Quantitative Application of Principal Component Analysis and Self-Modeling Spectral Resolution to Product Analysis of **Tetraphenylethylene Photochemical Reactions**

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Tetraphenylethylene readily undergoes photochemical reactions in room-temperature solutions. Principal component analysis and self-modeling spectral resolution are applied to the characterization of reaction products. On the basis of principal component analysis, the results show that only one product is formed in the reactions, and the absorption and fluorescence spectra of the product obtained from self-modeling spectral resolution match those of 9,10-diphenylphenanthrene. A new photophysical constraint is introduced as an additional criterion for justifying the results of the self-modeling spectral resolution. Relative photochemical efficiencies of tetraphenylethylene under different conditions are determined and discussed in terms of their mechanistic implications.

INTRODUCTION

In a product analysis of a chemical reaction, the objective is usually to determine the number of products in the reaction mixture and the concentration of each product. For many reactions, especially photochemical reactions, absorption and fluorescence spectroscopies serve as useful and efficient analytical methods. However, for systems in which the spectral responses of the products severely overlap, direct spectroscopic analysis becomes difficult due to the required separation of individual components. The separation can be achieved either by isolating individual products before analysis or through a quantitative resolution of the spectral responses of the components. The latter retains an important advantage of the spectroscopic method by being a direct analytical technique. A quantitative determination of contributions of individual components in a spectral mixture can be accomplished by the application of a computer-based chemometric technique such as principal component analysis (PCA) and self-modeling spectral resolution (SMSR).

Principal component analysis as one of the most widely used chemometric methods has widespread applications in analytical spectroscopy.¹ Recently, the method has also been employed to deduce a noise-attenuated best averaged spectrum from a one-component data matrix consisting of repeatedly measured weak spectra.² In the present study, the method will be applied to determining the number of products in a reaction mixture.

A combination of principal component analysis with selfmodeling yields a powerful spectral resolution technique (PCA-SMSR) that has found many interesting applications.^{1,3,4} Because self-modeling spectral resolution requires almost no knowledge of the underlying spectrum and involves only very limited assumptions, it is regarded as one of the most useful and also most challenging methods in chemometrics.¹

In exploiting applications of PCA and SMSR to chemical reactions, we have carried out a photochemical study of tetraphenylethylene (TPE) in solution. Upon photoexcitation, TPE undergoes an isomerization process along the excited singlet potential energy surface. Because TPE is symmetric with respect to isomerization, the process yields a product that is identical to the starting material.⁵ The isomerization process involves a presumably zwitterionic excited-state intermediate,⁶ corresponding to a geometry in which the central bond is twisted 90°. The lifetime of the initially formed excited singlet state of TPE is very short (5-15 ps),⁷ which is attributed to a very fast twisting of the central bond toward the formation of the twisted intermediate. While the mechanism on the photophysics of TPE appears reasonable, the photochemistry of TPE has yet to be taken into account. It will be shown that, in addition to the isomerization process, TPE has another efficient photochemical reaction which yields photoproducts different from the reactant as indicated by changes in the absorption and emission spectra after only a brief irradiation of a TPE solution. Questions concerning the nature and product distribution of the reaction and its competition with the isomerization process have to be addressed.

In this paper, we report a quantitative application of the PCA-SMSR method to the analysis of tetraphenylethylene photoproducts. It will be shown, on the basis of principal component analysis, that only one product is formed in the photochemical reaction. The absorption and fluorescence spectra of the product will be obtained through self-modeling spectral resolution and compared to results in the literature. A new photophysical constraint for self-modeling spectral resolution will be introduced and discussed.

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EXPERIMENTAL SECTION

Materials. Tetraphenylethylene (Aldrich 98%) was repeatedly recrystallized from hexane and ethanol. 9-Cyanoanthracene was used as a fluorescence standard after repeated recrystallization from ethanol. Spectrophotochemistry grade hexane (Burdick & Jackson) and ethanol (Curtin Matheson Scientific) were used as received.

Measurements. UV irradiation of samples was conducted using a xenon lamp (450 W). The wavelength of the irradiating light was selected by a monochromator with a band pass of 19 nm.

Absorption spectra were recorded on a computer-controlled Shimadzu UV-2101PC UV/vis spectrophotometer. The spectral files generated from the measurements were then exported to text files for further data processing.

Fluorescence and fluorescence excitation spectra were obtained using a SPEX Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source and a R928 photomultiplier tube. A right-angle geometry was used for solutions with optical densities ≤ 0.1 . For more concentrated solutions, emission spectra were obtained using a small angle (22.5°) front surface excitation geometry to avoid possible innerfilter effects. For some fluorescence measurements, a 395-nm color glass sharp cut filter (Schott, GG-395) was used in front of the emission monochromator to eliminate the overtone of the excitation Raman, and the spectra thus obtained were corrected for minor distortions in the 395-450-nm region using the transmittance profile of the filter. All fluorescence spectra were corrected for nonlinear instrument response⁸ using a predetermined correction factor unless specified otherwise. Fluorescence excitation spectra were collected using the ratio mode of the instrument (rhodamine-B as quantum counter) and further corrected using predetermined excitation correction factors. Fluorescence quantum yields were determined using integrated spectral area. All fluorescence spectral files were exported to text files using the software DM3000 supplied by SPEX for further treatment.

GC/MS analyses were conducted on an HP5890 GC equipped with a 5970 MSD using a 10 m \times 0.2 mm (0.33- μ m film thickness) HP-1 fused-silica capillary column. The injection port temperature was 180 °C, and the initial chromatography oven temperature was 100 °C (for 5 min), followed by a temperature ramp of 15 °C/min to 280 °C.

Data Analysis. Computations for principal component analysis and self-modeling spectral resolution were performed on an IBM-compatible 486-50 MHz personal computer using home-made software.

RESULTS AND DISCUSSION

Photochemical Reaction. Tetraphenylethylene readily undergoes photochemical reactions in room-temperature solutions upon irradiation with ultraviolet light. Spectral changes due to photochemical products can be observed even during a fluorescence scan on our emission spectrometer with a rather narrow excitation slit (0.5 mm).

A deoxygenated hexane solution of TPE was irradiated with a 450-W xenon lamp through a monochromator. At the wavelength used for irradiation (335 nm), the optical density of the solution was 0.3 at time zero. During irradiation, an absorption spectrum of the solution was recorded every 5 min. As shown in Figure 1, the spectra change significantly with irradiation time, with a progressive decrease in the red onset and a gradual increase in the wavelength region around 255 nm. There is also an isobestic point at 283.5 nm. Fluorescence spectra of the solution were also recorded at the same time interval during irradiation, and the results with excitation at 286 nm are shown in Figure 2. Upon irradiation, there is a rapid growth of a structured fluorescence band due to the photoproducts at the blue side of the broad fluorescence spectrum of TPE. With continued irradiation, the new structured band quickly becomes predominant.



Figure 1. Experimental absorption spectra of irradiated TPE solutions: (A) in a deoxygenated hexane solution at irradiation times of 0, 15, 35, 55, 75, 95, 115, 135, and 155 min (in the order of decreasing absorption in the longer wavelength region); (B) in a hexane-ethanol mixture at irradiation times of 0, 15, 35, 55, 75, 95, and 115 min.



Figure 2. Fluorescence spectra in a deoxygenated hexane solution ($\lambda_{exc} = 286$ nm) at irradiation times of 1, 15, 35, 55, 75, 95, 115, 135, and 155 min (in the order of increasing intensity). The inset is an expanded view of fluorescence spectra in the 400–700-nm region obtained with a 395 sharp cut filter at the emission side.

Similar measurements were also carried out for TPE in an air-saturated hexane solution and a 50% (v/v) hexane-ethanol solvent mixture under the same photochemical conditions. While the results from the air-saturated solution are similar to those from the deoxygenated solution, spectral changes in the hexane-ethanol mixture are much slower than those in hexane solutions (Figure 1).

Principal Component Analysis. Principal component analysis determines the number of significant components in a linear system and enables the representation of m exper-

⁽⁸⁾ Park, C. A. Photoluminescence of Solutions; Elsevier: Amesterdam, 1968.



Figure 3. Experimental combination coefficients and limits for the data matrix consisting of absorption spectra in a deoxygenated hexane solution.

imental spectra in a k-dimensional vector space $(k \le m)$ where each of the m spectra is a linear combination of k underlying components.⁹ For a data matrix **D** $(m \times n)$, in which each row represents an experimental spectrum and different rows are spectra obtained under different experimental conditions, a coordinate in the vector space can be constructed by k eigenvectors of the matrix, which correspond to k nonzero eigenvalues. In practice, k significant eigenvectors (corresponding to k significant eigenvalues) are obtained and the other eigenvectors represent primarily experimental noise. An experimental spectrum D_i can therefore be represented as following:

$$D_i = D_i' + R_i \tag{1}$$

where R_i is a residual vector. D_i' is the noise-attenuated spectrum regenerated from the eigenvectors $(V_j, j = 1, k)$ for the experimental spectrum D_i ,

$$D_i' = \sum_{i=1}^k c_j V_j \tag{2}$$

The combination coefficients c_j (j = 1, k) are the coordinate values in the vector space.

Absorption Spectra. A data matrix consisting of absorption spectra in a deoxygenated hexane solution as a function of irradiation time was constructed. It consisted of 51 rows and 212 columns (221.2-390 nm with 0.8-nm increments). Principal component analysis of the matrix yielded the following first four large eigenvalues: 0.390, 0.719 $\times 10^{-2}$, 0.206 $\times 10^{-5}$, and 0.330 $\times 10^{-6}$. By using the criteria based on the relative magnitude of eigenvalues, we can safely conclude that this is a two-component system. The combination coefficients for experimental spectra, denoted as a_i and b_i for spectrum *i*, are shown in Figure 3. Because the spectra are normalized, the combination coefficients satisfy the following normalization condition,

$$a_i(\sum v_a) + b_i(\sum v_b) = 1$$
(3)

where v represents elements of the eigenvectors. The coefficients in Figure 3 apparently adhere to the normalization line (eq 3) very closely, which further confirms a well-defined two-component system. Thus, principal component analysis reveals that there is only one product in the reaction mixtures.

Principal component analysis was also applied to two other data matrices consisting of absorption spectra in an airsaturated hexane solution and in a 50% (v/v) hexane-ethanol mixture, respectively. The eigenvalues from the two matrices (Table I) show that each corresponds to a well-defined twocomponent system. Plots of the combination coefficients for the two matrices are also in support of the conclusion that only one photoproduct is formed in the irradiation of a TPE solution.

In order to examine the consistency of the underlying photoproduct absorption spectrum in three different data matrices, a global data matrix consisting of all 155 experimental spectra was constructed for principal component analysis. The first four large eigenvalues listed in Table I also point to a well-defined two-component system. While the combination coefficients show a close adherence to the normalization line, there are small deviations (Figure 4), presumably due to nonlinear effects from slightly different spectra in the hexane-ethanol solvent mixture. Nevertheless, the conclusion from the results is again that only a single photoproduct is generated in the irradiation of TPE under three different conditions.

Self-Modeling Spectral Resolution. As discussed above, principal component analysis of the absorption spectral matrices revealed that there are two components (TPE and a photoproduct) in the spectral mixtures. A determination of the pure-component spectra can be accomplished by selfmodeling spectral resolution.

For a two-component system, combination coefficients of the experimental spectra adhere to the normalization line (Figure 3). Obviously, the two sets of combination coefficients for the two pure-component spectra also fall on the line, and they should lie outside the two extremes of the experimental coefficients because both underlying components have positive contributions to the experimental spectra. A determination of the pure-component coefficients, often called limits, requires two boundary conditions.

The most commonly applied conditions are due to Lawton and Sylvestre.¹⁰ If the two pure-component spectra do not completely overlap over the entire wavelength region, i.e., if there is at least one wavelength where component 1 has a contribution and component 2 does not and there is one other wavelength where the reverse applies, they can be used as boundary conditions. For our spectral resolution, only one boundary condition is required because one of the two components (TPE) is known.

From Figure 1, it is obvious that the onset of the absorption spectrum decreases as irradiation progresses, indicating that the photoproduct has a much smaller contribution in that wavelength region. Therefore, it can be assumed that there is at least one wavelength where TPE has an absorption contribution but the photoproduct does not. This serves as a boundary condition for the self-modeling of the photoproduct absorption spectrum. Spectra generated from different sets of combination coefficients were examined by stepping along the normalization line at the end corresponding to the photoproduct. The set of coefficients corresponding to the spectrum with zero absorption contribution in the onset wavelength region was selected as the limit. The results thus obtained are shown in Figures 3 and 5. The absorption spectrum of the photoproduct is in excellent agreement with the literature result of 9,10-diphenylphenanthrene (DPP),¹¹ which is a cyclization product of TPE.

Spectral resolution was also performed for the other two data matrices (TPE in an air-saturated hexane solution and in a hexane-ethanol mixture) and for the global matrix. Shown in Figure 6 is a comparison of results from these different matrices. While the spectra in deoxygenated and airsaturated hexane solutions are essentially identical, the spectrum in the 50% (v/v) hexane-ethanol mixture is slightly different. The difference is likely a result of solvent effects. The spectrum from the global data matrix is close to those

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Table I. Eigenvalues from Principal Component Analysis of Absorption and Fluorescence Spectral Matrices									
spectral matrix	<i>e</i> ₁	e_2	e ₃	e4					
absorption, hexane (–O ₂)	0.390	0.719×10^{-2}	0.206×10^{-5}	0.330 × 10−6					
absorption, hexane (air)	0.262	0.218×10^{-2}	0.702×10^{-6}	0.191 × 10-6					
absorption, hexane-ethanol	0.324	0.545×10^{-3}	0.280×10^{-6}	0.169 × 10 ⁻⁶					
absorption, global	1.450	0.208×10^{-1}	0.184×10^{-4}	0.329×10^{-4}					
fluorescence (400-700 nm)	0.408	0.199	0.972×10^{-3}	0.363×10^{-4}					
fluorescence (320–550 nm)	0.194	0.700×10^{-2}	0.130 × 10− ³	0.100×10^{-4}					



Figure 4. Experimental combination coefficients and limits for the global data matrix consisting of 155 absorption spectra.



Figure 5. Absorption spectrum of DPP, obtained using self-modeling spectral resolution, from the data matrix consisting of spectra in a deoxygenated hexane solution. The spectrum of TPE regenerated from eigenvectors is also shown for comparison.

from the hexane solutions as a result of favorable statistical weight (a larger number of spectra).

With the determination of a pure-component spectrum, relative absorbance at a given wavelength can be calculated. However, in order to obtain relative concentrations of the two components, their molar absorptivity values have to be determined. At the isobestic point (283.5 nm),

$$\epsilon_{\rm TPE}^{iso} = \epsilon_{\rm DPP}^{iso} \tag{4}$$

where ϵ denotes molar absorptivity. A ϵ_{DPP} value of 47 500 M^{-1} cm⁻¹ at the absorption spectral maximum (257.5 nm) was thus obtained from the ϵ_{TPE} value of 14 700 M^{-1} cm⁻¹ at the first band maximum (309 nm).

In order to further confirm the identification of the photoproduct, a GC/MS analysis of an irradiated TPE solution was performed, which yielded two chromatographic peaks. The one with the shorter retention time belongs to the reactant TPE and the other one is due to the photoproduct. The MS trace of the photoproduct matches well with the



Figure 6. Comparison of absorption spectra of DPP from three different data matrices: - - -, in a deoxygenated hexane solution; - · · -, in an ethanol-hexane mixture; and —, global matrix. The spectrum in an air-saturated hexane solution (not shown) is identical to the spectrum in a deoxygenated hexane solution.

description of 9,10-diphenylphenanthrene,¹² consistent with the assignment made on the basis of spectroscopic results.

Fluorescence Spectra. As shown in Figure 2, fluorescence spectra of irradiated TPE solutions are also mixtures, with contributions from both TPE and DPP. Two data matrices consisting of fluorescence spectra in different wavelength regions were used for principal component analysis. At an excitation wavelength of 286 nm, the first set of fluorescence spectra was recorded with a 395-nm sharp cut filter at the emission side to eliminate the overtone of the excitation Raman (Figure 2, inset). The second set of spectra was recorded without the filter, but only covering the 300-550nm wavelength region in order to avoid the overtone (Figure 2). Principal component analysis of both matrices yielded eigenvalues clearly corresponding to a two-component system (Table I). Shown in Figure 7 is a plot of combination coefficients for the first data matrix, which closely adhere to the normalization line.

Because the fluorescence spectrum of TPE is available, self-modeling is only required for the determination of the DPP fluorescence spectrum. Application of the Lawton-Sylvestre constraint discussed above is quite straightforward in this case because it is certain that the spectrum of DPP does not overlap the spectrum of TPE in the red region. Fluorescence spectra generated from different sets of combination coefficients were examined by stepping along the normalization line at the end corresponding to DPP (Figure 7). The set of coefficients corresponding to the spectrum without contribution in the red region was selected as the limit. The results of DPP combination coefficients and the fluorescence spectrum in the 400-700-wavelength region are shown in Figure 7.

A similar treatment was performed for the second fluorescence spectral matrix. Because spectra in this matrix cover the 300–550-nm wavelength region, a full fluorescence spec-

⁽¹²⁾ Eigth Peak Index of Mass Spectra, 3rd ed.; The Mass Spectrometry Data Centre, The University, The Royal Society of Chemistry: Nottingham, UK, 1983; Vol. 2, Part 2.



Figure 7. Experimental combination coefficients and limits (\Box , from the Lawton–Sylvestre constraint; \diamond , from the optimization of eq 10) for the first fluorescence spectral matrix (400–700 nm). The corresponding spectral results (uncorrected) are shown in the inset.



Figure 8. Fluorescence spectrum of DPP from self-modeling spectral resolution. The portion represented by a dashed line demonstrates an excellent agreement between the results from the two fluorescence spectral data matrices covering different wavelength regions. The spectrum of TPE regenerated from eigenvectors is also shown for comparison.

trum of DPP was determined from self-modeling. As shown in Figure 8, the 400-550-nm portion of the spectrum is identical to that obtained from the first spectral matrix.

The DPP fluorescence spectrum shown in Figure 8 is in excellent agreement with the result in the literature.¹³ It further confirms that DPP is the photoproduct.

A Photophysical Constraint for Self-Modeling. For an experimental absorption spectrum with combination coefficients (a_i, b_i) , fractional contributions of the two components can be calculated as follows:

$$x_{\rm A1} = \frac{\begin{vmatrix} a_{\rm i} & a_{\rm 2} \\ b_{\rm i} & b_{\rm 2} \end{vmatrix}}{\begin{vmatrix} a_{\rm i} & a_{\rm 2} \\ b_{\rm 1} & b_{\rm 2} \end{vmatrix}} \tag{5}$$

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Table II. A Criterion	for Self-Modeling Spectral
Resolution due to the	Independence of Fluorescence
Quantum Yield Ratio	on Irradiation Time
inned.	in a d

time	$\Phi_{F,DPP}^{a}$	$\Phi_{F,DPP}^{b}$	time	$\Phi_{F,DPP}^{a}$	$\Phi_{F,DPP}^{b}$
(min)	$\Phi_{F,TPE}$	$\Phi_{F,TPE}$	(min)	$\Phi_{F,TPE}$	$\Phi_{F,TPE}$
5	19.34	19.29	95	24.39	23.93
15	25.47	25.37	105	24.85	24.30
25	25.21	25.08	115	24.92	24.28
35	24.70	24.55	125	25.09	24.35
45	24.35	24.17	135	25.61	24.72
55	24.23	24.00	145	26.31	25.24
65	23.87	23.61	155	26.46	25.21
75	23.69	23.37	165	23.97	22.79
85	23.75	23.38	av	24.48	23.98

^a From the Lawton-Sylvestre constraint. ^b From the optimized limit (eq 10).

$$x_{A2} = 1 - x_{A1} \tag{6}$$

where a_1 , b_1 and a_2 , b_2 are combination coefficients for the two pure components. When both components contribute to an absorption spectral mixture at a given wavelength,

$$A_1/A_2 = (x_{A1}/x_{A2})(A_1^{\circ}/A_2^{\circ})$$
(7)

where A_1/A_2 is absorbance ratio at the wavelength, with $A_1 + A_2 = A$ (the observed absorbance at the wavelength). A_1°/A_2° is the corresponding absorbance ratio from the two normalized pure-component spectra. Similar equations can be derived for the fluorescence spectra,

$$F_1/F_2 = x_{\rm F1}/x_{\rm F2}$$
 (8)

where F represents integrated fluorescence spectral area. Therefore, the relative fluorescence quantum yields of the two components can be written as follows:

$$\Phi_{\rm F1}/\Phi_{\rm F2} = (F_1/F_2)(A_2/A_1) = (x_{\rm F1}/x_{\rm F2})(x_{\rm A2}/x_{\rm A1})(A_2^{\rm o}/A_1^{\rm o}) \quad (9)$$

For TPE and DPP, the fluorescence quantum yields are independent of irradiation time, so that Φ_{F1}/Φ_{F2} should be a constant. As shown in Table II (second column), the Φ_{F1}/Φ_{F2} values from eq 9 are almost constant with respect to irradiation time, indicating that the selection of limits for the absorption and fluorescence spectra of DPP was correct. A further improvement, though not significant in this particular case, by adjusting the limit for either the absorption or fluorescence spectrum of DPP to minimize the following standard deviation is possible.

$$Q = \sum_{i=1}^{m} \{ (\Phi_{\rm F1}/\Phi_{\rm F2})_i - [(1/m)\sum_{r=1}^{m} (\Phi_{\rm F1}/\Phi_{\rm F2})_r] \}^2 \qquad (10)$$

Consequently, this equation can be used as an additional criterion for self-modeling. For the determination of the DPP absorption spectrum, the accuracy of the Lawton-Sylvestre constraint at the onset region could be questioned because there is a possibility that the contribution of DPP in the wavelength region is small but nonzero. In order to accommodate such an assumption, the limit for the DPP absorption spectrum (Figure 3) has to be moved inward. A systematic examination of this possibility yielded an increase in the standard deviation (eq 10), indicating that the limit for the DPP absorption spectrum determined using the Lawton-Sylvestre constraint is correct.

With the limits for the absorption and fluorescence spectra of TPE and the limit for the absorption spectrum of DPP fixed, the standard deviation defined in eq 10 can be optimized by adjusting the limit for the fluorescence spectrum of DPP (Figure 7). The coefficients for the optimized limit and the corresponding spectrum are also shown in Figure 7. The limit from optimization of eq 10 is very close to the one from the



Figure 9. Relative concentrations of DPP and TPE as a function of irradiation time: O, in a deoxygenated hexane solution; ∇ , in an air-saturated hexane solution; \Box , in a hexane-ethanol mixture.

Lawton-Sylvestre constraint, and their corresponding spectra are nearly indistinguishable. In fact, the difference between the limits from the two different methods is within the uncertainty range of the experiments and the spectral resolution methods. If the limit from optimization is chosen, a ratio of fluorescence quantum yields (Φ_{F1}/Φ_{F2}) of 24 is obtained. With the TPE fluorescence yield of 2 × 10⁻³, determined using a hexane solution of 9-cyanoanthracene ($\Phi_F = 1.0$)¹⁴ as a fluorescence standard, the fluorescence quantum yield of DPP is 5 × 10⁻².

While the photophysical constraint (eq 10) serves as an additional criterion for justifying or refining the selection of limits in this study, it can also be used as an independent boundary condition for self-modeling spectral resolution when the Lawton-Sylvestre constraint is not applicable. If the absorption spectrum of DPP was known and the spectrum of TPE had to be determined, self-modeling could not be achieved on the basis of the Lawton-Sylvestre constraint by searching for zero absorbance in the shorter wavelength region. In such a case, the TPE limit could be obtained by applying the photophysical constraint. The actual procedure is to step along the normalization line to calculate Φ_{F1}/Φ_{F2} by use of the corresponding limiting coefficients. The standard deviation defined by eq 10 will show a minimum, which corresponds to the optimized limit. This boundary condition will be useful to many self-modeling spectral resolution problems, especially in product analyses of chemical reactions.

The photophysical constraint can in principle be extended to systems with more than two components, but practical applications will be more complicated. Research toward a generalization of the method to multicomponent systems is in progress.

Mechanistic Consideration. With the determination of the absorption spectrum and molar absorptivity, the relative concentrations of DPP in the reaction mixtures can be calculated, and a comparative examination of efficiencies of the photochemical reaction under different conditions becomes possible. As shown in Figure 9, efficiencies of the reaction in deoxygenated and air-saturated hexane solutions are nearly identical, indicating that the reaction is from the excited singlet state of TPE.

The nearly identical photochemical efficiencies of TPE in the hexane solution with and without the presence of oxygen are also interesting with respect to the mechanism. It was proposed¹⁵ that a photochemical generation of DPP from TPE is a two-step process, and the conversion from the intermediate (unorthodox diphenyldihydrophenanthrene) to DPP requires the presence of oxygen or an oxidant. While our results appear to contradict the proposed mechanism, it is quite possible that a small amount of oxidant present as impurities in the hexane solvent may be responsible for the oxidation process.¹⁶



The photochemical reaction is considerably slower in a hexane-ethanol mixture (50% v/v) than in neat hexane. One possible explanation is solvent polarity effects. On the basis of a fluorescence study of TPE and derivatives in pentane, it was suggested¹⁷ that part of the emission is from a planar excited state of TPE thermally populated from the twisted state. The lifetimes of the twisted-state in pentane and hexane are rather long, 1.7 and 1.5 ns, respectively,⁶ so that the proposed thermal process can be facilitated. However, in a polar solvent, the twisted state lifetime is faster by at least a factor of 10,6 making the thermal population of the planar state impossible. If the proposed mechanism is correct, the results in Figure 9 suggest that the photochemical reaction of TPE in hexane could be from more than one excited singlet state, with a portion from the thermally generated planar excited state. Which excited singlet state is responsible for the rest of the photochemical reaction in hexane and in the hexane-ethanol mixture remains a question. They could be from the same planar excited state generated promptly from the vertical excited state or from the vertical excited state directly. The latter scenario is particularly interesting because it implies that the photochemical reaction can compete with the fast twisting motion of the central bond toward the formation of the twisted excited state. A time-resolved photochemical study of TPE in different solvents is required to further address the issue.

In summary, the PCA-SMSR method can be applied to studies of chemical reactions. However, the method requires the mixtures to be linear combinations of the reactant and product spectra. Although fluorescence analysis is somewhat easier with respect to self-modeling resolution, absorption spectra can provide more straightforward information. For absorption spectral matrix, the Lawton–Sylvestre constraint is often not applicable to one of the components. The photophysical constraint can be very helpful in this regard, but it requires accurate determination of both absorption and fluorescence spectra. Further effort is needed in order to extend the method to multicomponent systems.

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