

Stilbene photocycloaddition reactions: ion pair and electron transfer dynamics

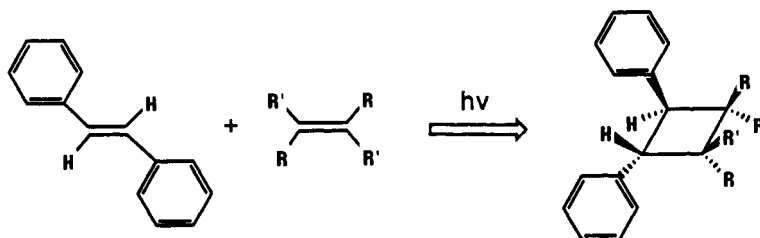
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Abstract- The quenching dynamics of the first excited singlet state of trans-stilbene by fumaronitrile has been examined by picosecond laser spectroscopy. The intrinsic rate for the electron transfer is $1.9 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$. The electron is transferred when the two molecules are in contact, producing a contact ion pair.

INTRODUCTION

During the past four years our research group has been interested in the mechanism of the photocycloaddition reactions of trans-stilbene with alkenes to produce substituted cyclobutanes.



One particularly interesting aspect of this reaction is the dependence of the quantum yield for reaction upon the structure of the alkene. In the presence of high concentrations of the electron rich alkene, tetramethylethylene, the quantum yield for photocycloaddition is 1.0 (ref. 1) while in the presence of the electron deficient alkene, fumaronitrile, the quantum yield for photocycloaddition is approximately 0 (ref. 2). These observations are difficult to rationalize based upon thermochemical considerations of the reactants and products. Clearly other factors govern the course of the reaction.

It has been shown that the mechanism of the photocycloaddition reactions of trans-stilbene involve the intervention of a charge-transfer species (ref. 2). When the excited singlet state of trans-stilbene is quenched by an alkene through an electron transfer, an ion pair intermediate is formed whose production has been shown to correlate with the cycloaddition products (ref. 2). If one begins to understand the factors that control the fate of the ion pair, then greater insight into the mechanism of photocycloaddition will be gained.

We begin addressing the mechanism of trans-stilbene photocycloaddition by examining the quenching of the excited singlet state of trans-stilbene by fumaronitrile. Three questions will be discussed. First, what is the intrinsic rate of the electron transfer from trans-stilbene to fumaronitrile to produce the stilbene radical cation and the fumaronitrile radical anion? Secondly, when the electron is transferred does it occur when the two molecules are in contact, to form a contact ion pair, or can it occur long range to produce a solvent separated ion pair? Finally, once the ion pair is produced, what are its subsequent dynamics?

EXPERIMENTAL

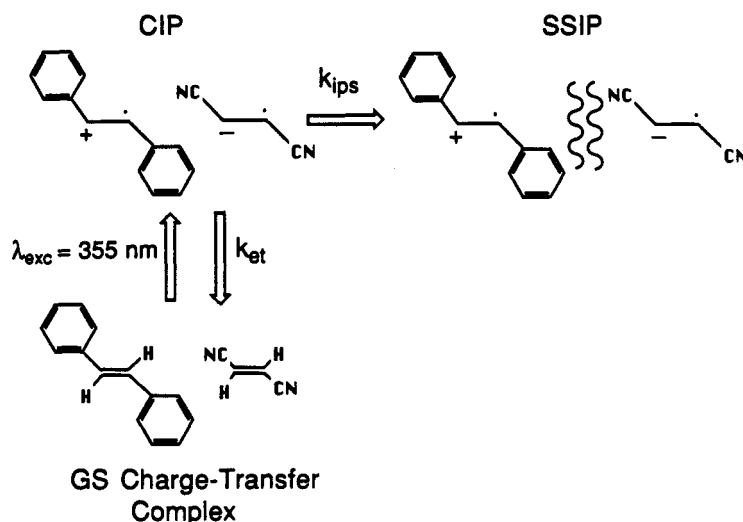
The experiments described in this paper were performed on a 25 psec and a 1 psec absorption spectrometers. The 25 psec absorption spectrometer is based upon a 25 psec Nd:YAG laser, operating at 10 Hz, to produce light pulses at 355 nm for excitation and continuum light ranging from 450 to 750 nm for probing the dynamics of transient species. Spectra were recorded by a vidicon interfaced to a spectrograph. A complete description of the experiment can be found in ref. 3. The 1 psec absorption spectrometer utilizes a mode-locked

Nd:YAG laser to synchronously pump a rhodamine 6G dye laser producing 600 nm, 1 psec light pulses. The output is passed through a three stage dye amplifier resulting in 2.0 mJ 600 nm pulse with a temporal width ranging from 1 to 2 psec. This light is frequency doubled to 300 nm, the pump pulse, and is used to produce continuum white light from 450 nm to 750 nm. A narrow band filter coupled with a polarizer at the magic angle determines the wavelength of the probe pulse. This probe pulse is delayed with respect to the 300 nm pump pulse using a stepping motor delay line. The probe pulse is split into two beams, an I and I₀, and the two signals are detected by two photodiodes in tandem with box car integrators.

RESULTS AND DISCUSSION

The dynamics of the trans-stilbene radical cation (TS⁺) and the fumaronitrile radical anion (FN⁻) in acetonitrile are deduced from the experiment depicted in Scheme 1.

Scheme 1



In an acetonitrile solution of 60 μM trans-stilbene/0.1 M fumaronitrile, a ground state charge-transfer complex is formed between trans-stilbene and fumaronitrile having an absorption at 355 nm. Irradiation of the charge-transfer complex with a 25 psec, 355 nm light pulse produces an contact ion pair within the time frame of the laser pulse (ref. 4). The contact ion pair (CIP), composed of TS⁺ and FN⁻, decays by two pathways: back electron transfer to reform the original charge-transfer complex, k_{et} , and ion pair diffusion to form a solvent separated ion pair (SSIP), k_{ips} . The kinetic parameters that govern the lifetime of the CIP, k_{et} and k_{ips} , can be measured by monitoring the decay dynamics of TS⁺. The TS⁺ has an absorption maximum at 480 nm. When the CIP decays by back electron transfer, k_{et} , there will be an accompanying decay in the TS⁺ absorption spectrum. However, when the CIP undergoes ion pair separation, there will be no change in the TS⁺ absorption intensity. Thus the decay of the CIP by two pathways should lead to biphasic behavior in the time-dependence of the TS⁺ absorption. Such behavior is observed, Fig. 1.

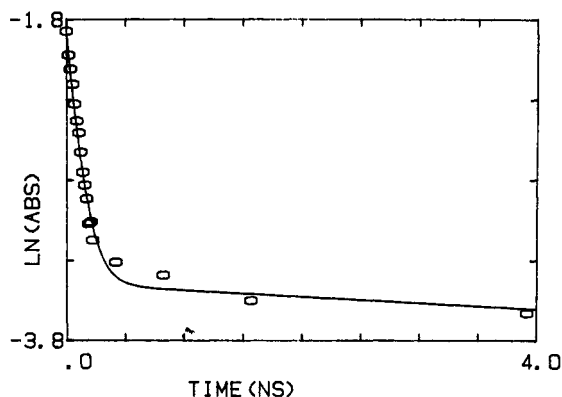
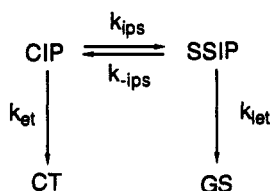


Fig. 1. Decay kinetics of trans-stilbene cation, 480 nm, following 25 psec irradiation of charge-transfer complex. O - experimental points; solid line - calculated decay kinetics.

Scheme 2



In order to analyze this kinetic data we assumed the kinetic model depicted in Scheme 2. The coupled differential equations for the time dependence of the concentrations of CIP and SSIP, shown in Scheme 2, were solved numerically with a fourth order Runge Kutta algorithm. Assuming that the absorption at $t=0$ is due to CIP alone and that the extinction coefficients of TS^+ in the CIP and SSIP are the same, we find that $k_{et} = 6.2 \times 10^9 \text{ sec}^{-1}$ and $k_{ips} = 1.3 \times 10^9 \text{ sec}^{-1}$. The rates for collapse of the SSIP to form the CIP, k_{-ips} , and long range electron transfer to form ground state reactants, k_{1et} , could not be resolved. The limit for these two processes is $k_{-ips} + k_{1et} < 0.05 \times 10^9 \text{ sec}^{-1}$.

We will next examine the quenching of the first excited singlet state of trans-stilbene (S_1) by fumaronitrile (FN)(ref. 5). The dynamics of S_1 following 300 nm excitation of trans-stilbene in the absence of fumaronitrile are monitored at 570 nm, near the absorption maximum of the $S_n \rightarrow S_1$ transition, Fig. 2. Assuming a Gaussian instrument response function,

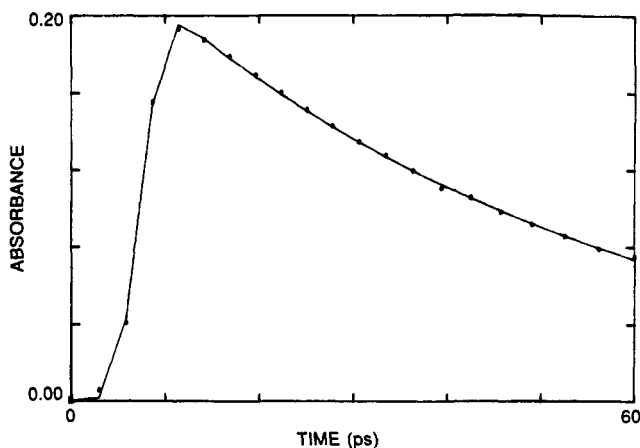


Fig. 2. Decay of trans-stilbene first excited single state. Pump - 300 nm, probe - 570 nm. Points - experimental, solid curve - calculated decay.

the decay of S_1 may be fit to a single exponential decay with a lifetime of 48 ± 3 psec. In the absence of FN, S_1 decays by isomerization upon the excited surface followed by internal conversion to the ground state surface to form both cis and trans-stilbene. However, in the presence of the electron deficient alkene FN, an electron is transferred from S_1 to the alkene. The quenching of S_1 by fumaronitrile as a function of concentration of alkene is shown in Fig. 3.

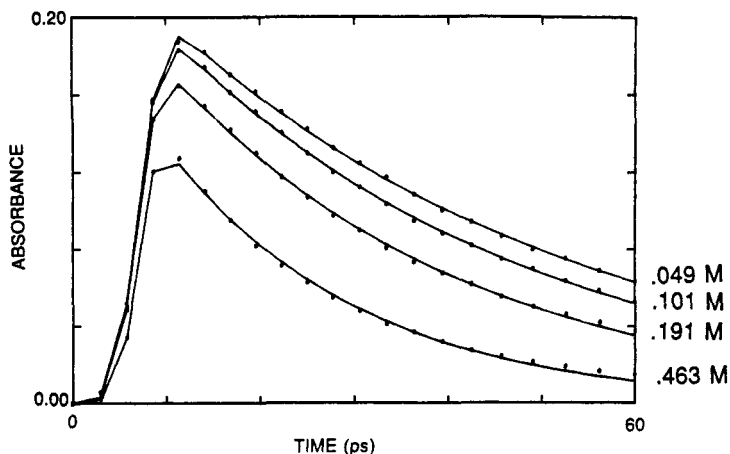


Fig. 3. Dynamics of quenching of the first excited singlet state of trans-stilbene by fumaronitrile, as a function of concentration. Pump - 300 nm, probe - 570 nm. Points - experimental data, solid curves - calculated decays assuming equation 1 for the rate constant.

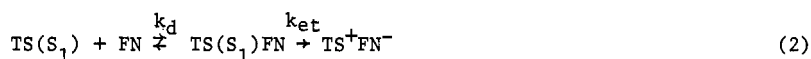
The rate of decay of S_1 in the presence of FN, k_{obs} , may be expressed as

$$k_{obs} = k_1 + k_{et}(FN) \quad (1)$$

where k_1 is the rate of decay of S_1 in the absence of FN and k_{et} is the rate constant for the electron transfer from S_1 to FN. Analysis of the data in Fig. 3, assuming a Gaussian instrument response function, leads to a second order rate constant for quenching of S_1 by FN of $k_{et} = 6.2 \pm .04 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$.

It is interesting to note that the quality of the fit to the data in Fig. 3 decreases with increasing concentration of FN. This is best illustrated by examining the 0.48 M FN kinetic data where the calculated curve overestimates the absorbances at early times and underestimates the absorbances at later times, Fig. 3. A linear least squares analysis of the 0.48 M FN kinetic data finds that as the time interval narrows from 23-60 psec to 37-60 psec, the second order rate constant increases by 17%. This behavior indicates that the rate constant for the quenching of S_1 by FN, k_{obs} , is time-dependent and can not be described by equation 1.

The origin of the time-dependence for the quenching of S_1 by FN may be understood within the formalism developed by Marcus and Siders (ref. 7). They considered an electron transfer process that is coupled to diffusion.



If the conditions of the experiment are such that the rate of the electron transfer, k_{et} , is much greater than the rate of diffusion, k_d , then as the time for observation approaches zero, $t \rightarrow 0$, the observed rate constant $k_{obs} = k_{et}$. Thus the early time behavior of the quenching directly reflects the kinetics of electron transfer. The time-dependent rate constant $k_{obs}(t)$ is expressed as

$$k_{obs}(t) = (1/(k_{et}^{-1} + k_d^{-1}))(1 + (k_{et}/k_d) \exp(y^2) \text{erfc}(y)) \quad (3)$$

where $\text{erfc}(y)$ is the complementary error function

$$\text{erfc}(y) = (2\pi^{-1/2}) \int_y^\infty \exp(-u^2) du \quad (4)$$

and

$$y = (Dt)^{1/2} R^{-1} (1 + k_{et}/k_d) \quad (5)$$

The parameter R is the distance for the electron transfer and D is the sum of the reactants diffusion coefficients. The diffusion rate constant k_d is expressed as

$$k_d = 4\pi DRN_a \quad (5)$$

where N_a is Avogadro's number. There are only two unknowns in equations 2-5; the intrinsic rate of electron transfer, k_{et} , and the distance for the electron transfer, R . The diffusion coefficients for trans-stilbene and fumaronitrile in acetonitrile were determined using the chronocoulometric mode on a BAS 100 Electrochemical Analyzer and ferrocene as the standard (ref. 5). The value of D is $3.1 \times 10^{-5} \text{ cm}^2/\text{sec}$.

The experimental data in Fig. 3 was analyzed using a time-dependent rate constant $k_{obs}(t)$, equation 3, and the results are shown in Fig. 4. The kinetic data is extremely well reproduced with the best fit corresponding to the parameters $k_{et} = 1.9 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ and $R = 8.5 \text{ \AA}$.

From the analysis of the time-dependent quenching data, it was deduced that the distance for the electron transfer is 8.5 \AA . This distance does not uniquely define the nature of the ion pair formed upon electron transfer. One possible geometry would have the trans-stilbene and fumaronitrile placed end on, forming a CIP upon electron transfer. Another possible geometry would have the two molecules plane parallel separated by 8.5 \AA which would lead to a SSIP upon electron transfer. Thus the distance of 8.5 \AA does not reveal the nature of the ion pair formed upon electron transfer.

More direct information regarding the nature of the ion pair formed upon electron transfer is in the resulting ion pair dynamics monitored at 480 nm. From our previous kinetic study, we found that the trans-stilbene/fumaronitrile CIP and SSIP have different kinetic behavior. In acetonitrile, the CIP has a lifetime of 133 psec while the SSIP is stable on the picosecond timescale. Thus in order to determine whether electron transfer occurs over short or long range, we will assume two kinetic models for the electron transfer. The first, Scheme 3, assumes that quenching S_1 produces only CIP while the second model, Scheme 4, assumes that quenching S_1 produces only SSIP.

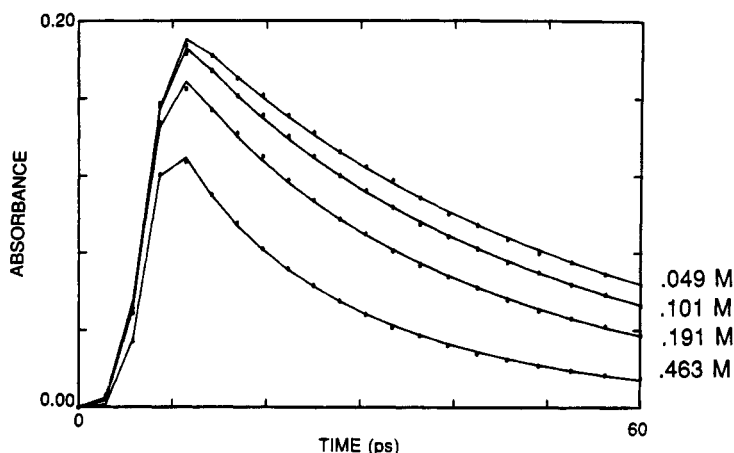
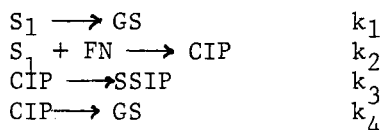
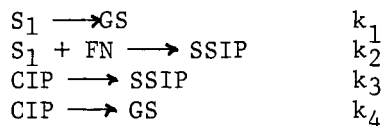


Fig. 4. Dynamics of quenching of the first excited singlet state of trans stilbene by fumaronitrile, as a function of concentration of fumaronitrile. Pump - 300; probe - 570 nm. Points - experimental data, solid curves - calculated using equation 3 for time-dependent rate constant.

Scheme 3



Scheme 4



In Scheme 3, the CIP is formed through irradiation of the charge-transfer band at 300 nm and through short range electron transfer. In Scheme 4, the SSIP is produced through both long range electron transfer, k_2 , and through the separation of the CIP, k_3 , which was initially produced through irradiation of the charge-transfer band at 300 nm.

Given the two models in Schemes 3 and 4, it is possible to calculate the time-dependence of the absorption of the TS^+ at 480 nm as all the kinetic parameters are known from previous experiments. In addition, the equilibrium constant for the formation of the charge-transfer complex at 300 nm is known from a Hildebrand/Benesi analysis (ref. 6). The results of the calculation are shown in Fig. 5 along with the experimental data at 480 nm.

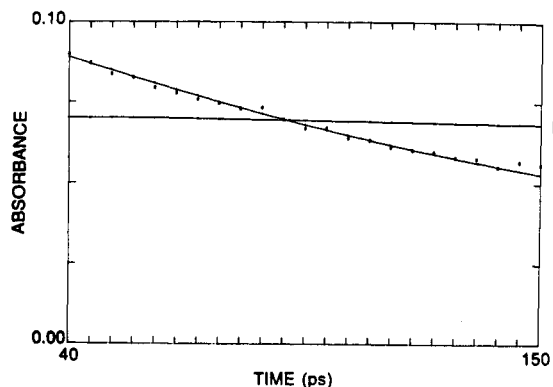
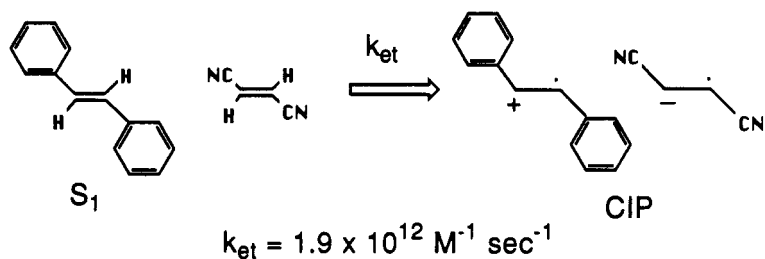


Fig. 5. Dynamics of trans-stilbene radical cation at 480 nm following 300 nm excitation of an acetonitrile solution of 30 μ M trans-stilbene/fumaronitrile. The points are experimental data. Curve A is calculated from Scheme 3 and Curve B is calculate from Scheme 4.

Clearly, Scheme 4 gives the superior fit to the experimental data suggesting that the electron is transfer when the two molecules are in contact, forming the CIP.

CONCLUSION

The results of the above study are summarized as follows:



The intrinsic rate of the electron transfer between the first excited singlet state of trans-stilbene and fumaronitrile is $k_{et} = 1.9 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ and the electron is transferred when the two molecules are in contact to produce a contact ion pair. This rate constant is two orders of magnitude greater than the diffusion controlled rate constant and could only have been obtained by examining the early picosecond dynamics of the electron transfer. This methodology will allow us to measure the rate of electron transfer between a variety of substituted stilbenes and alkenes in order to examine the Marcus theory of electron transfer (ref. 7).

Acknowledgements

This work is supported by a grant from the National Science Foundation (CHE 8418611)

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