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Transient Species in Photochemistry of Enones. The Orthogonal Triplet State Revealed by Laser Photolysis

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Abstract: Transient species having lifetimes of the order of tens of nanoseconds are observed in the laser photolysis of methyl vinyl ketone, acetylcyclohexene, cycloheptenone, cyclohexenone, cyclopentenone, and testosterone. On the basis of the lifetime of the transients and of quenching experiments, these species are identified as orthogonal or twisted triplet states, the angle of twisting varying with the rigidity of the molecule. These relaxed triplet species do not appear to be the reactive intermediate leading to cyclodimerization of cyclohexenone and cyclopentenone. In the case of cyclopentenone, a second transient species is observed and identified as the biradical dimer, an intermediate species between the reactive triplet and the final cyclodimer. The lifetime of the reactive triplet and its reactivity with cyclopentenone ground state, obtained from a study of the yield of formation of the biradical intermediate as a function of added quenchers, are in good agreement with those previously obtained from the effect of quenchers on the yield of the overall reaction.

Introduction

The photochemistry of enones has been and still is a matter of widespread interest.[1] Cyclic α,β-unsaturated ketones such as cyclopentenone, -hexenone, and -heptenone and steroidal enones are the most frequently studied compounds. Typical reactions are cycloaddition to olefins, dimerization (a special case of cycloaddition), nucleophilic additions, hydrogen abstraction, and rearrangements.

Most of these reactions are common to all the enones mentioned above, but the nature of the reactive intermediate and the mechanism of a given reaction can be completely different from one compound to another. For instance, both cyclopentenone and cycloheptenone photodimerize but it was shown that the reaction proceeds via a very long-lived "trans" form of cycloheptenone in its ground state[2] and via a very short-lived triplet state for cyclopentenone.[3]

Even in molecules where steric hindrance inhibits the appearance of a "trans" form, the nature of the reactive intermediate is not well defined. In most cases it is a triplet state, but its exact nature ($n\pi^*$, $\pi\pi^*$, $\pi\pi^*$ twisted along the $>C{=}C<$) is not known. Furthermore, in some cases where two types of reactions are in competition, both proceeding via a triplet state, the relative efficiency of the two reactions can be modified by changing the solvent or adding a quencher.[4,5] This behavior could mean that, at the very least, two types of triplet states are involved, each of them giving a particular reaction. But as long as the mechanisms of these reactions are not fully established, no definite conclusion can be drawn.

The lifetimes of the reactive triplet state of cyclohexenone and cyclopentenone, as estimated by quenching experiments, are in the nanosecond range.[3] It should therefore be possible to observe them by laser flash photolysis. Using 30-ns light pulses provided by a laser, Goldfarb[6] observed transient species of cycloheptenone, cyclohexenone, and acetylcyclohexene, which absorb in the range 260–270 nm. He identified them as "non-cis" isomers of the starting compounds. Recently reexamining the case of acetylcyclohexene we found that the transient species observed by Goldfarb is a precursor of the "trans" acetylcyclohexene ground state and we tentatively identified this precursor as an orthogonal triplet state, i.e., a triplet state relaxed by a 90° twist of the $>C{=}\dot{C}<$ double bond.[7]

We report in this paper the observation of similar transient species in a series of enones and the study of some of their properties. A comprehensive analysis of the results supports the identification of the observed transients as orthogonal or twisted triplet states and gives insight about the nature of the reactive triplet state involved in the photochemistry of some enones.

Experimental Section

Methyl vinyl ketone, cycloheptenone, acetylcyclohexene, and testosterone are commercially available and were used as received or after distillation. Commercial cyclohexenone (Aldrich) contains an impurity absorbing in the 260–270-nm region. We used samples of cyclohexenone, prepared according to the procedure of Garbisch[8] and purified by repeated preparative GPC. Samples purified in this manner do not contain this impurity. Cyclopentenone was similarly prepared and purified.

Cyclohexane, methylcyclohexane, ethanol (Prolabo, UV spectroscopy grade), and acetonitrile (Merck, Uvasol grade) were used as solvents. The solute concentrations were adjusted to get, on a 1-cm optical path, an absorbance around 1.5 at the excitation wavelength (either 265 nm in polar solvent or 353 nm in nonpolar solvents). On account of the extinction coefficient values at these wavelengths, this gives enone concentrations in the range 10^{-2}–10^{-1} M.

The laser-photolysis apparatus was set in a crossed-beam arrangement, the excitation laser beam and the analytical beam arriving from two perpendicular directions on a 10 × 10 mm quartz cell. For the study of very concentrated solutions ($\simeq$1 M), this square 10-mm cell was replaced by a 1 × 10 mm cell oriented at 45° with respect to the excitation and analytical beams. The analytical beam was provided by a 75-W xenon arc, pulsed at 90 V for 1 ms, and the photomultiplier was a IP28 RCA tube, specially wired on five dynodes only, in order to get a response time as short as 1 ns.[9]

In most experiments, the response time of the detection system was about 5 ns, limited by the 3.5-ns rise time of the oscilloscope (Tektronix 466) and by the 3-ns duration of the laser excitation pulse. In some cases, a faster oscilloscope (Tektronix 485) with a 1-ns rise time was used and the laser was operated in a mode-locked configuration, providing 200-ps light pulses, so that the overall response time of the system was less than 2 ns.

The laser, a Quantel instrument, including a Nd-YAG oscillator, a pulse slicer, a Nd-YAG amplifier, and two Nd-glass amplifiers, can be operated either in passive Q-switch or in mode-locked configurations. In the first case a 3-ns pulse can be extracted from the 18-ns output by the pulse slicer; in the second case the same pulse slicer isolates from the picosecond train a single 200-ps pulse. In both cases, energies of several tens of millijoules are obtained at 265 or 353 nm after frequency conversion.

Results

Upon excitation at 265 or 353 nm, all the enones studied give rise to transient absorptions in the 260–350-nm wavelength range which decay in a few tens of nanoseconds. In addition, much longer lived transient species appear when solutions of acetylcyclohexenone or cyclopentenone are flashed.

The long-lived species can easily be assigned from previous

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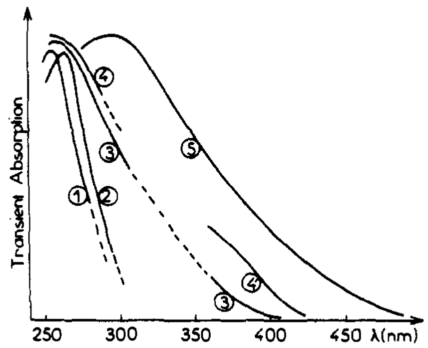


Figure 1. Absorption spectra of the transient species produced by laser photolysis of (1) methyl vinyl ketone; (2) cycloheptenone; (3) cyclohexenone; (4) cyclopentenone; (5) testosterone.

work. Indeed, for acetylcyclohexene this transient species has an absorption spectrum peaking at 345 nm and a lifetime around 15 μs in nonreactive solvents, such as acetonitrile or cyclohexane, but only 0.34 μs in methanol. It appears during the decay of the short-lived transient and has already been identified as the "trans" form of the acetylcyclohexene ground state.[7] In the case of cycloheptenone, the two transient species have very similar absorption spectra but they can easily be distinguished by their lifetime. The longer lived species, lasting as long as several seconds in nonreactive solvents, has already been identified as the "trans" cycloheptenone ground state and its main properties have been reported.[2]

Cyclohexenone does not give rise to a transient species that can be assigned to a "trans" ground state.

(1) Absorption Spectra of the Short-Lived Transients. The absorption spectra of the short-lived transient species observed after flashing the enones are given in Figure 1. Measurements at all wavelengths higher than 270 nm could be made for testosterone, excited at 265 nm in polar solvent, since the ground-state absorption is low. The other enones were excited at 353 nm, on the red side of the $n\pi^*$ absorption band, which constitutes in all cases a wavelength range where no transient absorption could be measured using the cross-beam arrangement adopted in this study. No correction was made for the absorption of the ground state since this correction would probably be negligible. Indeed, in the range of wavelengths investigated, the ground-state extinction coefficients are low ($<10^2$ M^{-1} cm^{-1}), whereas, regarding the transient absorption with respect to the excitation energy, the extinction coefficients of the transients must be high. The product of the quantum yield of formation of the transient, Φ, by the extinction coefficient of the transient, ϵ, was evaluated as follows. The transient absorption, ΔOD, produced by a laser pulse of energy E in solutions of cyclohexenone or cyclopentenone in cyclohexane and of benzophenone in benzene was measured at 270 nm for the enone solutions or at 535 nm, the maximum of absorption of triplet benzophenone. In each case, $\Delta OD = A\Phi\epsilon E\alpha$, where A is a factor depending on geometrical parameters, which are the same for the three experiments. The concentrations of the three solutions have been adjusted in order to get the same ground-state absorption at the excitation wavelength so that the fraction of the laser pulse absorbed in the analyzed volume, α, is also the same. Thus one can write

$$\Phi_1\epsilon_1/\Phi\epsilon = \Delta OD_1 E/\Delta OD E_1$$

By measuring ΔOD, ΔOD_1, E, and E_1 and with $\Phi_1 = 1$ and $\epsilon_1 = 7600$ at 535 nm for benzophenone[10] one gets $\Phi\epsilon = 2.1 \times 10^3$ for the cyclohexenone transient and 1.9×10^3 for the transient of cyclopentenone, at 270 nm so that $\epsilon_{270} \gtrsim 2 \times 10^3$ for both transient species.

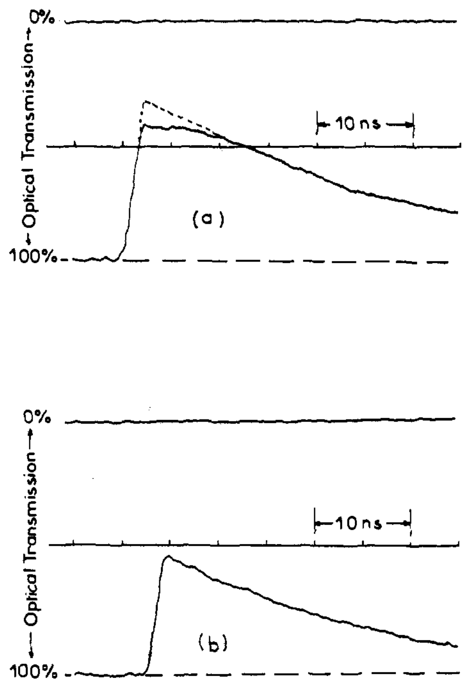


Figure 2. Reproduction of oscilloscope traces showing the growing and the first part of the decay of the transient absorption in the case of cyclohexenone in cyclohexane, sweep rate 5 ns/div: (a) no quencher added (the dashed line is an extrapolation of the regular decay observed after 20 ns); (b) butadiene added, 4.4×10^{-2} M.

Measurements below 250 nm were not possible, owing to the steeply rising absorption of the ground state for wavelengths shorter than 260 nm. In the 250–260-nm range, the slits of the monochromator have to be opened so wide that the apparent maximum of the transient spectra around 260 nm is not quite significant. However, considering the different absorption spectra, it is obvious that the transient absorptions are red shifted as the rigidity of the enone system increases.

(2) Growing of the Transient Absorption. For all the enones studied, with the exception of testosterone, the short-lived transient absorption is fully developed within the response time of the analytical system, when a 100-MHz oscilloscope and 3-ns excitation pulses are used. This means that any precursor of the transient species must have a lifetime shorter than 5 ns. Examining more carefully the case of cyclohexenone using a 200-ps excitation pulse and a 350-MHz oscilloscope, it can be seen that, during the first 10 ns, the decay of the transient absorption is not as fast as expected from the decay kinetics for the 10–50-ns period (see Figure 2a). This could indicate the existence of a process of formation of the transient species via a precursor having a lifetime of a few nanoseconds which partially compensates for the normal decay of the transient species.

For testosterone the formation of the transient via a precursor having a few-nanosecond lifetime becomes obvious. In the 260–280-nm region it appears only by a modification of the rate of decay during the first tens of nanoseconds but, in the 310–330-nm region, there is clearly a "slow" growing of absorption during 20 ns (see Figure 3).

(3) Decay of the Transient Absorption. The transient absorptions observed in the 260–280-nm region decay according to an apparent first-order law and the corresponding lifetimes ($1/e$) are given in Table I.

The lifetimes of the cyclohexenone and cyclopentenone transients, measured at 270 nm, are almost insensitive to temperature changes from −30 to +30 °C. They are also nearly unaffected by increasing the enone concentration from 10^{-1} up to 1 M.

For cyclopentenone in deaerated cyclohexane, the lifetime measured in the 360–380-nm range (τ = 45 ns) is larger than that measured in the 260–280-nm region (τ = 30 ns). The

Table I. Kinetics Properties of the Transient Species of the Enone Compounds

	methyl vinyl ketone	cycloheptenone	acetylcyclohexene	cyclohexenone	cyclopentenone	testosterone
lifetime in deaerated cyclohexane, τ, ns	8	11	16	25	30	440[a]
quenching by O_2 k_Q, $M^{-1}\,s^{-1}$	b	b	3.5×10^9	5×10^9	5×10^9	2.2×10^9
quenching by piperylene k_Q, $M^{-1}\,s^{-1}$	inefficient (see ref 6)			4×10^7 [c]	$<10^8$ [c]	$\sim 10^9$

[a] Measured in ethanol. Eventual reaction with the solvent would shorten the lifetime with respect to the one that would be measured in cyclohexane. [b] Oxygen decreases the lifetime but the quenching rate constant was not measured. [c] A chemical reaction may account for the decrease of the lifetime.

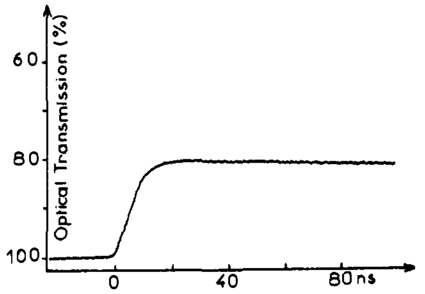


Figure 3. Reproduction of an oscilloscope trace showing the "slow" growing of the transient absorption in the case of testosterone in ethanol, sweep rate 20 ns/div.

lifetime measured at 365 nm depends slightly on the solvent polarity: 45 ns in benzene, 42 ns in ethanol, and 30 ns in acetonitrile. No similar effect was noticed at 270 nm.

(4) **Influence of Oxygen.** In aerated solutions, the lifetimes of the transient species are slightly shorter than in N_2-saturated solutions. In O_2-saturated solutions, the measured lifetimes are markedly shortened, giving thus a clear evidence for a quenching of the transient species by oxygen. This is contrary to what has been previously reported.[6] Approximate values of the quenching rate constant, k_Q, calculated from the lifetimes measured at 270–280 nm in N_2-, air-, and O_2-saturated solutions are listed in Table I.

The transient species of cyclopentenone observed in the 360–380-nm region is also quenched by oxygen with a rate constant equal to 5×10^9 $M^{-1}\,s^{-1}$ (assuming that oxygen concentration is equal to 10^{-2} M in O_2-saturated acetonitrile).

(5) **Influence of Dienes. (a) On the Testosterone Transient.** Addition of piperylene strongly decreases both the lifetime and the amount of the testosterone transient. From a study of the effect of piperylene concentration upon the lifetime of the transient, the rate constant for quenching the transient is found to be around 10^9 $M^{-1}\,s^{-1}$.

(b) On the Cyclohexenone Transient. Addition of piperylene has only a very weak influence on the lifetime of the cyclohexenone transient, measured at 280 nm. Plots of the reciprocal lifetime vs. the piperylene concentration are poorly linear (but this could be due to experimental uncertainty; see section 6) and yield an apparent quenching rate constant in the range 4×10^7 to 2×10^8 $M^{-1}\,s^{-1}$. Butadiene also decreases the lifetime of the cyclohexenone transient with a rate constant around 1.5×10^8 $M^{-1}\,s^{-1}$.

Addition of piperylene or butadiene at concentration as low as 4×10^{-2} M suppresses the irregularity observed in the decay of the transient during the first 10 ns after the excitation and which is tentatively related to the existence of a precursor (see Figures 2a,b). Taking into account the very short lifetime of this precursor and the efficiency of low diene concentrations to suppress its effect, the rate constant of quenching of the precursor by dienes should have a minimum value around 10^{10} $M^{-1}\,s^{-1}$.

The amount of transient absorption at 280 nm, ΔDO, is also slightly decreased by addition of piperylene, but plots of $1/\Delta$DO vs. the piperylene concentration are not linear: a small concentration of diene (3–5×10^{-2} M) decreases ΔDO by about 15% but further additions of quencher (up to 0.3 M) are much less efficient. The effect of the addition of piperylene upon the transient absorption of cyclohexenone may be accounted for by either a single or two species responsible for the absorption. In the first case, the single species is produced by two pathways, the minor one (~20%) involving a short-lived (<5 ns) intermediate efficiently quenched by dienes, whereas the major pathway (~80%) does not involve any species quenchable by piperylene. In the second case the transient absorption is due to two species having a similar lifetime (~25 ns), the formation of the major one being insensitive to dienes, whereas the minor one is formed via a short-lived intermediate efficiently quenched by piperylene. But it must be emphasized that the observed changes in lifetime or absorption intensity are small (≃20% for high piperylene concentrations) and become rapidly comparable to the measurement uncertainty at low quencher concentrations. Therefore, the nonlinearity of the quenching plots is not firmly established: it just appears as a general tendency in a great number of experiments.

(c) On the Cyclopentenone Transient. Piperylene does not affect greatly the cyclopentenone transient species observed in the 260–280-nm region: even for piperylene concentrations around 10^{-1} M, the lifetime of this species decreases very slightly ($k_q < 10^8$ $M^{-1}\,s^{-1}$) and the amount of transient absorption remains nearly constant.

On the other hand, the amount of transient absorption observed at 365 nm is strongly decreased by addition of piperylene. This indicates that the transient species absorbing at 365 nm is formed via a precursor which has a nonnegligible lifetime, τ, and which is quenched by the diene with a large rate constant, k_Q. The value of the product $k_Q\tau$ is obtained from plots of $\Delta(OD)_0/\Delta(OD)$ vs. the piperylene concentration. $\Delta(OD)_0$ and $\Delta(OD)$ are the amounts of transient absorption observed in the absence and in the presence of quencher. Typical results are shown in Figure 4. They clearly indicate that the value of the product $k_Q\tau$ depends on the cyclopentenone concentration, as shown quantitatively in Figure 5. Assuming that k_Q is constant, the lifetime of the precursor of the transient species absorbing at 365 nm is given by

$$1/\tau = 1/\tau_0 + k_{SQ}[\text{cyclopentenone}]$$

and with $k_Q = 10^{10}$ $M^{-1}\,s^{-1}$ in acetonitrile, $1/\tau_0 < 5 \times 10^7$ s^{-1} (i.e., $\tau_0 > 20$ ns) and $k_{SQ} \simeq 1.2 \times 10^9$ $M^{-1}\,s^{-1}$.

(6) **Limits to the Precision of the Kinetic Measurements.** Lifetimes measurements are reproducible within ±0.5 ns. This accuracy is satisfactory in most cases. However, this 0.5-ns uncertainty in the lifetimes leads to a large uncertainty in the quenching rate constants when poorly efficient quenchers are used at low concentration since the lifetimes measured in the presence and in the absence of quencher are close to each other.

The measurements at 270 nm of the lifetime of the transients of cyclohexenone and cyclopentenone as a function of the enone concentration, made in order to investigate the role of these transients in the photodimerization process, call for an additional comment. The study of the more concentrated solutions

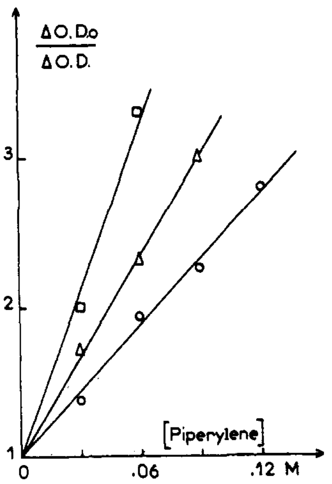


Figure 4. Stern-Volmer plots for the quenching by piperylene of the formation of the transient species of cyclopentenone which absorbs at 365 nm, solvent acetonitrile. Cyclopentenone concentration: (○), 0.55; (△), 0.35; (□), 0.25 M.

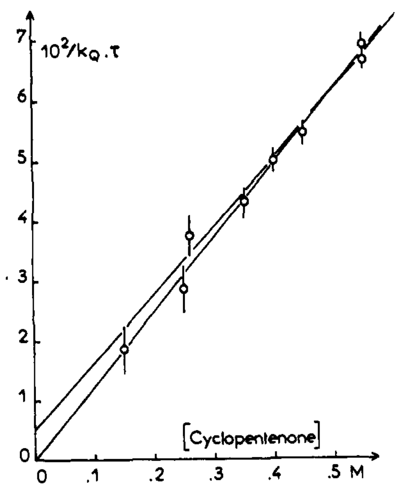


Figure 5. Variation of the lifetime of the triplet species of cyclopentenone, precursor of the transient which absorbs at 365 nm, as a function of cyclopentenone concentration. Values of $k_Q\tau$ are obtained from Stern-Volmer plots as those shown in Figure 4.

requires a modification of the optical arrangement (see Experimental Section). This change in the geometry of the setup, associated with the spatially nonuniform distribution of the energy in the cross section of the laser beam, can lead to small variations in the measured lifetimes.[11] We therefore consider that a 10% decrease of the lifetime of the transient when the enone concentration is changed from 10^{-1} to 1 M may have escaped our observation. This means that the self-quenching rate constant is smaller than 5×10^6 M^{-1} s^{-1} for the transients species of cyclohexenone and cyclopentenone absorbing at 270 nm.

Discussion

Besides the long-lived transoid ground state of flexible enone molecules, three short-lived species have been detected or suspected in this study.

The first one, I, is observed in the 260–280-nm range for all the enones. Arising from a precursor, II, which is not directly observed, another species, III, appears between 360 and 400 nm for cyclopentenone only.

Let us first consider transients II and III of cyclopentenone. The properties of II, deduced from measurements on III, are quite similar to the properties of the reactive triplet involved in photodimerization of cyclopentenone, deduced by Wagner and Bucheck[3] from measurements on the quantum yield of the overall reaction. Making the same assumption as these authors on the rate constant of quenching by piperylene ($k_Q = 10^{10}$ M^{-1} s^{-1} in acetonitrile) we found a lifetime ($\tau_0 > 20$ ns) and a self-quenching rate constant ($k_{SQ} = 1.2 \times 10^9$ M^{-1} s^{-1}) close to those they obtained ($\tau_0 = 25$ ns and $k_{SQ} = 6.9 \times 10^8$ M^{-1} s^{-1}). Therefore, species II is assumed to be the reactive triplet state involved in photodimerization.

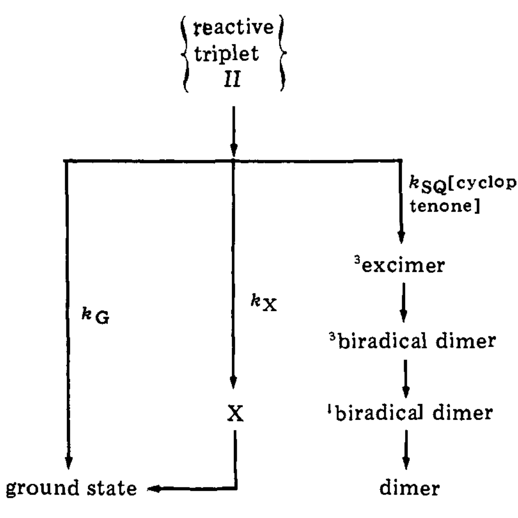
It is then tempting to identify transient III, which is produced from II, as an intermediate on the pathway of dimerization, either a triplet excimer or a biradical dimer. But it could be the product of a side reaction of the reactive triplet, noted X, in Scheme I.

With the values of τ_0 ($1/\tau_0 = k_G + k_X$) and k_{SQ} given above, the yield of conversion of II into a triplet excimer or a biradical dimer should be large and slightly increase (from 82 to 94%), whereas the yield of formation of X should be small and decrease strongly (from less than 18 to less than 6%) when the cyclopentenone concentration rises from 0.15 to 0.55 M. Experimentally, the transient absorption at 365 nm (i.e., the amount of III) increases slightly with the cyclopentenone concentration. But the fraction of the laser light absorbed in the cell also increases in the same time. This change in the density of excitation can easily account for the variations of the transient absorption if one assumes a nearly constant yield of formation of III, but it could certainly not if the yield of formation of III were decreasing by a factor of 3. We therefore conclude that III is either the triplet excimer or the biradical dimer involved in the photodimerization process.

We consider a triplet excimer as a possible intermediate by analogy with the triplet exciplex postulated in photocycloaddition of olefins to cyclohexenone and cyclopentenone.[12] Does this "triplet excimer" really exist or is the biradical formed from an "encounter complex"? The answer depends on the energy of stabilization of the "^{3}enone-enone" pair but, even in a triplet excimer, this energy is probably small so that a triplet excimer should be quenched by piperylene. Therefore the lifetime of a triplet excimer should be very short (<1 ns) since Stern-Volmer plots for quenching of the photodimerization by dienes are linear,[3,12] whereas the quenching of two sequential species (namely, the reactive triplet and the triplet excimer) should lead to nonlinear Stern-Volmer plots at high concentration of quencher. The observed species, III, has a lifetime around 40 ns and is not quenched by piperylene: it cannot be a triplet excimer.

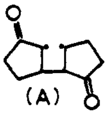
On the other hand, the triplet biradical dimer may have a 40-ns lifetime since the step ^{3}biradical → ^{1}dimer is spin forbidden and first requires a spin inversion from triplet biradical to singlet biradical. This spin-inversion process generally proceeds with a rate constant in the range 10^7–10^8 and leads

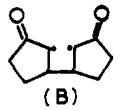
Scheme I

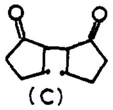


to lifetimes from 10 to 100 ns for most of the known triplet biradicals, such as those generated in Norrish type II reactions[13] or the biradical orthogonal triplet state of styrenes.[14] Oxygen quenches triplet biradicals with rate constant around 5×10^9 M^{-1} s^{-1} [13,14] as it quenches transient III.

Three types of biradicals can be envisaged leading to the HT dimer (A) and HH dimer (B and C). It seems unlikely that structure C can give rise to an absorption in the 350–380-nm range, whereas structures A and B, which both possess the chromophore -ĊH-CO-, could. That does not imply that biradical C is not formed but only that transient III must be identified as biradicals A or B or a mixture of both.


(A)


(B)


(C)

The small variations of the lifetime of III as a function of the polarity of the solvent may be tentatively related to the variations of the percentage of HH and HT dimers in various solvents. In nonpolar solvents where HT dimer is the major one, biradical A must be predominant and has perhaps a longer lifetime than biradical B.

The biradical dimer of cyclohexenone was not observed but that can easily be accounted for. The yield of formation of this species as calculated from the lifetime of the reactive triplet and the rate constant of self-quenching given by Wagner[3] must be very low in our experimental conditions. With 0.1 M cyclohexenone, this yield should be only 3%, obviously too small to be detected in our study.

Let us now consider transient I, the species which absorbs in the 260–280-nm range with a lifetime ranging from 10 ns for the very flexibles enones to 30 ns for cyclopentenone and increasing up to 440 ns for the rigid testosterone. The molecular skeleton of testosterone is assumed to be more rigid than that of the cyclopentenone (at least as far as twisting of the double bond is concerned) since testosterone phosphoresces at low temperature[15] whereas cyclopentenone does not. The lack of phosphorescence of cyclopentenone is probably related to energy dissipation via molecular distortion since rigidified cyclopentenones do phosphoresce.[16]

Considering the similarity of the properties of transient species I produced by irradiation of the various enones, we assume that the same type of species is observed in all cases.

It was shown, in the case of acetylcyclohexene, that the kinetics of decay of this species and of formation of the metastable "trans" ground state are identical within the experimental error, implying that the transient I is the precursor of the "trans" form.

The following assignments for the transient species I have been considered.

(a) The first was an excited singlet state (this can be discarded from a consideration of the lifetimes of the transients).

(b) The second was a "nontwisted" $n\pi^*$ or $\pi\pi^*$ triplet state.

These two states are supposed to be very close in energy[15–17] and from theoretical calculations as well as from spectroscopic and energy-transfer measurements it is known that they are approximately 70 kcal/mol above the planar ground state. Thus, these "nontwisted" triplet states should be quite efficiently quenched by energy transfer to piperylene, with a rate constant around or larger than 5×10^9 M^{-1} s^{-1}. For the cyclohexenone transient I, the measured quenching rate constant is one or two orders of magnitude smaller than this value. Addition of piperylene also has a very weak influence on the lifetime of the cycloheptenone and acetylcyclohexene transients.

Only the testosterone transient is efficiently quenched by piperylene. However, identification of the testosterone transient as a "nontwisted" triplet is not quite satisfactory. First, on the basis of reversible energy transfer theory[18] the experimental quenching rate constant is consistent with a 60 kcal/mol energy gap between the transient and the ground state, whereas the 0–0 band of the testosterone phosphorescence is around 400 nm, i.e., 70 kcal/mol.[15] Second, such an identification would raise some difficulty about the nature of the precursor of the testosterone transient since this precursor has a lifetime much too long to be an excited singlet state of a carbonyl compound.

(c) A biradical species resulting from the opening of the ring and very rapidly recyclizing to give both "cis" and "trans" ground states was also considered. Such a biradical species should probably give many rearrangements products, which are not observed in the relatively simple photochemistry of cyclohexenone, for instance. Furthermore, such as an intermediate should not exist in the case of methyl vinyl ketone.

(d) Identification of the transient species I as an orthogonal or highly twisted form of the triplet state does not suffer from the inconsistencies which led us to discard the assignments presented above.

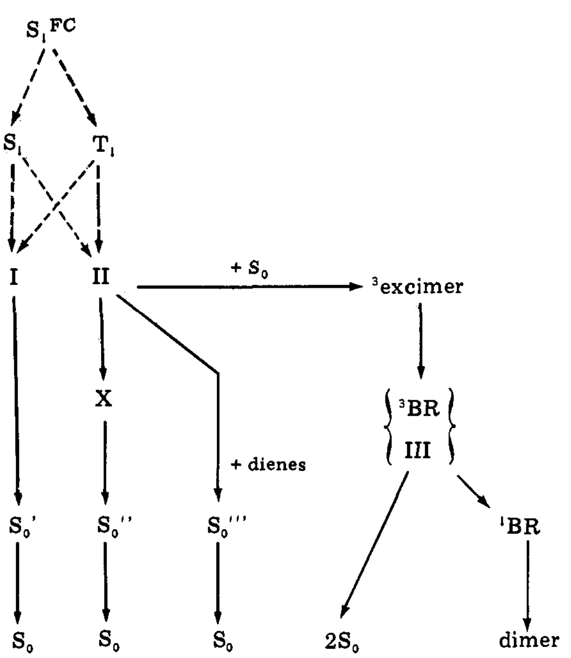
Molecules such as methyl vinyl ketone, cycloheptenone, or acetylcyclohexene, in which the ground state can be twisted by more than 90°, can easily reach the orthogonal configuration in their triplet state. The energy of the orthogonal triplet state is probably a few kcal/mol below that of the planar triplet, i.e., about 60–65 kcal/mol above the planar ground state, whereas the orthogonal ground state probably lies between 30 and 50 kcal/mol above the planar ground state.[19] Thus the energy available from the orthogonal triplet state in a "vertical energy transfer" process is much less than the 60 kcal/mol required for an efficient energy transfer to piperylene. The inefficient quenching of transient I of cyclohexenone and cyclopentenone by dienes may be related either to an inefficient "nonvertical" energy transfer or, more probably, to a chemical reaction such as addition of the diene to the C═C double bond of the enone system.[20]

The orthogonal triplet state can be efficiently quenched by oxygen. The triplet state of stilbene,[21] substituted stilbenes,[22] and styrenic compounds[14] in which the double bond is twisted by 90° are also quenched by O_2 with rate constants in the range $5\text{-}7 \times 10^9$ M^{-1} s^{-1}. These orthogonal triplet states may be considered as 1,2 triplet biradicals and it can be recalled that 1,4 triplet biradicals generated in Norrish II reactions are also quenched by O_2 with rate constants in the range $5\text{-}8 \times 10^9$ M^{-1} s^{-1}.[13]

For the more rigid systems, such as cyclopentenone and testosterone, a true perpendicular triplet state is certainly impossible but the C═C double bond can probably suffer a large twist leading to a stabilized conformation of the triplet state (see Figures 6a and 6b). It may be predicted from considerations schematically represented in Figure 6b that the energy gap between the triplet and ground states will increase as the twist angle of the double bond, in the minimum energy configuration of the triplet state, will decrease. For cyclopentenone the energy of the twisted triplet should remain smaller than 60 kcal/mol since the cyclopentenone transient is not efficiently quenched by piperylene. For the more rigid testosterone, the energy of the less twisted triplet should reach a value around 59–60 kcal/mol, in agreement with the order of magnitude of the rate constant of quenching of the testosterone transient by piperylene.

Lifetime considerations also fit in with the assignment of the observed transient to perpendicular or twisted triplet species. The orthogonal triplet state is expected to have a very short lifetime, owing to a strong coupling between triplet and ground states resulting from the small energy difference between these two states in the perpendicular configuration. An

Scheme II



increase of this energy difference, resulting from the limitation of the C=C twist angle by rigidification of the molecule, should increase the lifetime of a twisted triplet with respect to that of a similar perpendicular triplet. The measured lifetimes, ranging from 10 ns for very flexible systems to more than 400 ns for testosterone, agree with these views. A similar influence of the molecule rigidity on the triplet lifetime is observed in a series of styrenic compounds.[23] These lifetimes range from 25 ns for styrene and 55 ns for 1-phenylcyclohexene (orthogonal triplet) to ~1.5 μs for 1,2-dihydronaphthalene and 2-phenyl-2-norbornene (twisted triplet). It may be noticed that the lifetimes measured in the enone and the styrenic series are quite similar.

In the cases of cyclohexenone and cyclopentenone, the reactive triplet II is not formed from the twisted triplet I since the formation of biradical III, which arises from II, is much faster than the decay of I. Inversely the twisted triplet I is not formed from II since piperylene quenches II without decreasing significantly the formation of I. However, a very slight conversion from II into I could explain the anomalies observed in the behavior of the cyclohexenone transient in the presence of piperylene. Both the irregularity in the decay, shown in Figure 2, and the nonlinear quenching reported in the Results section, 5b, may be explained by assuming that a small fraction of the absorption at 280 nm, assigned to I, appears from a precursor having a few-nanosecond lifetime and is efficiently quenched by dienes. This precursor could be the reactive triplet II but we need further experiments, with a different laser, to test this hypothesis.

Thus, to a first approximation, the triplet species I and II must be populated concurrently with quantum yields Φ_I and Φ_{II} and do not interconvert. The product $\Phi_I\epsilon$ was estimated to be 2×10^3 for both considered enones. Assuming that ϵ, the extinction coefficient of species I at 270 nm, is not larger than 2×10^4 one gets $\Phi_I \geq 10\%$ and therefore $\Phi_{II} \leq 90\%$. The quantum yield Φ_{II} has been previously measured by two groups of the authors.[3,12] They both found $\Phi_{II} \simeq 1$ for cyclohexenone and cyclopentenone by using the same method: quantum yield of cis–trans isomerization of 1,3-pentadiene, sensitized by the cycloenones, extrapolated to infinite diene concentration. Although the plots given in Figure 1 of ref 3 and Figure 2 of ref 12 seem quite good, a 10% uncertainty in the extrapolated values seems possible.

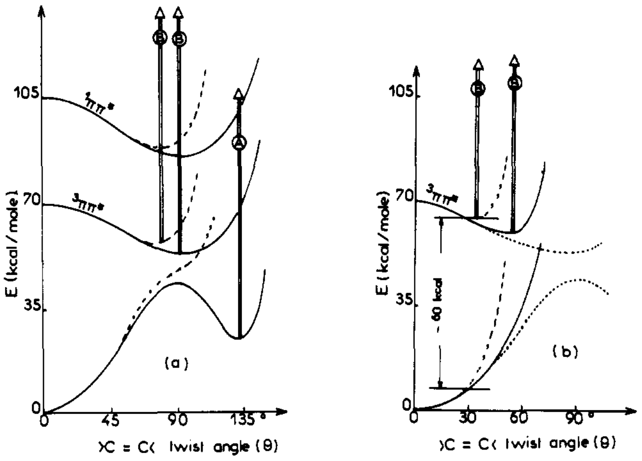


Figure 6. Schematic potential energy curves along the coordinate of twisting of the C=C double bond for the ground state and the ππ* singlet and triplet state of (a) cycloheptenone (—) and cyclohexenone (---); (b) cyclopentenone (—) and testosterone (---). The double arrows indicate the transient absorptions assigned to the "trans" ground state (A) and the twisted triplet (B).

It was suggested by Wagner[3] that the large decrease of the lifetime of the reactive triplet when going from cyclopentenone to cyclohexenone was related to the ability of the reactive triplet to give "an E′ species with considerable twisting about the double bond, the rate constant for formation of such a twisted species being expected to increase with ring size". We fully agree with this view and we find no better argument to account for the very short lifetime of the reactive triplet. But the E′ species postulated by Wagner cannot be identified with the twisted triplet I that we observed since the yield of formation of E′ should be quenched by dienes, whereas the yield of formation of I is not. One should note that Wagner's E′ species plays the same role as the X species appearing in Scheme I, which is not observed in our experiments.

Thus Scheme I must be completed to account for the existence of the twisted triplet, I, and the concurrent formation of species I and II. This gives Scheme II, in which dashed arrows indicate several possible pathways for population of the triplet species I and II from the Franck-Condon excited singlet state.

One must therefore assume that there are two distinct twisted triplets and we have to account for the existence of at least three metastable conformations of the triplet state of cyclohexenone and cyclopentenone: one reactive triplet and two twisted triplet species. This seems impossible if one considers only the relaxation by twisting of the double bond and a ππ* triplet as shown in Figure 6.

We have to consider at least one other relaxation mode of the enone excited states, for instance, a modification of bond lengths from a system C=C—C=O to a system such as C⩦C=C⩦O. This relaxation was theoretically studied by Devaquet[17] in addition of the twist of the double bond. The potential energy surfaces of nπ* and ππ* triplet states present a stabilization by twisting and change in the bond lengths. They intersect each other, determining a complex energy sheet for the lowest triplet with valleys, saddle points, and ridges, the orbital nature changing from one valley to the other. The shape of this energy surface strongly depends on small variations of parameters such as the energy gap between the pure nπ* and ππ* triplets at the Franck-Condon geometry (experimentally unknown and, probably, these pure states have no real existence) or the energy of constraint of the cycle upon twisting the double bond. However, the general trends are that (1) for appreciable twist and little bond elongation, the lowest triplet T_A has a ππ* character; (2) for small twist angle and a large bond elongation, the lowest triplet T_B has a nπ* character; (3) both T_A and T_B are stabilized by a further twist of the double bond

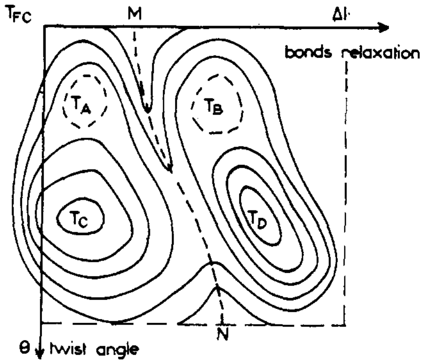


Figure 7. A possible representation, as a relief map, of the energy surface of the lowest triplet state of an α,β-enone system accounting for the existence of several metastable conformations. Considered relaxation modes are twisting of the C═C double bond (θ) and change in bond lengths (Δl). Triplet nature is $\pi\pi^*$ on the left side of the MN line, $n\pi^*$ on the other side. Metastable conformations (energy minima) are T_C, T_D, and either T_A or T_B or both T_A and T_B. See text and ref 17.

to give T_C and T_D (respectively described as $T\pi'y$ and Tny by Devaquet).

Figure 7 shows a possible representation for the energy surface of the lowest triplet state, drawn as a relief map. It closely resembles Figure 9 of Devaquet's paper.[17] The ridge MN represents the intersection of the original pure $n\pi^*$ and $\pi\pi^*$ triplet surfaces. The shape of the isoenergetic curves is arbitrary and only chosen in order to account for the three general trends given above. Depending on the nature of the lowest Franck-Condon triplet, T_{FC}, point M will be on the Δl axis ($T_{FC} = \pi\pi^*$) or on the θ axis ($T_{FC} = n\pi^*$), but this is unimportant. The only important feature is the presence of two valleys, one in the $\pi\pi^*$ region, the other in the $n\pi^*$ domain, and the existence of two minima in one valley at least.

Assuming, for instance, that T_B and T_D are two minima in the $n\pi^*$ valley leads to the following interpretation of the experimental results: T_B would be identified as the reactive triplet, T_D as the twisted species X, and T_C as the twisted triplet I. Intersystem crossing would yield about 10% of $\pi\pi^*$ triplet (left side of the MN limit) which, if T_A is not a minimum, would very rapidly relax to T_C, and about 90% for $n\pi^*$ triplet which goes to T_B. The lifetime of T_B would be determined by the energy barrier between T_B and T_D, which may be dependent on the size of the cycle.

Alternatively, it may be assumed that the valley presenting two minima is on the $\pi\pi^*$ side, in which case T_A would be the reactive triplet, T_C the species X, and T_D the species I. The existence of two minima on the $\pi\pi^*$ surface seems hardly conceivable if one considers only the twisting of the double bond, i.e., along the θ axis. But combination of several modes of relaxation (we have only considered two of them, but some other ones may also be important) may explain the existence of a minimum around T_A.

We wish to emphasize that no precise information about the nature or the geometry of the different triplet species can be obtained from Figure 7. This figure only shows how the existence of several metastable triplet species is made possible by the conjunction of three properties of the enone system: (1) the molecular system is rather flexible; (2) there are two triplet states very close in energy; (3) these two triplet states being of different nature are stabilized in a different manner by the various modes of geometrical relaxation.

The shape of the energy surface described in Figure 7 and therefore the stability, the geometry, and the chemical reactivity of the various triplet species are probably very sensitive to small variations of the relative energies of the $n\pi^*$ and $\pi\pi^*$ triplet states. This may explain why, in some cases, the photochemistry of enones is very sensitive to small modifications of the molecular structure.

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References and Notes

(1) See, for instance, the related chapters by W. H. Horspool, *Spec. Period. Rep.: Photochem.*
(2) R. Bonneau, P. Fornier de Violet, and J. Joussot-Dubien, *Nouv. J. Chim.*, **1**, 31 (1977).
(3) P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, **91**, 5090 (1969), and references cited therein.
(4) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).
(5) O. L. Chapman, "Organic Photochemistry", Vol. 3, Marcel Dekker, New York, 1973, p 223.
(6) T. D. Goldfarb, *J. Photochem.*, **8**, 29 (1978).
(7) R. Bonneau and P. Fornier de Violet, *C. R. Acad. Sci.*, **284**, 631 (1977).
(8) E. N. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965).
(9) G. Beck, *Rev. Sci. Instrum.*, **47**, 537 (1976).
(10) R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).
(11) J. W. Boag, *Proc. R. Soc. London, Ser. A*, **308**, 677 (1968).
(12) R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, **99**, 3559 (1977).
(13) R. D. Small and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).
(14) R. Bonneau, *J. Photochem.*, **10**, 439 (1979).
(15) (a) C. R. Jones and D. R. Kearns, *J. Am. Chem. Soc.*, **99**, 344 (1977); (b) G. Marsh, D. R. Kearns, and K. Schaffner, *ibid.*, **93**, 3129 (1971).
(16) (a) R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and K. Saltiel, *Mol. Photochem.*, **1**, 301 (1968); (b) R. L. Cargill, W. A. Bundy, D. M. Pond, A. B. Sears, J. Saltiel, and J. Winterle, *ibid.*, **3**, 123 (1971); (c) S. W. Beavan and D. Philipps, *ibid.*, **8**, 311 (1977).
(17) A. Devaquet, *J. Am. Chem. Soc.*, **94**, 5160 (1972).
(18) K. Sandross, *Acta Chem. Scand.*, **18**, 2355 (1964).
(19) See the activation energies for thermal cis–trans isomerization of conjugated olefins: *Prog. React. Kinet.*, **2**, 165 (1964).
(20) T. S. Cantrell, *Chem. Commun.*, 1656 (1970).
(21) F. Dainton, E. A. Robinson, and G. A. Salmon, *J. Phys. Chem.*, **76**, 3897 (1972); M. Sumitani, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 2503 (1978).
(22) D. V. Bent and D. Schulte-Frohlinde, *J. Phys. Chem.*, **78**, 446 (1974).
(23) R. Bonneau, unpublished results.