplet decay was controlled by the usual first-order kinetics while ion generation resulted from a smaller bimolecular triplet decay term.

Table I
Triplet–Triplet Ionization

(1)	$^3M_1 + {}^3M_1 \rightarrow (MM)^{*a}$	$k_1[^3M_1]^2$	
(2)	$^3M_1 \rightarrow {}^1M_0$	$k_2[^3M_1]$	
(3)	$(MM^*) \rightarrow (MM)'^b$	$k_3[(MM)^*]$	$\xi^d = \dfrac{k_3}{k_3 + k_4}$
(4)	$(MM^*) \rightarrow$ uncharged states[c]	$k_4[(MM)^*]$	
(5)	$(MM)' \rightarrow {}^2M^+ + {}^2M^-$	$k_5[(MM)']$	$\eta^d = \dfrac{k_5}{k_5 + k_6}$
(6)	$(MM)' \rightarrow$ uncharged states[c]	$k_6[(MM)']$	
(7)	$^2M^+ + {}^2M^- \rightarrow (MM)''^e$	$k_7[^2M^+]$	
(8)	$(MM)'' \rightarrow$ uncharged states[c]		

[a] $(MM)^*$ = a double molecule excited encounter complex. [b] $(MM)'$ = a double molecule excited complex relaxed into conformation of large charge-transfer character. [c] For many substances the uncharged states are or lead to the parent molecules, so that no net chemical change has occurred. The possible processes of step 4 include the reverse of step 1. [d] The specific rates k_1, k_2, k_7 and product $\xi\eta$ have been measured. k_1 and k_7 are diffusion limited. [e] $(MM)''$ = a double molecule complex formed from fully solvated ions. $(MM)''$ may be electronically excited.

In gas-phase or dilute solutions motion of the triplet excitation occurs by molecular diffusion while in crystals motion occurs by an exciton migration dependent on exchange interaction between adjacent excited triplet state and ground singlet state. In some pure fluids such as naphthalene the triplet exciton diffusivity exceeds the molecular diffusivity by 10 to 100 times,[14] presumably because there may be larger probability than in a crystal for an unexcited neighbor to be in an intermolecular conformation which optimizes exchange interactions. In media of low dielectric constant the delayed fluorescence path usually dominates ionization.

Ion Escape Probability

The factors concerned in ionization following a trip-

(9) (a) M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, *Phys. Rev. Lett.*, **10**, 12 (1963); (b) C. L. Braun and G. M. Dobbs, *J. Chem. Phys.*, **53**, 2718 (1970); (c) J. Jortner, *Phys. Rev. Lett.*, **20**, 244 (1968). The last article compares a number of possible singlet–singlet interactions, especially autoionization of X*.

(10) Th. Förster, *Z. Naturforsch, A*, **4**, 321 (1949).

(11) S. I. Choi and S. A. Rice, *Phys. Rev. Lett.*, **8**, 410 (1962).

(12) C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc., Ser. A*, **269**, 574 (1962); B. Stevens, M. S. Walker, and E. Hutton, *Proc. Chem. Soc. London*, 62 (1963); R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, *Phys. Rev. Lett.*, **10**, 400 (1963).

(13) A. Kawada and R. C. Jarnagin, *J. Chem. Phys.*, **44**, 1919 (1966); L. P. Gary, K. deGroot, and R. C. Jarnagin, *ibid.*, **49**, 1577 (1968).

(14) P. Avakian and R. F. Merrifield, *Mol. Cryst.*, **5**, 37 (1968); H. Baessler, *J. Chem. Phys.*, **49**, 5198 (1968); P. Holzman and R. C. Jarnagin, *ibid.*, **51**, 2251 (1969).

Table II
Triplet to Free Ion Probabilities (25°)[g]

Solute	Solvent	Dielectric constant, κ	R_c, Å	$\frac{[^2M^+]}{[^3M_1]}$	$\xi\eta$	η calcd[f]
Anthracene[c]	Hexane	1.89	296	$<10^{-5}$ [a]	$<10^{-4}$ [a]	1.3×10^{-13}
Phenanthrene[b]	Methyltetrahydrofuran	6.2	90	0.0005	1.9×10^{-4}	4.5×10^{-4}
Phenanthrene	Tetrahydrofuran	7.4	76	0.0027	1.9×10^{-3}	1.9×10^{-3}
Naphthalene	THF	7.4	76	0.0024	1.4×10^{-2}	1.9×10^{-3}
Anthracene	THF	7.4	76	0.0071	1.4×10^{-2}	1.9×10^{-3}
Pyrene	THF	7.4	76	0.0041	1.3×10^{-3}	1.9×10^{-3}
Phenanthrene[b]	C_7H_6CN	26.5	21	0.100	6.4[d]	0.16
Phenanthrene[b]	CH_3CN	36.7	15	0.096	0.41	0.24
Tetracene[e]	THF	7.4	76	$<10^{-5}$ [a]	$<10^{-4}$ [a]	1.9×10^{-3}
Tetracene[e]	CH_3CN	36.7	15	$<10^{-5}$ [a]	$<10^{-4}$ [a]	0.24

[a] Photocurrent signal was below minimum detectable limits represented by these figures. [b] Photocurrent due to ions and optical absorption of $^3M_1$ was obtained simultaneously; others were done on separate exciting flashes. [c] Similar results were obtained for anthracene in cyclohexane and for naphthalene or phenanthrene in hexane and cyclohexane. [d] Benzonitrile may be an adequate electron acceptor so as to allow electron transfer through several solvent molecules. [e] The triplet populations in these cases were at least 25 times larger than in the others. [f] The value of R_0 was 9 Å. [g] Data from ref 13.

let–triplet encounter in fluids are similar to those for dissociation of excited complexes formed in fluids by any means and are presented as illustration. A mechanism consistent with the experimental results is given in Table I. In Table II are given values for the ratio of free ion concentration observed at the maximum of a photocurrent transient to the initial concentration of $^3M_1$ as formed by a brief intense light flash. These ratios do not represent free ion yield. An output to input yield is not meaningful because the formation of free ions is biphotonic and the ion to triplet ratio is intensity dependent. Also included in Table II are experimental values for the probability that a triplet–triplet encounter results in a pair of free ions, $\xi\eta$. This probability is the important quantity for biphotonic encounters.

The term free ions or free charges is used in the sense free of the Coulomb field of its countercharge. Heuristically this may be described in terms of a relatively long Coulomb range. A pair of oppositely charged particles separated by a distance less than $R_c = e^2/\kappa kT$ do not contribute to a steady current but behave as an orientable dipole, although they may contribute to the optical absorption of the radical ions and to their chemical reactivity. Using the Coulomb range in the above sense and the Einstein relation between diffusion constant and electric mobility allows the familiar diffusion-limited specific rates to be transformed into those in which R_0, the short range of interaction between uncharged molecules, is replaced by R_c or by R_c and a Boltzmann factor. The limiting formulas are listed in Table III. In solids similar forms prevail with replacement of molecular or ion diffusivity by exciton diffusion constant or hole and electron mobility.

Using the results contained in Table III allows estimation of the probability for dissociation into free charges, η. From Table II it is seen that the experimental values of $\xi\eta$ are roughly paralleled by the calculated η values and that, with the exception of tetracene, ξ must be near unity for the hydrocarbons tested.

Table III
Convenient Diffusion-Limited Specific Rates

	$M_a + M_b \rightarrow Z$
Short range	$k = 4\pi(D_a + D_b)R_0$
Long range	$k = 4\pi(\mu_+ + \mu_-)(k_BT/e)R_c$
	$Z \rightarrow M_a^{\mp} + M_b^{\pm}$
Short range	$k = 4\pi(D_a + D_b)R_0/V$
Long range	$k = 4\pi(\mu_+ + \mu_-)(e/V)\exp(-R_c/R_0)$
	$V = (4/3)\pi R_0^3$; $R_C = e^2/\kappa k_B T$

$$\eta = [1 + (R_0/R_c)\exp(+R_c/R_0)]^{-1} \simeq (R_c/R_0)\exp(-R_c/R_0) \quad (10)$$

The quantity R_0 which enters into the probability for escape from (MM)′ to free charges is the distance between the charged components at the start of their thermal motion to freedom; *i.e.*, the short-range interaction of step 1 as altered by the relaxation of step 3 illustrated in Table I. An R_0 value of 9 Å has been found for the excited complex formed from two phenanthrene triplets,[13] while Weller[1] finds 7 Å for the distance separating the components for $^1(M^{\pm}N^{\mp})^*$ formed from aromatic hydrocarbon and diethylaniline. The value for phenanthrene is more than twice the average hard sphere radius of a pair of phenanthrene molecules of about 5.4 Å. For any solute–solvent system, the complete change from (MM)′ to free ions occurs when the ions no longer share a volume $(4/3)\pi R_c^3$. Within the volume $(4/3)\pi R_0^3$ fast relaxation of (MM)* to a variety of excited conformational complexes may occur. One of these excited complexes is (MM)′, whose energy is near $(E_{ions} - e^2/\kappa R_0) \leq 2E_T$. The relaxation of (MM)* to (MM)′ must compete with eq 4 and must be fast compared to about 10^{-10} sec as obtained from the second equation of Table III, using $D_a = D_b = 2 \times 10^{-5}$ cm² sec^{-1} and $R_0 = 9$ Å. (MM)′ is probably that state of the conformationally

Table IV
Selected Mobilities[a]

Medium (25°)	Carrier	Mobility, $cm^2\ V^{-1}\ sec^{-1}$ [h]
Liquid Ar (at triple point, 87°K)	e^-	520[g]
Germanium (intrinsic crystal)	e^-	93
Tetramethylsilane	e^-	93[b,c]
Neopentane	e^-	55[b]
Hexamethyldisilane	e^-	20[c]
2,2-Dimethylbutane	e^-	10[b]
2-Methylbutene-2	e^-	3.6[d]
Tetraethylsilane	e^-	0.5[c]
Hexane	e^-	0.1[b,e]
Water	e_{aq}^-	0.0018[f]
Tetramethylsilane	$^2T^-$	0.0014[b]
Tetramethylsilane	$^2TMPD^+$	0.0012[c]

[a] In hydrocarbon-like fluids the values in the references below[b,d,e] are most reliable, having been determined from a transit time measurement. The relative values in the silane series are more reliable than their magnitude. [b] W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, **52**, 4788 (1970). [c] Reference 19. [d] With the permission of H. T. Davis (to be published), L. D. Schmidt, and H. T. Davis. [e] R. M. Minday, L. D. Schmidt, and H. T. Davis, *J. Chem. Phys.*, **50**, 1473 (1969). [f] K. H. Schmidt and W. L. Buck, *Science*, **50**, 70 (1966). [g] J. L. Jahnke, L. Meyer, and S. A. Rice, *Phys. Rev.*, **3**, 734 (1971). [h] To convert to associated diffusion constant multiply by 0.026 V at 25°.

relaxed states of (MM)* which introduces maximum charge-transfer character. Since ξ is near unity for some hydrocarbons, then the rate of relaxation is not significantly limiting. (MM)′ can dissociate into ions or neutral excited states or radiate. An approximate upper limit to k_5^{-1} can be estimated in several ways. The experimental lifetime of anthracene sandwich excimer in rigid matrix is 225 nsec, while that for anthracene–diethylaniline exciplex in fluid toluene is 100 nsec. Thus k_6^{-1} is of the order of 100 nsec, and for effective competition k_5^{-1} must be smaller. Using the second equation of Table IV, $R_0 = 9$ Å, $\kappa = 7.4$, and $\mu_+ = \mu_- = 4 \times 10^{-4}$ cm² V sec^{-1}, then $k_5^{-1} = 70$ nsec. From either viewpoint $k_5^{-1} < 100$ nsec.

The failure to observe ions from tetracene in either tetrahydrofuran or acetonitrile in which η was large must be placed on a small value of ξ. This follows because the energetics of tetracene triplet are favorable for ion formation by several tenths of a volt, because transient absorption demonstrated that large triplet concentration was present and because the triplets disappear in part by second-order processes.

Observed free ion to triplet ratios of about 10% are possible in fluids of dielectric constant greater than about 15. Molecules with singlet to triplet yields of about 0.1 or greater may produce a reasonable density of free ions by a bimolecular triplet mechanism. Exceptionally high light intensities need not be available. If the system or a small region of a composite system such as a thin film or micellular organizate will support triplet lifetime of a few hundred microseconds, then the integration effect of a steady light can produce small but catalytically significant densities of radical ions. Even if free ion production is negligible, ions within the Coulomb volume may be expected to react chemically as though they were free.

Electron Ejection within Solids and Fluids

Absorption of a second photon by a molecule during the lifetime of one of its excited states can result in the ejection of an electron, as indicated in conjunction with eq 3. The intramolecular details of the ejection can proceed in either of two ways: by a direct transi-

$$M^* + h\nu_2 \longrightarrow 2M^+ + e^- (E_e \geq 0) \qquad (11)$$

tion to a continuum state or by an indirect transition *via* a bound state imbedded in the continuum. If the terminal states in eq 11–13 are nearly isoenergetic, then

$$M^* + h\nu_2 \longrightarrow M^{**} \qquad (E^{**} \geq IP) \qquad (12)$$

$$M^{**} \longrightarrow {}^2M^+ + e^- (E_e \geq 0) \text{ (autoionization)} \qquad (13)$$

a complete description should be one superimposing all three states; however, because of small overlap between the components or because of small energy differences between them it is often a useful approach to consider the components as discrete. Taking the states as discrete, then the absorptive transitions 11 and 12 must be considered as competitive and the transition of 13 must be considered in competition with all nonejecting channels of decay of M** (see ref 9c). The yield of separated charge is fixed by the intramolecular probability for each transition pattern, eq 11 or 12, 13, times the extramolecular probability for the charge to escape from the vicinity of $^2M^+$. The extramolecular probability may be dominant. Equation 14 illustrates the escape problem.

$$^2M^+ (E_i = {}^3/_2kT) + e^- (E_e > {}^3/_2kT;\ R \approx 3\ \text{Å}) \longrightarrow {}^2M^+ (E_i = {}^3/_2kT) + e^- (E_e = {}^3/_2kT;\ R) \qquad (14)$$

Electron-ejecting transitions result in terminal states in which the electron is not localized and in which the electron may be "hot" by a few volts of kinetic energy. In condensed media inelastic scattering is frequent, so that the departing electron may be thermalized in a distance much less than the Coulomb range. If the electron is to become free its subsequent escape must be driven by the thermal field. If the initial kinetic energy of the electron was in excess of that for electronic transitions of the solid or fluid, then inelastic losses corresponding to these transitions will occur. Ultimately the electron energy will fall into the range of vibrational and librational transitions and more frequent losses in smaller increments must occur for thermalization to be complete. Only the latter loss modes are likely to be significant for an ejection energy less than the lowest electronic transition of the medium. The identity of the effective loss modes is unknown, although they have been considered sufficiently efficient that freeing of charge by electron ejection through absorption of visible or near-ultraviolet photons has been neglected as a photochemical trigger.

During a very short time following the ejecting transition, the hot electron will come into thermal equilibrium with the lattice (order 10^{-12} sec). Then during an interval it has an existence as an *unbound nonsolvated species* which is contained within the medium by electronic polarization responding at optical frequencies. At some time after thermalization the electron may be localized through solvation by the medium; however, in polar media such as alcohols and water the thermalization and solvation processes are probably synonomous, occurring during a period on the order of molecular relaxation times of the medium. The result is a localized solvated electron or polaron which is subject to further fast reactions. In nonpolar hydrocarbon-like fluids near room temperature solvation has an unclear meaning since the polaron binding energy is comparable to kT. There will also occur electron localization by formation of specific ionic species in both solids and fluids. The latter times are dependent on concentration of the localizing sites. The two general modes of localization will be denoted as trapping.

The trapping phenomena often dominate the electron behavior. Radiolysis and photolysis studies in various media but especially in aqueous and ammoniacal media have clearly identified the solvated electron and measured many of its properties,[15] but until recently the observation of the electron subsequent to localization had not been achieved. Examination of the trapped electron by magnetic and optical techniques results in information about the trapping site. An example is a recent Account in which photoejection from the previously excited triplet state of tetramethylparaphenylenediamine (TMPD) in rigid hydrocarbon matrix was discussed.[16]

Other examples of multiphotonic electron ejection from excited states are available. The effective photon capture cross section, $\epsilon' = \eta\epsilon$, being the product of the escape probability, η, with the absorption coefficient, ϵ, connecting the triplet state of crystalline anthracene to the charge ejected state, has been estimated to be $2\ M^{-1}\ \text{sec}^{-1}$ averaged over the range 4700–5500 Å. Distinction betweeen direct and autoionization was not possible.[17]

Electron ejection from singlet exciton in anthracene crystal has been identified at very high photon fluxes.[18a,b] The absorption of 6943-Å light resulted in an effective capture cross section, $\epsilon' = 60\ M^{-1}\ \text{sec}^{-1}$.[18b] Distinction between direct and autoionization was not possible.

In rigid media electrons localized in traps are immobile. Trapped electrons in fluids have mobility values similar to those of ions, while nonlocalized electrons may have mobility which is orders of magnitude larger (Table IV). Because of this large difference in mobility it has been possible to apply the sensitivity of fast transient conduction techniques to seek the untrapped electron in dielectric fluids.

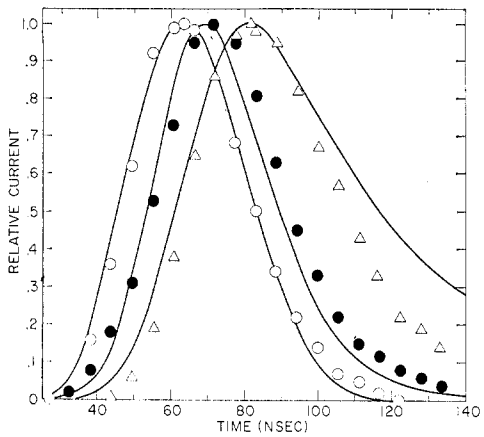

Figure 1. Relative transient photocurrent: photoejection from ^{3}TMPD by 3471-Å light. Flash peaks at 45 nsec and terminates at 90 nsec. Triplet life = 30 μsec. Maximum dose 2.4×10^{16} photons cm^{-2}. ———, calculated from ref 19; ○, experimental 100% dose; ●, experimental 17% dose; △, experimental 3% dose.

In Figure 1 are shown experimental and calculated transient photocurrents resulting from electron ejection from ^{3}TMPD in tetramethylsilane at 25°.[19] The current for the first few hundred nanoseconds is entirely due to high-mobility electrons. The current after the first few hundred nanoseconds is due primarily to localized electrons and is slowly decreasing by recombination (eq 17). The rapid current decay is due to localization of mobile electrons to become negative species of smaller mobilities (eq 16) and at the higher intensities to electron–ion recombination (eq 15). The

$$e^- \text{ (thermal)} + {}^2\text{TMPD}^+ \longrightarrow \text{TMPD (may be excited)} \quad (15)$$

$$e^- \text{ (thermal)} + \text{T} \longrightarrow {}^2\text{T}^- \text{ (trapping by any means)} \quad (16)$$

$${}^2\text{TMPD}^+ + {}^2\text{T}^- \longrightarrow \text{TMPD} + \text{T (either may be excited)} \quad (17)$$

$$i(t) \propto (\mu_e[e^-] + \mu_+[{}^2\text{TMPD}^+] + \mu_-[{}^2\text{T}^-]) \quad (18)$$

ratio of specific rates for recombination of ion and electron to that for recombination between ion and trapped electron is $(\mu_e + \mu_+)/(\mu_- + \mu_+)$. To within an order of magnitude the thermal electron mobility is given by the ratio of the observed current at peak to that at about 1 μ sec.

Electron Escape Probability

The probability for obtaining free charge once the initial charge pair is formed is similar to that for the separation of excited molecular complexes into ions. Equation 10 and related escape probabilities are independent of the rate of charge motion. Ion separation

(15) E. J. Hart, *Accounts Chem. Res.*, **2**, 161 (1969).
(16) A. C. Albrecht, *ibid.*, **3**, 238 (1970).
(17) P. Holzman, R. Morris, R. C. Jarnagin, and M. Silver, *Phys. Rev. Lett.*, **19**, 506 (1967).
(18) (a) R. G. Kepler, *ibid.*, **18**, 951 (1967); (b) E. Courtens, A. Bergman, and J. Jortner, *Phys. Rev.*, **156**, 948 (1967). The ionization was $^1\text{M}_1 + h\nu_3 \rightarrow e^- + h^+$. $^1\text{M}_1$ was generated by simultaneous two-photon absorption, $^1\text{M}_0 + 2h\nu_1 \rightarrow {}^1\text{M}_1$, so that the overall ionization was a three-photon process.
(19) S. Takeda, N. Houser, and R. C. Jarnagin, *J. Chem. Phys.*, **54**, 3195 (1971).

Table V
Yield of Free Electrons

Distance parameter, Å	Photon energy, E, eV	Yield, 25°	Activation energy, eV Obsd	Calcd
	TMPD–TMS			
$\sigma = 55\sqrt{E - 4.7}$[a]	4.77	2.3×10^{-5}	0.16	0.16
	4.96	3.3×10^{-4}	0.12	0.12
	5.17	3.0×10^{-3}	0.12	0.09
	5.39	1.0×10^{-2}	0.10	0.07
	TMPD–Hexane			
$\sigma = 16\sqrt{E - 4.7}$[a]	5.06	8.0×10^{-8}	0.34	0.26
	5.28	2.0×10^{-6}	0.27	0.20
	5.64	3.2×10^{-5}	0.18	0.16
	5.90	4.0×10^{-5}	0.17	0.16
	Anthracene (crystal)			
$R_0 = 80$[b]	4.2		0.060	
91[b]	4.68		0.053	
117[b]	5.28		0.041	
141[b]	5.9		0.034	

[a] $D(R) = (4/\sigma^3\sqrt{\pi})R^2 \exp[-R^2/\sigma^2]$. [b] $D(R) = 4\pi R^2 \cdot (2\pi R_0^2)^{-1}\delta(R - R_0)$; ref 22.

from excited complex has each charge pair start at the same initial separation of 7 to 9 Å. In the case of cation and photoejected electron there is no single value of R_0; rather there is a distribution of values. The distribution of these values is presumably determined by relaxation of the electron, considered as an independent particle, into a thermal equilibrium with the lattice but not with the parent ion. In nonpolar media values for the separation at first thermalization as large as 100 Å have been indicated (Table V). These large values make it seem unlikely that electron escape results only from an interaction between excited molecular state and solvent, although some weak interaction is necessary to induce transition from excited molecule to independent ion–electron state. In contrast, a strong specific interaction between excited molecular state and solvent may account for forming e_{sol}^- from excited solute in water and other polar media in a manner analogous to forming ions from excited complex.

The free charge yield is determined by summing over the product of escape probability, P, and the distribution of initial thermal separations, $D(R)$. The escape probability is given by $P = [1 + (eR_c/2kT)E] \cdot \exp(-R_c/R)$[20] to powers linear in applied electric field E. The linear field dependence has been tested for ejection from ^{3}TMPD in hexane ($\kappa = 1.89$)[21] and similar fluids and for ejection from ground state in crystalline anthracene ($\kappa = 3.02$).[22] At room temperature the field-driven term for $E = 1$ kV/cm is less than 6% in hexane and less than 10% in anthracene. For sufficiently low fields the yield is then

$$\eta = \int_0^\infty D(R) \exp[-R_c/R]dR \qquad (19)$$

(20) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).
(21) N. Houser and R. C. Jarnagin, *ibid.*, **52**, 1069 (1970).
(22) R. H. Batt, C. L. Braun, and J. F. Hornig, *ibid.*, **49**, 1967 (1968).

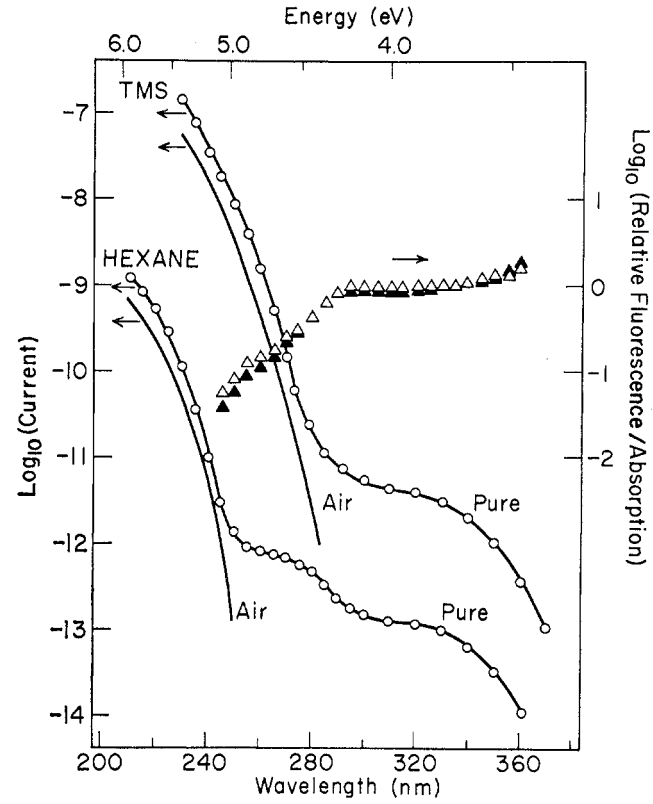

Figure 2. Biphotonic and monophotonic ionization: steady-state photocurrent normalized to 8×10^{14} photons cm^{-2} sec^{-1}. Relative fluorescence normalized to 320 nm; TMPD at 3.3×10^{-6} M; triplet life in pure solvents 37 μsec; current in amperes. See ref 19.

The yield should be unaffected by moderate trap densities. At large trap density ejection and thermalization converge in time, and the form of eq 19 should be maintained but become trap sensitive.

In the absence of severe trapping $D(R)$ may be expected to be determined by diffusive motion of the hot electron and of form $(4/\sigma^3\sqrt{\pi})R^2 \exp[-R^2/\sigma^2]$. If an autoionizing state is the ejection source, then $D(R)$ must contain the probability for process 13 and may reflect the spatial extent of the autoionizing state probability density. The latter may also be expected for an ejection from a Rydberg-like state of the donor induced by interaction with the medium.

$D(R)$ has been neither experimentally nor theoretically resolved for low-energy photoionization, although some progress is in hand for high-energy radiation.[23] Attempts toward experimental resolution of $D(R)$ are in progress. In Figure 2 is shown a montage of photocurrent *vs.* photon energy obtained under steady-state excitation. The response in the 320–380-nm range is due to the ^{3}TMPD biphotonic ionization. At higher photon energy the response is due to monophotonic ejection from TMPD ground state. The added efficiency of the monophotonic process arises because there is no limitation due to triplet lifetime, not because of significant change in $D(R)$. The addition of an O_2 trap causes quenching of ^{3}TMPD and the biphotonic

(23) A. Mozumder, *Advan. Radiat. Chem.*, **1**, 1 (1969).

contribution but has relatively little effect on the monophotonic ejection. The rise of monophotonic current contribution and the fall of relative fluorescence indicate that channels for ejecting transition are available above about 4.5 eV.

For the monophoton ejection the effective absorption coefficient for free charge ejection, $\epsilon'(\lambda)$, can be obtained from the observed current. Associating the ratio of effective cross section to optical absorption coefficient with yield allows $\eta(\lambda,T)$ to be estimated. Reasonable fits of the observed data to a gaussian $D(R)$ have been obtained, but must be more carefully examined. Some preliminary results are in Table V. The calculated activation energy was obtained by considering all the temperature dependence to be in R_c. Table V also includes results obtained on ejection from ground state of crystalline anthracene[22] for which $D(R)$ was approximated by a δ function.

Electrons ejected from donor molecules into dielectric media with initial kinetic energy in the 0–2-V range may travel to distances of 10 to 100 Å before thermalization is complete. The time required for the thermalization is apparently only a few vibrational periods. Following thermalization the electron exists as a highly mobile entity suffering scattering from density and dielectric fluctuations and after a time becomes trapped as a solvated electron or specific ionic species. The trapping time in hydrocarbon-like media of high purity has been observed in the range 50–1000 nsec. In aqueous media in which strong solvation is mandatory the trapping time appears to be in the picosecond range[24] and to occur simultaneously with thermalization; however, in these media the thermalization distance must approximate or exceed the Coulomb range and neither geminate nor free recombination is as significant as in nonpolar fluids.

One may speculate that biolayer structures may exist or thin film structures may be devised across which electrons could be ejected. The recombination of the trapped higher energy ions could then be forced to seek alternate paths. Fluids which support electron states of high mobility and containing suitable donor solutes could lead to thin-layer liquid-state devices of fast-switching characteristics.

Problems and Possibilities

Some monophotonic and biphotonic ionizations in solids and fluids have been reviewed. Parallels between ionization due to excited complex dissociation in both solids and fluids as well as parallels due to electron ejection in solids and fluids were noted. It seems likely that photochemical reactions may be found which involve the radical ions resulting from excited complex dissociation. It is also clear that even in fluids of low dielectric constant ionization by electron ejection in the near-ultraviolet can be sufficiently efficient for these processes to be considered as generators of reactive intermediates.

There are no satisfactory theories for the thermalization of low-energy electrons in fluids. Which modes of vibration and rotations are significant and which collective modes of the fluid are significant for inelastic loss processes are yet to be determined. The character of the ejecting transition has also not been determined. An even greater challenge lies in forming the mechanisms for photoliberation of charge and its transport into controllable units which mimic the supramolecular organization nature finds favorable for the control of light stimuli.

The National Science Foundation, the Advanced Research Projects Agency, and the U. S. Atomic Energy Commission have supported portions of this work.

(24) M. J. Bronskill, R. K. Wolff, and J. W. Hunt, *J. Chem. Phys.*, **53**, 4201, 4211 (1970).

Additions and Corrections

Volume 4, 1971

Paul G. Gassman: The Thermal Addition of Carbon–Carbon Multiple Bonds to Strained Carbocyclics.

Page 135. Add to reference 34: "Recent studies have shown that what appears to consist of a formal symmetry-allowed thermal $_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$ addition to **67** is a stepwise process in which the tetracyanoethylene is *not* involved in the rate-determining step: H. H. Westberg, E. N. Cain, and S. Masamune, *ibid.*, **91**, 7512 (1969)."