

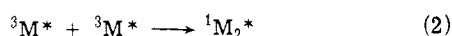
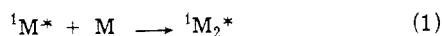
# Excimer Fluorescence of *trans*-Stilbene and Diphenylacetylene

Brian Brocklehurst,\* David C. Bull, Margaret Evans, Peter M. Scott, and Gillian Stanney<sup>1</sup>

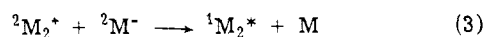
Contribution from the Department of Chemistry, The University, Sheffield, S3 7HF, England. Received September 21, 1974

**Abstract:** Excimer fluorescence from *trans*-stilbene ( $\lambda_{\max} = 430$  nm) and diphenylacetylene (390 nm) is reported. A new method of detecting labile excimers was used: emission spectra were measured on warming solutions in squalane after  $\gamma$  irradiation at 77°K. Excimers are formed by neutralization of dimer cations and are stabilized against further reaction by the high viscosity.

Excimers are normally formed from excited monomers by the diffusion-controlled reactions 1 or 2.<sup>2</sup> Some years



ago, excimer emission was observed in the thermoluminescence of solutions after irradiation with  $\gamma$ -rays in the glassy state at 77°K;<sup>3</sup> it was ascribed to the neutralization of dimer cations (reaction 3). It was clear that this reaction



might be used to detect new excimers: it has the advantages that the two molecules are already bound together, and the low temperature and the high viscosity (estimated at  $10^9$  P) of the softening glass may prevent dissociation or formation of a chemical dimer. (Processes 1 and 2 are diffusion controlled and require low viscosity.) However, the alkanes used initially as solvents (isopentane plus methylcyclohexane) are not good solvents for the larger aromatic hydrocarbons;  $\sim 10^{-2}$  molar solutions are required for strong excimer emission. After preliminary trials with *o*-terphenyl and cumene, it has been found that squalane (2,6,10,15,19,23-hexamethyltetracosane) is a good solvent for this purpose,<sup>4</sup> though its glass transition ( $\sim 180^\circ\text{K}$ ) is relatively high. The application of this method to *trans*-stilbene and diphenylacetylene is described here.

## Experimental Section

Squalane was purified by passing it down columns of activated silica gel at 80°. Zone-refined *trans*-stilbene was obtained from Aldrich Chemical Co.; diphenylacetylene was purified by vapor-phase chromatography. Solutions in high-purity silica cells were degassed on the vacuum line (a few millimeters of nitrogen was added to maintain thermal contact), immersed in liquid nitrogen and exposed to <sup>60</sup>Co  $\gamma$ -rays (dose rate  $\approx 5 \times 10^{15}$  eV g<sup>-1</sup> sec<sup>-1</sup>). Samples were transferred to an empty, precooled, silica dewar and allowed to warm up, while the emission spectrum was scanned repeatedly. Initially, an Aminco-Bowman spectrofluorimeter was used. For the final measurements, higher resolution was obtained with a Hilger D 330 monochromator (band width, 5.2 nm) and an E.M.I. 9558 photomultiplier, using a chopper, amplifier, and phase-sensitive detector. Normal fluorescence spectra and fluorescence excitation spectra were measured using the latter instrument with a xenon arc and a D330-331 Hilger double monochromator to excite the sample. Further details of the thermoluminescence experiments are given elsewhere.<sup>3,4</sup>

## Results

The thermoluminescence spectra of *trans*-stilbene are shown in Figure 1: the structural fluorescence is ascribed to the monomer, the broad band at 430 nm to the excimer. The monomer emission predominates in the early part of

the glow peak and the excimer in the later: the excimer was weaker at lower concentrations. This behavior exactly parallels that of naphthalene in alkane mixtures<sup>3</sup> and squalane;<sup>4</sup> it has been argued previously<sup>3</sup> that the early part of the glow is due to close ion pairs ( $M^+ + M^-$ ), the later to pairs further apart; the latter form dimer cations before they neutralize. (Nearly all recombination is "geminate" under these conditions.)

Preliminary experiments with other commercial samples of *trans*-stilbene showed several structured emissions in the region 380–500 nm. Similar results were obtained when zone-refined stilbene samples were irradiated for 20 min or more, or if they had been irradiated previously. These emissions were shown to be due to impurities or irradiation products by observing their photofluorescence in the glasses at 77°K: their excitation spectra were different than stilbene's. The broad band at 430 nm could not be excited in this way, either in the glass or in the liquid; concentrated solutions ( $10^{-1}$ – $10^{-2}$  molar) in methylcyclohexane, between 298 and 218°K, were tried. In low-dose experiments with zone-refined material (Figure 1) emissions of impurities, etc., were negligible.

The ready excitation of impurities in small quantities is probably due to their reabsorption of the stilbene monomer fluorescence; the samples are thick (15 mm) and usually cracked (so that reflections increase the light path), and radiolysis produces excitation right through the sample unlike ultraviolet light which is absorbed in the surface layers of concentrated solutions. Under some conditions, impurity emission was observed in the glow curve but was then replaced by the excimer. Presumably monomer fluorescence was reabsorbed but not the longer wavelength excimer. If the impurity was scavenging charges and being excited directly on neutralization the interference would increase late in the glow when the ions traverse larger distances.

Similar results were obtained with diphenylacetylene, a new broad band appearing at 390 nm. Again, impurities and irradiation products interfered but these were largely removed by purifying the material and using low doses. Tests with likely impurities (anthracene, phenanthrene, *cis*-stilbene) showed that their structured fluorescence could be readily distinguished at high resolution. The 390-nm band could not be excited directly in the glass or in liquid solution.

## Discussion

The observed separations between the monomer 0-0 bands and the excimer maxima ( $\sim 6800$  cm<sup>-1</sup> for *trans*-stilbene,  $\sim 7300$  cm<sup>-1</sup> for diphenylacetylene) are very similar, as would be expected, and are comparable with those of other excimers;<sup>2</sup> this further supports the assignment. However, it should be noted that, in general, dimer cations may

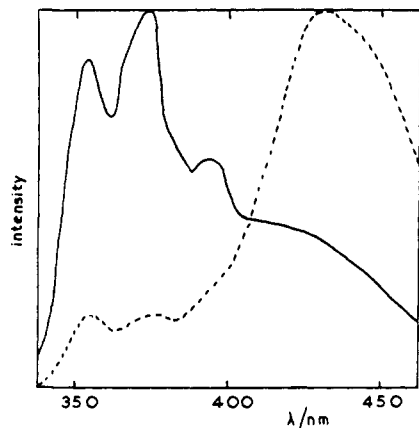


Figure 1. Spectra (uncorrected) of thermoluminescence of  $10^{-2}$  molar zone-refined *trans*-stilbene in squalane after 2 min of  $\gamma$  irradiation: (—) early in glow peak; (- - -) late in glow peak.

not have a "perfect sandwich" structure;<sup>5</sup> the same may be true of excimers formed from them.

Crystalline 2,4-dichloro-*trans*-stilbene gives excimer emission,<sup>6</sup> but there appear to be no reports of excimer emission from stilbene or its derivatives in solution. Stilbene is known to dimerize via the singlet excited state;<sup>7</sup> probably

the excimer is an intermediate which reacts in fluid solution much faster than it fluoresces. Similarly, excited diphenylacetylene is known to form products derived from two, three, or four monomer molecules;<sup>8</sup> the excimer is likely to be formed first.

This method is being extended to other compounds and should be a useful one for sufficiently soluble materials. In general, trace impurities are not likely to give spurious results since the ions are not mobile in the solid and only travel short distances ( $\sim 100$  Å) before neutralization. As noted above, impurities able to absorb the fluorescence of the substrate interfere strongly, but their presence is readily detected in photofluorescence.

#### References and Notes

- (1) The authors thank the Science Research Council (U.K.) for financial support for one of them (D.C.B.) and for an equipment grant.
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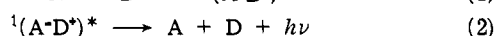
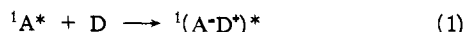
## Electrogenerated Chemiluminescence. XXII. On the Generation of Exciplexes in the Radical Ion Reaction

Su Moon Park and Allen J. Bard\*

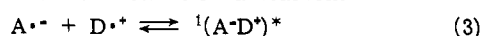
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received September 23, 1974

**Abstract:** Exciplex emission from systems containing tri-*p*-tolylamine (TPTA) as a donor molecule and various acceptor molecules was observed in both acetonitrile (ACN) and tetrahydrofuran (THF) solutions during electrogenerated chemiluminescence (ecl) studies. Systems containing naphthalene as an acceptor and five donor molecules also showed exciplex emission in ACN solutions. Triplet quenching experiments, magnetic field effect measurements, and temperature studies demonstrated that the exciplex is formed directly in the radical ion reaction. The energy of the exciplex emission showed a linear correlation with the cyclic voltammetric peak potentials for reduction of the acceptor molecules and for oxidation of the donor molecules. Studies of the ecl of the dibenzoylmethane (DBM)-TPTA system in six different electrochemical solvents, where only exciplex emission is observed, demonstrated the importance of solvent dielectric constant on exciplex emission intensity. The role of exciplexes in the general ecl scheme is also discussed.

Exciplexes are excited molecular complexes which are dissociated in the ground state.<sup>1</sup> They are usually produced by reaction of a photoexcited singlet species ( $^1A^*$ ) with a ground state molecule, D; exciplex emission is usually structureless and red shifted from that of  $^1A^*$  by about 6000  $\text{cm}^{-1}$ .<sup>1,2</sup>



Previous studies of radical-ion annihilation chemiluminescence (cl)<sup>3,4</sup> reactions and electrogenerated chemiluminescence (ecl)<sup>5,6</sup> in low dielectric constant solvents, such as tetrahydrofuran (THF), have demonstrated the formation of exciplexes by the direct reactions of radical ions



and it has been suggested that an exciplex may be an intermediate in other cl or ecl reactions, even when exciplex

emission is not observed.

It has generally been felt, however, that emission from exciplexes will not be observed in polar solvents, such as acetonitrile (ACN), where dissociation of the exciplex into the radical ions (the reverse of reaction 3) becomes more important.<sup>7</sup> We describe here ecl experiments with a number of acceptor and donor molecules in both THF and ACN which demonstrate the formation of exciplexes and show that the energy of the exciplex emission correlates with the redox potentials of the reactant molecules. Preliminary experiments on the effect of magnetic field, solvent, and temperature variations on the ecl behavior in these systems are also discussed.

#### Experimental Section

**Chemicals.** Tri-*p*-tolylamine (TPTA) and tri-*p*-anisylamine (TPAA), kindly provided by Professor R. N. Adams (University of