Figure 3. Plot of the change in the temperature of the calorimeter vs. the millimoles of solid tetracene dianion salt in the evacuated glass bulbs.

In THF both the dianions and anion radicals are ion associated with the sodium cation.[1] However, in the solid state the questions of crystal lattice energies replace those of ion association and ion solvation. Very little is known about dianion crystal lattice energies, but it appears that the crystal lattice energies of anion radicals do not vary much from one polyacene anion to another.[9] The solid-state disproportionation enthalpy is a sensitive function of crystal lattice energies (U) and electron affinities (EA) as shown in Scheme I.

The values for EA_1 are well known,[11] and those for U_1 can be calculated from the enthalpies of reaction of the anion radical salts with water as previously described,[9] Table II. Neither the second electron affinities nor the dianion crystal lattice energies are known,

(11) Becker, R. S.; Chen, E. *J. Chem. Phys.* **1966**, *38*, 1873.
(12) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

Table III. Volume of THF in the Initial Sample Divided by the Volume Remaining after Evaporation (A) and the Ratios of the Double Integrals of the ESR Spectra of the Anthracene Anion Radical in Solution (B)

A	B	A	B
1.00	1.00	1.53	1.68
1.19	1.49	2.79	2.62
1.47	1.47		

but from Table II it appears that even the relatively small differences in the crystal lattice energies and in the electron affinities combine to generate large differences in the disproportionation enthalpies for the solid polyacene anion radicals. A combination of crystal lattice energies and electron affinities results in the most exothermic disproportionation enthalpy yet observed (−13.6 kcal/mol for the solid pyrene anion radical). For all of the anions studied in both phases, the enthalpy of disproportionation in the solid state is between 24 and 10 kcal/mol more exothermic than in solution.

Two impurities that may have existed in the solid dianion solutions are neutral sodium metal caused by electron transfer back to the metal from the dianion and anion radical together with the neutral hydrocarbon. The first possibility has been eliminated, since the addition of water to the solid salts does not yield any hydrogen gas. The possibility that the anion radicals could change to neutral molecule and dianion as the THF was being evaporated also had to be eliminated. From Table III it is clear that the relative intensity of the ESR signal after THF evaporation does not decrease relative to the ratio of the initial THF volume to the final THF volume. In fact, the data would indicate that the anion radical concentration was increasing even faster than can be accounted for by concentration effects. However, the double integration method does incorporate relatively large errors. In the last sample, when more than 60% of the THF had been evaporated, some precipitation of the solid anion radical could be observed.

Study of the Photolysis of Dimethyl-*s*-tetrazine Using a Holographic Technique

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Abstract: A holographic technique is used to investigate the photochemical action spectrum of the second step in the two-photon photodissociation of dimethyl-*s*-tetrazine (DMST) in poly(vinylcarbazole) (PVK). We are able to show from these measurements that the previously observed transient absorption in the 600–700-nm spectral region is not directly involved in the second step absorption that leads to photodissociation. Furthermore, from the very fact that holograms can be produced with modest laser powers in this system, we are able to conclude that the intermediate in the second step cannot have a lifetime on the nanosecond or shorter time scale.

The photodissociation of tetrazine and its substituted derivatives has been the subject of many recent investigations.[2-8] This interest

has been stimulated by the suggestion that the photodissociation might be useful as a means of isotope separation.[3b] It has also

(1) Institute of Physical Chemistry, University of Munich, D-8000-Munich-2, West Germany.
(2) (a) J. H. Meyling, R. P. van der Werf, and D. A. Wiersma, *Chem. Phys. Lett.*, **28**, 364 (1974); (b) R. M. Hochstrasser and D. S. King, *Chem. Phys.*, **5**, 439 (1974); R. M. Hochstrasser, D. S. King and A. C. Nelson, *Chem. Phys. Lett.*, **42**, 8 (1976); D. S. King, C. T. Denny, R. M. Hochstrasser and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 271 (1977); J. Pacansky, *J. Phys. Chem.*, **81**, 2240 (1977); D. Coulter, D. Dows, H. Reisler and C. Wittig, *Chem. Phys.*, **32**, 429 (1978).

(3) (a) R. M. Hochstrasser and D. S. King, *J. Am. Chem. Soc.*, **98**, 5443 (1976); R. M. Hochstrasser, D. S. King, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 3923 (1977). (b) R. R. Karl, Jr., and K. K. Innes, *Chem. Phys. Lett.*, **36**, 275 (1975); R. M. Hochstrasser and D. S. King, *J. Am. Chem. Soc.*, **97**, 4760 (1975); B. Dellinger, D. S. King, R. M. Hochstrasser, and A. B. Smith, III, *ibid.*, **99**, 3197 (1977).
(4) H. deVries and D. A. Wiersma, *Phys. Rev. Lett.*, **36**, 91 (1976); H. deVries and D. A. Wiersma, *Chem. Phys. Lett.*, **51**, 565 (1977).
(5) G. Castro, D. Haarer, R. M. Macfarlane, and H. P. Trommsdorf, U.S. Patent 4 101 976, 1978.
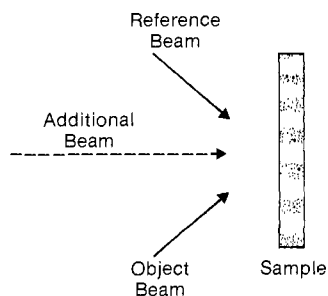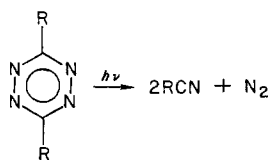
Figure 1. Diagram of the three-beam holographic experiment. The interfering reference and object beams produce a spatial modulation of the light intensity in the sample. This light intensity variation results in varying amounts of photochemical bleaching in the sample represented by the shaded and unshaded regions.
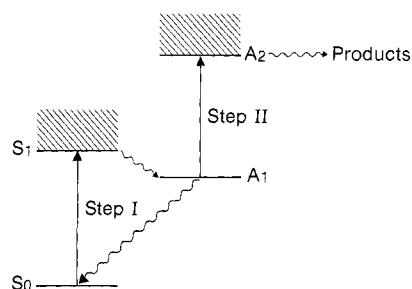

Figure 2. Four-level two-photon photochemical scheme that describes the DMST photodissociation. Step I involves absorption from the ground state S_0 to the lowest singlet state S_1. A radiationless transition, represented by the wavy line, produces the intermediate A_1. A_1 absorbs a photon in step II to produce an excited state A_2, ultimately resulting in photochemical products.

been shown that very narrow holes can be "burned" into the absorption spectrum,[4] and it has been proposed that this hole-burning technique can form the basis of an extremely high-density optical memory system.[5]

Originally the photodissociation was thought to involve

Later it was shown that for several phenyl- and methyl-substituted tetrazines, the reaction in rigid matrices proceeded by the step-wise absorption of two laser photons.[6,7] The first photon converts the tetrazine into an as yet unknown intermediate, and the second photon results in the dissociation of the intermediate. Transient absorption was observed and attributed to one of the intermediates in the photochemical process.[7,8] It is fair to say, however, that at this point the details of the tetrazine photochemistry are not understood. One would like to know the number of intermediates in the process, their nature, and their precise role in the photochemistry. An interesting question that has recently been raised[9] in this regard is whether the observed transient absorption[7,8] is to be identified with the intermediate directly involved in the second step of the photochemistry or with one occurring somewhere else along the reaction pathway. Recently, Paczkowski, et al.[14] have shown that the observed transient absorption is probably not associated with the second photon absorption.

So that more information on the tetrazine photodissociation could be provided, the system dimethyl-*s*-tetrazine (DMST) in a poly(vinylcarbazole) (PVK) host polymer has been investigated with the use of a new holographic technique.[10] In this technique the photochemical process is investigated by following the temporal growth of a hologram resulting from the photochemistry. The method is used in the present case to obtain an action spectrum for the second step of the two-step tetrazine photodissociation. Information is thus obtained on the wavelength region for the second step.

Theory of Photochemical Holography

The details of the production of a hologram by a photochemical reaction[11] and the use of this technique to obtain information about the reaction itself[10,12] have been previously discussed. A diagram

of the experiment to be described here is shown in Figure 1. Consider first the case where one has only two coherent beams, a reference and an object beam. As a consequence of the photochemistry that occurs in the recording medium, the fringe pattern resulting from the interference of these two beams is impressed into the medium as local changes in absorption and index of refraction. The hologram is then read by blocking the object beam and detecting the fraction of the reference beam deflected into the direction of the object beam. The growth of the hologram as measured by its efficiency η (the intensity in the deflected beam divided by the incident light intensity) is given by eq 1[10] where

$$\eta(t) = a(\mathcal{J})t^2 \qquad (1)$$

t represents time, $a(\mathcal{J})$ is proportional to $\mathcal{J}^{2n}$ where $\mathcal{J}$ is the light intensity and n is 1 or 2 depending on whether the photochemistry occurs with the absorption of one or two laser photons. $\mathcal{J}$ also depends, as will be shown below, on the molar extinction coefficient ϵ, and the quantum yield ϕ. Equation 1 is only valid during the initial portion of the hologram growth.

Next consider the application of the above equation to the four level, two-photon photochemical scheme shown in Figure 2. This scheme corresponds in overall outline to the photodissociation process in substituted tetrazines.[8] In the first step the tetrazine molecule is excited from its ground state S_0 to its lowest excited singlet state S_1. From the S_1 state the system proceeds to an as yet unknown intermediate state A_1. The second step in the photochemical process involves the absorption of a second photon, converting the intermediate to an excited state A_2 from which photodissociation occurs. The overall reaction requires the stepwise absorption of two photons, thus n above is 2.[6]

To apply eq 1 to the present case it will be helpful to separate $a(\mathcal{J})$ into factors corresponding to steps I and II in Figure 2. In the case where only the reference and object beams are present in a two-photon process

$$a'' = Cb_{I,1}b_{II,1}\mathcal{J}_1^4 \qquad (2)$$

Here the double prime indicates that the expression describes a two beam experiment. The roman numeral subscripts I and II on b refer to the respective photochemical steps shown in Figure 2. The arabic subscripts 1 and 2 refer to the particular light beam whose effect on the hologram growth is described by the factor b. The subscript is 1 when b describes the growth of the hologram due to interfering reference and object beams. It is 2 when the factor describes the growth enhancement by the additional third beam (see below).

The b factors are proportional to the extinction coefficient ϵ and quantum yield ϕ for the photochemical steps.[10]

$$b = [2303\phi\epsilon]^2 \qquad (3)$$

Finally C in eq 2 is a proportionality constant containing all of those factors not of relevance to the present discussion. a'' will

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(7) B. Dellinger, M. A. Paczkowski, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **100**, 3242 (1978).

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(11) W. J. Tomlinson, *Appl. Opt.*, **11**, 823 (1972); **14**, 2456 (1975); W. J. Tomlinson and E. A. Chandross, *Adv. Photochem.*, **12**, 201 (1980).

(12) Chr. Bräuchle, D. M. Burland, and G. C. Bjorklund, *J. Phys. Chem.*, **85**, 123 (1981).

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be 0 and no hologram will be produced unless the photons in the two intefering beams have an energy greater than the S_0-S_1 separation. In the case of substituted tetrazines this threshold energy is also sufficient to initiate step II.

If an additional beam at a different frequency is added, the holographic growth rate may be enhanced according to eq 4. In

$$a''' = a'' + C(b_{I,1}b_{II,2} + b_{I,2}b_{II,1})\mathcal{J}_1^2\mathcal{J}_2^2 \tag{4}$$

addition to the normal two beam holographic growth given by a'', the growth rate may be enhanced by the additional beam in two ways represented in eq 4 by the two terms between the parentheses. The additional beam can be absorbed in the second step (II) while the two interfering beams produce the hologram in the first step. This is represented by the term $b_{I,1}b_{II,2}$. Conversely the additional beam can be absorbed in the first step described by the $b_{I,2}b_{II,1}$ term. Note that the additional beam by itself cannot produce a hologram. There are thus no terms in eq 4 proportional to $\mathcal{J}_2^4$.

As a specific example consider the case where the interfering object and reference beams have sufficient energy to result in both absorption steps in Figure 2. The hologram will then grow in a manner described by a'' in eq 2. If the additional beam can only result in step II, that is, it is not absorbed by the S_0 state, then $b_{I,2}$ is 0 since the extinction coefficient ϵ_I is 0 for this wavelength. The additional beam thus results in an increase in the holographic growth rate described only by the term involving $b_{I,1}b_{II,2}$ in eq 4. When the additional beam can produce both steps in the process, the full equation is necessary to describe the hologram growth. A useful parameter for analyzing the experimental data is defined in eq 5. When the photons from all three beams have sufficient

$$B = \left[\frac{a'''}{a''} - 1\right]^{1/2}\frac{d_1}{d_2} = \left[\frac{b_{II,2}}{b_{I,1}} + \frac{b_{I,2}}{b_{II,1}}\right]^{1/2} \tag{5}$$

energy to promote both photochemical steps, both square root terms in eq 5 are nonzero. The first term corresponds to the additional beam promoting step II and the second term to the case where the additional beam promotes step I. If, as discussed above, the additional beam does not have sufficient energy to promote step I, $b_{I,2}$ is 0 and B has only a single term. B is thus simply a measure of the fractional change in growth rate for three vs. two beams and may be easily obtained from experiment.

By measuring B as a function of the wavelength of the additional beam it can be seen that one obtains a photochemical action spectrum for the second step in the two-photon process. For such a photochemical action spectrum, only $b_{I,2}$ and $b_{II,2}$ in eq 5 change with wavelength.

The other two factors $b_{I,1}$ and $b_{II,1}$ are constant. Since $b_{I,2}$ is proportional to the square of the $S_0 \rightarrow S_1$ extinction coefficient ϵ_I times the quantum yield for this step and $b_{II,2}$ is proportional to the square of the second step extinction coefficient ϵ_{II} times the photochemical quantum yield, the first square root term in eq 5 yields the photochemical action spectrum. The second term represents a spectrum that is proportional to the product of the $S_0 \rightarrow S_1$ absorption spectrum and the appropriate quantum yield.

Experimental Details

A. Sample Preparation. Dimethyl-*s*-tetrazine (DMST) was prepared from the reaction of acetaldehyde and hydrazine[13] and purified by vacuum sublimation. Cast polymer films of 200–300-μm thickness were prepared by dissolving DMST in viscous solutions of polyvinylcarbazole (PVK) in toluene. Holograms grown in these films showed no decrease in efficiency over a period of 24 h nor was there a difference between the experimental results obtained with freshly prepared films and films that were several weeks old. These results indicate that the photochemically-active species do not diffuse on these time scales.

B. Holographic Apparatus. The apparatus used to record the holograms is shown in Figure 3. An argon ion laser operating at 514 nm was used to provide the reference and object beams. About 10% of the laser output was split off for this purpose by a glass plate. The remainder of the 514-nm radiation was used to pump a tunable CW ring dye laser. The dye laser using rhodamine 6G had a tuning range of 560–630 nm.
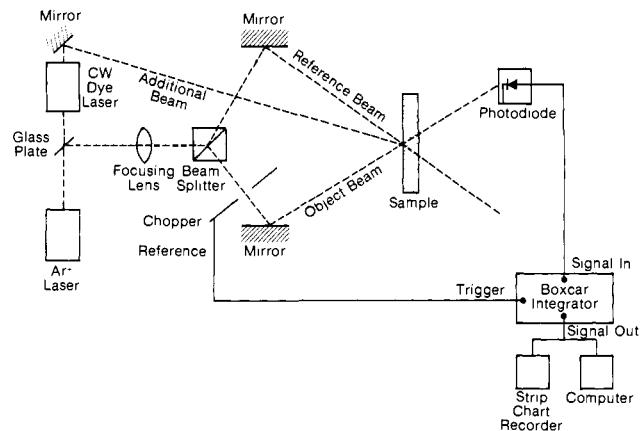
(13) W. Skorianetz and E. Kovats, *Tetrahedron Lett.*, 5067 (1966).

Figure 3. Experimental apparatus used in the three-beam holographic experiments. The dotted lines represent the light paths of the various laser beams and the solid lines represent electrical pathways.
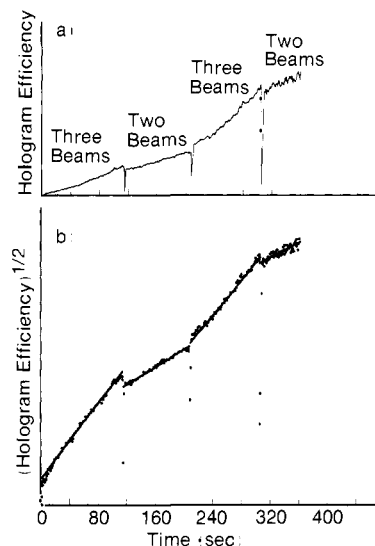

Figure 4. (a) Hologram efficiency vs. time when the sample is exposed to three or two laser beams. Reference and object beams are at 514 nm and the additional beam at 562 nm. Interfering beams have powers of 0.55 mW and the additional beam 3.3 mW. Both beams are focused to a spot size of $\sim$0.1 cm^2. The discontinuities in the growth curves represent points at which the system was switched from two to three beam exposure and vice versa. (b) Square root of the hologram efficiency vs. time for the system described in (a). The points are experimental values and the solid lines represent a linear least-squares fit to the data.

The dye laser radiation was used to provide the third (additional) beam.

The split-off portion of the 514-nm beam was passed through a beam splitter and then the object beam passed through a chopper operating at 200 Hz. The two beams produced by the beam splitter were recombined and focused at the sample to a spot area of typically 0.1 cm^2. After passing through the sample, the object beam was intercepted by a photodiode. The signal from the photodiode was used as the input to a boxcar integrator. This signal was sampled during a 2-ms interval while the chopper was blocking the object beam. In this way the output of the boxcar integrator recorded the growth of the holographic image of the object beam as read by the reference beam. The output from the boxcar integrator was sent to a strip chart recorder and was also digitally recorded in an IBM Series/1 computer.

It should be noted that photochemistry continues due to the reference beam alone during those periods when the object beam is blocked. However, this single beam does not form interference fringes and thus cannot by itself cause hologram growth. It can however, lead to a depletion of the DMST and thus to eventual erasure of the hologram. All of the work reported here was done at early stages in the hologram growth where depletion of DMST was negligible.

Results

An example of the raw experimental data is shown in Figure 4a. The first portion of the holographic growth curve was re-
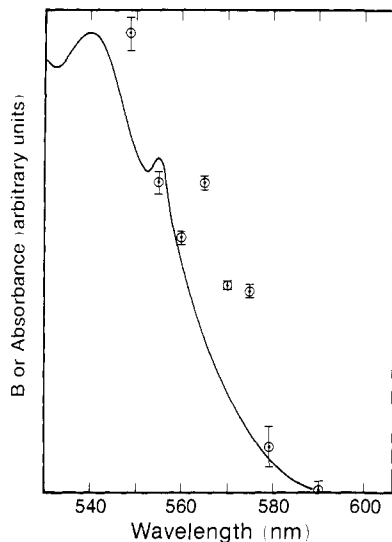
Figure 5. Plot of the parameter B and the absorbance vs. wavelength for DMST in PVK. The solid line is the DMST absorption spectrum. Values of B at various wavelengths are represented by open circles. The error bars represent the range of experimental values obtained in from three to five measurements for each point.

corded with all three beams, the second segment with only the object and reference beam, and the third with three beams again. Note that the additional beam clearly increases the growth rate. This is in spite of the fact that the additional beam by itself cannot cause hologram growth. This was checked by allowing a hologram to grow with three beams and then blocking the object beam. No hologram growth was observed with just the additional beam and the reference beam.

The square root of the hologram intensity vs. time is shown in Figure 4b. According to eq 1 this should result in a linear functional relationship. Also shown in the figure is a linear least-squares fit to the experimental data. Note that as expected the data is well approximated by a linear relationship. One can also see from the figure that the two segments of the curve produced by three beams have similar slopes as do those segments produced by two beams.

From curves of this type it is possible to obtain the values of a'''/a'' needed to evaluate B in eq 5. B as a function of wavelength is shown in Figure 5. Each point in the figure is an average of from 3 to 5 different measurements. The range of these measurements is represented by the error bars in the figure. Also shown in the figure is the absorption spectrum of DMST in PVK.

The first point to note about the spectrum of B in Figure 5 is that there is no enhancement of the holographic growth beyond 600 nm. This is in spite of the fact that at least one of the reaction intermediates has an observed transient absorption spectrum in this region.[7,8]

The second point to note is that the wavelength dependence of B is not simply proportional to the $S_0 \rightarrow S_1$ absorption spectrum. This is not immediately obvious from Figure 5, but we have tried to scale the $B(\lambda)$ data so as to overlap the DMST absorption spectrum. No scaling can bring the two sets of data into reasonable coincidence. From this it can be concluded that the second step photochemical action spectrum differs from the $S_0 \rightarrow S_1$ absorption. Since both the interfering object and reference beams and the additional beams can produce photochemistry in this wavelength region, both terms in eq 5 are necessary to describe the temporal growth of the hologram. It is not possible in this case to obtain a pure step II photochemical action spectrum.

Discussion

Several possibilities exist as to the nature of the intermediate that absorbs the second photon in the DMST photodissociation. The intermediate may be the DMST lowest singlet state S_1, the lowest triplet state T_1, an unrelaxed vibronic level of S_1 or T_1, higher triplet level, or a distinct photochemical species. Along

with the question of the identity of this intermediate is associated the question of the relationship between the transient absorption observed in the 600–700-nm region and the two-photon photochemistry. For example, deVries et al.[9] have recently suggested that this absorption is due to an intermediate that is produced after the absorption of the second photon and is thus not directly involved in the photochemistry. From the results discussed in this paper, it is possible to provide information on the nature of the photochemical intermediates.

First consider the question of the identity of the photochemical intermediate (A_1 in Figure 2). The very fact that two-photon holograms can be observed in DMST at modest laser power levels[10] allows us to make an estimate of the lifetime of the intermediate involved in the photochemistry. The rate k of a two-photon photochemical process may be written[8] as in eq 6 where ϕ_I is the

$$k = \phi_I \frac{\mathcal{J}_I \sigma_I \tau}{\hbar \omega_I} \frac{\phi_{II} \mathcal{J}_{II} \sigma_{II}}{\hbar \omega_{II}} \tag{6}$$

quantum yield for the production of the intermediate A_1 from S_1 and ϕ_{II} is the quantum yield of the photodissociation from A_2. $\mathcal{J}_I$ and $\mathcal{J}_{II}$ are the intensities of the exciting light at frequencies ω_I and ω_{II}, respectively. σ_I and σ_{II} are the absorption cross-sections for the two steps, and τ is the lifetime of the intermediate.

For a laser intensity $\mathcal{J}_I = \mathcal{J}_{II}$ of 1 W/cm², experiments indicate that about 50% of the material has reacted in less than 1 min.[10] This means that k in eq 6 is roughly 0.02 s⁻¹. Taking these values and the following reasonable values for the other parameters

$$\sigma_I = 2 \times 10^{-18} \text{ cm}^2 \ (\epsilon = 500)$$

$$\sigma_{II} = 10^{-17} \text{ cm}^2 \ (\epsilon = 10\,000)$$

$$\hbar \omega_I = 4 \times 10^{-19} \text{ J} \ (496 \text{ nm})$$

$$\phi_I = \phi_{II} = 1.0$$

one can obtain a rough estimate of the intermediate state lifetime. For these values τ is 0.8 ms. This value of τ may be off by 1 or 2 orders of magnitude because of considerable uncertainties in the parameters used. The arguments below only require that the estimate for τ be accurate to within 5 orders of magnitude.

Paczkowski et al.[14] in a very recent paper have left open the possibility for their vapor-phase results that the intermediate state is the lowest singlet state S_1. This possibility is clearly ruled out for our condensed-phase experiments by the above estimate for τ. The S_1 lifetime for DMST has been determined to be 6 ns.[2a] Clearly well away from the estimated millisecond lifetime for the intermediate. Not only does the above estimate for τ rule out the S_1 state as a candidate, it would also seem to rule out any vibronic S_1 or T_1 state and any higher triplet states. These states would all be expected to have subnanosecond lifetimes. It should be emphasized that these conclusions strictly apply only to the condensed phase for DMST. Another possibility is that the intermediate is the vibrationally relaxed lowest triplet state T_1. This state is known to have a lifetime of 85 μs at 1.6 K.[3a] Although one cannot completely rule the T_1 state out as a possibility, the results of Hochstasser, et al.[3a] showing that T_1 is very inefficiently populated by indirect excitation into S_1 would seem to make this state an unlikely candidate.

Next we turn to the relationship between the observed 600–700-nm transient absorption[7,8] and the photochemistry. The photochemical action spectrum clearly shows that the second step in the photochemistry occurs only for light of wavelengths shorter than 600 nm. No photochemistry is observed when one attempts to excite the second step in the wavelength region of the observed transient absorption. These results provide direct experimental evidence that the long wavelength transient absorption is not directly involved to any significant extent in the DMST photochemistry. Paczkowski et al.[14] have also obtained evidence in this regard. They find that the concentration of the absorbing transient

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(14) M. Paczkowski, R. Pierce, A. B. Smith, III, and R. M. Hochstrasser, *Chem. Phys. Lett.*, **72**, 5 (1980).

is too low to be directly involved in the photochemical reaction. It is impossible from either of these experimental results to say whether the transient species is produced after the absorption of the first or the second photon in the two-photon photochemical process.

Although the absorption and photochemical action spectrum are similar they cannot, by suitable normalization, be superimposed as would be the case if $b_{II,2}$ in eq 5 were 0. This allows us to conclude that the second-step photochemical-action spectrum includes the region from 600 to 560 nm. Using lines from the Ar^+ laser, we have shown that the second-step absorption extends at least to 488 nm. Whatever the nature of the photochemical intermediate, its absorption spectrum in the 488–600-nm region is similar to but not identical with the DMST $S_0 \rightarrow S_1$ absorption.

Conclusions

In this paper we have used a new holographic technique to provide information about the two-photon photodissociation of

DMST in PVK. The very fact that holograms can be produced in this system with modest CW laser powers means that the intermediate produced in the photochemical process cannot have a lifetime on the nanosecond or shorter time scales. This rules out vibrationally unrelaxed excited states and the lowest singlet state. The lowest triplet state also seems an unlikely candidate.[3a] This means that the intermediate is most likely a distinct metastable chemical species.

We have also investigated the photochemical action spectrum of this intermediate. The action spectrum is similar to but not identical with the $S_0 \rightarrow S_1$ DMST absorption. The action spectrum does not extend to the long-wavelength side beyond 600 nm. This clearly rules out the possibility that the previously observed transient with absorption in the 600–700-nm region[7,8] is involved directly in the second step of the photochemistry.

Acknowledgment. We wish to thank D. C. Alvarez for his valuable technical assistance in the work described here.

Free-Energy Relationships for Reversible and Irreversible Electron-Transfer Processes

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Abstract: The relationship between the free-energy change and the activation energy for electron-transfer reactions is examined. Two general classes of processes, reversible and irreversible, are discussed, and the relation between them is studied. An analysis of the differences between linear and nonlinear free-energy relationships is presented.

I. Introduction

It is frequently observed that for a set of related chemical reactions there is a relationship between the free energy of activation, $\Delta G^\ddagger$, and the standard free-energy change, ΔG. The formulation and meaning of such free-energy relationships (FER) have been widely discussed in the past, particularly as they pertain to proton[2]- and electron[3]-transfer processes where extensive kinetic data are available. The introduction of electronically excited molecules as reactants in electron-transfer processes has generated new sets of data, and this has caused renewed interest in the experimental and theoretical aspects of FER.

Electron-transfer processes have been studied in our laboratories using different substrates (organic peroxides[4] and transition metal complexes[5]) and pursuing different aims (elucidation of the

mechanism of bioluminescent and chemiluminescent displays[4] and the design of systems for the conversion of light into chemical energy[5]). In several cases these studies have led us to observe correlations between kinetic and thermodynamic quantities and to use these correlations as a means for obtaining deeper insight into these reaction mechanisms. In two independent papers[6,7] we recently discussed some general aspects of electron-transfer kinetics and apparently arrived at contradictory conclusions about the validity and the meaning of *linear* FER. The purpose of this paper is to analyze and to compare our different approaches in order to clarify their scope and limitations with the aim of removing the apparent contradiction.

II. Kinetic Scheme

An electron-transfer reaction originating from a weak interaction[8] between a donor and an acceptor can be discussed on the basis of the scheme in eq 1, where the electronic states of D and

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(8) Classical cases of weak-interaction electron-transfer processes are outer-sphere electron-transfer reactions of transition metal complexes in polar solvents.[3]