Nonvertical Triplet Excitation Transfer to Arylalkene Acceptors: Further Evidence That Double Bond Torsion Is Unimportant

C. M. Brennan,[†] **R. A. Caldwell,**[*] **J. E. Elbert,**[‡] **and D. J. Unett**

Contribution from the Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75083

Received November 26, 1993[®]

Abstract: Time-resolved kinetic absorption spectrophotometry and photoacoustic calorimetry have been employed in a study of the kinetics and energetics of triplet excitation transfer to a series of arylalkene acceptors. Both the *cis* and *trans* isomers of β-methylstyrene are able to achieve significant relaxation in the triplet state. Nonvertical behavior is observed only for the *cis* isomer, for which single-bond torsions are expected to contribute to the measured relaxation. A comparison of the behavior of tetraphenylallene and its model, 1,1-diphenylethylene, is also revealing. Relaxation through double bond torsion in the allene triplet state leads to an "allyl–vinyl" biradical of particularly low energy. Measured energy transfer rate constants for the two molecules display a close correspondence. These results provide further compelling evidence for a recently proposed model for the nonvertical excitation transfer process dominated by single bond torsional modes.

Introduction

In nonvertical triplet excitation transfer (NVT), spectroscopic energies of donor and acceptor triplets predict an endothermic process, but the rate constant for excitation transfer is enhanced relative to that to be expected were the spectroscopic energy deficit simply to be made up by thermal activation. The initial proposals[1–3] for the process were intended to explain the rate enhancements. They postulated that a geometrical change in the acceptor triplet toward some conformation at which its energy was relaxed, i.e. lower than the known spectroscopic energy, occurred during the excitation transfer.

For *cis*-stilbene (*c*-S), the motion suggested was torsion of the double bond toward a perpendicular geometry, in line with the long-understood torsional relaxation of the ethylene triplet. Subsequent discussions of the origins of the NVT process, as it pertains to flexible π-systems, have focused extensively on the details of the mode of access to these perpendicular triplets.[4–11]

Recently Gorman *et al.*[12–14] have offered a different interpretation. They noted that all acceptors for which NVT was claimed possessed significantly nonplanar π-systems in the ground state as a result of steric crowding.[15–17] The exception, *trans*-stilbene,[4,7] is discussed below. The strain induced by this crowding is relieved primarily through single bond torsions (phenyl–vinyl torsion in *cis*-stilbene). Low-frequency oscillations about these single bonds at ambient temperatures enable these systems to explore more nearly planar ground state conformations which are expected to possess reduced spectroscopic triplet energies as a consequence of excited state stabilization. This interpretation therefore outlines a simple mode by which these systems achieve access to a lower entry point on the triplet surface and the rate enhancements characteristic of NVT. Taking *c*-S as a case in point, Gorman *et al.*[12] showed that its analog 2,3-diphenylnorbornene (DPN), differing from *c*-S in being incapable of significant double bond twisting but like *c*-S in being able to stabilize in the triplet state by phenyl–vinyl single bond torsion, afforded a near-exact correspondence with *c*-S in rate constants of excitation transfer from standard triplet donors. Subsequent work[18] showed that relaxed DPN triplet was some 10 kcal mol^{-1} lower than the spectroscopic DPN triplet state, the relaxation being assigned primarily to phenyl–vinyl torsion.

This paper reports further studies of excitation transfer kinetics to arylalkene acceptors in which the fully relaxed triplet state of the acceptor differs substantially in geometry from the spectroscopic state. We have sought a more rigorous test of the lack of importance of double bond torsion in assisting NVT to alkenes. Of great interest as an acceptor in this connection is *trans*-β-methylstyrene (*t*-MS), expected to be planar in the ground state yet known to be perpendicular at the double bond in the triplet state.[19,20] It possesses the capability to relax in the triplet from some 60.5 (spectroscopic) to 53.2 kcal mol^{-1} by double bond torsion, but it has no single bond torsion in the ground state able to assist NVT. We find that *t*-MS behaves as a classical vertical acceptor whereas *cis*-β-methylstyrene (*c*-MS), a nonplanar

---

[†] Present address: I.C.I. Specialties, Blackley, Manchester, U.K.

[‡] Present address: Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[®] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) Hammond, G. S.; Saltiel, J. *J. Am. Chem. Soc.* **1963**, *85*, 2516.

(2) Hammond, G. S.; Saltiel, J.; Lamola, A. A.; Turro, N. J.; Bradshaw, J. S.; Cowan, D. O.; Counsell, R. C.; Vogt, V.; Dalton, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 3197.

(3) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.

(4) Saltiel, J.; Charlton, J. L.; Mueller, W. B. *J. Am. Chem. Soc.* **1979**, *101*, 1347.

(5) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

(6) Orlandi, G.; Monti, S.; Barigelletti, F.; Balzani, V. *Chem. Phys.* **1980**, *52*, 313.

(7) Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144.

(8) Ramamurthy, V.; Liu, R. S. H. *J. Am. Chem. Soc.* **1976**, *98*, 2935.

(9) Wagner, P. J.; Scheve, J. *J. Am. Chem. Soc.* **1977**, *99*, 2888.

(10) Lamola, A. A. *Energy Transfer and Organic Chemistry*; Interscience: New York, 1969.

(11) Saltiel, J.; D'Agostino, J. D.; Megarity, E. D.; Metts, L.; Neuberger, K.; Wrighton, M. S.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

(12) Gorman, A. A.; Beddoes, R.; Hamblett, I.; McNeeney, S. P.; Prescott, A. L.; Unett, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 963–964.

(13) Gorman, A. A.; Hamblett, I.; Rushton, F. A. P.; Unett, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 983–984.

(14) Forward, P. J.; Gorman, A. A.; Hamblett, I. *J. Chem. Soc., Chem. Commun.* **1993**, 250–251.

(15) Gorman, A. A.; Hamblett, I.; Jensen, N.-H. *Chem. Phys. Lett.* **1984**, *111*, 293.

(16) Gorman, A. A.; Hamblett, I.; Irvine, M.; Raby, P.; Standen, M. C.; Yeates, S. *J. Am. Chem. Soc.* **1985**, *107*, 4404.

(17) Gorman, A. A.; Lambert, C.; Prescott, A. L. *Photochem. Photobiol.* **1990**, *51*, 29.

(18) Caldwell, R. A.; Riley, S. J.; Gorman, A. A.; McNeeney, S. P.; Unett, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 4424.

(19) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

(20) Bonneau, R.; Herran, B. *Laser Chem.* **1983**, *4*, 151–70.

0002-7863/94/1516-3460$04.50/0

Table 1. Rate Constants for Triplet Energy Transfer from Selected Sensitizers to *trans*-β-Methylstyrene, *cis*-β-Methylstyrene, 1,1-Diphenylethylene, and Tetraphenylallene

sensitizer (E_T/kcal mol^{-1})[a]	k_{et}(*t*-MS)/L mol^{-1} s^{-1}	k_{et}(*c*-MS)/L mol^{-1} s^{-1}	k_{et}(DPE)/L mol^{-1} s^{-1}	k_{et}(TPA)/L mol^{-1} s^{-1}
xanthone (74.1)			7.1×10^9	6.2×10^9
p-methoxyacetophenone (71.81)		7.6×10^9	6.0×10^9	
benzophenone (68.6)	4.3×10^9	2.4×10^9	3.9×10^9	2.5×10^9
thioxanthone (65.5)	4.3×10^9	4.1×10^9	4.8×10^9	3.2×10^9
phenanthrene (61.9)	2.6×10^9	2.0×10^9	1.9×10^9	1.9×10^9
naphthalene (60.9)		2.3×10^8	1.0×10^9	2.5×10^8
9-cyanophenanthrene (58.1)[b]	3.0×10^8	3.2×10^7	1.6×10^8	3.0×10^7
3-methoxy-9-cyanophenanthrene (57.0)[b]	3.2×10^7	3.7×10^6	4.0×10^7	4.3×10^6
chrysene (56.6)	3.2×10^7	3.7×10^6		
3,9-dicyanophenanthrene (55.5)[b]			3.2×10^7	3.2×10^6
fluoranthene (54.2)	3.8×10^5		8.7×10^5	1.1×10^6
fluorenone (53.3)[c]	1.9×10^5	1.8×10^5	6.3×10^5	
1,2,3,4-dibenzanthracene (50.8)			2.5×10^5	

[a] Unless otherwise stated the data are from the following: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. [b] Caldwell, R. A.; Creed, D.; Maw, T.-S. *J. Am. Chem. Soc.* **1979**, *101*, 1293. [c] Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, NY, 1966; p 298.

molecule, is a nonvertical acceptor, thus providing further confirmation of Gorman's hypothesis.

We have also compared tetraphenylallene (TPA) as an acceptor to 1,1-diphenylethylene (DPE), for which the π-system should be essentially the same, and have determined the relaxed triplet energy of TPA by time-resolved photoacoustic calorimetry.[21-24] Double bond torsion in the TPA triplet state produces an "allyl–vinyl" biradical structure of particularly low energy, and if this were important to NVT, the rate of excitation transfer to TPA should have been enhanced relative to DPE. In contrast, rates of triplet energy transfer to TPA and DPE are closely comparable and they suggest NVT involving only the phenyl–vinyl torsions.

Experimental Section

Materials. Triplet sensitizers were available commercially or were prepared earlier in these laboratories and were purified by recrystallization. Solvents were HPLC or spectro grade and were used without further purification. *t*-MS and DPE were purified by vacuum distillation. Preparation of *c*-MS was by photoisomerization of the *trans* isomer using α-naphthyl phenyl ketone as a photosensitizer. Purification was effected via column chromatography to remove the sensitizer followed by preparative gas chromatography. A sample of *t*-MS was also purified by preparative GC without significant change in the observed kinetics. Tetraphenylallene was purified by recrystallization.

Kinetic absorption spectrophotometry was used to determine the rate constants for excitation transfer. The experimental configuration is well-known. The apparatus used was a continuum YG671C-10 Nd:YAG Q-switched laser with pulse width fwhm = 5 ns, typically operated at 2–3 mJ/pulse. An Osram Model XBO 150 W/I high-pressure xenon lamp provided the monitoring excitation which was focused onto a 2 mm × 1 mm aperture at the front of a 5 mm × 10 mm cuvette. A matching aperture at the rear allowed the monitoring light to exit and be focused onto the entrance slit of a CVI Digikrom 240 monochromator. The signal from a Hamamatsu R928 phototube in a housing modified as previously reported was received, after baseline zeroing using a backoff box, by a Tektronix DSA602 digital signal analyzer and transferred to a 386 PC clone for analysis by the PC RAD and KS01 programs.

Solutions were maintained under a continuous nitrogen sparge and the volume was monitored to ±5%. Energy transfer rate constants were determined in toluene or cyclohexane, the latter solvent being employed for the higher energy ketone sensitizers. All energy transfer rate constants for TPA were determined in benzene. The acceptor (quencher) was added by microliter syringe, either as neat liquid or as a dilute solution depending on the range of concentration required. Triplet states of sensitizers with little or no ground state absorption at 355 nm were generated by sensitization using either benzophenone or thioxanthone. Such sensitizers were used in concentrations sufficient to yield the desired triplet states on a time scale calculated to be rapid in comparison to the subsequent energy transfer to the desired quencher.

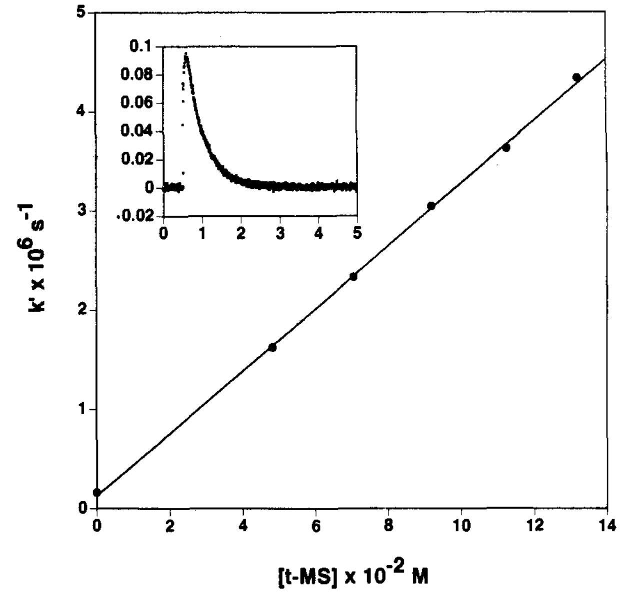

Figure 1. First-order rate constants for chrysene triplet decay vs *t*-MS concentration. Inset: Decay profile of chrysene triplet monitored at 575 nm. *x*-axis, 1 μs/division.

Photoacoustic calorimetry employed a 1-MHz transducer and followed procedures previously described.[23,25]

The **oxygen perturbed absorption spectrum** of *cis*-β-methylstyrene was obtained using a high-pressure absorption cell and Hewlett-Packard Model 8450A diode array spectrometer. The procedure and cell design have been reported previously.[23]

Results

Rate constants for triplet excitation transfer are given in Table 1. A representative rate constant plot is reproduced in Figure 1. The k_{et} values in general are reproducible to ±10%. Plots of log k_{et} as a function of sensitizer triplet energy are shown in Figures 2–4. The rationale for such plots is well-known;[3,26] the details are discussed subsequently.

Tetraphenylallene triplet was observed following excitation transfer from thioxanthone or benzophenone sensitizer. Its lifetime of 97 ns (Figure 5) was independent of sensitizer and laser power, was identical at 0.059 and 0.015 M, and was identical in benzene or CCl_4 solvent. The absorption spectrum of the TPA triplet state (Figure 6) was also identical in the two solvents,

---

(21) Braslavsky, S. In *Photoacoustic and Photothermal Phenomena*; Hess, P., Pelzl, J., Eds.; Springer Verlag: Berlin, 1988; Vol. 58, pp 508–13.

(22) Melton, L. A.; Ni, T.; Lu, Q. *Rev. Sci. Instrum.* **1989**, *60*, 3217–23.

(23) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457–64.

(24) Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849.

(25) Arnaut, L. G.; Caldwell, R. A.; Elbert, J. E.; Melton, L. A. *Rev. Sci. Instrum.* **1992**, *63*, 5381–5389.

(26) Sandros, K. *Acta Chem. Scand.* **1973**, *27*, 3021.

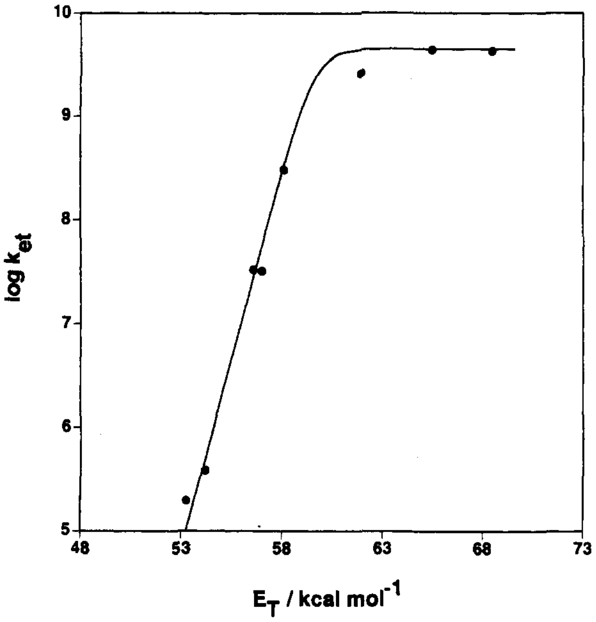

Figure 2. Plot of log k_{et} for triplet energy transfer from selected sensitizers to *trans*-β-methylstyrene. The solid line is that expected[31] for a vertical acceptor with a triplet energy of 59.6 kcal mol^{-1} assuming diffusion at 6 × 10^9 L mol^{-1} s^{-1}.

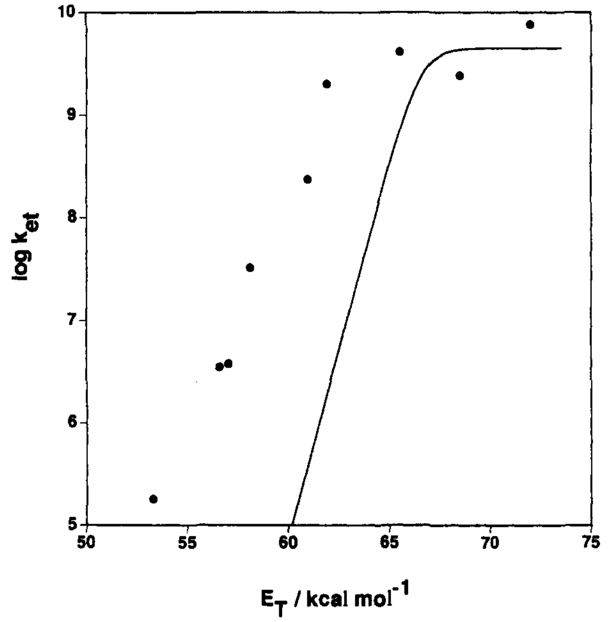

Figure 3. Plot of log k_{et} for triplet energy transfer from selected sensitizers to *cis*-β-methylstyrene. The solid line is that expected[31] for a vertical acceptor with a triplet energy of 66.5 kcal mol^{-1} assuming diffusion at 6 × 10^9 L mol^{-1} s^{-1}.

showing a broad absorbance centered around 390 nm. The triplet was quenched by oxygen with rate constants of 1.7 × 10^9 L mol^{-1} s^{-1} in benzene and 1.8 × 10^9 L mol^{-1} s^{-1} in CCl$_4$.

The relaxed triplet energy of TPA was determined using benzophenone sensitization in benzene by time-resolved photoacoustic calorimetry using techniques already described.[22,23,27] The triplet lifetime afforded by this technique was 90.3 ± 1.8 ns and the relaxed triplet energy was 40.2 ± 0.7 kcal mol^{-1}. The spectroscopic and relaxed triplet energies of the acceptors examined in this work are summarized in Table 2.

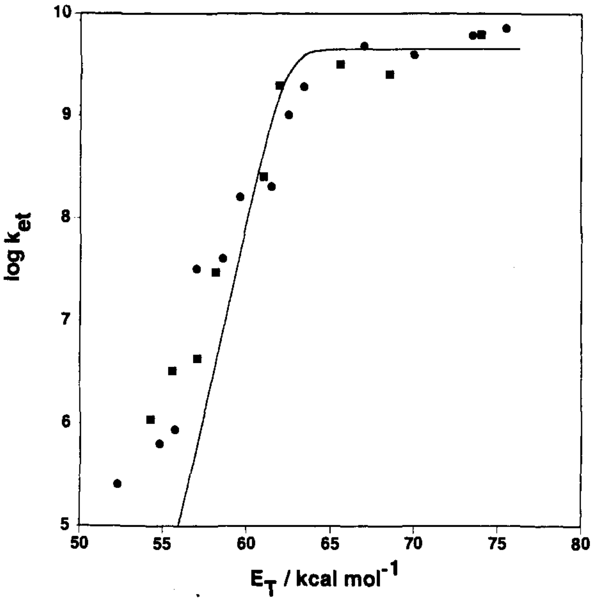

Figure 4. Plot of log k_{et} for triplet energy transfer from selected sensitizers to 1,1-diphenylethylene (●), shifted as described in text, and to tetraphenylallene (■). The solid line is that expected[31] for a vertical acceptor with a triplet energy of 62.3 kcal mol^{-1} (*vide infra*) assuming diffusion at 6 × 10^9 L mol^{-1} s^{-1}.

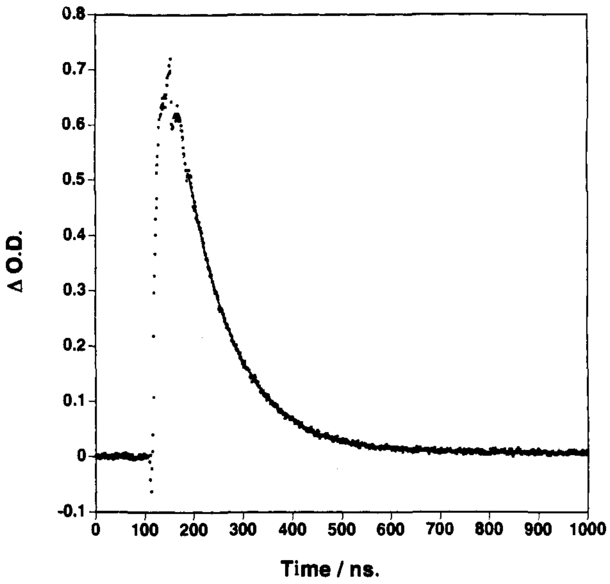

Figure 5. Decay profile of tetraphenylallene triplet state monitored at 400 nm following thioxanthone sensitization with a tetraphenylallene ground state concentration of 14.2 mM.

Discussion

Spectroscopic (Vertical) and Relaxed Acceptor Triplets. The data in Table 2 for *t*-MS and DPE are taken from our previous work[23] and show 7.3 and 8.7 kcal mol^{-1} relaxation relative to the respective vertical triplets. The spectroscopic triplet energy of *c*-MS was calculated from its oxygen perturbed singlet–triplet absorption spectrum. The spectrum contained no vibrational fine structure. The assigned value is that corresponding to the longest wavelength at which absorption was recorded (430 nm) and is probably accurate to ±10 nm (±1.6 kcal mol^{-1}). The energy assigned to the relaxed *c*-MS triplet is based on that measured for the *trans* isomer using photoacoustic calorimetry and is reported relative to the *cis* ground state which is 1.3 kcal mol^{-1} higher than the less strained *trans* ground state according to MMX (PCMODEL, Serena Software). The *c*-MS triplet is therefore able to relax by some 15.6 kcal mol^{-1}.

---

[27] Brennan, C. M.; Caldwell, R. A. *Photochem. Photobiol.* **1991**, *53*, 165–170.

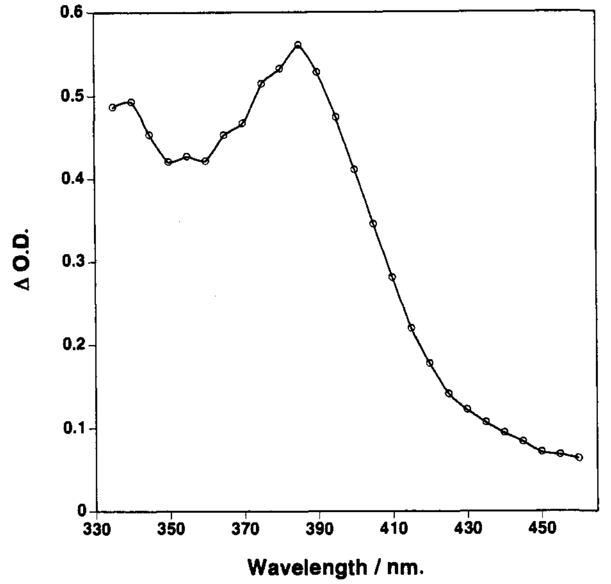

Figure 6. Tetraphenylallene triplet–triplet absorption spectrum recorded 72 ns after the laser pulse following thioxanthone sensitization.

Table 2. Spectroscopic and Relaxed Triplet Energies of Acceptors

quencher	E_T(spec)/kcal mol^{-1}	E_T(rel)/kcal mol^{-1}
t-MS	60.5[a]	53.2 ± 2.4[a]
c-MS	66.5[b]	50.9 ± 2.4[d]
DPE	60.8[a]	52.1 ± 1.8[a]
TPA	57.4[c]	40.2 ± 0.7[b]

[a] Reference 23. [b] This work. [c] Reference 35. [d] Relaxed triplet energy relative to *c*-MS ground state.

The available evidence suggests that relaxed styrene-type triplets adopt a perpendicular geometry.[19,20,23] In addition, one would also expect a tendency toward planarity across the phenyl–vinyl single bond even greater than in the ground state due to increased π-bond order in the excited state. For *t*-MS we therefore suggest that essentially all the relaxation can be accounted for by double bond torsion simply because we see no other available modes of relaxation. For *c*-MS and DPE, a contribution from phenyl–vinyl torsion might be included since each of these apparently (*vide infra*) begins with a nonzero phenyl–vinyl dihedral angle.

The opportunity for phenyl–vinyl torsion to assist in NVT requires a nonzero dihedral angle in the relaxed geometry of the ground state. We have examined *t*-MS, *c*-MS, and DPE using MMX and find dihedral angles of 1.34°, 42.99°, and 39.2°, respectively. It is therefore clear that *t*-MS has no opportunity for NVT by phenyl–vinyl torsion, whereas *c*-MS and DPE do.

Relaxation of TPA is a special case. The allyl–vinyl geometry calculated by Johnson[28-30] as the lowest energy point of the allene triplet surface can only be reached by a full 90° rotation of one of the orthogonal diphenylethylene chromophores with respect to the other. When in the allyl–vinyl structure, the extensive conjugation of the tetraphenylallyl radical chromophore and the strain relief engendered by the rehybridization of the allenic carbon provide a ready rationale for the reasonably low relaxed triplet energy of TPA.

If the entire 17.2 kcal mol^{-1} of relaxation available to TPA were to contribute to NVT, this extraordinary driving force should cause rates of excitation transfer to be much faster than to DPE. However, if phenyl–vinyl torsion is all that is relevant, the two may be regarded as possessing effectively identical chromophores and should show nearly the same rate constants for the same sensitizer.

Sandros Plots. The original plot by Sandros[31] of log (triplet excitation transfer rate constant) against the triplet energy of the donor, for transfers of excitation involving biacetyl, revealed basically two regions. In examples of exothermic triplet excitation transfer, rates were essentially independent of donor structure and the rate constant approached 10^{10} L mol^{-1} s^{-1}, nearly the rate constant for diffusion. The slope of the plot in the region of endothermic excitation transfer was essentially equal to $(RT \ln 10)^{-1}$ at room temperature. The interpretation of this and other similar outcomes is that thermal energy is used to make up a spectroscopic energy deficit, leading to an expected rate constant expressible as $A \exp(-\Delta E/RT)$, with constant A.

Very clearly only Figure 2 (for *t*-MS) fits this criterion, and we believe the present data demonstrate conclusively, by an accepted method, that *t*-MS is a vertical acceptor. Many years ago we had reached the same conclusion using secondary deuterium isotope effects reinforced by fragmentary rate constant data obtained from quenching plots.[32] It should be noted that the best fit to the *t*-MS data was obtained using a triplet energy of 59.6 kcal mol^{-1}. This is 0.9 kcal mol^{-1} lower than the spectroscopic value reported in Table 2. This small discrepancy is, however, within the reported experimental error of this measurement given the generally poor resolution of vibrational fine structure in the singlet–triplet absorption spectra of olefins. In addition, Lamola and Hammond[33] have also assigned a value of 59.8 kcal mol^{-1} to the *t*-MS triplet energy, a value in excellent agreement with that reported here, from their own spectroscopic measurements.

Though double bond torsion of *t*-MS is available in its triplet state with substantial exothermicity from vertical to relaxed triplet (Table 2), no rate enhancement of endothermic triplet excitation transfer is apparent from Figure 2. In contrast, the Sandros plot for *c*-MS given in Figure 3 displays the characteristic features of a nonvertical acceptor. Rates of energy transfer in the endothermic region are significantly enhanced relative to the predicted behavior. The obvious conclusion is that the introduction of steric interactions between the phenyl and β-methyl substituents in this acceptor produces the conditions necessary for NVT, i.e. a nonzero phenyl–vinyl dihedral angle. Furthermore, NVT is not observed (in *t*-MS) when only double bond torsion is available, yet is observed (in 2,3-diphenylnorbornene[12]) when only phenyl–vinyl single bond torsion is likely. Accordingly, we rule out double bond torsion as having substantial significance for NVT to arylalkenes.

From a study of activation parameters for substantially endothermic excitation transfer to the stilbenes from anthracene and 9,10-dichloroanthracene, Saltiel *et al.* have proposed that *trans*-stilbene is a nonvertical acceptor. It was suggested by these authors that adherence to the Sandros equation may not provide a sufficient criterion for vertical behavior when a compensation between enthalpic and entropic activation parameters occurs. Although, without temperature studies, we cannot rule out the potential application of such an argument to the experiments with *t*-MS, there are important differences between the two studies. The activation parameters reported by Saltiel *et al.* were determined for two sensitizers from which energy transfer is expected to be significantly endothermic regardless of the point of entry onto the stilbene triplet surface and for which room temperature rate constants were quite low (ca. 10^3–10^4 M^{-1} s^{-1}). In contrast, the present study concentrates on sensitizers with triplet energies sufficient to populate the relaxed styrene triplet exothermically and with rate constants in excess of 10^5 M^{-1} s^{-1}. Even if double bond torsion contributes significantly when the rate is so slow, we do not believe it necessary that that mechanism contribute when rates are much larger as in the case of *t*-MS.

---

(28) Johnson, R. P. *Org. Photochem.* **1985**, *7*, 75–147.
(29) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3963.
(30) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.
(31) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.
(32) Caldwell, R. A.; Sovocool, G. W.; Peresie, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 1496–1502.
(33) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

Our position is therefore not inconsistent with the preferred variable energy mechanism of Saltiel *et al.* We believe that the best resolution of the issue is that single bond (phenyl–vinyl) torsion is the dominant feature controlling the kinetics of NVT unless two conditions are met: (1) there are no sterically congested single bonds which are able to provide a rate enhancement, and (2) excitation transfer is so slow that modes normally of lesser importance, such as double bond torsion, must be called upon to assist. In other cases, although double bond torsion and single bond torsion may be coupled and may both contribute, the available evidence seems to demonstrate that the contribution of the latter by itself is sufficient to rationalize the kinetics. These are the cases which comprise by far the majority of examples of NVT.

The energy transfer data for DPE and TPA are presented together in Figure 4. Both molecules clearly behave as nonvertical acceptors. Görner[34] has previously reported a reasonable degree of adherence to the Sandros equation for DPE, leading to the conclusion that this molecule behaves as a classical acceptor. While the present results are largely in agreement with the earlier report, there is clearly a significant deviation from Sandros behavior in the more extensive data set reported here. To facilitate the comparison, the data points for DPE have been shifted to the right by 1.5 kcal mol^{-1}. This suggests a triplet energy for TPA somewhere around 62.3 kcal mol^{-1} which is significantly higher than a previously reported[35] value presented in Table 2. This comparison is, of course, less accurate than one in which two vertical acceptors are examined as there are no clear linear regions in the data. Indeed, this particular comparison is only possible due to the high level of correlation of the two data sets. The errors in the estimation of this higher triplet energy are, however, not significantly greater than those normally associated with the absorption measurements for reasons mentioned earlier.

Of particular interest is the possible effect of a double bond torsion in TPA. As described earlier, an enormous exothermicity is associated with full relaxation from the vertical triplet. However, as Figure 4 demonstrates, the differences in absolute rate constants for excitation transfer between TPA and its model (DPE) are quite modest. The putative advantage of double bond torsion to be gained for TPA is in actuality nil. The conclusion that double bond torsion is largely irrelevant to NVT is thereby reinforced.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant AT-532) for financial support. Laser flash photolysis equipment was purchased with support of the National Science Foundation (NSF CHE 8820268 and 9121313) and the Permanent Fund of the University of Texas. We thank Dr. A. A. Gorman for helpful discussions and Drs. R. M. Wilson and K. A. Schnapp for the sample of tetraphenylallene.

---

(34) Görner, H. *J. Phys. Chem.* **1982**, *86*, 2028.

(35) Ullman, E. F.; Henderson, W. A., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4390.