fluorocarbons in exhibiting a much larger excess volume than is predicted by theory.[11]

Alternatively, the discrepancies noted may be related to the large positive values of X_{12} for the hydrocarbon–perfluorocarbon systems. Thus, the theory may become inaccurate when applied to *any* system for which X_{12} is large. In opposition to this hypothesis, it is to be observed that the previous investigations of solutions[2] offer no intimation of a disparity between observed and calculated excess volumes which increase with X_{12}.

Among nonpolar mixtures for which adequate equation-of-state data for the pure components are available, the hydrocarbon–perfluorocarbon systems appear unfortunately to be unique in being characterized by large positive interactions X_{12}. It is difficult therefore to reach a decision between alternative explanations attributing the error in the calculated excess volumes to a peculiarity of the fluorocarbons on the one hand or to the large values of X_{12} for their mixtures with hydrocarbons on the other. Detailed experimental studies on systems exhibiting LCST's would be informative in this connection.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Contract No. AF49(638)-1341.

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[11] An inverse dependence of the intermolecular energy E_0 on the volume V has been assumed in the derivation[1,3] of eq 1. If instead we write $E_0 = -\text{constant}/V^m$ with $m > 1$ (*ca.* 1.3 for n-C_6H_{14}–n-C_6F_{14}), the calculated excess volume is increased and values calculated for other excess quantities also are brought into better agreement with observation. The parameter C, then given by $C = (\gamma v/R)/[1 + 3m + 3/\alpha T]$, is diminished somewhat as well. However, representation of the equation of state for both the fluorocarbon and the hydrocarbon components is rendered less satisfactory by such revision, which would also entail introduction of an additional parameter. For these reasons we have not made use of this device.

A Kinetic Study of the Photochemical Reaction of Phenanthrenequinone with Olefins

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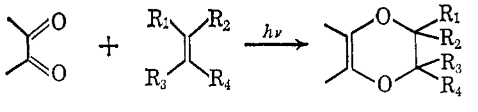
Contribution from the Photochemistry and Spectroscopy Laboratory, Northeastern University, Boston, Massachusetts 02115. *Received February 16, 1966*

Abstract: Quantum yields at 405 mμ for the addition of phenanthrenequinone to stilbene, diphenylethylene, and triphenylethylene in benzene solution are independent of the olefin concentration over a wide range but vary with the structure of the olefin. *cis*-Stilbene and *trans*-stilbene react at different rates but give rise to a common product. This reaction is accompanied by *cis–trans* isomerization for which $\Phi_{CS \rightarrow TS} \approx \Phi_{TS \rightarrow CS}$. The system reaches a stationary *trans/cis* isomer ratio of 0.7 ± 0.05, which is close to that reported for some photostable, high-energy sensitizers, but which in this case represents a balance between the rates of isomerization and adduct formation. Measurements with α,α'-stilbene-d_2 indicate a kinetic isotope effect for adduct formation. The results are consistent with the formation of the spectroscopic triplet state of *trans*-stilbene by classical energy transfer and of a short-lived common association complex between triplet quinone and the *cis*- or *trans*-olefin, which is partitioned between decay to a nonspectroscopic excited state and collapse to adduct. The intersystem-crossing efficiency for phenanthrenequinone is inferred to be unity.

Phenanthrenequinone (PAQ) adds photochemically to olefins. This is a general reaction for certain 1,2-diketones which was first reported by Schönberg and Mustafa[1] and which has been carried out on a preparative basis with a large number of olefins. The reaction yields adducts of structure I (eq 1). It was established by Pfundt and Schenck that only excitation of PAQ leads to adduct I; separate excitation of the olefin produces no conversion of PAQ.[2,3] On the basis of limited kinetic measurements, these authors propose a mechanism in which an excited state of PAQ forms a biradical intermediate with the olefin. Adduct is postulated to result from the interaction of this intermediate with a second, ground-state PAQ molecule.[3]



(1)

I

PAQ has a triplet energy of 48.8 kcal/mole,[4] and it was anticipated and found that, with the stilbenes, adduct formation is accompanied by *cis–trans* isomerization. Sensitized olefin isomerization is well documented, but the detailed mechanism of this process can by no means be regarded as established.[5] The question arises as to whether there is a relation between adduct formation and isomerization and whether, in general, olefin-sensitizer intermediates participate in the isomerization brought about by low-energy sensitizers. The detailed kinetic study of the reaction of PAQ with stilbene and with two other phenyl-substituted ethylenes was undertaken to firmly establish a mechanism for the addition reaction and to shed light on the role of

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[1] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 387 (1944).

[2] G. O. Schenck, O. Neumüller, and R. Koch, *Strahlentherapie*, **114**, 22 (1961).

[3] G. Pfundt, Doctoral Dissertation, Göttingen, 1962.

[4] This value was obtained from the emission spectra of PAQ in aliphatic hydrocarbons at 77°K; *cf.* N. A. Shcheglova, D. N. Shigorin, and M. V. Gorelik, *Zh. Fiz. Khim.*, **39** (4), 893 (1965).

[5] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964). This paper cites earlier references.

olefin-sensitizer intermediates. Further mechanistic information was sought by measurements with the 1,2-dideuteriostilbenes.

Experimental Section

Materials. Purities were established by gas chromatography (gc) using an F & M Model 720 temperature-programmed instrument with columns packed with appropriate substances (silicon grease, Carbowax 1500, and Triton X-305, 20% on Chromosorb-P, and by thin layer chromatography (tlc) on aluminum oxide coatings.

A. Solvents. Acetone and chlorobenzene were purified by fractional distillation. Ethyl acetate was treated with acetic anhydride prior to distillation, and acetic acid was distilled from phosphorus pentoxide. Carbon tetrachloride and tetrachloroethylene (both spectral grade) were used without further purification. *t*-Butyl alcohol was dried over sodium sulfate, refluxed over sodium, and finally distilled from sodium. Benzene satisfactory for the kinetic experiments was obtained by preparative-scale gas chromatography of CP benzene (16 ft × 1 in. column of 18% Triton X-305 on Chromosorb-P at 70°) and subsequent distillation.

B. Reactants. Commercial PAQ, after initial recrystallization from benzene or ethanol, was chromatographed on silica gel. The PAQ eluted with ethyl acetate and recrystallized from benzene was free of detectable impurities. *trans*-Stilbene (Eastman Kodak) was converted into its dibromide[6] from which it was regenerated by treatment with zinc.[7] Analysis of material prepared in this manner by tlc and gc showed it to be free of the *cis* isomer. In some kinetic experiments scintillation grade *trans*-stilbene containing less than 2% of the *cis* isomer as the sole impurity was used without further purification. *cis*-Stilbene (Eastman Kodak) was freed of the *trans* isomer by chromatography on alumina.[8] Pure samples of 1,1-diphenylethylene were obtained by gc of commercial material (4 ft × 0.25 in. column of 20% silicone grease on Chromosorb-P at 270°). Triphenylethylene (Eastman Kodak) was recrystallized from ethanol. 2-Acetonaphthone and naphthalene from the same source were recrystallized from ligroin and ethanol, respectively.

Deuterated Stilbenes.[9] Diphenylacetylene[10] in hexane was allowed to react with deuterium (99.5% purity) in the presence of 10% palladium-on-charcoal until 1 molar equiv of the gas was absorbed. The *cis*-stilbene-1,2-d_2 was freed from small amounts of the *trans* isomer and diphenylacetylene by chromatography on alumina using hexane as eluent. The fraction used for kinetic work contained at least 99.85% of the *cis* isomer (gc). *trans*-Stilbene-1,2-d_2 was obtained by the iodine-catalyzed photoisomerization, which can be conveniently followed by periodic spectral measurements, of the *cis* compound.[9] The material had mp 122.5–124° after recrystallization from ethanol (lit.[9] 123.8–125°) and contained at least 97% of the *trans* isomer (gc). Analysis by the falling-drop method indicated 16.40 atom % of deuterium[11] (calculated 16.67 atom %).

PAQ–Stilbene Adduct. Preparative-scale irradiations of PAQ were carried out in a modified version of the immersion apparatus described by Schenck.[12] A filter solution (1×10^{-4} *M* naphthalazine in xylene) served to exclude light below 390 mμ. PAQ (0.226 g, 1.09 mmoles) and *trans*-stilbene (1.075 g, 5.96 mmoles) in 280 ml of *t*-butyl alcohol were deoxygenated with a stream of nitrogen in the irradiation assembly, which was maintained at 30° by the circulation of water from a constant-temperature bath. The vigorously agitated suspension of PAQ was irradiated with a 250-w mercury lamp. After 15 min the PAQ had dissolved and a solid began to separate which was filtered after a total of 90 min of irradiation. Recrystallization from ethanol furnished 0.094 g (22%) of colorless adduct, mp 245–247° (lit.[13] 225°).

Similarly, *cis*-stilbene gave an adduct in 9% yield, mp 244–250°, after 45 min of irradiation. Every test applied showed the two adducts to be identical. A mixture melting point showed no depression, and the ultraviolet, infrared,[13] and nmr spectra were indistinguishable. Further, tlc under several conditions failed to effect a separation.

Apparatus and Procedure for the Kinetic Measurements. The monochromatic irradiation assembly[14] consists of a 500-w mercury lamp, a grating monochromator, a shutter, lenses to provide a collimated beam of light, a constant-temperature cell holder (±0.1°), and an Eppley thermopile with a basic sensitivity of 0.124 mv/mw cm^{-2}. These components are linearly arranged in the order given, with the thermopile directly behind the cell holder. The output of the thermopile is recorded on a strip chart recorder which is calibrated with reference signals from a precision potentiometer. At 405 mμ, the wavelength utilized in the kinetic experiments, this apparatus furnishes intensities of about 2 mw/cm^2 (4×10^{15} quanta/cm^2 sec).

The irradiations were carried out in rectangular Pyrex spectrophotometer cells of 1-cm path length. Since only an accurately masked area was illuminated, the solution was agitated throughout the photolysis by means of a magnetic stirrer. Separate tests established that the mixing was complete and rapid enough so as not to affect instantaneous measurements of the transmitted intensity. Solutions for kinetic runs were prepared by introducing aliquots of stock solutions of the reactants into a bulb to which the irradiation cell is attached. The solvent was completely removed on a high-vacuum line; pure, degassed benzene, which was stored over calcium hydride, was distilled into the bulb. The assembly was then sealed under vacuum. The initial concentration of PAQ and the volume of the solution were determined from its optical density at 407 mμ. Data recorded for each experiment were: (1) the dark response (shutter closed) and the intensity of the unattenuated light beam before and immediately after photolysis, (2) the intensity transmitted by the cell and solvent (I_0), and (3) the intensity transmitted by the cell and solution during photolysis (I) as a function of time. It can be readily shown that the total intensity of light absorbed at any time (I_{abs}) is given to a good approximation[14] by

$$I_{\mathrm{abs}} = F(I_0 - I) \tag{2}$$

where F is constant factor which includes the area irradiated, a correction for variations in intensity across the beam, and corrections for reflections from glass–air interfaces. Optical densities ($D = \log I_0/I$) measured with the irradiation apparatus agree to ±0.01 with values obtained with a spectrophotometer. Runs under a given set of conditions were made at least in duplicate. Quantum yields were computed from the least-squares slopes of $\log [(I_0/I) - 1]$ *vs.* time plots (see Results).

Since it was established that at very high olefin-to-PAQ ratios (~100:1) air had a negligible effect on the reaction,[15] the rate of isomerization of the stilbenes was measured in nondegassed solutions. The irradiation cell was provided with a serum-cap-covered opening through which microliter samples were withdrawn periodically during irradiation. The *cis–trans* isomer distribution was determined by gc using a 4 ft × 0.25 in column of 20% silicone grease on Chromosorb-P at 250°. By varying the column temperature it was shown that no thermal isomerization occurs.

Spectral Measurements. These were made with a Beckman DK-1 spectrophotometer using a constant-temperature cell block. Under the conditions of the kinetic experiments (concentrations were PAQ ~ 5×10^{-4} *M* and olefins ~10^{-2} *M*), only the PAQ absorbed light at wavelengths greater than 390 mμ. The adduct spectra in benzene are all very similar and show maxima near 350 and 370 mμ with $\epsilon \approx 1.6 \times 10^3$. The maximum of PAQ at 407 mμ (ϵ 1.86×10^3, benzene) conveniently almost coincides with a mercury emission line. Adherence to Beer's law in the range 1–5 × 10^{-4} *M* was found for PAQ at 367 and 407 mμ and for the stilbene photoadduct at 367 mμ. It was shown by comparing the calculated and observed densities of mixtures that there is no ground-state complex formation between the quinone and stilbene, and that the spectra of the quinone and its adduct are additive. A degassed solution of PAQ and *trans*-stilbene showed no spectral changes on standing in the dark for 80 days.

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(6) "Organic Syntheses," Coll. Vol. 3, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 350.

(7) W. M. Schubert, B. S. Rabinovitch, and N. R. Larson, *J. Am. Chem. Soc.*, **74**, 4590 (1952).

(8) M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

(9) *Cf.* N. Tunkel, Doctoral Dissertation, Rutgers University, 1955.

(10) Reference 6, p 377.

(11) Measured by Josef Nemeth, Urbana, Illinois.

(12) G. Schenck, *Dechema-Monograph.*, **24**, 105 (1955). The modified design, which was suggested by Dr. H. Köller, is described in the M. S. thesis of D. H. Lambert, Northeastern University, 1964.

(13) A. Butenandt, L. Karlson-Poschmann, G. Failer, U. Schiedt, and E. Bickert, *Ann.*, **575**, 123 (1951).

(14) A detailed description of this apparatus will be published (H. P. Wolf, J. J. Bohning, P. A. Schnieper, and K. Weiss).

(15) *Cf.* also S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

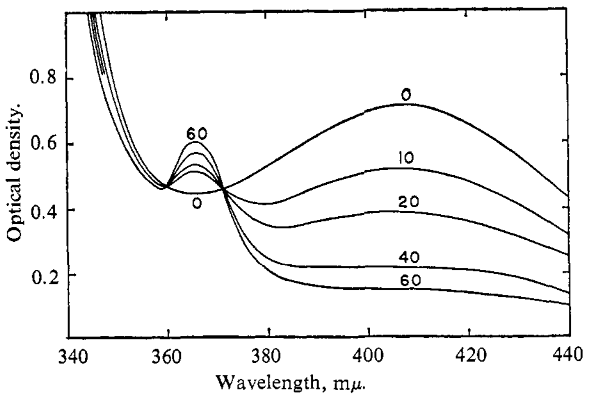

Figure 1. Photolysis of PAQ and *trans*-stilbene in benzene. The initial concentrations were PAQ 4×10^{-4} *M* and *trans*-stilbene 4×10^{-2} *M*. The numbers on the curves represent the irradiation time in minutes.

Results

Addition Reaction. To obtain meaningful rate data, it was first necessary to establish conditions under which adduct formation is the predominant reaction. Under preparative conditions, the isolated yields of adduct were found to be low even when light absorption was confined to the PAQ. The photolysis of PAQ in a number of purified and thoroughly outgassed solvents resulted in its disappearance even in the absence of olefin. In two cases (acetic acid, acetone) about 50% of the PAQ was regenerated when the cells were opened to air. This is indicative of the formation of 9,10-dihydroxyphenanthrene, which is known to undergo rapid air oxidation.[16] With respect to reactivity and the solubility of the reactants, benzene appeared most suitable. Its further purification by preparative-scale gas chromatography provided a solvent which was adopted for the kinetic work in view of the following facts.

1. Irradiation of PAQ in this solvent under standard kinetic conditions results in the disappearance of only 25% in 60 min, and oxygen regenerates 60% of the reacted PAQ. In the presence of 10^{-2} *M trans*-stilbene, 86% of the PAQ reacts in the same time and none is re-formed with oxygen.
2. In the absence of olefin, irradiation gives rise to isosbestic points at 354 and 365 mμ and a new peak at 357 mμ. With *trans*-stilbene, isosbestic points appear at 357 and 372 mμ, and the photoadduct peak appears at 367 mμ[3,17] (Figure 1).
3. Using the decrease in optical density at 407 mμ as a measure of the PAQ which has reacted in conjunction with the extinction coefficients at 367 mμ for PAQ and adduct, 90–95% yields of adduct can be calculated from the optical densities at 367 mμ of stilbene reaction mixtures.

Clearly the olefin almost completely suppresses the side reaction with the solvent, the nature of which remains obscure.

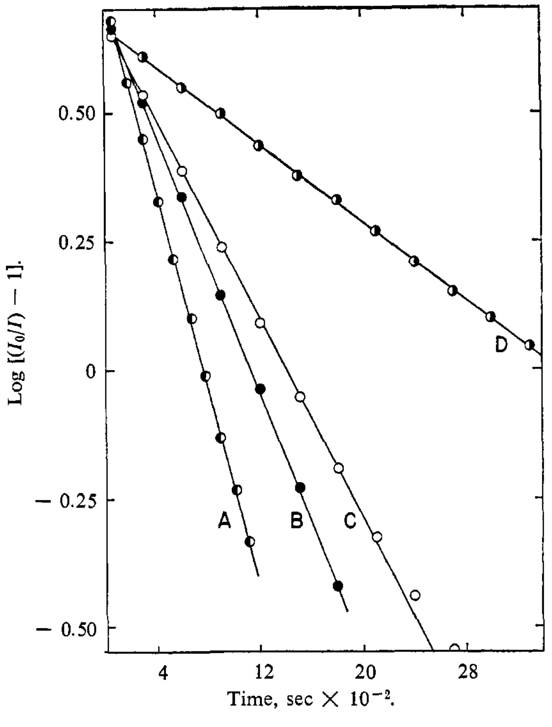

Figure 2. Determination of Φ_A according to eq 3. Initial concentrations were PAQ $\sim 5 \times 10^{-4}$ *M* and olefins $\sim 5 \times 10^{-2}$ *M*: (A) *cis*-stilbene, (B) triphenylethylene, (C) *trans*-stilbene; (D) 1,1-diphenylethylene.

In the presence of an excess of olefin, the disappearance of quinone follows the simple rate law $-d[Q]/dt = \Phi_A I_{abs}$ ([Q] = PAQ concentration, Φ_A = quantum yield) for 75–80% of reaction.[18] Introducing the definition $I_{abs} = I_0' - I' = I_0'[1 - \exp(-2.3\epsilon[Q]d)]$, where *d* is the path length in cm, ε is the extinction coefficient of PAQ at 405 mμ, and I_0' and I' represent the incident and transmitted light intensities (einsteins/l. sec) corrected according to eq 2, and integrating lead to

$$\log [(I_0/I) - 1] = \log [(I_0/I) - 1]_{\text{initial}} - \Phi_A I_0' \epsilon t \quad (3)$$

Some representative plots of eq 3 with PAQ:olefin ratios of 100 are shown in Figure 2, while Table I lists the quantum yields for all the olefins studied.

Table I. Quantum Yields for the Addition of PAQ to Olefins[a]

Olefin	Quantum yield (Φ_A)[b]
trans-Stilbene	0.066 ± 0.002[c]
cis-Stilbene	0.14 ± 0.005
α,α′-*trans*-Stilbene-d_2	0.069 ± 0.002
α,α′-*cis*-Stilbene-d_2	0.17 ± 0.005
Triphenylethylene	0.11 ± 0.004
1,1-Diphenylethylene	0.035 ± 0.001

[a] With 405-mμ light, in benzene at 25°. Initial PAQ and olefin concentrations are $\sim 5 \times 10^{-4}$ and $\sim 5 \times 10^{-2}$ *M*, respectively. [b] Slope (eq 3) divided by $I_0'\epsilon$. [c] Average of ten determinations with intensities in the range 1.5–3.3 × 10^{-6} einstein/l. sec.

At this point it is pertinent to examine why there are deviations from eq 3 toward the end of the photolysis. It should be noted that the plots invariably curve upwards; *i.e.*, there is an apparent decrease in quantum yield. The effect is particularly noticeable with *trans*-stilbene, where the appearance of *cis*-stilbene as the reaction proceeds cannot be responsible since this isomer is more reactive. Apart from mechanistic con-

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(16) P. Ramart-Lucas, J. Matti, T. Guilmart, and M. Grumey, *Bull. Soc. Chim. France*, 1215 (1948).

(17) *Cf.* also G. O. Schenck, *Strahlentherapie*, **115**, 597 (1961).

(18) 1,1-Diphenylethylene, the least reactive olefin, was only followed for 60% of reaction.

siderations, other causes to be explored are: (1) the fact that the adduct or a product of side reactions is a more efficient quencher of excited PAQ than stilbene, and (2) the formation of side products which show absorption in the 400-mμ region. With respect to the first possibility it was found that added adduct at twice the PAQ concentration has essentially no effect on the *trans*-stilbene reaction ($\Phi_A = 0.063$). Naphthalene and 2-acetonaphthone, which have been reported to quench benzophenone triplets at close to diffusion-controlled rates,[19] and which seemed to constitute reasonable model quenchers of PAQ in view of an early estimate of its triplet energy as ~65 kcal,[20] produced no change in Φ_A for the *trans*-stilbene reaction.

Case 2 appears to account for the lack of linearity at high conversion. Thus when a second charge of PAQ (as solid) is added to a photolyzed *trans*-stilbene–PAQ (100:1) reaction mixture and the solution is rephotolyzed, the apparent quantum yield is about 20% lower than for the initial photolysis. Subsequent additions of PAQ and photolyses show increasingly smaller decreases in the slopes, as if the component responsible for the change was gradually being eliminated. This behavior is entirely consistent with the appearance of a small amount of absorption in the 400-mμ region which would cause the actual PAQ concentrations to be significantly lower than the apparent concentrations at high conversion.

The quantum yields quoted in Table I are independent of the olefin concentration provided that a reasonable excess of olefin is maintained. With *trans*-stilbene, there is no appreciable decrease in rate until the olefin: PAQ ratio is less than 3:1. Under conditions where the reaction rate is independent of the olefin concentration, it is also insensitive to oxygen. As shown in Table II, the quantum yields for the stilbene reactions show a small temperature dependence.

Table II. Temperature Dependence of the Stilbene–PAQ Reaction[a]

Temp, °C	Φ_A *trans*-Stilbene	*cis*-Stilbene
11	0.067 ± 0.002	0.16 ± 0.01
26	0.065	0.14
40	0.061	

[a] Stilbene:PAQ ratio is 100:1.

***cis–trans* Isomerization.** Data for the stilbene reactions in which *ca.* 4 × 10^{-4} *M* PAQ was photolyzed under standard conditions are presented in Table III. Isomerization quantum yields were determined from the initial rates of light absorption and the initial slopes of the isomerized stilbene concentration *vs.* time curves, in each case starting with the pure isomer (Table IV). The estimated uncertainty of ~5% in the quantum yields leads to the conclusion that $\Phi_{\mathrm{CS-TS}} \approx \Phi_{\mathrm{TS}\rightarrow\mathrm{CS}}$ for stilbene.[23]

Table III. PAQ-Sensitized *cis–trans* Isomerization of Stilbenes[a]

Initial concentrations PAQ × 10^4	Total stilbene × 10^2	*trans/cis* ratio Initial	Final
4.49	4.51	0.054	0.077
4.59	4.61	0.32	0.35
4.06	4.00	1.11	1.02
4.73	4.74	4.26	2.70
4.33	4.32	330	16.2
4.35	4.33[b]	25.9	9.5
4.31	4.30[c]	0.0084	0.039

[a] At 25° in benzene. Solutions were irradiated for 45 min. [b] α,α′-*trans*-Stilbene-d_2. [c] α,α′-*cis*-Stilbene-d_2.

Table IV. Quantum Yields for the PAQ-Sensitized Isomerization of Stilbene[a]

Starting isomer	Quantum yield
cis	0.45 ± 0.03
trans	0.43 ± 0.03

[a] In benzene at 25°, PAQ and stilbene concentrations ~5 × 10^{-4} and 5 × 10^{-2} *M*, respectively.

The data of Table III indicate that a stationary *trans-/cis*-stilbene ratio (*R*) is ultimately reached. A series of consecutive PAQ additions and photolyses were carried out with solutions in which the initial values of *R* were close to 1, and the stationary ratios $R_S = 0.7$ for stilbene and $R_S = 0.8$ for α,α′-stilbene-d_2 were obtained by the extrapolation of plots of *R* against the reciprocal of the total amount of PAQ reacted. The uncertainty in these values is again large (at least ±0.05). The sensitized isomerization is not quenched by the adduct.

Discussion

Consideration must first be given to the Pfundt–Schenck mechanism,[8] for which the key steps are

$$\mathrm{Q} \overset{h\nu}{\rightleftharpoons} \mathrm{Q}^* \tag{4}$$

$$\mathrm{Q}^* + \mathrm{C{=}C} \longrightarrow \mathrm{X} \tag{5}$$

$$\mathrm{X} + \mathrm{Q} \longrightarrow \mathrm{A} + \mathrm{Q} \tag{6}$$

$$\mathrm{X} \longrightarrow \mathrm{C{=}C} + \mathrm{Q} \tag{7}$$

Here Q and Q* represent ground-state and excited PAQ, respectively, X a "biradical" addition complex,[24] and A the adduct. Even if modified for the occurrence of isomerization by expanding eq 5 and 6 into separate steps for *cis* and *trans* isomers, the mechanism gives $\Phi_A = a[\mathrm{Q}]/(b + [\mathrm{Q}])$, where *a* and *b* are constants if a large excess of olefin is employed. We propose that this mechanism is inapplicable because (1) within the limitations imposed by minor side reactions, Φ_A is independent of the PAQ concentration;[25] (2) the mech-

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(19) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(20) This value was based on the stationary-state *trans/cis* ratio of piperylene achieved by sensitized isomerization.[21] The large discrepancy between this and the spectroscopic value[4] is undoubtedly due to the photochemical addition of PAQ to the 1,3 diene.[22]

(21) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *ibid.*, **66**, 1144 (1962).

(22) G. O. Schenck, *Z. Elektrochem.*, **64**, 997 (1960).

(23) For stilbene-d_2, $\Phi_{\mathrm{CS}\rightarrow\mathrm{TS}} > \Phi_{\mathrm{TS}\rightarrow\mathrm{CS}}$ barely within the error limits. The possible occurrence of an isotope effect in *cis–trans* isomerization is obviously highly pertinent to the mechanism of this process, and to the problem of radiationless transitions in general. Further isomerization experiments with deuterated substrates, unsensitized and sensitized with stable compounds, are in progress.

(24) *Cf.* G. O. Schenck, Plenary Lecture, Fifth International Symposium on Free Radicals, Uppsala, Sweden, 1961.

(25) The side reactions could obscure dependence on [Q]. However, since they are small in extent (~5%) we believe that, with *b* of significant magnitude, dependence on [Q] would lead to lack of linearity in plots of eq 3 at much smaller conversions than is actually the case.

anism ascribes a specific "quenching" role to ground-state PAQ (eq 6) (if participation by a third molecule is necessary, any molecule, *i.e.*, solvent, olefin, or adduct, should be satisfactory); (3) Φ_A being invariant with changes in olefin concentration implies that the reverse step of eq 4 is unimportant. The model then predicts identical Φ_A values for *cis* and *trans* isomers. In fact, it can be readily shown that any mechanism in which a single intermediate is partitioned between decomposition into isomers and formation of adduct leads to Φ_A independent of *R*.

A meaningful discussion of the kinetic results is possible in terms of a simple mechanism (eq 8 to 17) which includes many of the steps proposed by Hammond and co-workers for sensitized *cis–trans* isomerization.[5] In these equations, the symbols not defined previously have the following significance: Q'', excited singlet state of PAQ; p, a nonspectroscopic excited state of stilbene as defined by Hammond;[5] TS and CS, *trans*- and *cis*-stilbene; Q' and TS', the spectroscopic triplet states. The direct excitation process CS → CS' is not included in view of the sizable energy difference between Q' (48.8 kcal) and CS' (57 kcal).[26,27] The scheme includes a collision complex (X) of finite lifetime between Q' and olefin, which is implied in the original discussion of the p state,[28] and which provides a link between energy transfer and Schenck's "biradical" mechanism.[29] With stable sensitizers (benzophenone, etc.) X decays only to p and ground-state sensitizer. With a reactive sensitizer such as PAQ, X is partitioned between decay to p and collapse to product. We take the physical identity of the products isolated from *cis*- and *trans*-stilbene to be strong evidence for the existence of a common intermediate. It is reasonable to suppose that the change in geometry leading to nonplanar p takes place in the complex X. Freedom of torsional motion in energy-rich X would be expected to furnish the same distribution of adducts Ia and Ib, which differ with respect to geometry about the 2,3 bond of the dioxene ring, from the *cis*- and *trans*-olefins.[30] The energy of TS' (50 kcal)[26] is approximately matched with that of Q'. Classical energy transfer (eq 12) must be invoked, for in its absence the quantum yields of adduct formation become independent of *R*.

$$\mathrm{Q} \underset{k_2}{\overset{h\nu}{\rightleftharpoons}} \mathrm{Q''} \tag{8}$$

$$\mathrm{Q''} \xrightarrow{k_3} \mathrm{Q'} \tag{9}$$

$$\mathrm{Q'} + \mathrm{TS} \xrightarrow{k_4} \mathrm{X} \tag{10}$$

$$\mathrm{Q'} + \mathrm{CS} \xrightarrow{k_5} \mathrm{X} \tag{11}$$

$$\mathrm{Q'} + \mathrm{TS} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{TS'} \quad \mathrm{Q} \tag{12}$$

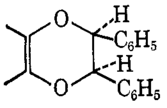
$$\mathrm{X} \xrightarrow{k_7} \mathrm{A} \tag{13}$$

$$\mathrm{X} \xrightarrow{k_8} \mathrm{p} + \mathrm{Q} \tag{14}$$

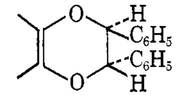
$$\mathrm{TS'} \xrightarrow{k_9} \mathrm{p} \tag{15}$$

$$\mathrm{p} \xrightarrow{k_{10}} \mathrm{TS} \tag{16}$$

$$\mathrm{p} \xrightarrow{k_{11}} \mathrm{CS} \tag{17}$$



Ia



Ib

Application of the steady-state hypothesis to transient species leads to the rate equation

$$-\frac{\mathrm{d}[\mathrm{Q}]}{\mathrm{d}t} = \frac{I_{\mathrm{abs}}K_3K_7(k_4R + k_5)}{(k_4 + ak_6)R + k_5} \tag{18}$$

where, for convenience, we have defined $K_3 = k_3/(k_2 + k_3)$, $K_7 = k_7/(k_7 + k_8)$, and $a = k_9/(k_9 + k_{-6}[\mathrm{Q}])$. The appearance of *a* in eq 18 introduces a rate dependence on [Q] such that the quantum yields decrease with increasing conversion. However, we can reason that the extent of transfer between TS' and Q is negligibly small.[31] Thus *a* can be taken as unity, and we can generate the expressions listed in Table V for the conditions $R >> 1$ and $R << 1$, corresponding to reactions which start with *trans*-stilbene and *cis*-stilbene, respectively. As Table III shows, when these conditions apply initially, they remain unchanged for a significant part of the reaction. Numerical values for ratios of constants were computed from the expressions of Table V and the experimentally determined quantities, and are listed in Table VI. The ratio k_4/k_5 was obtained by applying the stationary-state condition $\mathrm{d}R/\mathrm{d}t = 0$.[32]

Table V. Expressions for the Quantum Yields Base on Eq 18[a]

	$R_{\mathrm{initial}} >> 1$	$R_{\mathrm{initial}} << 1$
Φ_A	$\dfrac{K_3K_7k_4}{k_4 + k_6}$	K_3K_7
$\Phi_{\mathrm{CS}\rightarrow\mathrm{TS}}$		$K_3K_8K_{10}$
$\Phi_{\mathrm{TS}\rightarrow\mathrm{CS}}$	$\dfrac{K_3K_{11}[K_8(k_4 + k_6) + K_7k_6]}{k_4 + k_6}$	

[a] With $a = 1$; $K_8 = 1 - K_7$; $K_{10} = k_{10}/(k_{10} + k_{11})$; $K_{11} = 1 - K_{10}$.

Within experimental error, the intersystem-crossing efficiency for PAQ (K_3) is unity and $k_{10} \approx k_{11}$ for stil-

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[26] D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

[27] Only the minimum number of steps required to account for the results are included. Steps such as TS' → TS and TS' → CS, which are potentially significant, are omitted because their inclusion leads to composite constants from which no information can be gleaned which is not also available from the simple scheme. It is obvious that the change TS' → CS requires passage through a nonplanar state such as p.

[28] G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

[29] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

[30] In a private communication, G. O. Schenck and G. Pfundt have indicated that the adduct of mp 245–250° isolated by us from reactions with *cis*- and *trans*-stilbene has the *trans* configuration Ib. The *cis* adduct (structure Ia) melts ~80° lower, and in benzene or *t*-butyl alcohol the isometric adducts are formed in comparable amounts: G. O. Schenck and S. Farid, *Tetrahedron*, in press.

[31] Thus we already know that $k_{-6}[\mathrm{Q}] >> k_9$ cannot hold, for then $a \approx 0$ and Φ_A becomes independent of *R*. The range of [Q] is 5×10^{-4} to 1×10^{-4} *M* during photolysis. This is about two orders of magnitude lower than the sensitizer concentrations employed in Hammond's extensive study of stilbene isomerization,[5] and on the basis of these data is close to the infinite dilution limit. In fact, the data on quenching by azulene[5] indicate that $k_{-6} \approx 10^2k_9$ is reasonable. This gives $a \approx 0.95$–0.99 during the decomposition of 4×10^{-4} *M* of PAQ.

[32] $[\mathrm{TS}] + [\mathrm{CS}] = S_0 - ([\mathrm{Q}]_0 - [\mathrm{Q}])$, where S_0 is the total initial substrate concentration. This equation yields $(R_S + 1)\,\mathrm{d}[\mathrm{CS}]/\mathrm{d}t = \mathrm{d}[\mathrm{Q}]/\mathrm{d}t$ which, with appropriate substitution, affords k_4/k_5 as a function of experimentally measured parameters.

Table VI. Rate Constant Ratios for the PAQ–Stilbene Reaction

System	k_4/k_6	k_4/k_5	$\frac{k_6}{k_4 + k_6}$	K_8	K_7	K_{10}
Stilbene	0.89 ± 0.05	0.7 ± 0.1	0.5 ± 0.1	0.98 ± 0.06	0.14 ± 0.01	0.53 ± 0.03
α,α'-Stilbene-d_2	0.70 ± 0.04				0.17 ± 0.01	

bene. The data further indicate that all the processes which deactivate the PAQ triplet proceed at comparable rates. Since the decay of X is heavily in favor of the formation of the p state ($K_8 = 0.86$), adduct formation can be viewed as a minor deactivating path, and the nonspectroscopic excitation of stilbene occurs at about the same rate as the classical energy transfer. The small temperature dependence of K_7 (*cf.* Table II) indicates that the decay of X to p and Q is favored at higher temperature and hence involves some activation energy. The temperature variation of the ratio $K_7k_4/(k_4 + k_6)$ is in the same direction as that of K_7, but the magnitude is too small to detect a significant influence of $k_4/(k_4 + k_6)$.

The stationary *trans/cis* ratio, $R_S = 0.7$, is close to that reported for high-energy sensitizers.[5] However, in the present case it represents a balance between the rate of isomerization and the rate of addition. Since the addition of PAQ to *cis*-stilbene is faster than to *trans*-stilbene, it is clear that for isomerization only R_S would be much smaller than 0.7.

Since the association complex X resembles the transition state of thermal reactions, the appearance of secondary deuterium isotope effect in adduct formation is not surprising. The formation of X may not only involve the appearance of torsional freedom about the central C–C bond of the olefin, but may also cause the geometry at the central carbon atoms to change from that appropriate for an sp^2 hybridization to a configuration between sp^2 and sp^3. In this case $(k_4)_D > (k_4)_H$ is expected,[33] but the data indicate that $(k_4/k_6)_D < (k_4/k_6)_H$. Consequently there is a strong implication that $(k_6)_D > (k_6)_H$, *i.e.*, that the classical energy transfer occurs at less than the diffusion-controlled rate and is subject to an isotope effect.[34] That $(K_7)_D > (K_7)_H$ can be readily accommodated if the olefinic carbon configuration in X is closer to sp^2 than to sp^3, and if the configuration in X and p are similar. Under these circumstances $(k_8)_D \approx (k_8)_H$ and $(k_7)_D > (k_7)_H$. These arguments imply that an activation energy is involved in the formation of X and in its passage into adduct.

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(33) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, Co., New York, N. Y., 1960.

(34) G. W. Robinson and R. P. Fosch, *J. Chem. Phys.*, **38**, 1187 (1963), predict on theoretical grounds that only a very small isotope effect can be expected if the energy difference between the initial and final states is small.

Excited Singlet Molecular Oxygen in Photooxidation

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Abstract: Competitive photooxidation of three pairs of unsaturated compounds yields a single set of relative reactivities, whether sensitized by a dye (methylene blue or rose Bengale) or by the aromatic substrates themselves. This result seems, except in case of a remarkable coincidence, uniquely consistent with excited singlet oxygen as the reactive species and inconsistent with a series of biradical-like "moloxides" which would be different for each sensitizer. In pyridine, the relative reactivities with singlet oxygen are as follows: tetramethylethylene, 1.0; 9,10-dimethylanthracene, 1.0; 9,10-diphenylanthracene, ~0.2; rubrene, 2.25; and 1,3-diphenylisobenzofuran, 38.5. Direct addition to the triplet state of these acceptors is undetectable, with the possible exception of the last one where its contribution would be small. Energy considerations would indicate that the active molecules are in the $^1\Delta_g$ state.

The purpose of this note is to present additional experimental evidence for a mechanism *via* excited singlet oxygen molecules for the photooxidation in solution of organic compounds (acceptors) such as the polyacenes, in which a transannular peroxide is formed. This type of reaction has attracted much attention.[1] It is generally agreed that it does not proceed by direct addition of a ground-state oxygen molecule to a singlet excited molecule of the acceptor during the fluorescence quenching step. On the basis of the complex kinetic data previously accumulated, three

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(1) For recent discussions of photooxidation, see E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963); and C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3880 (1964).