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THE TRIPLET STATE OF METHYL 1,2-DIPHENYLCYCLOPROPENE-3-CARBOXYLATE

WILLIAM G. HERKSTROETER, DONALD P. SPECHT and SAMIR FARID
Research Laboratories, Eastman Kodak Company, Rochester, NY 14650 (U.S.A.)
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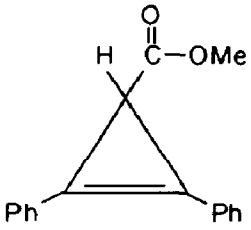
Summary

Methyl 1,2-diphenylcyclopropene-3-carboxylate (CP), which is of special interest because of its role as a monomer in photo-cross-linkable polymers, was selected as a representative example of a substituted cyclopropene for investigation of its triplet state. Flash photolysis was used to view the CP triplet directly and to measure the rate constants for energy transfer to CP from a series of triplet sensitizers. Because the intersystem crossing quantum yield of CP is only 5×10^{-3}, the triplet state can be populated efficiently only by energy transfer from an appropriate sensitizer. In benzene solution the triplet lifetime of CP is 360 μs, and the rate constant for reaction with ground state CP to form dimers is 3.8×10^{7} M^{-1} s^{-1}. The 0–0 energy of the triplet state is 51.0 kcal mol^{-1} (17.8 kilokaysers), determined from a plot of the energy transfer data according to the Balzani equation. The profile of this plot shows that the ground and triplet state geometries of CP are different, probably because of partial relief in the triplet state of the considerable ground state strain energy.

1. Introduction

The photochemistry of substituted cyclopropenes has attracted considerable attention in recent years. These small ring compounds undergo electron transfer reactions, rearrangements, additions and dimerizations [1 - 16]. Furthermore, the singlet and triplet excited states have distinct chemistries.

Methyl 1,2-diphenylcyclopropene-3-carboxylate (CP)



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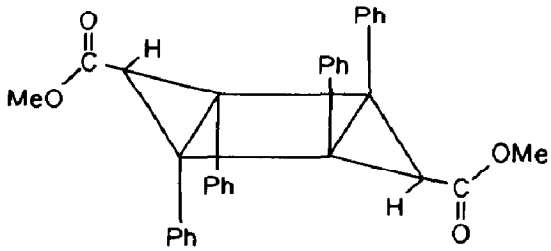
undergoes photochemical dimerization [6, 14]:

$$S \xrightarrow{h\nu} {}^3S^* \quad (1)$$

$${}^3S^* + CP \longrightarrow S + {}^3CP^* \quad (2)$$

$${}^3CP^* + CP \longrightarrow \text{dimer} \quad (3)$$

This reaction proceeds in the presence of appropriate triplet sensitizers, but not upon direct excitation of CP [6]. In this scheme S represents the sensitizer. Only a single dimer is formed and it has the following structure [6]:



This dimerization is of special interest to us because it is the cross-linking reaction in light-sensitive polymers when CP is incorporated as the cross-linking reagent [17]. As in solution, appropriate sensitizers in the polymers efficiently dimerize CP. Cross-linking in polymers proceeds efficiently in the presence of several ketocoumarin triplet sensitizers [18] with triplet energies as low as 48.5 kcal mol^{-1} (16.9 kilokaysers).

That ketocoumarin sensitizers of such low energy should dimerize CP by the energy transfer mechanism of eqn. (2) seemed inconsistent with a literature report of the triplet energy of CP. On the basis of an energy transfer measurement from triplet chrysene to CP, DeBoer *et al.* [6] reported that the triplet energy of CP exceeds that of *cis*-stilbene (57.0 kcal mol^{-1} or 19.9 kilokaysers), that CP does not undergo "non-vertical" energy transfer and that the efficacy of relatively low energy triplet sensitizers such as 1,2-benzanthracene (E_T = 47.2 kcal mol^{-1} (16.5 kilokaysers)) in photodimerizing CP cannot be explained by energy transfer from the sensitizer to CP.

In a more recent report [14] the triplet energy of CP was estimated to be 53.0 kcal mol^{-1} (18.5 kilokaysers) on the basis of the kinetics of reversible energy transfer between CP and certain triplet sensitizers.

An attempt to measure phosphorescence from 1,2,3-triphenylcyclopropene (TPCP) had placed the triplet energy of this CP analog near 72 kcal mol^{-1} (25 kilokaysers) [3], whereas the determination of quantum yields of dimer formation with this same molecule using a series of triplet sensitizers led to an estimate of about 50 kcal mol^{-1} (17 kilokaysers) for the triplet state energy [5]. Certainly the wide divergence in the literature values of the triplet energy for CP and TPCP emphasizes the need for a definitive determination of the triplet energy of a representative cyclopropene.

Also germane to triplet state dimerization of CP and reported in the literature, although based on indirect measurements, are a lower limit to the lifetime of $^3CP^*$ and the rate constant for eqn. (3). The former is 100 μs and the latter is 1.1×10^8 M^{-1} s^{-1} [6].

Our goals were to measure some of the properties of the triplet state of CP including a definitive measurement of the triplet energy and to determine what factors control dimerization efficiency. We used flash photolysis to observe directly photochemically generated metastable species such as lowest excited triplet states. Although CP was the only cyclopropene with which we worked, the triplet state properties of this molecule should not be very different from those of related molecules containing the cyclopropene chromophore.

2. Results and discussion

Initial experiments were run to see whether CP formed any observable transients upon direct excitation. None were formed with CP in degassed benzene solution after flash excitation with near-UV light from xenon flashlamps. Even far-UV excitation of CP in acetonitrile solution in a quartz cell led to no detectable transient. In the presence of any of a number of triplet sensitizers, however, a transient attributable to CP was observed after flash excitation. At low concentration the lifetime of this species exceeded 300 μs, but decreased linearly as the CP concentration was raised. Figure 1 illustrates this linear dependence; extrapolation to zero CP concentration shows a limiting lifetime of 360 μs.

Because $^3CP^*$ had been reported to have a lifetime of greater than 100 μs [6], it seemed likely that this was indeed the species we were observing. Other considerations allowed more positive identification. The slope of the plot in Fig. 1 gives the rate constant for the interaction between the metastable species and CP to be 3.8×10^7 M^{-1} s^{-1}. DeBoer *et al.* [6] reported the rate constant for the triplet-sensitized dimerization of CP to be 1.1×10^8 M^{-1} s^{-1}. As this value is based upon an indirect determination, the agreement with our more direct measurement is satisfactory.

It is generally agreed that the quantum yield for intersystem crossing in substituted cyclopropenes is low, and this explains our failure to see any CP transient after direct excitation with xenon flashlamps. A frequency-doubled ruby laser at 347 nm, however, did produce some of this same metastable species. Considerably more was observed when a triplet sensitizer was present. From the quantum output of the pulsed laser, the initial transient absorbance and an estimate for the extinction coefficient of the metastable species the quantum yield for direct formation of the metastable species is $(5 \pm 3) \times 10^{-3}$. A quantum yield this low precludes direct observation of the transient with our conventional flash photoelectric apparatus. This agrees with the conclusion of DeBoer *et al.* [6] that the quantum yield for intersystem crossing in CP is negligibly small.

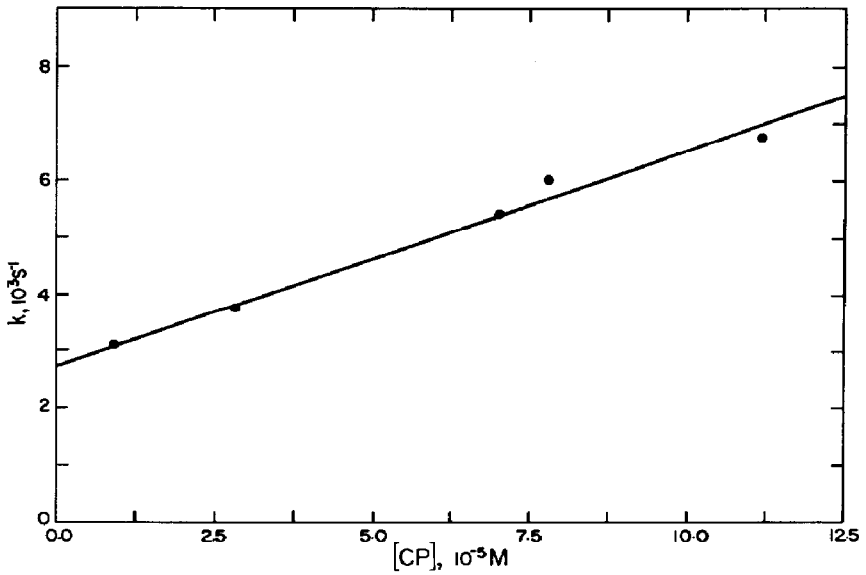


Fig. 1. Plot of the rates of disappearance of $^3CP^*$ as a function of the CP concentration. The slope gives the rate constant for CP dimerization and the intercept gives the rate constant for first-order decay of $^3CP^*$:

$$^3CP^* \xrightarrow{k_f} CP$$

$$^3CP^* + CP \xrightarrow{k_s} \text{dimer}$$

$$k = k_f + k_s[CP]$$

intercept = $k_f = 2.75 \times 10^3\ s^{-1}$

slope = $k_s = 3.8 \times 10^7\ M^{-1}\ s^{-1}$

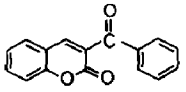
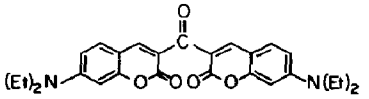
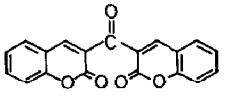
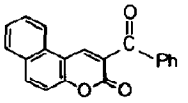
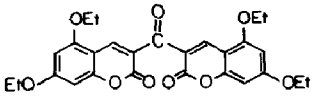
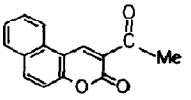
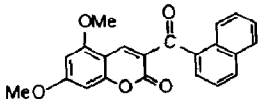
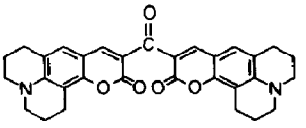
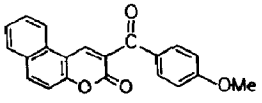
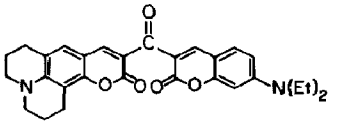
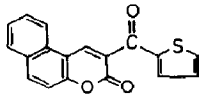
The overall behavior of the flash-generated metastable CP species is consistent with it being the lowest excited triplet state, and we confidently make this assignment.

Experiments to determine the energy level of the triplet state of CP showed that CP neither phosphoresces nor shows any absorption unequivocally assignable to ground state excitation directly to the triplet state. We then turned to the energy transfer method. Lamola [19] has noted the reliability of the energy transfer method for triplet energy determination when other methods fail or give equivocal results.

As noted above, DeBoer *et al.* [6] have measured energy transfer from the sensitizer chrysene to CP. A series of sensitizers whose triplet energies span a broad range is required, however, to pinpoint the triplet energy of the energy acceptor. The ketocoumarins were our choice for such a series of sensitizers because they have high yields of intersystem crossing, large extinction coefficients and easily monitored triplet–triplet absorption and they are known to photodimerize CP. The ketocoumarins shown in Table 1 were used in this role; aromatic hydrocarbon sensitizers were selected to fill energy

TABLE 1

Ketocoumarin sensitizers

Structure	*Designation*	*Structure*	*Designation*
	K-1		K-7
	K-2		K-8
	K-3		K-9
	K-4		K-10
	K-5		K-11
	K-6		

gaps for which no ketocoumarin sensitizers were available and also to compare and verify results obtained with the ketocoumarins.

Flash photolysis experiments were run with degassed benzene solutions of the reagents under consideration. It was necessary to establish that CP shortened the lifetimes of each of the sensitizer triplets and that the degree of shortening was a linear function of CP concentration. Because $^3CP^*$ has a lifetime of 360 μs, reversible energy transfer enters the picture as the forward energy transfer becomes isoenergetic or endothermic:

$$^3K^* + CP \rightleftharpoons K + {}^3CP^* \qquad (4)$$

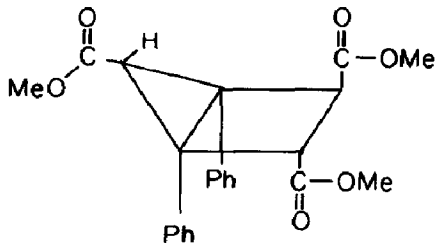
where K represents an appropriate ketocoumarin sensitizer. If reversible energy transfer were to occur, the desired linear relationship between the observed rate of $^3K^*$ disappearance and CP concentration would not hold. Because the ketocoumarins have large extinction coefficients, these sensitizers can be used at concentrations as low as 2×10^{-6} M to minimize the

reverse reaction of eqn. (4). Nevertheless, it would be a mistake to ignore this reaction.

Reverse energy transfer can be circumvented completely by adding a reagent to react with $^3CP^*$ to shorten its lifetime. Such a reagent is dimethylfumarate (F), which adds to $^3CP^*$ [14]:

$$^3CP^* + F \longrightarrow \text{adducts} \quad (5)$$

Of the several isomeric adducts from this reaction, the principal adduct has the following structure:



The triplet energy of F is sufficiently high [16, 20] that this molecule does not interfere in the energy transfer from triplet sensitizer to CP.

Figure 2 is a plot of the rate of disappearance of $^3CP^*$ as a function of [F]. The slope of this plot yields the constant for the reaction of $^3CP^*$ and F; it is 3.3×10^7 M^{-1} s^{-1}. Depending upon the concentration of the particular sensitizer, F at 0.01 M or higher was added to the experimental solutions to ensure that the rate of the reverse reaction of eqn. (4) would remain negligible in competition with the rate of disappearance of $^3CP^*$ via other reactions.

Ketocoumarin sensitizer K-7 (Table 1) was selected to probe the effect of CP on the sensitizer triplet lifetime in the presence of 0.01 M F. Figure 3 is a plot of the rate of disappearance of flash-generated ^{3}K-7* as a function of CP concentration; the required linear dependence is confirmed. Once again the slope of the plot gives the rate constant of interest, this time for energy transfer from ^{3}K-7* to CP; it is 7.0×10^8 M^{-1} s^{-1}.

The remaining ketocoumarin sensitizers and aromatic hydrocarbon sensitizers were also used to measure rate constants for triplet energy transfer to CP. In all cases the rate of disappearance of the sensitizers' triplet state was increased by the addition of CP but the actual degree of increase and consequently the rate constant depended upon the triplet energy of the sensitizer. Table 2 gives these energy transfer data in terms of the rate constants k_q for energy transfer from each individual sensitizer to CP. The error limits for these rate constants are ±15%.

With sensitizers K-7, K-10 and K-11, second transient species were observed in addition to the triplet states, and these second transients disappeared by second-order kinetics. We have not yet identified these second species, but their absorption bands were narrower than their triplet–triplet

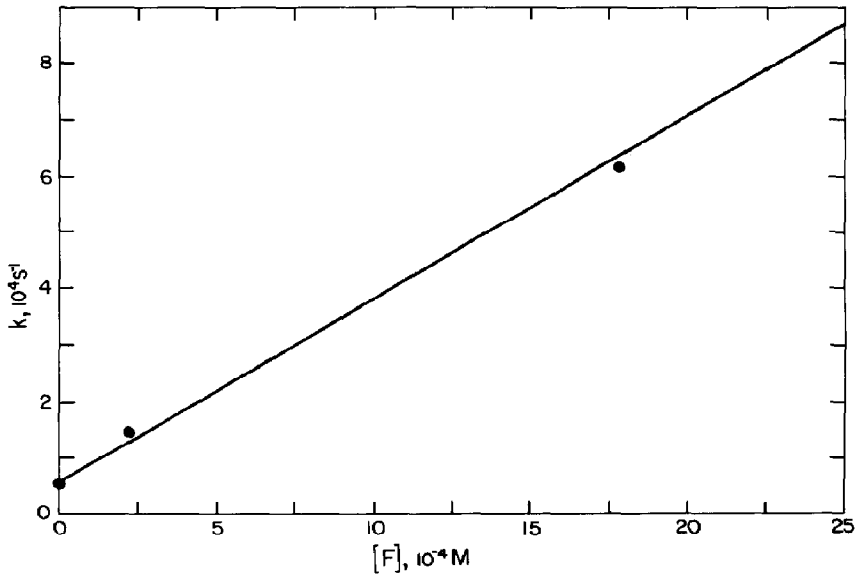


Fig. 2. Plot of the rates of disappearance of $^3CP^*$ as a function of the F concentration. The slope gives the rate constant for adduct formation between $^3CP^*$ and F (the concentration of CP was 7.7×10^{-5} M):

$$^3CP^* \xrightarrow{k_f} CP$$

$$^3CP^* + CP \xrightarrow{k_s} \text{dimer}$$

$$^3CP^* + F \xrightarrow{k_a} \text{adduct}$$

$$k = k_f + k_s[CP] + k_a[F]$$

$$\text{intercept} = k_f + k_s[CP]$$

$$\text{slope} = k_a = 3.3 \times 10^7 \, M^{-1} \, s^{-1}$$

absorption bands so that the triplets could be monitored at wavelengths where the second-order species did not interfere.

It was necessary to establish a limiting value for k_q when the sensitizer has a substantial excess of energy for exciting CP to its triplet state. These requirements were met by phenanthrene and triphenylene for which the measured rate constants for energy transfer are slightly less than 5×10^9 M^{-1} s^{-1}, which is the limiting value found for many, but not all, organic and organometallic acceptor molecules undergoing energy transfer in benzene solution. Although none of the ketocoumarin sensitizers has a triplet energy high enough to transfer energy to CP at the maximum rate, this same limiting value prevails for energy transfer from a representative ketocoumarin to the known triplet state quenchers azulene [27], ferrocene [27] and a pyrazolone azomethine dye [28, 29]. The results are listed in Table 3.

Figure 4 was constructed from CP energy transfer data by plotting the logarithm of the rate constant for energy transfer *versus* the triplet energy of

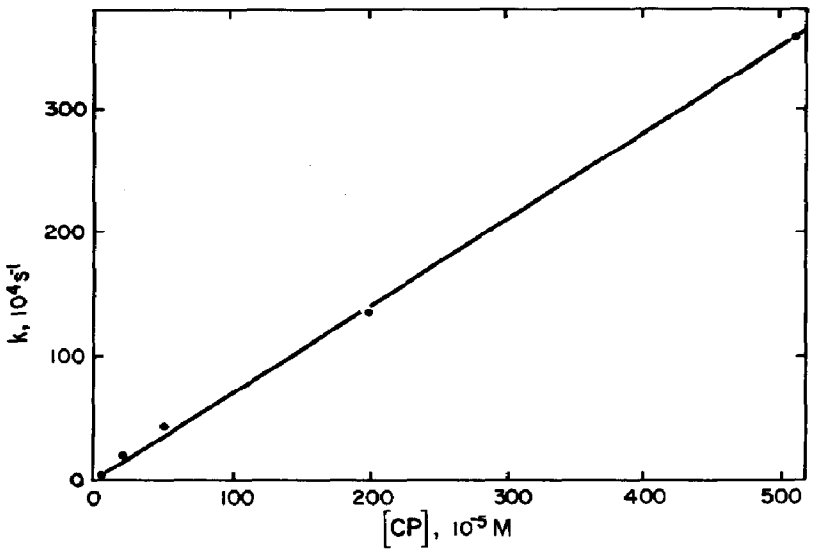


Fig. 3. Plot of the measured rates of disappearance of ^{3}K-7* as a function of the CP concentration. The slope gives the rate constant for energy transfer from ^{3}K-7* to CP (F was present at a concentration of 1×10^{-2} M):

$$^3\text{K-7}^* \xrightarrow{k_f} \text{K-7}$$

$$^3\text{K-7}^* + \text{CP} \xrightarrow{k_q} \text{K-7} + {}^3\text{CP}^*$$

$$k = k_f + k_q[\text{CP}]$$

$$\text{slope} = k_q = 7.0 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$$

the sensitizer. Such plots are well established in the literature [22, 27 - 37]. The full curve (theoretical, as will be explained below) matches the experimental data and shows a monotonic increase in the rate constants with the triplet energy of the sensitizer; this provides additional evidence that the experimental rate constants result from energy transfer from the photoexcited sensitizers to CP. Furthermore, the rate constants obtained from the two different sensitizer groups, ketocoumarins and hydrocarbons, mesh well in the plot.

Two important types of information can be extracted from these plots: the triplet energy of the acceptor molecule and the degree of geometrical change in the acceptor molecule as it is excited from the ground state to the triplet state. This latter phenomenon, termed "non-vertical" energy transfer [20, 37], is known to occur in many acceptor molecules.

The Sandros equation [30] is the traditional equation relating the rate constant for energy transfer to the triplet energy difference between the sensitizer and the acceptor:

$$k_q = \frac{k_d}{1 + \exp(\Delta G/RT)} \tag{6}$$

TABLE 2

Rate constants for energy transfer to methyl 1,2-diphenylcyclopropene-3-carboxylate

Sensitizer	E_T [a] (kcal mol^{-1})	*Monitoring wavelength* [b] (nm)	k_q (M^{-1} s^{-1})
Triphenylene	66.5 [c]	630	4.7×10^9
Phenanthrene	61.9 [c]	490	4.7×10^9
K-1	58.9 [d]	550	3.0×10^9
K-2	57.9 [d]	630	3.6×10^9
K-3	56.0 [d]	620	3.1×10^9
K-4	55.4 [e]	630	3.0×10^9
Fluoranthene	53.0 [c]	670	2.1×10^9
1,2,5,6-dibenzanthracene	52.2 [c]	542	1.2×10^9
K-5	51.6 [e]	620	5.9×10^8
K-6	51.6 [e]	620	5.9×10^8
K-7	51.5 [f]	725	7.0×10^8
K-8	51.3 [e]	630	3.8×10^8
1,2,3,4-dibenzanthracene	50.8 [c]	615	2.8×10^8
K-9	50.7 [e]	620	2.5×10^8
Tetrabenzonaphthalene	49.4 [c]	585	8.6×10^7
K-10	48.6 [d]	725	3.4×10^7
K-11	48.5 [d]	725	1.9×10^7
1,2-benzanthracene	47.2 [c]	640	3.3×10^6
9,10-dimethyl-1,2-benzanthracene	44.3 [g]	640	5.6×10^4

[a] Based on the 0–0 band in low temperature phosphorescence measurements.
[b] Wavelength where triplet–triplet absorption in the sensitizer was monitored. This wavelength is not necessarily the maximum in the triplet–triplet absorption spectrum.
[c] From ref. 21.
[d] From ref. 18.
[e] This work.
[f] When using the phosphorescence-determined value of 50.8 kcal mol^{-1} for the K-7 data point in the plot of Fig. 4, we observed a seemingly significant deviation from the experimental curve. We then checked to see whether the solution triplet energy of K-7 had shifted relative to that measured in a glass at liquid nitrogen temperature. Such a phenomenon is known, for example, for benzil [22]. Unlike benzil, however, K-7 does not phosphoresce in degassed benzene solution. To answer the question we had posed, we calibrated the solution triplet energy of K-7 on the basis of its rate of energy transfer to biacetyl. Since biacetyl has a well-defined plot of the logarithm of its rate constant for energy acceptance *versus* the triplet energy of the sensitizer, the triplet energy of K-7 could be pinpointed by this technique. Reverse energy transfer was prevented by adding tetramethylethylene to the experimental solution. This substance reacts with triplet biacetyl, but its triplet energy is high enough to prevent its accepting energy from ^{3}K-7* [23 - 25]. We found the solution triplet energy of K-7 to be 51.5 kcal mol^{-1}, a value that gave a satisfactory fit of the K-7 data point to the Fig. 4 plot.
[g] From ref. 26.

Here k_q and k_d are the rate constants for actual energy transfer and for diffusion-limited energy transfer respectively and the free-energy change ΔG for the energy transfer can be taken to be equal to the triplet energy difference between the energy donor and acceptor.

TABLE 3

Rate constants for energy transfer from ^{3}K-7* to low energy quenchers

Quencher	k_q (M^{-1} s^{-1})
Azulene	5.3×10^9
Ferrocene	4.8×10^9
4-((4-aminophenyl)imino)-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one	5.3×10^9

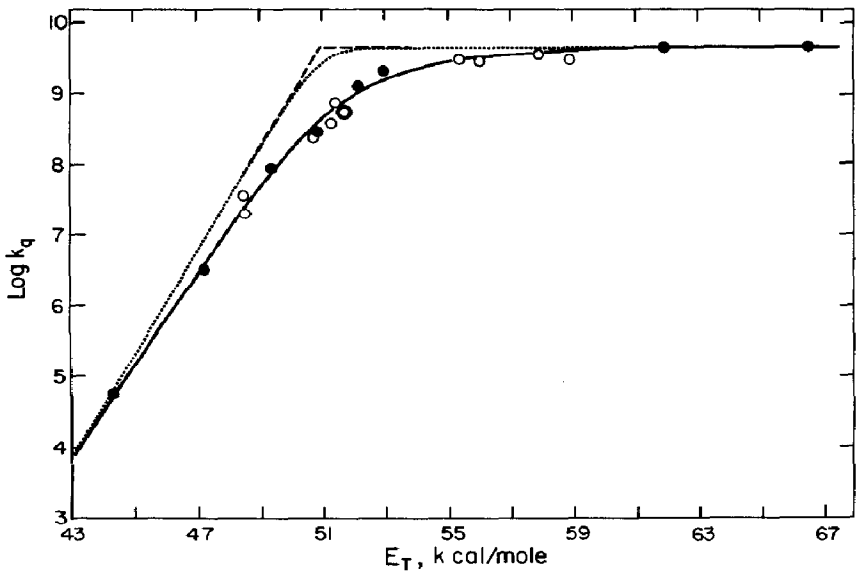


Fig. 4. Plot of the logarithm of the rate constants for energy transfer from a series of triplet sensitizers to CP *vs.* the triplet energy of the sensitizers: ○, ketocoumarin sensitizers; ●, hydrocarbon sensitizers; ——, the theoretical curve predicted by eqn. (8) for $\Delta G = 0$ at 51.0 kcal mol^{-1} and $\Delta G^{\ddagger}(0) = 1.7$ kcal mol^{-1}; ·····, the theoretical curve for $\Delta G^{\ddagger}(0) = 0$; — — —, linear extrapolations from the exothermic and endothermic limits of the theoretical curve which intersect at the assigned triplet energy of CP.

Sandros' treatment of energy transfer applies strictly only when non-vertical energy transfer is negligible. For CP as well as many other acceptor molecules investigated by energy transfer, non-vertical energy transfer is significant, and the treatment of their energy transfer data can be satisfied by an equation recently published by Balzani and coworkers [38, 39].

Balzani extended the treatment of electron transfer in fluid solution to energy transfer quenching. The energy transfer scheme and the corresponding equations are

$$D + A \xrightarrow{h\nu} {}^3D^* + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^3D^*A \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} D^3A^* \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} D + {}^3A^* \tag{7}$$

$$k_q = \frac{k_d}{1 + k_{-d}/k_{en} + \exp(\Delta G/RT)} \tag{8}$$

where D and A represent the energy donor and acceptor respectively and k_q is the overall rate constant for energy transfer. ΔG is the free-energy change for the energy transfer step; in most cases ΔG can be taken to be equal to the triplet energy difference between donor and acceptor.

Two different theoretical bases were used to calculate k_{en}. The first is based upon the Eyring theory of absolute reaction rates and leads to k_{en} being defined as [38]

$$k_{en} = k^{\circ}_{en} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{9}$$

The standard free energy $\Delta G^{\ddagger}$ of activation is given by

$$\Delta G^{\ddagger} = \Delta G + \frac{\Delta G^{\ddagger}(0)}{\ln 2} \ln\left\{1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^{\ddagger}(0)}\right)\right\} \tag{10}$$

Distortions in the triplet state relative to the ground state are accommodated by the empirical parameters k°_{en} and $\Delta G^{\ddagger}(0)$. The former is defined as a pre-exponential factor and the latter as a measure of the barrier to reorganization of the nuclear positions that occur to make energy transfer possible.

Balzani's second theoretical basis [39] extends the Ulstrup–Jortner quantum mechanical description of electron transfer reactions to triplet–triplet energy transfer. This leads to k_{en} being defined as the product of electronic and nuclear terms. The electronic term is equal to the square of the electron exchange interaction between D* and A in the encounter complex, and the nuclear term represents the Franck–Condon factor for the energy transfer.

Balzani's method has successfully matched experimental rate constants for triplet energy transfer with the corresponding calculated values using both definitions of k_{en}. For such molecules as the stilbene isomers, ferrocene and ruthenocene [38], experimental plots of energy transfer data were matched with calculated curves by trial-and-error selection of ΔG to find the proper position along the ordinate as well as with the empirical parameters k°_{en} and $\Delta G^{\ddagger}$ to determine the appropriate curve shape. Application of the second definition of k_{en} requires knowledge of the spectral properties of both D and A, including the frequency of the dominant modes, the bandwidth and the displacement parameters. Where these properties were known, as with stilbene and azobenzene, the calculated and experimental energy transfer curves coincided quite well [36, 39].

Because of the lack of CP spectral data necessary to apply Balzani's second method to this molecule, we used only his first method to calculate rate constants for triplet energy transfer to CP. Using eqn. (8), we tried to find the theoretical curve that best fits the experimental data points of Fig. 4. The parameters to be satisfied were k_d, k_{-d}, k°_{en}, $\Delta G^{\ddagger}(0)$ and ΔG.

The term k_d is the rate constant for the diffusion-controlled reaction whereas k_{-d} is a dissociation rate constant; the significance of both rate constants in energy transfer is shown in eqn. (7). The former rate constant is given by the Debye equation [40] and the latter by the Eigen equation [38,

39, 41]. We took the same values for k_d and k_{-d} that Balzani used for the stilbene isomers, namely 1.0×10^{10} M^{-1} s^{-1} and 1.2×10^{10} s^{-1} respectively.

We measured a maximum k_q for CP of slightly less than 5×10^9 M^{-1} s^{-1}. It is of course established that the limiting rate constants for energy transfer will be less than diffusion controlled [38, 42]. This inefficiency in energy transfer can be accommodated in the Balzani equation by proper selection of k°_{en}. Because the limiting k_q values for the stilbene isomers are also near 5×10^9 M^{-1} s^{-1} [22], it seems appropriate for us to use the same k°_{en} value that Balzani used for stilbene, namely 1×10^{10} s^{-1}.

To determine the curve shape, we selected by trial and error various values of $\Delta G^\ddagger(0)$ and found a satisfactory fit with $\Delta G^\ddagger(0) = 1.7$ kcal mol^{-1} (0.6 kilokaysers). The best position along the ordinate occurs with $\Delta G = 0$ at 51.0 kcal mol^{-1} (17.8 kilokaysers). This value becomes our assigned triplet energy for CP.

An alternative method for determining the triplet energy of CP and $\Delta G^\ddagger(0)$ is based on measuring the slope of a plot according to the Balzani equation [43]. The slope of a tangent to a curve representing the Balzani equation [44] is given by

$$RT\frac{d(\ln k_q)}{d(\Delta G)} = \frac{1}{1 + \exp\{-\ln(2\,\Delta G)/\Delta G^\ddagger(0)\}}$$

For $\Delta G = 0$ the slope of the equation will be 0.5; for $\Delta G = \Delta G^\ddagger(0)$ the slope will be 0.67. If, from experimental data plotted according to $RT \ln k_q$ *versus* ΔG (or its equivalent E_T in this situation), we then determine the best-fitting quadratic equation we can find the energies for slopes with these values. For the CP data presented in this paper and plotted on both axes in units of electronvolts the best-fitting quadratic equation is $y = 1.1791x^2 + 5.7519x - 6.4461$. The first derivative is $y' = -2.3582x + 5.7519$. Here $y' = 0.5$ for $x = 2.227$ eV, and $y' = 0.67$ for $x = 2.156$ eV. These values translate to E_T for CP of 51.4 kcal mol^{-1} and $\Delta G^\ddagger(0)$ of 1.6 kcal mol^{-1}. The close agreement between these values and those determined by the other method is encouraging.

Our best-fitting theoretical curve is given by the full curve in Fig. 4. To show the influence of geometrical change on curve shape, we generated another theoretical curve according to Balzani's equation with $\Delta G^\ddagger(0) = 0$ and included it as the dotted line in Fig. 4. The triplet energy of 51.0 kcal mol^{-1} is also the intersection point along the ordinate of the broken lines extrapolated from the high and low energy limiting portions of the dotted curve.

As pointed out by Balzani *et al.* [38], molecules really have three distinct triplet energies. There is a triplet energy based on vertical absorption, another based on vertical emission or phosphorescence and a third, the 0–0 triplet energy, based on the energy difference between the minima in both states. These three distinct energy values are illustrated schematically in Fig. 5 where, for a hypothetical molecule, potential energy surfaces of both the ground state and triplet states are plotted as a function of changes in

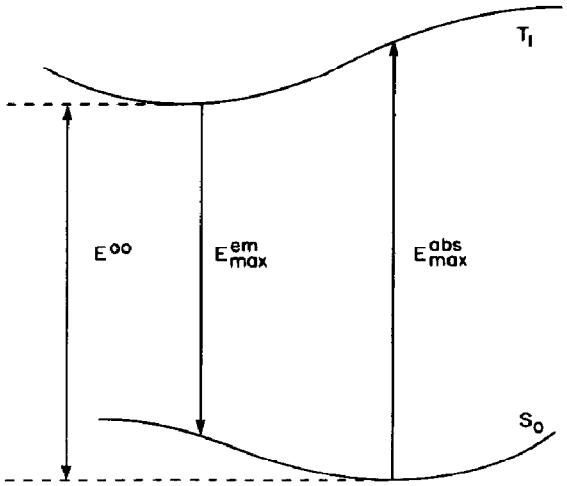


Fig. 5. The potential energy surfaces for the ground singlet state and lowest excited triplet state of a hypothetical molecule as functions of the molecular configuration. The measured energy gap between the two states depends upon the method of measurement.

molecular geometry. For molecules that do not change their configurations in the triplet state, these three triplet energies will be identical. However, these triplet energy differences are meaningful when molecules take on different configurations in the different electronic states. It is the 0–0 triplet energy that is obtained from the Balzani equation by the method described above.

Two possible explanations of geometrical changes upon excitation of CP from the ground state to the triplet state are changes in the dihedral angles between the phenyl substituents and the cyclopropene ring or changes in the bond lengths within the ring itself. Because of the considerable strain energy in the cyclopropene ring, the latter proposal seems more likely, although a combination of the two is also possible. We know from thermal measurements on unsubstituted cyclopropene that the ground state of this molecule has a substantial strain energy of 54.5 kcal mol^{-1} and that this strain is reduced by 26 kcal mol^{-1} by addition across the double bond [15, 45]. Intuitively, we might expect that stretching of the CP double bond would provide the geometrical change between the ground and triplet states that our energy transfer plots require. Certainly, such stretching occurs in stilbene upon excitation to its triplet state [46 - 48]. However, to the extent that we can extrapolate Pincock and Boyd's calculations on unsubstituted cyclopropene [10] to CP, this is not the case. Their molecular orbital calculations show that relief to this ground state strain occurs by the breaking of one of the single bonds in the lowest excited singlet state, but in the triplet state there is a 13 kcal mol^{-1} barrier to the breaking of this bond. Vinylcarbene is thus formed in the singlet state, whereas the triplet state has a sufficient lifetime to dimerize. The relatively small barrier to the breaking of one of the single bonds in the triplet state leads to the conclusion that these bonds offer probable stretching modes.

Although most molecules known to undergo non-vertical energy transfer either rotate or invert about a central isomerizable bond [22, 28, 36], there is a precedent for bond stretching as the reason for excited state configurational change. Ferrocene in its lowest excited triplet state undergoes a symmetrical expansion of a ring–metal stretching vibration [49, 50]. Many isomerizable molecules undoubtedly also stretch or loosen their double bonds in the triplet state *en route* to a perpendicular triplet state configuration. With CP, however, rotation about any ring bond is precluded by the σ framework of the molecule so that any triplet state configurational change in the ring must be confined to bond stretching alone. A consequence of the inability of CP to rotate about any of its ring bonds is the triplet lifetime of greater than 300 μs in fluid solution; this is in marked contrast with the submicrosecond or even subnanosecond triplet lifetimes of many isomerizable molecules.

To summarize our results, we have used flash photolysis to look directly at the triplet state of CP and to measure the rate constants for quenching by CP of the triplet states of a series of sensitizers. Triplet state CP has a lifetime of 360 μs; it reacts with ground state CP with a rate constant of 3.8×10^7 M^{-1} s^{-1} and with F with a rate constant of 3.3×10^7 M^{-1} s^{-1}. A plot of the rate constants for quenching of the sensitizer triplet states by CP *versus* sensitizer triplet energy is a relatively smooth function of the latter, showing that triplet energy transfer is the mode of quenching even for sensitizers previously regarded to be too low in energy to excite CP to its triplet state. This plot also shows that CP undergoes a change in geometry concomitant with energy transfer. The configuration of CP in the triplet state is different from that in the ground state, probably because of the stretching of one of the ring bonds to give partial relief to the considerable ground state strain energy.

Factors that control the efficiency of the triplet state dimerization of CP include the rate of energy transfer to CP and the concentration of CP. The ketocoumarin sensitizers function well in dimerizing CP because of their high triplet state yields [18] and because even those with relatively low energy triplets such as K-10 and K-11 still transfer energy to CP at a satisfactory rate if the concentration of CP is high enough. A sufficient concentration of CP is also required to make certain that all $^3CP^*$ will find a reaction partner for dimerization instead of decaying unreacted to the ground state.

3. Experimental section

Triplet–triplet absorption and energy transfer were measured on a flash photoelectric apparatus. Two xenon flashlamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inner walls were coated with highly reflective paint (Eastman white reflectance coating). The flash discharge energy was 156 J, correspond-

ing to a 2 μF capacitor charged to 12.5 kV. Glass color filters (Corning 9863) were placed between the flashlamps and the sample cell holder. The monitoring source was a quartz–halide 100 W lamp (Osram 64625) powered by a regulated d.c. power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens and a monochromator 0.25 m long (Jarrell–Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity was measured as a function of time using a photomultiplier tube (RCA 4463) mounted on the exit slit of the monochromator. The photomultiplier output was fed into a cathode follower amplifier and then into a wide-band digital storage oscilloscope (Nicolet model 1090). The output voltage of the photomultiplier, read directly in digital form on the oscilloscope screen as a function of time, was linear with regard to the light intensity transmitted by the sample so that an observed change in voltage after flash excitation could be readily converted mathematically to a change in absorbance in the sample. Transient lifetimes were measured by the recovery rate of the monitoring beam after the excitation flash. The kinetic analysis was performed using the method of Linschitz and Sarkanen [51, 52].

The procedures for phosphorescence measurements have been described elsewhere [18].

The solvents in the energy transfer experiments were Mallinckrodt Nanograde benzene and Mallinckrodt Analytical Reagent acetonitrile and were used as received.

CP was prepared according to the method of Breslow *et al.* [53].

The sources and purification methods for all but four of the hydrocarbon sensitizers are listed elsewhere [28]. Triphenylene was purchased from the Aldrich Chemical Company and was recrystallized from ethanol. Zone-refined phenanthrene was purchased from James Hinton Ph.D. Fluoranthene was obtained from Kodak Laboratory Chemicals and was recrystallized three times from ethanol. Tetrabenzonaphthalene was purchased from Chemicals Procurement Laboratories Inc. and was used as received.

The synthesis, purification and properties of the ketocoumarin sensitizers K-1, K-2, K-3, K-7, K-10 and K-11 are described elsewhere [18]. The other ketocoumarin sensitizers were synthesized by adding 60 drops of piperidine to 10 mmol each of the appropriate 2-hydroxy-1-naphthaldehyde and the corresponding β-ketoester in 30 ml of warm ethanol. The mixture was heated at reflux on a steam bath for 15 - 30 min (4 h for K-4). After cooling, the product was collected, washed with alcohol and recrystallized from alcohol–acetonitrile.

Melting points were determined using a Thomas–Hoover Uni-Melt apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were measured using a Varian EM-390 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained using an LKB type 9000 mass spectrometer. Absorption spectra were measured using a Hitachi–Perkin–Elmer model 320 spectrophotometer.

The analytical results for 5,7-dimethoxy-3-(1-naphthoyl)coumarin (K-4) are as follows: melting point, 210 - 211 °C; NMR (solvent, $CDCl_3$) (δ, ppm), 3.81 and 3.83 (overlapping —OCH_3 singlets (s)), 6.23 (doublet (d); H(6); J = 2.25 Hz), 6.41 (d; H(8); J = 2.25 Hz), 7.30 - 7.45 (multiplet (m); H(2′), H(3′), H(4′), H(5′), H(6′), H(7′), H(8′)), 8.51 (s; H(4)); mass spectrum (MS) (m/e (percentage relative intensity)), 360 (M^+, 100%), 359 (29%), 343 (15%), 332 (34%), 331 (37%), 315 (15%), 301 (10%), 289 (10%), 233 (46%), 180 (15%), 155 (44%), 149 (15%), 127 (80%); absorption maximum (benzene), 358 nm; $\epsilon = 21.9 \times 10^3\ M^{-1}\ cm^{-1}$.

The analytical results for 3-anisoylbenzo[f]coumarin (K-5) are as follows: melting point, 209 - 210 °C; ^1H NMR (solvent, $CDCl_3$) (δ, ppm), 3.87 (s, —OCH_3), 6.92 (d; H(3′), H(5′); J = 9.0 Hz), 7.46 (d; H(10); J = 9.12 Hz), 8.87 (d; H(2′), H(6′); J = 8.70 Hz), 8.03 (d; H(9); J = 9.0 Hz), 8.20 (broad d; H(5); J = 7.8 Hz), 8.79 (s; H(4); MS (m/e (percentage relative intensity)), 330 (M^+, 73%), 315 (5%), 302 (14%), 310 (9%), 299 (4%), 223 (5%), 165 (9%), 139 (9%), 135 (100%), 107 (9%), 92 (12%); absorption maximum (benzene), 373 nm; $\epsilon = 13.9 \times 10^3\ M^{-1}\ cm^{-1}$.

The analytical results for 3-(2-thenoyl)benzo[f]coumarin (K-6) are as follows: melting point, 241.5 - 242.5 °C; MS (m/e (percentage relative intensity)), 306 (M^+, 93%), 278 (10%), 277 (44%), 276 (23%), 250 (8%), 223 (8%), 195 (23%), 153 (10%), 139 (30%), 111 (100%), 83 (13%); absorption maximum (benzene), 376 nm; $\epsilon = 12.9 \times 10^3\ M^{-1}\ cm^{-1}$. The NMR data are not reported for K-6 because some of the protons could not be assigned unequivocally.

The analytical results for 3-benzoylbenzo[f]coumarin (K-8) are as follows: melting point, 209 °C; ^1H NMR (solvent, $CDCl_3$) (δ, ppm), 7.31 - 7.96 (m; H(6), H(7), H(8), H(10), H(2′), H(3′), H(4′), H(5′), H(6′)), 8.04 (d; H(9); J = 8.7 Hz), 8.19 (d; H(5); J = 7.2 Hz), 8.82 (s; H(4)); MS (m/e (percentage relative intensity)), 300 (M^+, 100%), 299 (13%), 272 (71%), 271 (37%), 223 (20%), 195 (21%), 139 (26%), 105 (73%), 77 (57%); absorption maximum (benzene), 375 nm; $\epsilon = 12.1 \times 10^3\ M^{-1}\ cm^{-1}$.

The analytical results for 3-acetylbenzo[f]coumarin (K-9) are as follows: melting point, 188 - 189 °C; ^1H NMR (solvent, $CDCl_3$) (δ, ppm), 2.75 (s; —CH_3), 7.38 (d; H(10); J = 9.0 Hz), 7.49 - 7.94 (m; H(6), H(7), H(8)), 8.01 (d; H(9); J = 9.12 Hz), 8.27 (broad d; H(5); J = 7.68 Hz), 9.18 (s; H(4)); MS (m/e (percentage relative intensity)), 238 (M^+, 79%), 223 (100%), 210 (8%), 195 (25%), 168 (11%), 149 (25%), 139 (39%); absorption maximum (benzene), 387 nm; $\epsilon = 13.8 \times 10^3\ M^{-1}\ cm^{-1}$.

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