

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_0 . Table V also includes results obtained on ejection from ground state of crystalline anthracene²² 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 range²⁴ 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 bilayer 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)."