

PRIMARY PROCESSES IN THE PHOTOISOMERIZATION OF A NITROCHROMENE STUDIED BY NANOSECOND LASER PHOTOLYSIS

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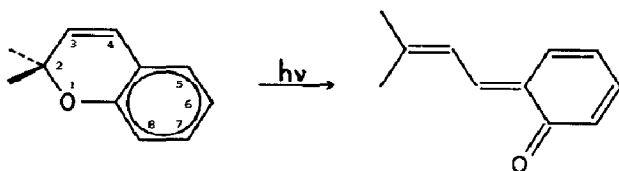
Summary

The primary processes in the photoisomerization of 6-nitro-8-methoxy-2,2,3-trimethyl-2*H*-chromene (Chr) in toluene were studied from -3 to 55 °C by measuring the transient absorption changes produced by neodymium glass laser excitation at 353 nm (third harmonic) with a full width at half-maximum of 6 ns. The results indicate that the formation of a long-lived (about 50 s at 24 °C) coloured isomer (I) occurs owing to C—O bond opening, partly directly from the excited singlet state of Chr and partly via the triplet state. A novel result is the observation that bond opening in triplet Chr leads to a cisoid isomer in the triplet state (³X) which subsequently transforms into the coloured isomer. The lifetimes of ³Chr and ³X are about 80 ns and 450 ns respectively at 24 °C. The activation energies of the ³Chr → ³X and ³X → I reactions are about 8 kcal mol⁻¹ and about 10 kcal mol⁻¹ respectively. The use of Chr as a model system for studies of spiro-pyran photochromism is discussed.

1. Introduction

The chromenes are closely related to the spiropyrans which form an important class of photochromic compounds. This similarity is reflected in their photochemistry since it is known [1] that they undergo essentially the same photoisomerization reaction as that responsible for the photochromism of the spiropyrans, *i.e.* the formation of an isomer due to opening of the C(2)—O(1) bond:

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For this reason, and because of their relatively simple structure, the chromenes have attracted interest as model systems in photochemical investigations of the spiropyrans. A fluorescence study by Becker *et al.* [2] indicated that the photochemistry of 2,2-dialkylchromenes occurs from the excited singlet state. Photochemical reactions involving the triplet state of natural chromenes have also been reported [3]. Recently Appriou *et al.* [4] have studied the absorption and emission properties of a number of chromenes and Le Beuze *et al.* [5] have calculated the excited singlet and triplet energy levels using the complete neglect of differential overlap spectroscopic method. Balny *et al.* [6] have used the flash photolysis method to study the decay of the coloured photoisomers of chromenes. However, no detailed studies of the primary photochemical reactions of chromenes appear to have been performed by time-resolved techniques.

The purpose of the present study was to investigate the primary steps in the photoisomerization of a chromene by means of nanosecond laser photolysis. 6-nitro-8-methoxy-2,2,3-trimethyl-2*H*-chromene (Chr) was chosen as a representative model for the photoactive moiety of spiropyrans of practical interest. The results show that the coloured quinoid isomer is formed from both the singlet and the triplet manifolds. In addition to the isomer, two intermediates of triplet character were detected. It was found that these triplet species were not formed simultaneously but appeared consecutively. We propose that this evolution on the triplet energy surface corresponds to the opening of the pyran ring.

2. Experimental details

2.1. Materials and preparation

Chr was synthesized according to the method described in ref. 7. Toluene (Merck Uvasol) was chosen as the solvent because chromenes are known to have less tendency to aggregate in this solvent than in most other common solvents [8]. Indeed, no deviation from Beer's law could be detected by spectrophotometry at Chr concentrations of 10^{-5} - 10^{-3} M. In addition, the absence of a concentration effect in the kinetic study indicated that association did not occur on laser excitation. A Chr concentration of 10^{-4} M was used in the present study.

The samples, which were contained in silica cells of cross section 10 mm \times 10 mm with polished windows, were purged for 15 min with argon to remove dissolved oxygen. Some photodegradation was observed and the samples were therefore renewed frequently.

2.2. Laser photolysis apparatus

An Nd³⁺-doped glass laser (CILAS VD 231; maximum energy, 60 J; emission at 1060 nm; full width at half-maximum (FWHM), 30 ns) was used as the excitation light source. Laser pulses of 353.3 nm wavelength and 6 ns FWHM pulse width were obtained using potassium dihydrogen phosphate crystals and a Pockels cell (CILAS DL11). A small fraction of the laser light was extracted by means of a beam splitter and was directed onto a pyroelectric joulemeter (Laser Precision Corporation model Rk3230 with an RE548 probe).

The laser beam, which was shaped to a cross section of approximately 3 mm × 10 mm by means of cylindrical lenses, entered the reaction cell through a frosted silica plate. Laser-induced transient transmission changes were monitored perpendicularly to the laser beam using a xenon flashlamp (Verre et Quartz VQX65N) as the analysis light source. A section 2 mm wide close to the laser entrance window was probed. The analysis flash was synchronized such that the laser pulse occurred during the maximum emission of the flashlamp. In this way a constant light intensity (within 2%) was obtained during the first 50 μs after laser excitation.

The probe light passing through the solution was focused at the entrance slit of a 0.25 m monochromator (Jarrell-Ash; *f*, 3.5; spectral bandwidth, 2 nm). A photomultiplier tube (RCA 1P28 or HTV R928 cabled with four dynodes; load, 50 - 150 Ω) was used to measure the light intensity at the exit slit. The photomultiplier signal was displayed on an oscilloscope (Tektronix 7844 provided with a P6021 field effect transistor probe). The oscilloscope screen was scanned using a high sensitivity video camera (Sofretec CF123V) and the video signal was digitized using a converter (Thomson CSF TSN1150) for storage on magnetic tape in a Tektronix 4051 computer.

Within a few runs the flashlamp was replaced by a constant light source (Osram XBO150) which allowed measurements to be made in the time range of milliseconds to seconds. Nine dynodes were used in the photomultiplier in this case (load, 15 kΩ).

Kinetic analysis of the transient signals was performed using a best fitting procedure and a non-linear least-squares method.

2.3. Triplet quantum yields

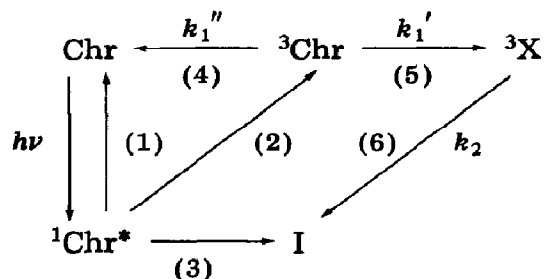
The triplet yield was obtained by comparing the amount of triplet populated after laser excitation of the chromene with that found on excitation of a reference compound of known triplet quantum yield at the same laser energy. Acridine in benzene was chosen as the reference; its triplet quantum yield is reported to be 0.73 (±0.07) and the triplet extinction coefficient at 442 nm (triplet absorption peak) is $2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [9]. In these measurements the laser energy was kept sufficiently low for light saturation effects to be avoided; less than 15% of the chromene was converted to the triplet state. The acridine concentration was chosen to give the same optical density (OD) at 353 nm as the chromene (0.16 across the 2 mm

width of the analysis beam). The triplet concentration of Chr was monitored at 520 nm using a triplet extinction coefficient of $8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (see Section 3.1) and that of acridine at 442 nm.

3. Results

3.1. Reaction scheme

Solutions of 10^{-4} M Chr in toluene were studied by nanosecond laser photolysis in the temperature range $-3 - 55^\circ \text{C}$ in the presence and absence of oxygen. The results are consistent with the occurrence of the processes described in the following reaction scheme:



where $^1\text{Chr}^*$ represents the excited singlet state, ^3Chr the lowest triplet state, I the most stable of the possible isomers formed after C—O bond opening and ^3X the triplet state of a transient X intermediary in structure between Chr and the isomer I. The reactions are referred to by the numbers in parentheses. The arguments which have led to the proposal of this scheme are developed in the following sections.

3.2. Spectra and kinetics

Transient light transmission changes were observed in the wavelength range 290 - 720 nm on laser excitation of deaerated Chr solutions at 24°C . The amplitude of these changes was found to be directly proportional to the laser energy at low energies whereas a saturation effect was evident at higher energies. This behaviour is typical of a monophotonic excitation process with light saturation due to the depletion of ground state molecules. In most of the runs the excitation level was chosen to produce approximately 40% depletion of ground state chromene at the end of the laser pulse.

Figure 1 shows typical oscillograms recorded at different wavelengths and temperatures during the first $2 \mu\text{s}$ after excitation. It is seen from these oscillograms that the change in OD produced during the laser pulse is followed by further development lasting 100 - 200 ns. A second slower phase lasting for 1 - $2 \mu\text{s}$ is also apparent. The OD still remains strongly modified at the end of this phase. Kinetic analysis showed that the OD changes at all wavelengths and conditions could be fitted to the expression

$$\Delta(\text{OD}) = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \quad (\text{I})$$

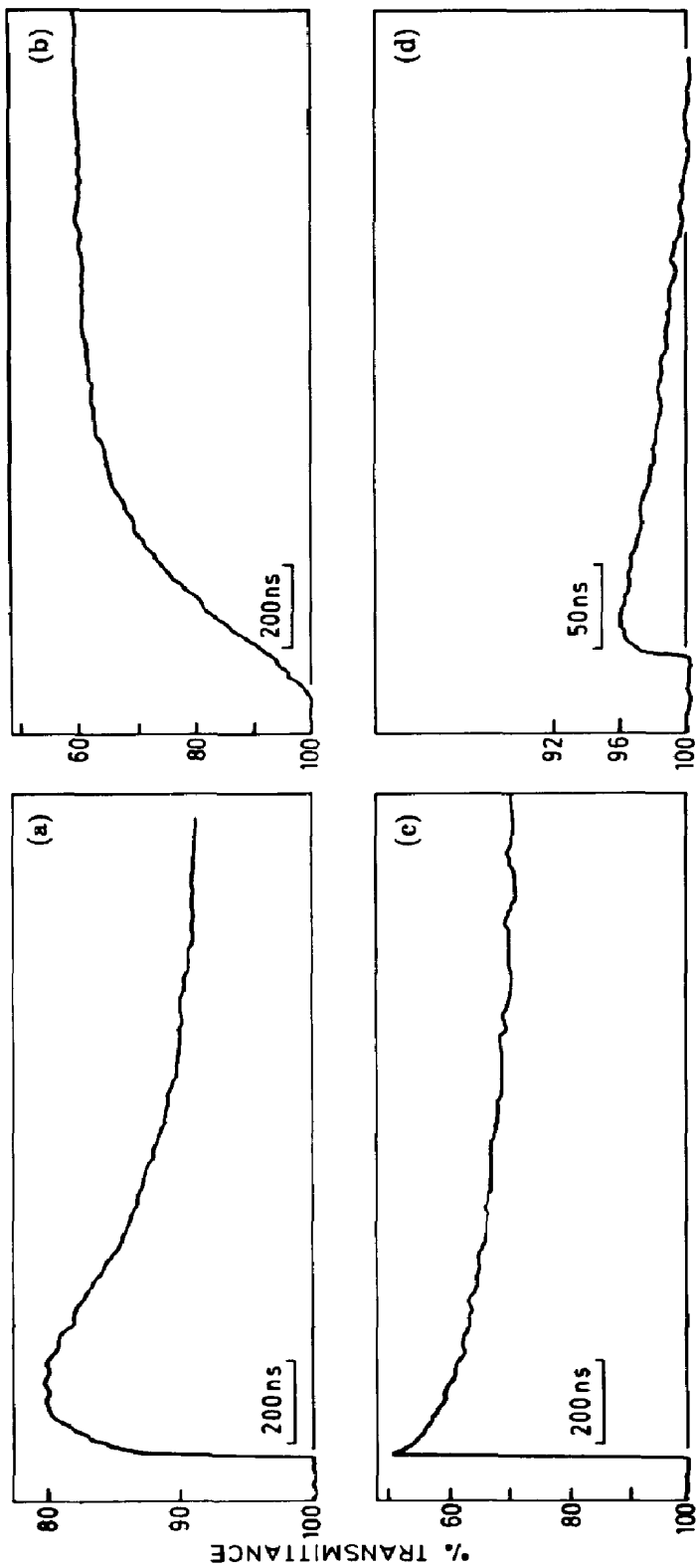


Fig. 1. Oscillograms showing the variation in the optical transmission at different wavelengths λ of 10^{-4} M Chr in degassed toluene on excitation by a 353 nm laser pulse of 6 ns duration (the transmission before excitation is referred to as 100% transmittance): (a) 340 nm and 24 °C; (b) 380 nm and 24 °C; (c) 520 nm and 24 °C; (d) 700 nm and 55 °C.

where t is the time after the end of the laser pulse, $\Delta(\text{OD})$ is the difference between the OD at time t and that before excitation, the k_n are wavelength-independent parameters and the a_n are wavelength-dependent parameters. The values $k_1 = (1.2 \pm 0.3) \times 10^7 \text{ s}^{-1}$ and $k_2 = (2.2 \pm 0.5) \times 10^6 \text{ s}^{-1}$ were obtained at 24°C .

Difference spectra were constructed from the oscillograms at three characteristic times defined by the kinetics: $t = 0$ (end-of-pulse spectrum), $t = 160 \text{ ns}$ (end of fast variation) and $t = 2 \mu\text{s}$ (end of slower phase). These spectra are shown in Fig. 2. The combined spectral and kinetic results indicate that three different species (^3Chr , ^3X and I in the reaction scheme) are formed in this time range. To obtain the pure spectra of these species from the difference spectra it was necessary to determine their concentrations at the corresponding times. According to the reaction scheme both ^3Chr and I are present at $t = 0$. The results of oxygen quenching and temperature studies (see Sections 3.3 and 3.4) show that the initial I concentration was a factor of 0.2 of that of ^3Chr . The concentrations of the three species present at $t = 160 \text{ ns}$ were calculated using the rate constants k_1 and k_2 and the observation (see Section 3.4) that a fraction 0.2 of ^3Chr decays directly to the ground state (reaction (4)). The proportions of ^3Chr , ^3X and I at this time were 0.53, 0.33 and 0.14 respectively. Only I remains at $t = 2 \mu\text{s}$. Knowing these values, we calculated the ^3Chr spectrum from the end-of-pulse difference spectrum, the ^3X spectrum from the spectrum at $t = 160 \text{ ns}$ and the I spectrum from the spectrum at $t = 2 \mu\text{s}$. Since the initial depletion of Chr was known from the light saturation behaviour (a factor of 0.4 of the Chr concentration), absolute values of the absorption intensities were obtained. However, the approximate nature of these values, because of the many corrections involved, must be stressed.

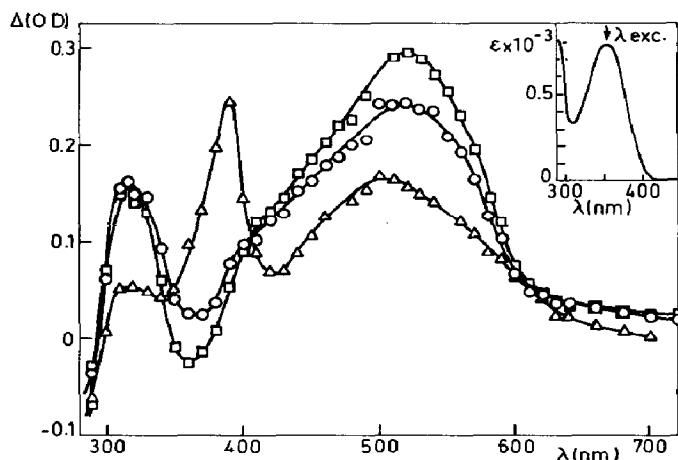
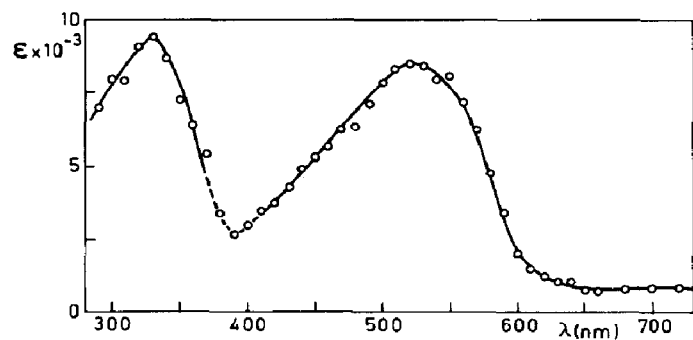
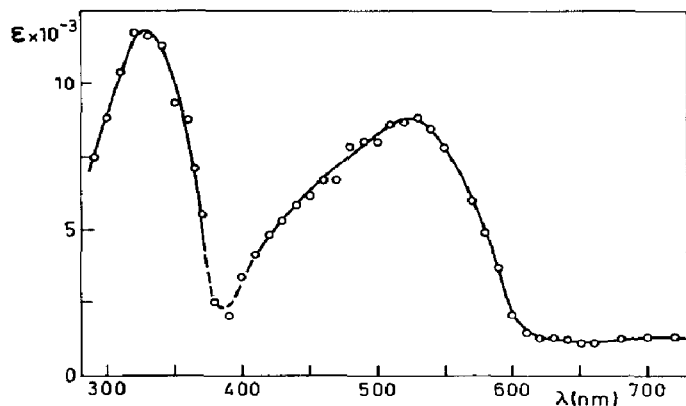


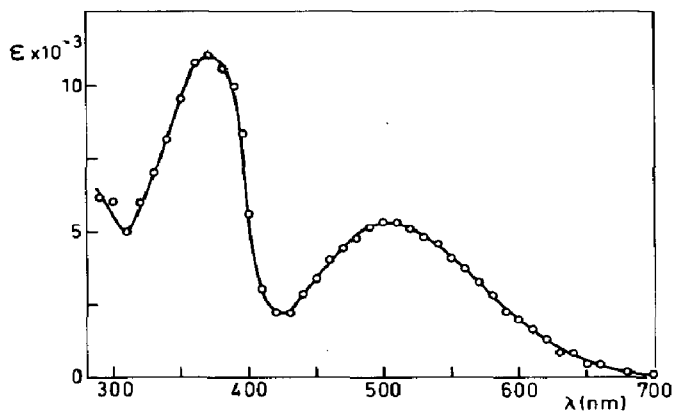
Fig. 2. Difference spectra observed on excitation of 10^{-4} M Chr in degassed toluene at 24°C by a 353 nm laser pulse: \square , at the end of the pulse ($t = 0$); \circ , at $t = 160 \text{ ns}$; \triangle , at $t = 2 \mu\text{s}$. The values are the average of at least two measurements. The extinction coefficients ϵ ($\text{M}^{-1} \text{ cm}^{-1}$) of Chr in toluene with the laser wavelength λ_{exc} indicated are shown in the inset.



(a)



(b)



(c)

Fig. 3. Extinction coefficients ϵ ($M^{-1} \text{ cm}^{-1}$) of Chr phototransients calculated from the difference spectra (---, uncertainty due to strong interference from the I absorption peak): (a) the lowest triplet state of Chr (^3Chr); (b) the intermediate ^3X ; (c) the long-lived isomer I.

The spectra of the three transient species are shown in Fig. 3. It is seen from this figure that the spectra of ^3Chr and ^3X are very similar. They are both characterized by two absorption bands peaking at 330 nm and 520 nm

and a weak absorption extending into the near IR. The extinction coefficients for ^3Chr and ^3X at 330 nm are about $1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and about $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ respectively; the corresponding values at 520 nm are about $8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and about $9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Indeed, the assignment of these spectra to different species is based on kinetic evidence (biexponential OD changes) rather than on differences in the spectral structure.

The spectrum of the isomer I (Fig. 3(c)) also has two absorption maxima (at 370 and 500 nm) and an absorption extending in the red to 700 nm. The peak extinction coefficients are about $1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 370 nm and about $5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm.

It is easily seen that the reactions described in the reaction scheme should give the biexponential kinetics observed experimentally and that the rate-determining parameters are the rate constants of decay of ^3Chr and ^3X respectively. We thus find that the total rate of decay of ^3Chr ($k_1' + k_2''$) is equal to k_1 which has a value of $1.2 \times 10^7 \text{ s}^{-1}$ at 24 °C, and that the rate constant of decay of ^3X is equal to k_2 which has a value of $2.2 \times 10^6 \text{ s}^{-1}$. (The corresponding lifetimes for ^3Chr and ^3X are 80 ns and 450 ns respectively.)

According to the reaction scheme, the decay of ^3Chr is due mainly to the formation of ^3X (reaction (5)). This conclusion is based on the observation that the transient OD at 700 nm increases during the first 50 ns after excitation. (This effect is particularly evident at 55 °C as shown in Fig. 1(d).) Chr does not absorb at this wavelength, and the absorption increase must therefore be due to the gradual formation of a secondary species from the initial transient(s). The rate of appearance of this species was the same as the rate of disappearance of ^3Chr , which justifies the conclusion that it is formed from the latter transient.

The spectrum of the isomer I was found to remain constant in the time range 10^{-6} - 10^{-1} s. However, the transient nature of I appeared from measurements over several seconds. Small sample volumes were used in these runs to allow probing of the entire sample by the analysis light and thus avoid problems due to material diffusion in this time range. It was found that the isomer I disappeared in approximately 50 s at 24 °C.

3.3. Oxygen effects

Runs using oxygen-saturated solutions ($9 \times 10^{-3} \text{ M O}_2$ [10]) showed that the decays of both ^3Chr and ^3X were drastically accelerated under these conditions. Also, the amplitude of the ^3X absorption decreased as well as that of the I absorption which remained 2 μs after excitation. These effects were also observed in air-saturated solution although they were less pronounced. The rate constants k_q for the quenching of ^3Chr and ^3X were calculated from the kinetic results (the accuracy of these determinations was low because the values of the two rate constants of the biexponential decay approached each other in the presence of oxygen, thus making the separation of the components difficult). The high values obtained ($k_q(^3\text{Chr}) = (5 \pm 2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_q(^3\text{X}) = (2 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are typical of

triplet quenching by oxygen and can be considered as proof of the triplet nature of these transient species.

The decrease in isomer formation on addition of oxygen directly indicates that ^3Chr and ^3X are deactivated to the chromene ground state by this quencher. This hypothesis was used to calculate the expected effect of oxygen on the yield of isomer formed in the reaction $^3\text{Chr} \rightarrow ^3\text{X} \rightarrow \text{I}$ from the experimentally determined rate constants k_1 , k_2 , $k_q(^3\text{Chr})$ and $k_q(^3\text{X})$. Compared with the isomer yield for oxygen-free solutions, the yields for oxygen-saturated and air-saturated solutions were calculated to be $r_{\text{ox}} = 0.02$ and $r_{\text{air}} = 0.13$. The experimental values were 0.21 and 0.45 respectively. The discrepancy between these values disappears if we assume that a fraction of approximately 0.2 of the isomer I is formed directly from the excited singlet state and the remainder is formed via the triplet states. However, there is the alternative possibility that only one of the triplets is quenched to the chromene ground state by oxygen and that the other gives an isomer on oxygen quenching. Indeed, it has been shown [11] that the quenching of spiropyran triplets by oxygen can lead to enhanced isomer formation. A calculation based on the assumption that the quenching of ^3Chr and ^3X by oxygen produces Chr and I respectively gave the values $r_{\text{ox}} = 0.23$ and $r_{\text{air}} = 0.60$. The r_{air} value obtained is sufficiently different from the experimental value for this hypothesis to be rejected.

Summarizing, we assume on the basis of these results that both ^3Chr and ^3X are quenched to the chromene ground state by oxygen and that a small fraction (about 0.2) is formed directly from the excited singlet state.

3.4. Temperature effects

The effect of temperature on the kinetics was studied from -3 to 55°C . The results are in agreement with the proposed reaction scheme throughout this range. The end-of-pulse spectrum was found to be independent (both in intensity and structure) of the temperature, and we can therefore conclude that both the triplet yield and the yield of isomer directly formed from the excited singlet state (reaction (3)) are constant in this temperature range. However, the amplitude of the $2\ \mu\text{s}$ spectrum increased on going from the low to the high temperature limit (see inset in Fig. 4). We conclude from this result that a loss reaction which competes with the formation of the isomer I exists and that this reaction has a smaller activation energy than that for isomer formation. In the following it is assumed that this loss process corresponds to the fast decay of ^3Chr directly to the ground state (reaction (4)). (The alternative possibility of the fast decay of ^3X to the ground state was rejected because anomalously high frequency factors were obtained for the isomer formation reaction (6) when this assumption was applied, as can be deduced from the results presented in the following.)

Although the isomer yield increases with temperature, the inset in Fig. 4 provides evidence that a saturation effect exists at the highest temperatures. This result directly shows that the isomer formation (reaction (6)) dominates the loss reaction (4) at the high temperature limit. It is easily

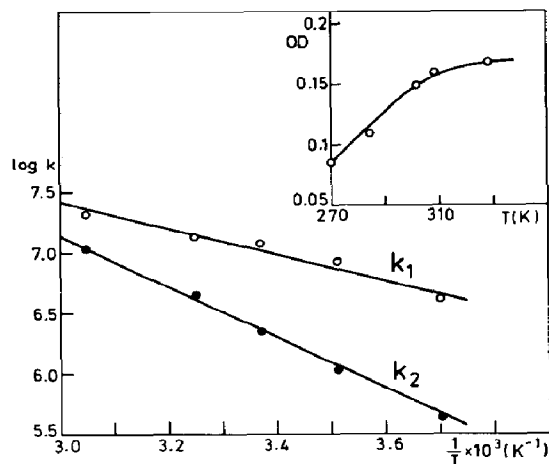


Fig. 4. Arrhenius plots of the ^3Chr (k_1) and ^3X (k_2) decay rate constants. The temperature dependence of the OD at 520 nm of the fraction of isomer I formed via the triplet pathway is shown in the inset.

shown that the ratio $a(k_1')/a(k_1'')$ of the frequency factors for these reactions as well as the difference $E_{\text{act}}(k_1') - E_{\text{act}}(k_1'')$ between their activation energies can be obtained from the curvature of the curve in the inset in Fig. 4. Since $k_1' + k_2'' = k_1$, it is then possible to obtain the values of a and E_{act} for each of the two reactions by combining the results of the above calculation with the results of the experimental determination of k_1 as a function of temperature. The temperature dependences of both k_1 and k_2 were obtained by analysis of the biexponential kinetics measured at 340, 380 and 520 nm. It must be stressed that k_1 and k_2 approach each other closely at the higher temperatures, making their separation difficult and the results very approximate. An Arrhenius plot of k_1 is shown in Fig. 4. By combining this result with the frequency factor ratios and activation energy differences calculated from the isomer saturation curve, we obtain approximate a and E_{act} values for k_1' and k_1'' . The values $a \approx 5 \times 10^{12} \text{ s}^{-1}$ and $E_{\text{act}} \approx 8 \text{ kcal mol}^{-1}$ for k_1' and $a \approx 5 \times 10^6 \text{ s}^{-1}$ and $E_{\text{act}} \approx 0.5 \text{ kcal mol}^{-1}$ for k_1'' gave the best fit to the experimental results.

These values were used to calculate the relative importance of reactions (4) and (5) at 24 °C. The results show that a fraction of approximately 0.8 of ^3Chr is transformed into ^3X at this temperature. This value was used in the calculation of the absorption spectra of the transients described in Section 3.2.

The a and E_{act} values for k_2 were obtained directly from the Arrhenius plot for k_2 in Fig. 4. The results are $a \approx 4 \times 10^{13} \text{ s}^{-1}$ and $E_{\text{act}} \approx 10 \text{ kcal mol}^{-1}$.

3.5. Quantum yields

The quantum yield of the ^3Chr population was determined by comparison of the triplet concentration obtained on excitation of chromene

solutions with that observed on excitation of acridine in benzene (see Section 2.3). A value of about 0.7 was obtained for Φ_T at 24 °C. No significant temperature effect on Φ_T was observed.

The Φ_T value was used to calculate the quantum yield Φ_I of the isomer I. The initial concentration of I was found to be a factor of 0.2 of that of ^3Chr (see Section 3.2). The yield for formation of I directly from the excited singlet state of Chr (reaction (3)) is thus $0.2 \times \Phi_T = 0.14$. It was also found that a fraction 0.8 of ^3Chr transforms into I via ^3X . The quantum yield of formation of I via the triplet pathway is then $0.8 \times \Phi_T = 0.56$. The total I yield is the sum of these values, *i.e.* $\Phi_I = 0.7$.

4. Discussion

The results show that the primary photophysical and photochemical processes of Chr are quite complex, involving isomerization via two different pathways and the formation of two different triplet species. The treatment of the data was difficult because of this complexity and also because of the strong overlap in the spectra of the different transients. The proposed reaction scheme therefore may not give an altogether complete description of the processes involved; however, the main features appear to be well substantiated.

The results show that the main process following photoexcitation of Chr (which is a non-fluorescent compound [4]) is intersystem crossing (ISC) with $\Phi_T = 0.7$. This behaviour is expected since nitroaromatic compounds generally have high ISC yields. Phosphorescence studies of Chr at 77 K have also shown that ISC is efficient: a phosphorescence quantum yield of 0.15 has been reported [4]. The π, π^* nature of the triplet was deduced from the phosphorescence spectrum and the triplet energy was determined (2.4 eV) [4].

In addition to ISC, pyran ring opening occurs directly from the excited singlet state with a quantum yield of 0.14. The sum of this yield and that of ISC is 0.84. It is seen that internal conversion is a minor process, if it is present, considering the small difference of this value from unity and the uncertainty in the quantum yield determination.

A novel striking result is the observation that the chromene triplet rapidly (in about 100 ns) transforms into the triplet of a transient product X which in turn is a precursor of the coloured isomer I. We identify the species X as the isomer formed directly on opening of the pyran ring, and further suggest that this isomer still retains almost the same geometry as that of Chr. Evidence for the latter hypothesis was obtained from the oxygen quenching results: if more extensive changes in configuration had occurred before the appearance of ^3X , we would not expect to find the observed decrease in the formation of I on the oxygen quenching of ^3X since the quenching should then favour further evolution to the stable isomer I.

Our interpretation of the nature of ^3X can be compared with the results of spiropyran photoisomerization studies. Heiligman-Rim *et al.* [12] first proposed that a cisoid isomer precedes the formation of the merocyanine. Murin *et al.* [13] observed in a nanosecond laser study of an indolinspiropyran that absorption changes occurred in the range of a few hundred nanoseconds, and they proposed tentatively that merocyanine is formed via a cisoid ground state isomer which disappears in this time range. In contrast, Vannikov and Kryukov [11], in studies of similar indolinspiropyran, reported the appearance of a transient which they attributed to a cisoid isomer in the triplet state which was the precursor of the merocyanine. However, they could not determine experimentally the evolution of the spiropyran triplet to the isomer triplet. The present results lend support to their hypothesis since we have directly established the possibility of C—O bond opening on the triplet energy surface in the case of chromene. It should also be noted that an electron paramagnetic resonance study of indolinspiropyran at 105 K [14] suggested that C—O bond cleavage occurred in the triplet state with multiplicity conservation; the observed strongly biradical character of the resulting triplet was assumed to be due to the orthogonality between the π electron systems of the indolino and benzene groups of the structurally unrelaxed isomer. A recent study of spiropyran photolysis at 4 K by optically detected magnetic resonance and luminescence methods [15] has provided further evidence for the appearance of an unrelaxed isomer formed on opening the C—O bond.

As mentioned in Section 3.3, we attributed the transient product formed from ^3Chr to a triplet state species because of its efficient quenching by oxygen. Additional support for this assignment comes from the observation of a high frequency factor for the $^3\text{Chr} \rightarrow ^3\text{X}$ process ($a \approx 5 \times 10^{12} \text{ s}^{-1}$) compatible with the absence of spin change. In contrast, the frequency factor for the radiationless deactivation of ^3Chr directly to Chr has the low value ($a \approx 5 \times 10^6 \text{ s}^{-1}$) expected for this spin-forbidden process.

The decay of ^3X was found to be associated with an increase in concentration of isomer I, and reaction (6) was proposed to account for this behaviour. Species I presumably corresponds to the structurally relaxed *trans-trans* form of the open isomer in view of its long lifetime. The rearrangement from the ^3X cisoid geometry to that of I probably occurs by stepwise isomerization with the formation of isomers of intermediate structures. Indeed, spectral studies of spiropyran photochromism have demonstrated the appearance of such intermediates in the formation of the merocyanine [16]. However, in the present case the transient spectra did not give any evidence for a similar stepwise structural evolution. The probable reason for this is that the lifetimes of the intermediates are too short compared with that of ^3X to make their observation possible.

An interesting finding is the observation of a high frequency factor ($a \approx 4 \times 10^{13} \text{ s}^{-1}$) of the rate constant k_2 determining the rate of the *cis-trans* isomerization of ^3X . The high value indicates that the geometrical change occurs without a corresponding change in the spin multiplicity, *i.e.* the

resulting isomer is initially formed in its triplet state. This result implies that the isomer triplet state is deactivated rapidly after this isomerization since the isomer triplet could not be observed experimentally. Such fast relaxations from the triplet to the ground state are frequently observed in molecules with conjugated double bonds undergoing isomerization reactions [17].

We have shown in the present study that the isomer I is formed not only via the chromene triplet state but also directly from the excited singlet state. A twofold pathway involving the same excited states has been reported [16, 18, 19] for the formation of merocyanine from spiropyran. This similarity in photochemical behaviour illustrates the usefulness of chromenes as model compounds in studies of spiropyran photochemistry.

Acknowledgments

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