NANOSECOND LASER PHOTOLYSIS STUDY OF THE REACTION MECHANISM IN THE PHOTOCHROMISM OF A PIPERIDINOSPIROPYRAN

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Summary

The primary processes in the photoisomerization of spiro[8-methoxy-6-nitro-$2H(1)$-benzopyran-2,2'-3',3'-dimethylpiperidine] (H-SP) in toluene were studied from 271 to 324 K by means of nanosecond laser photolysis using the third harmonic (353 nm) of an Nd–glass laser as the excitation light (pulses with a full width at half-maximum of 6 ns). The all-trans isomer, the photomerocyanine (lifetime, about 3 s at 297 K), is formed almost entirely from the lowest triplet T of H-SP by a stepwise process which occurs adiabatically on the lowest triplet surface. This process involves the sequential formation of three isomeric triplets one from the other: T, ^{3}Z and ^{3}A with lifetimes of 20 ns, 110 ns and 4 μs respectively at 297 K. ^{3}Z and ^{3}A are the triplets of open isomers with cisoid and transoid configurations respectively. ^{3}A decays to a ground state isomer of transoid geometry, which is converted into the more stable all-trans isomer (photomerocyanine). The activation energies of the T $\rightarrow$ ^{3}Z and ^{3}Z $\rightarrow$ ^{3}A processes are about 5 kcal mol^{-1} and about 6 kcal mol^{-1} respectively. The mechanism of photoisomerization for H-SP is compared with that previously established for the closely related system spiro[3-methyl-8-methoxy-6-nitro-$2H(1)$-benzopyran-2,2'-3',3'-dimethylpiperidine].

1. Introduction

Heterocyclic spiropyrans form an important class of photochromic compounds. The photochromism consists in a reversible photoisomerization involving C—O bond rupture of the non-coloured closed compound, upon UV excitation, to form a highly coloured open isomer, the photomero-

cyanine, which thermally (or photochemically) reverts to the initial colour-less form.
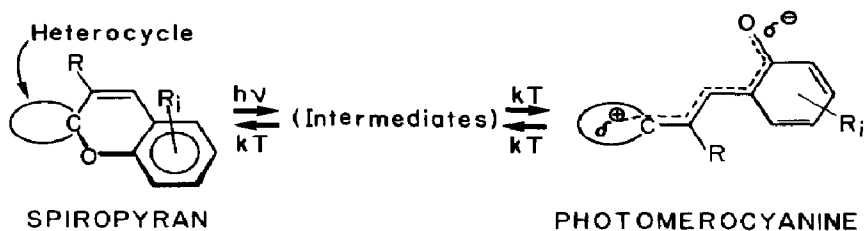
In the spiropyran the heterocycle and the benzopyran rings are orthogonal to each other, while the photomerocyanine has a planar configuration. It has been proposed [1] that the primary process associated with UV light absorption leads to benzopyran ring opening and is followed by a sequence of thermal steps involving extensive structural rearrangements before the all-trans isomer is reached. The photochromic properties of spiropyrans and in particular the indolino class have been extensively studied, especially in connection with practical applications, phototropic glasses [2], non-linear optics [3] etc. However, the primary processes of the photoisomerization have received less attention and are still not entirely understood. Different reaction schemes leading to the photomerocyanine have been proposed: the triplet pathway, involving an upper excited triplet [4] or the vibrationally relaxed lowest triplet [5 - 7] of the spiropyran, and the excited singlet pathway [6, 8, 9], involving as an intermediate a cisoid ground state isomer with an opened C—O bond. Such a ground state intermediate was proposed for the first time by Heiligman-Rim *et al.* [10] and has been very recently observed in time-resolved (picosecond and nanosecond) studies [8, 9]; this species retains a non-planar geometry and then converts to the planar all-trans coloured isomer.

A new class of photochromic spiropyrans which are piperidino derivatives was recently reported by Maguet *et al.* [11]. A representative compound of this class of spiropyrans is spiro[8-methoxy-6-nitro-2H(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] (H-SP).

H-SP
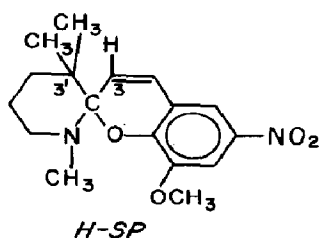
It has been shown that the photoisomer obtained in this case is an all-trans isomer (λ_{max} = 570 nm) similar to that of indolinospiropyrans.

However, if the hydrogen in position 3 is substituted by a methyl group to form spiro[3-methyl-8-methoxy-6-nitro-2H(1)-benzopyran-2,2'-3'3'-dimethylpiperidine] (Me-SP), the photoisomer obtained is not the all-trans isomer but is a cisoid form (λ_{max} = 440 nm), indicating that the isomerization process is blocked in this case at some intermediate stage, probably because of steric hindrance to rotation arising from the presence of the three methyl groups in positions 3 and 3'. In a previous nanosecond laser photolysis study [12], we investigated the photoisomerization mechanism of Me-SP. We obtained a long-lived cisoid isomer in agreement with the results of Maguet *et al.* [11] and showed that this isomer is formed exclusively from the first excited singlet state of Me-SP. In addition to this species, two triplets were detected, one formed from the other. The first, attributed to the lowest triplet of Me-SP, leads by C—O bond rupture to the triplet state of an isomer which retains a cisoid geometry close to that of the initial compound.

In the present study the primary processes in the photoisomerization of H-SP were investigated by means of nanosecond laser photolysis. The mechanism of photoisomerization is quite different from that for Me-SP. The all-trans isomer is formed almost entirely via a triplet pathway. A quite unusual feature of the mechanism is that the all-trans isomer is formed as a result of adiabatic evolution on the lowest triplet energy surface via three successive triplets; the first is the lowest triplet of the closed form and the other two are most probably the lowest triplets of open isomers with cisoid and transoid configurations.

2. Experimental details

2.1. *Laser apparatus*

The exciting light source was an Nd^{3+}-doped glass laser (CILAS VD 231) emitting at 1060 nm. Laser pulses of 6 ns full width at half-maximum at 353.3 nm were obtained using potassium dihydrogen phosphate crystals and a Pockels cell (CILAS DL 11). Relative measurements of the laser energy were performed by focusing a small fraction of the laser light on a pyroelectric joulemeter (Laser Precision Corporation model Rk 3230 with an RE 335 probe).

Cylindrical lenses were used to match the laser beam cross-section to the 3 mm × 10 mm section of the volume probed in the sample cell. A frosted silica plate was used to homogenize the laser light at the entrance of the cell. Transient transmission changes were monitored at right angles to the laser beam using a xenon flash lamp (Verre et Quartz VQX65N) as the probing light source. A constant-running xenon lamp (OSRAM XBO 75 W/2) was used to monitor transmission changes over times longer than 50 μs. The detection system consisted of a monochromator (Jarrell–Ash type 82-410; bandwidth, 2 nm), a photomultiplier (HTV R928) and a double-beam oscilloscope (Tektronix 7844). The electric signal from the photo-

multiplier was fed into the scope through a field effect transistor probe (Tektronix P6021). The time resolution of the detection system was 1 - 2 ns. The oscilloscope screen was scanned using a high sensitivity video camera (Sofretec CF123 V); the video signal was digitized using a converter (Thomson CSF TSN1150) and was stored on magnetic tape for kinetic analysis on a Tektronix 4051 computer.

2.2. Materials

H-SP was synthesized according to the method described in ref. 13. In order to avoid aggregation of the spiropyran, toluene (Merck Uvasol) was chosen as the solvent [14]. Spectrophotometric measurements confirmed the absence of any deviation from Beer's law for concentrations in the range 10^{-5} - 10^{-3} M. No concentration effects on the transients could be observed in the time-resolved study. A concentration of 9×10^{-5} M was used in the present study. The samples, contained in silica cells of cross-section 10 mm $\times$ 10 mm, were deoxygenated by bubbling with argon for 15 min. Even though there was no detectable photodegradation the samples were renewed frequently.

2.3. Triplet quantum yields

The triplet quantum yield was determined by comparing the triplet concentration obtained after laser excitation of H-SP with that formed on excitation at the same laser energy of acridine in benzene chosen as a standard; the triplet quantum yield for acridine in benzene is reported to be 0.73 ± 0.07 [15].

This method of determining triplet quantum yields is only valid provided that a small fraction of the molecules are excited; in these measurements less than 15% of the H-SP molecules were converted to the triplet state. The acridine concentration was chosen to give the same optical density (OD) at 353 nm as that of H-SP (0.15 across the 2 mm width of the analysis beam). The triplet concentration of H-SP was monitored at 560 nm using a triplet extinction coefficient of 5000 M^{-1} cm^{-1} (see Section 3.1); the triplet concentration of acridine was monitored at its absorption maximum of 442 nm using a triplet extinction coefficient of 2.7×10^4 M^{-1} cm^{-1} [15].

3. Results and discussion

Transient OD changes obtained on laser excitation at 353 nm of deoxygenated solutions of H-SP (9×10^{-5} M) in toluene at 297 K were monitored in the spectral range 300 - 750 nm over a time range extending from a few nanoseconds to a few seconds after the laser pulse. The OD changes were found to be linearly dependent on the laser energy at low energy but to saturate at higher laser energies, owing to ground state depletion. The linear relationship reflects the monophotonic character of the processes investigated. The saturation curves thus obtained showed that total depletion of

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the ground state of H-SP could be achieved. However, for practical reasons, the laser energy was kept to a value corresponding to 60% depletion of the ground state of H-SP.

3.1. Spectra and kinetics

Typical oscillograms are shown in Fig. 1. A transient absorption built up within the laser pulse decays partially over 50 ns (oscillogram 1(a)). Oscillograms 1(b) and 1(c) show that there are at least three phases in the evolution of the transient absorption at 430 nm: a phase lasting about 50 ns, another phase lasting about 400 ns and a third phase lasting about 40 μs. At 570 nm and 630 nm (oscillograms 1(d) and 1(e)) two components are visible
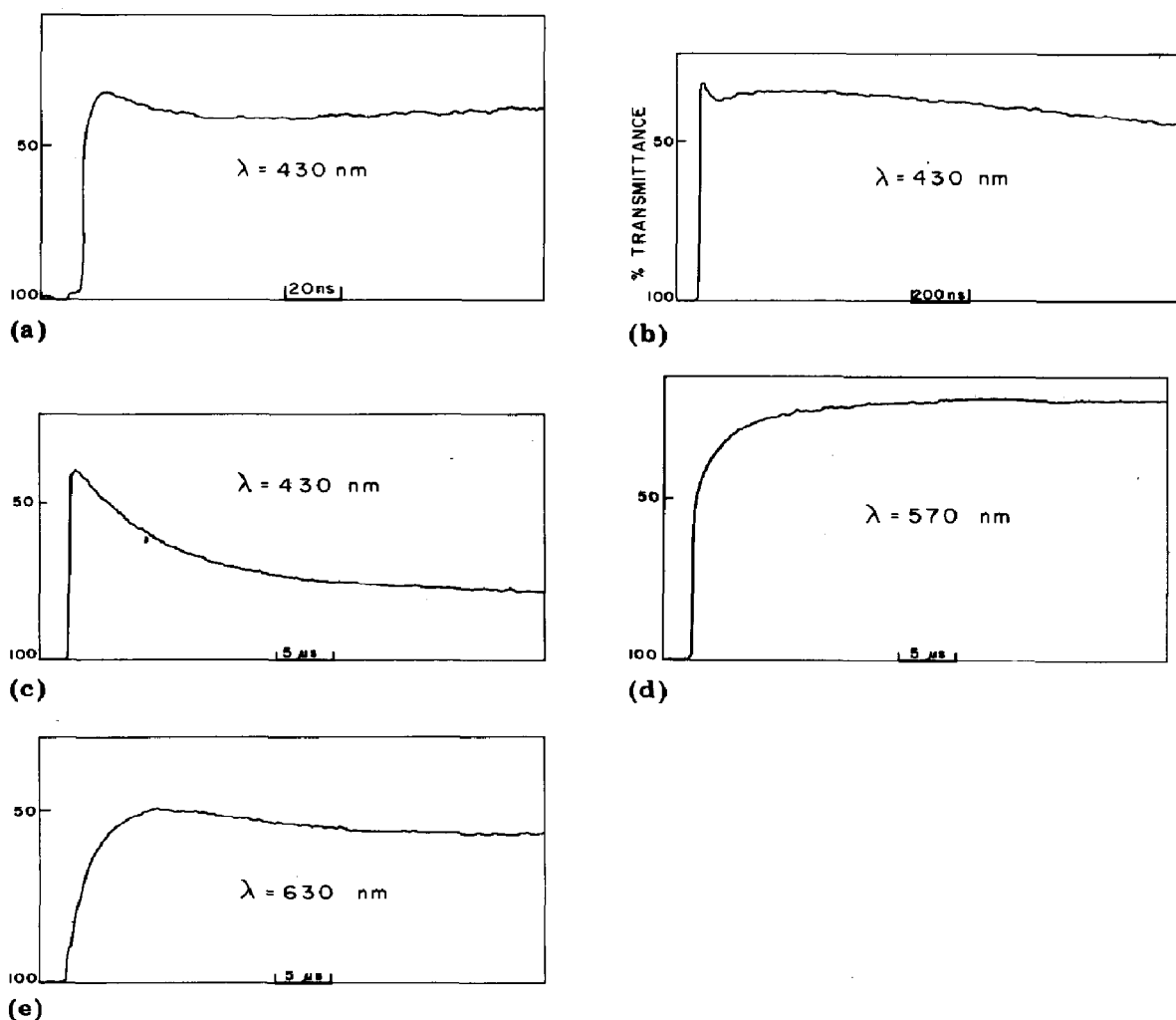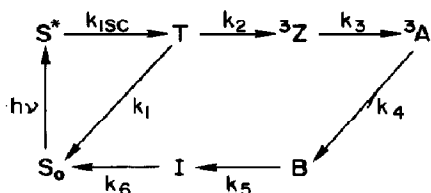

(a)

(b)

(c)

(d)

(e)

Fig. 1. Oscillograms showing the variation in the optical transmission at different wavelengths λ of 9×10^{-5} M H-SP in degassed toluene at 297 K on excitation by a 353 nm laser pulse of 6 ns duration.

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in the microsecond phase, the first component lasting 10 μs and the second component lasting about 30 μs. Runs over longer times show that the transient absorption still present at 40 μs after the laser pulse remains constant over a few tenths of a second then decays within 20 s, leading to complete recovery of the initial absorption of H-SP. Thus, no less than five phases may be distinguished in the OD evolution. Kinetic analysis (using biexponential analysis in the nanosecond and microsecond ranges and mono-exponential analysis in the seconds range) showed that these time phases can be associated at all wavelengths with the formation and the decay of five transient species with lifetimes of 20 ns, 110 ns, 4 μs, 12 μs and 3 s respectively at 297 K. The following scheme was deduced from these experimental results and those obtained from the observed effects of oxygen and temperature on the kinetics and the yields of the transient species. (See Sections 3.2 and 3.3.)

$$S^* \xrightarrow{k_{ISC}} T \xrightarrow{k_2} {}^3Z \xrightarrow{k_3} {}^3A$$
$$h\nu \uparrow \quad \swarrow k_1 \qquad\qquad \swarrow k_4$$
$$S_0 \xleftarrow{k_6} I \xleftarrow{k_5} B$$

In the above scheme S* represents the first excited singlet state of H-SP, T (lifetime, 20 ns) the lowest triplet state of H-SP, ^{3}Z (lifetime, 110 ns) the lowest triplet state of an isomer retaining the cisoid geometry reached after C—O bond opening, ^{3}A (lifetime, 4 μs) the lowest triplet state of an isomer of transoid configuration, B (lifetime, 12 μs) the ground state of ^{3}A or possibly an isomer which has relaxed further structurally and I (lifetime, 3 s) the most stable isomer of all-trans configuration, the photomerocyanine.

   In recent kinetic studies on indolinospiropyrans, singlet and triplet pathways have been proposed in the formation of the photomerocyanine [4, 5, 8, 16]. On the singlet pathway it has been shown that the photomerocyanine is formed through an intermediate which is a cisoid isomer of very short lifetime (picosecond or nanosecond range) [8, 9]. Also, in a previous paper on Me-SP [12], we have shown that a cisoid isomer is formed from the first excited singlet state. However, this species does not lead to the fully developed trans isomer: the isomerization is blocked at the cisoid stage, probably because of steric hindrance in this molecule. However, in the case of H-SP, the formation of I directly from the excited singlet state can be neglected on the basis of the results of the computation of the spectrum of T. Indeed, the absorption maxima of T and I in the visible range are very close to each other (560 and 570 nm), but the extinction coefficient of I is much higher ($\epsilon_{570} \approx 30\,000$ M^{-1} cm^{-1}) than that of T ($\epsilon_{560} \approx 5000$ M^{-1} cm^{-1}). Therefore any contribution of the singlet pathway to the formation of I should modify the spectrum of T. In fact the computed spectrum of T gives an unacceptable shape to the visible band if more than 10% of the total
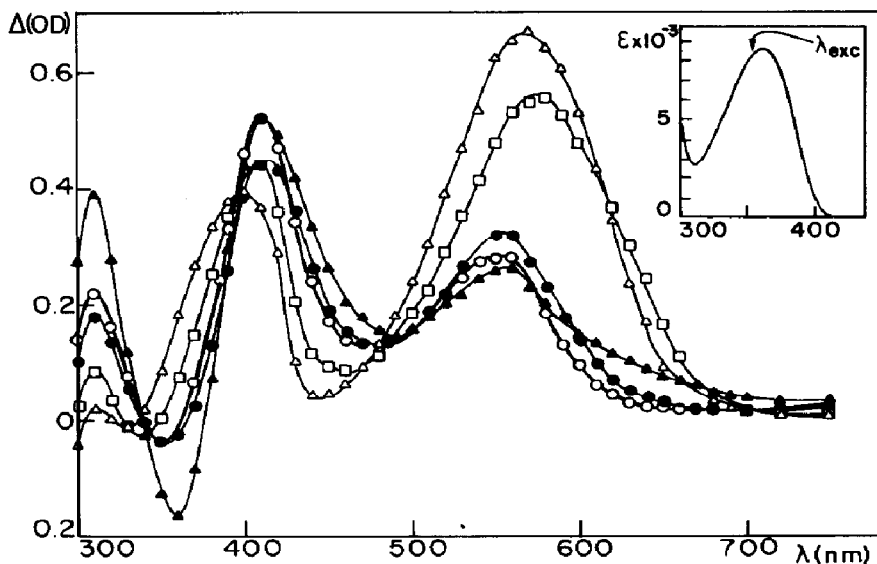
Fig. 2. Difference spectra observed on excitation of 9×10^{-5} M H-SP in degassed toluene at 297 K by a 353 nm laser pulse: ▲, at the end of the pulse ($t = 0$); ○, at $t = 40$ ns; ●, at $t = 500$ ns; □, at $t = 8$ μs; △, at $t = 40$ μs. The values are the averages of at least two measurements. The extinction coefficients ϵ (M^{-1} cm^{-1}) of H-SP in toluene with the laser wavelength λ_{exc} indicated are shown in the inset.

concentration of I is obtained from the singlet state. Consequently, in the following the singlet pathway for the formation of I will be assumed to be negligible.

Difference spectra (Fig. 2) were constructed from changes in the transient absorption measured at five different characteristic times defined by the kinetics: $t = 0$ (end of laser pulse), $t = 40$ ns, $t = 500$ ns, $t = 8$ μs and $t = 40$ μs (upon completion of formation of I which is then the only transient still present). The spectrum of T (Fig. 3(a)) was obtained from the difference spectrum measured at the end of the laser pulse. Since the concentration of T was 60% of the initial concentration of H-SP (9×10^{-5} M) (see Section 3), the extinction coefficients ϵ for T were thus obtained. The spectrum of T has three maxima: at 300 nm, 400 nm and 560 nm, with ϵ_{max} of 1.1×10^4 M^{-1} cm^{-1}, 1.0×10^4 M^{-1} cm^{-1} and 0.5×10^4 M^{-1} cm^{-1} respectively. The absorption extends into the IR region. It will be shown in Section 3.2 that T is a triplet state (T is assigned to the lowest triplet state of H-SP); indeed, since H-SP is non-fluorescent [13], the lifetime of the excited singlet state should be on the subpicosecond time scale and T should therefore be populated within the laser pulse duration. As expected, the spectrum of T is quite similar to that of the lowest triplet of Me-SP [12] with a UV band shift of about 20 nm and similar band ratios. The absolute spectra of the other transients (Fig. 3) were computed from the difference spectra using the kinetic scheme proposed and the values obtained for the rate constants of the processes involved. It must be stressed that the separation of the spectra was difficult because of the high degree of overlap. The spectrum of ^{3}Z (Fig.
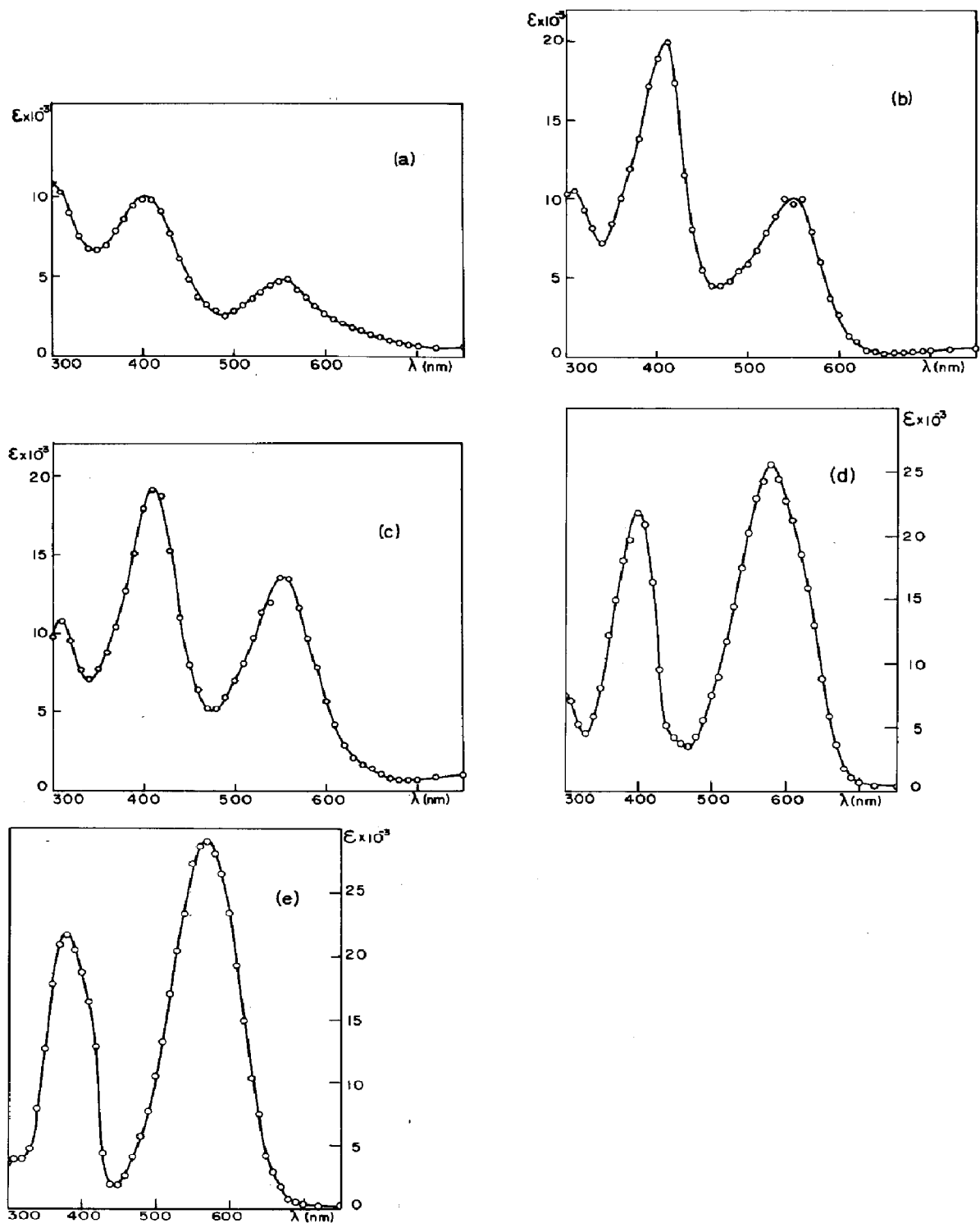
Fig. 3. Extinction coefficients ϵ (M^{-1} cm^{-1}) of H-SP transients calculated from the difference spectra: (a) the lowest triplet state T of H-SP; (b) the second triplet ^3Z; (c) the third triplet ^3A; (d) the first isomer B; (e) the long-lived isomer I (photomerocyanine).

3(b)) was obtained using the known branching ratio from T (see Section 3.3) and assuming full conversion from ^3Z to ^3A (see Section 3.3); this spectrum presents three bands at 310 nm, 410 nm and 550 nm with ϵ_{max} values of 1.0×10^4 M^{-1} cm^{-1}, 2.0×10^4 M^{-1} cm^{-1} and 1.0×10^4 M^{-1} cm^{-1} respectively. The spectrum of ^3A (Fig. 3(c)) was obtained assuming complete conversion from ^3A to B (see Section 3.3). This spectrum has three bands with the same wavelength maxima as the spectrum of ^3Z, but with different band ratios, ϵ_{max} being 1.1×10^4 M^{-1} cm^{-1} at 310 nm, 1.9×10^4 M^{-1} cm^{-1} at 410 nm and 1.4×10^4 M^{-1} cm^{-1} at 550 nm. Since T was assigned to the lowest triplet of the closed form (H-SP), it is suggested that ring opening occurs on the lowest triplet energy surface and leads consecutively to ^3Z and ^3A which are triplets of open form corresponding to different stages of configurational evolution. The shorter lived ^3Z is assumed to be the triplet of an isomer of cisoid geometry reached after C—O bond rupture; the observation of such a triplet has also been reported previously for Me-SP and nitrochromene [12, 17]. ^3A in turn decays to a ground state (the species B), probably of essentially trans geometry. The spectrum of the isomer B (Fig. 3(d)) was calculated under the assumption of complete conversion from ^3A to B. This spectrum has two bands, at 400 nm and 580 nm with ϵ_{max} values of 2.3×10^4 M^{-1} cm^{-1} and 2.7×10^4 M^{-1} cm^{-1} respectively; in a few microseconds B leads to the photomerocyanine I which lasts a few seconds. The spectrum of I (Fig. 3(e)) was calculated from the difference spectrum at 40 μs; at this time only I is present and its concentration at total ground state depletion is obtained on the basis of the kinetic scheme, knowing the branching ratio from T (see Section 3.3). The spectrum of I has maxima at 380 nm and 570 nm with ϵ_{max} values of 2.2×10^4 M^{-1} cm^{-1} and 2.9×10^4 M^{-1} cm^{-1} respectively. The high absorbance in the visible is consistent with that of the photomerocyanines of other classes of spiropyrans. The spectra of B and I have similar bands with high extinction coefficients; this is strong evidence for the trans character of both B and I configurations, with an important degree of delocalization and charge separation.

3.2. Oxygen effects

Oxygen is known to be an efficient quencher of triplet states. This feature was used to assess the triplet nature of the transients. Saturation of the solution with oxygen (9×10^{-3} M O_2 [18]) efficiently accelerated the decays of T, ^3Z and ^3A; the high value of the quenching rate constant, $k_q = (3 \pm 1) \times 10^9$ M^{-1} s^{-1}, was considered as evidence of the triplet character of these three species. In contrast, the decays of B and I were unaffected by oxygen, leading to the conclusion that B and I are ground state isomers. It was also found that the yields of ^3Z, ^3A and I decrease only to a limited extent even in an oxygen-saturated solution. The shape of the spectrum measured at 40 μs after the laser pulse in oxygen-saturated solution was identical with that of I in deoxygenated solution; however, its amplitude was 70% and 90% for oxygen-saturated and air-saturated solutions respec-

tively, as compared with deoxygenated solution. These experimental values reflect exclusively the quenching of T by oxygen and air as calculated from the k_q values. The possibility that oxygen enhances intersystem crossing of ^3Z to S_0 was discarded because there should then be a drastic reduction in the yield of I: the calculated values of the yield of I would be 20% and 60% for oxygen and air respectively as compared with deoxygenated solution; these calculated values are in complete disagreement with the experimental results given above. It was therefore concluded that ^3Z does not decay towards S_0, but decays towards B in the presence of oxygen. Vannikov and Kryukov in a study of indolinospiropyrans [7] also gave evidence for the occurrence of such an effect of oxygen on a triplet intermediate leading to the photomerocyanine. Thus the behaviour of the second triplet ^3Z in the case of H-SP is different from that of the second triplet ^3Y in the case of Me-SP [12]; ^3Y generated from the lowest triplet of the spiropyran (like ^3Z) is also an open form, but in the presence of oxygen it decays to the spiropyran instead of leading to an isomer of transoid configuration. From these observations, it may be inferred that in the case of H-SP the configuration of ^3Z has developed further away from the initial cisoid geometry while ^3Y probably retains this geometry.

As mentioned above, the decay of ^3A was also accelerated in the presence of oxygen. As it is known from the preceding results that the reduction in the yield of I in the presence of oxygen is only due to the quenching of T, and since no new transient formation concomitant with the quenching of ^3A was observed, it is inferred that ^3A decays towards B; this observation implies that the structure of ^3A is essentially trans.

3.3. Temperature effects

The effect of temperature on the kinetics and the yields of transients was studied in the range 271 - 324 K. The temperature dependence of the decays of the triplet states T, ^3Z and ^3A is shown in Fig. 4. The temperature effects were analysed on the basis of the kinetic scheme proposed (see Section 3.1). The results obtained from this analysis showed that these three triplets are formed consecutively one from the other.

Under the assumption (already made in the case of Me-SP [12]) that only part of the T population decays to ^3Z and the remainder to S_0, the observed decay (Fig. 4, k_T) is the result of two competing processes (described by k_2 and k_1 in the kinetic scheme). Comparison of experimental decays with calculations at various temperatures using this assumption leads to activation energies of 5 kcal mol^{-1} and 0.4 kcal mol^{-1} and pre-exponential factors of 2×10^{11} s^{-1} and 6×10^7 s^{-1} for k_2 and k_1 respectively. The high value obtained for the pre-exponential factor of k_2 is expected since there is no spin change in the formation of ^3Z from T. The process T $\xrightarrow{k_1}$ S_0 is characterized by a low pre-exponential factor, as expected for the spin change involved in the relaxation of T to a ground state. It was calculated from the computed k_1 and k_2 that a fraction 0.5 of the T population was converted to ^3Z at 297 K (this fraction was used in the calculations of the
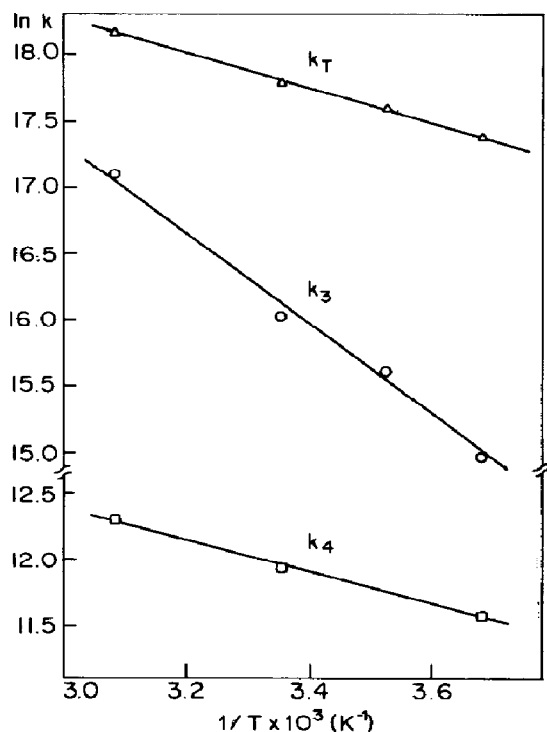
Fig. 4. Arrhenius plots of the decay rate constants of T (k_T), ^3Z (k_3) and ^3A (k_4).

absorption spectra of the transients given in Fig. 3). The activation energy of about 5 kcal mol^{-1} for C—O bond rupture in H-SP and Me-SP [12] is quite similar to that of nitrochromene [17], indicating that the mechanism of the ring opening is similar in piperidinospiropyrans and nitrochromene.

The concentrations of ^3Z, ^3A, B and I increase with temperature with the same exponential dependence; this observation leads to the conclusion that any branching from ^3Z towards B or I, or from ^3A towards I, in deoxygenated solutions should be unimportant. The decay of the triplet ^3Z towards ^3A (k_3 in the kinetic scheme) is characterized by an activation energy of about 6 kcal mol^{-1} and a pre-exponential factor of 3×10^{11} s^{-1}. The high value of this factor (similar to that of the decay of T to ^3Z) is consistent with the assumption that the triplet ^3A is formed from ^3Z as indicated in the kinetic scheme. The decay of ^3A to B (k_4 in the kinetic scheme) has an activation energy of about 2 kcal mol^{-1} and a pre-exponential factor of 5×10^6 s^{-1}; the low value of this factor is in agreement with the spin change involved in the relaxation of ^3A towards a ground state B. In summary, the effects of temperature on the decay of the different species observed experimentally show that the formation of the coloured isomers B and I involves three intermediates of triplet character. These triplet species are formed consecutively one from the other. Such a sequence of relaxed triplets appears to be a common feature of the opening of the pyran ring in nitrochromene [17], Me-SP [12] and H-SP. Direct evidence for such a

sequence has not been reported for other classes of spiropyrans. In the case of nitrochromene [17] and H-SP this opening is followed by cis–trans isomerization on the triplet energy surface.

3.4. Quantum yields

The quantum yield Φ_T of H-SP triplet formation was determined by comparison of the triplet concentration obtained on excitation of H-SP solution with that of acridine in benzene used as a standard [15] (see Section 2.3). A value of 0.7 ± 0.1 was obtained for Φ_T at 297 K. This value is comparable with that obtained for the Φ_T of the related molecule Me-SP ($\Phi_T = 0.5 \pm 0.1$). It may be noted that in the case of Me-SP there is competition between the formation of the triplet and the formation of the isomer generated from the first excited singlet state with a quantum yield of 0.2. Since H-SP and Me-SP are non-fluorescent compounds [13] it is seen that the same quantum yield of internal conversion (0.3) is obtained for the two compounds.

The Φ_T value was used to calculate the quantum yield Φ_I of formation of the isomer I. It was found from computed values (see Section 3.3) that a fraction 0.5 of the H-SP triplet population transforms to I via two other triplets ^3Z and ^3A; since the singlet pathway for the formation of I is negligible, the quantum yield of I is thus $0.5\Phi_T = 0.35$. In the case of nitrochromene [17], isomerization occurs via both singlet and triplet pathways: the triplet pathway is more efficient ($\Phi_I{}^T = 0.56$) than the singlet pathway ($\Phi_I{}^{S^*} = 0.14$). It appears that in both compounds the photoisomerization yields via the triplet pathway are of the same order of magnitude.

4. Conclusions

It is shown in this paper that the isomerization of H-SP to form a photomerocyanine proceeds essentially in the triplet manifold. Almost all ring-opened molecules isomerize adiabatically on the triplet surface until reaching a transoid triplet which decays towards the all-trans coloured isomer. Thus the primary photochemical processes of H-SP appear to be quite complex, involving isomerization via a sequence of three intermediate triplets.

This adiabatic evolution on a triplet surface appears to be an unusual process which we had previously observed in a study of a nitrochromene [17] and Me-SP [12]. In fact, only a few examples of adiabatic processes on the triplet energy surface have been reported, such as oxidative photocyclization of phenylenediamines [19] or photoisomerization of anthrylethylenes [20]. However, direct evidence for such a mechanism has not been reported for other classes of spiropyrans. The photoisomerization of H-SP constitutes a new illustration of this type of reaction.

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Note added in proof

After submission of the manuscript, we learned of a paper by Lenoble and Becker which has just been published [21]; these researchers found that ring opening in the triplet state of a 6'-nitroindolinospiropyran leads to the triplet state of a cisoid isomer, as in the case of the piperidinospiropyran reported here.

21 C. Lenoble and R. S. Becker, *J. Phys. Chem.*, *90* (1986) 62.