Picosecond Flash Photolysis of Photochromic Spiropyrans

S. A. KRYSANOV and M. V. ALFIMOV

Institute of Chemical Physics, USSR Academy of Sciences, 142432 Chernogolovka, Moscow Region, USSR

(Received February 16, 1983)

The transient species involved in photocoloration and photobleaching of indoline 6-nitrosubstituted spiropyran solutions at room temperature were studied by picosecond flash photolysis. Transient absorption spectrum of spiropyran colorless form consists of two bands peaked at 440 and 585 nm and is assigned to the photoinduced intermediate non-planar *cis* configuration with the broken C—O bond of the pyran ring. This transient is found to have the buildup time shorter than 10 ps and initial decay times of about 10 ns in benzene and 5 ns in ethanol. The colored form exhibits the transient absorption peaked at 460 nm with the lifetime of about 200 ps in ethanol which is assigned to $S_n \leftarrow S_1$ absorption of colored form. The predominant decay channel of the colored form S_1 state is shown to be internal conversion $S_1 \rightsquigarrow S_0$ with the quantum yield of about 0.70 ± 0.15 .

1. INTRODUCTION

Spiropyrans belong to the most important class of the organic photochromic compounds which are used in the light sensitive materials.¹ Intensive study of the spiropyran photochromism during three decades² has allowed us to appreciate the general photochemical reaction (for reviews see Refs. 3–5). The initial colorless form A with the orthogonal planes of two molecular halves suffer C—O bond breaking of the pyran ring under ultraviolet light. The final planar colored form B absorbing at about 600 nm is the mixture of four conformers of the trans isomer differing by the rotation angle about single bonds of the polymethene chain.

Though the structure of A and B forms is well established, there is no common point of view on the detailed mechanism of the photochromic reaction. The detailed mechanism is discussed usually⁴

in terms of the intermediate *cis* isomer X.² The X isomer represents the photoinduced non-planar configuration with broken C—O bond. Such intermediate must exist in both photochromic processes: in photocoloration, $A \rightarrow B$, after C—O bond breaking, and in the photobleaching, $B \rightarrow A$, before C—O bond restoration.

Much attention was given to the indoline nitrosubstituted ($R_2 = \text{NO}_2$) spiropyrans having a largest photocoloration efficiency.⁴ The transient absorption band with a peak at 440 nm with a lifetime of about 10^{-7} s was observed⁶ in the nanosecond studies of these compounds. This transient was founded to be formed both in photocoloration and photobleaching and was ascribed⁶ to the X isomer. The 440 nm band was ascribed to the triplet state of form A in other works.⁷ The transient species buildup was studied in Ref. 8 by means of the streak camera. The buildup times of the photoinduced final B (590 nm) and intermediate (440 nm) absorption bands were shown⁸ to be synchronous within several nanosecond and to coincide with the time resolution of the streak camera used. These results show that methods with the time resolution less than 10^{-9} s are needed for the primary processes study in the spiropyrans photochromic transformations.

In this paper we present experimental results on picosecond flash photolysis of the indoline nitrosubstituted spiropyran SP_1 ($R_1 = CH_3$; $R_2 = NO_2$).

2. EXPERIMENTAL

An undegassed solution of SP_1 in benzene and ethanol (10^{-3} M) in a 1 mm quartz cell at 295 K were used in the photo-coloration study. The ethanol solution of SP_1 was used in the photobleaching study since the thermostability of form B is increased considerably in polar solvents. The colored form was prepared by illumination of the solution of the initial form with the 265–313 nm lines of a 1000 W mercury lamp. The solution was illuminated before every laser shot to restore the form B concentration.

The apparatus used to measure picosecond transient absorbance spectra was the same as that described in detail elsewhere.⁹ Briefly, it includes a mode-locked Nd:phosphate glass laser on the basis of an unstable resonator configuration and amplifier system to produce single 6 ps, TEM₀₀ pulses at 1055 nm. The second 528 nm (an energy 1 mJ) and third 352 nm (an energy 0.5 mJ) harmonics were used as excitation pulses. For probing, the 1055 nm pulse generated in D₂O a broad-band continuum. The double-beam optical system consisting of the semi-transparent Al mirror and five miniature mirrors forms interrogating continuum pulses delayed by 10 ps, 400 ps, 1 ns, 2.5 ns, 5 ns with respect to the excitation pulse. The absorbance changes ΔA in a sample were detected photographically and calculated for each time using two alternate laser shots in presence (p) and absence (a) of the excitation pulse:

$$\Delta A = \gamma^{-1}[(D_1^p - D_2^p) - (D_1^a - D_2^a)]$$

where γ and D are the contrast and blackening of the film.

3. RESULTS AND DISCUSSION

The transient absorption with two peaks at 440 and 585 nm was detected on flashing the benzene solution of colorless form with a 352 nm picosecond pulse, as shown in Figure 1. The spectra measured

FIGURE 1 Transient absorbance spectra of the colorless form SP_1 in benzene at 295 K measured at 10 ps and 5 ns delays after excitation with a 6 ps, 352 nm pulse.

at 10 ps and 5 ns delays were normalized with respect to the short-wavelength band in this Figure. The shape and maximum position of these bands as seen do not depend on time. An absorbance increase of the long-wavelength band was only observed in the time region studied. The kinetic behavior of 440 and 585 nm bands in the benzene solution is shown in Figure 2. The angle between the polarization planes of the excitation and probe beams was arbitrary in this case, and the slow buildup during 400 ps is due to rotation relaxation. The transient absorption band 440 nm is seen to decay with the characteristic time of about 10 ns. The initial parts of the kinetic curves for the 440 and 585 nm bands coincide in the 10 ps–2 ns region and the increase of the 585 nm band absorbance is observed for the later delay times.

FIGURE 2 Absorbance kinetics at 440 and 585 nm of the SP_1 colorless form in benzene. The point with the zero absciss refers to the 10 ps delay time. Excitation with a 352 nm picosecond pulse when rotational relaxation is not eliminated.

An analogous transient absorption bands with the same maxima at 440 and 585 nm were observed for the ethanolic solution of the SP_1 colorless form. The only difference was that the spectra width for the ethanolic solution was larger than for the benzene one. The kinetic behavior of these bands in the ethanolic solution is shown in Figure 3. The rotational relaxation effects were eliminated here due to a proper adjustment of the angle between polarization planes (54.7°).¹⁰ Both transient bands are formed within the duration of the 6 ps excitation pulse and its optical density diminishes in the beginning with the same characteristic time of about 5 ns. The kinetic curves change later, namely, the long-wavelength band absorbance tends to increase and the short-wavelength band decay becomes slower.

The results of the SP_1 colored form study are represented in Figures 4 and 5. Excitation of a form *B* solution with a 528 nm pulse resulted in the immediate bleaching (negative ΔA , Figure 4) of the ground-state absorption band at 550 nm. The transient absorption band with the peak at 460 nm was formed simultaneously with the diminution of the 550 nm band. The 460 nm band decays completely within 1 ns (Figure 5). The recovery of the bleached 550 nm band occurs in the same time region. It is worthwhile mentioning that the 550 nm recovery is not complete and the stationary value ΔA_{550} forms 25% of the initial value measured at 10 ps.

FIGURE 3 Absorbance kinetics at 450 and 560 nm of the SP_1 colorless form in ethanol. Excitation with a 352 nm picosecond pulse under conditions of the rotational relaxation elimination.

FIGURE 4 Spiropyran SP_1 in ethanol at 295 K. Right-hand scale: ground-state absorption spectra of colorless A and colored B forms. Left-hand scale: transient absorbance spectrum of colored form B (open circles) measured at 10 ps delay after excitation with a 528 nm picosecond pulse.

Let us consider the assignment of the states which exhibit the transient absorption. The short-wavelength band peak 440 nm coincides exactly with that in the nanosecond experiments.⁶⁻⁸ This coincidence proves the identity of the transient species observed in nano- and pico-second flash photolysis experiments. As pointed out in the Introduction, the 440 nm is ascribed at present to two species: to the triplet state of the colorless form A^7 and to the *cis* isomer X .⁶ The data presented in Figures 2 and 3 entitle us to assign the transient absorption band 440 nm to the X isomer. Indeed, the lifetime of the

FIGURE 5 Absorbance kinetics at 460 and 550 nm of the SP_1 colored form in ethanol. Excitation with a 528 nm picosecond pulse under conditions of the rotational relaxation elimination.

form A triplet state in solid solutions at 7 K is of the order 0.1 s.¹¹ This lifetime in the room temperature solution can be diminished due to the quenching by oxygen to $\approx 2 \cdot 10^{-7}$ s at the usual oxygen concentration 10^{-3} M and diffusion-controlled quenching rate in ethanol $5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The measured times of the 440 nm band decay of about 10^{-8} s are much less than the triplet state lifetimes. Combining this result with that in nanosecond experiments⁶ we thus conclude that the X isomer decay is characterized by two decay times of about 10^{-8} and 10^{-7} s.

The fast decay was observed not only for the 440 nm band but also for the 585 nm band. The coincidence of the initial parts of the kinetic curves for these bands indicate that both bands belong to the same intermediate isomer X. The fast formation of the long-wavelength band within the 20 ns pulse duration was interpreted in the nanosecond experiments⁶ as the photocoloration occurring directly via the singlet state S_1 of form A without the intermediate form X involvement. The above assignment of the 585 nm band allows us to explain the photocoloration process in terms of only one primary transient, namely the X form. This assignment is supported further by the fact that the transient 585 nm band maximum differs from that of the ground-state absorption spectrum of form B at 550 nm in ethanol (Figure 4). The contribution of the final form B begins to manifest for delays more than 3–5 ns (Figures 2 and 3).

The present results reveal two properties of the transient X which have to be elucidated, namely the ultrafast formation of the X isomer and its two-component decay. Let us consider the known from the literature photoprocesses in spiropyrans to interpret the ultrafast X formation. The indoline and pyrans parts absorb approximately independently and the transfer energy between these parts can occur.^{12,13} The mechanism of the spiropyrans photochromism is determined first of all by the relative position of the energy levels. The indoline nitrosubstituted spiropyran SP_1 has the following state ordering: S_0 , $T_{\pi\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$, $S_{n\pi^*}$.¹³ The long-wavelength absorption and phosphorescence are due to $\pi\pi^*$ -transitions¹³ in pyran part of form A. Since the energy level of the $T_{n\pi^*}$ state is lower than the $S_{\pi\pi^*}$ state, the intersystem crossing probability is high (10^{11} s^{-1}) according to the systematization¹⁴ that results in both fluorescence quenching and effective population of the triplet state. An ultrafast formation of the transient X can thus be explained by the photodissociation

from the lowest triplet state of form A. This process would imply an absence of the form A phosphorescence. But the fact is form A possesses a phosphorescence^{3,12} and we have to conclude that the transient X formation must occur via an upper triplet state of form A. An ultrafast internal conversion between an upper triplet level can compete in this case with an ultrafast dissociation that results in the population of the phosphorescent level. This conclusion is in agreement with the results of the sensitized photocoloration experiments.^{3,15-17} The presence of two kinds of triplet levels, phosphorescent and photochemically active, with the energy difference of about 1500 cm^{-1} was shown in these works. In our opinion, a some upper vibrational level of the lowest $T_{\pi\pi^*}$ state can be responsible for the photochemical active level since the energy difference between the triplet $\pi\pi^*$ and $n\pi^*$ states of the pyran ring is of about 5000 cm^{-1} .¹³

The existence of two characteristic times of the isomer X decay allows us to choose the following kinetic scheme from the many one proposed for the photochromic processes analysis⁹ XXX:

where B_1 is the least stable *trans* isomer of the colored form, $B_{2,3,4}$ are the rest of the *trans* isomers with the increasing stability. We have for the times longer than $k_0^{-1} = 10\text{ ps}$:

$$X = \alpha \exp(-\lambda_1 t) + \beta \exp(-\lambda_2 t)$$

$$\lambda_{1,2} = \frac{1}{2}(k_1 + k_2 + k_3 + k_4) \mp [(k_1 + k_2 - k_3 - k_4)^2 + 4k_2k_3]^{1/2}$$

For the ethanolic solution $\lambda_1 = 3 \cdot 10^6\text{ s}^{-1}$ [6], $\lambda_2 = 2 \cdot 10^8\text{ s}^{-1}$. From the conditions $\lambda_1 \ll \lambda_2$ and $k_1 + k_2 + k_3 + k_4 = \lambda_1 + \lambda_2$ we obtained

$$\left(1 + \frac{k_1}{k_2}\right) \left(1 + \frac{k_4}{k_3}\right) \approx 1$$

that is satisfied at $k_2 \gg k_1$ and $k_3 \gg k_4$. We suppose further $k_3 < k_2$ since the process $B_1 \rightarrow X$ is connected with the potential barrier overcoming. Indeed, the X form has an energy of about 10^4 cm^{-1} ⁴ higher than the B forms.

We conclude from these estimates that (1) the transformation of the *cis* isomer X into the least stable *trans* isomer of form B is responsible for the fast X decay with $k_2 \approx 10^8\text{ s}^{-1}$; (2) large efficiency¹²

If the photocoloration in the indoline nitrosubstituted spiropyrans⁴ is due to the fast transition of the X isomer into the colored form ($X \rightarrow B_1$) in comparison with the back process ($X \rightarrow A$).

As for the transients in the photobleaching $B \rightarrow A$ process, we assign the transient absorption band 460 nm (Figure 4) to the $S_n \leftarrow S_1$ transition from the lowest excited singlet state of the colored form. Indeed, the 460 nm band is formed for the time shorter than 10 ps and its decay time 200 (100 ps) is close to the fluorescence lifetime of form B (400 ps in ethanol³). Moreover, the 460 nm band decay is accompanied by recovery of the ground-state absorption band 550 nm in the same time region. An incomplete recovery of the 550 nm band is ascribed naturally to an intersystem crossing in form B and the above given value 25% for the stationary rest ΔA_{550} determines just the quantum yield of intersystem crossing. In view of the small fluorescence quantum yield (0.02^3) we conclude that internal conversion with the quantum yield of 0.70 ± 0.15 is the predominant decay channel of the lowest excited singlet state S_1 of form B. An absence of the X form absorption in the time region up to 5 ns is due to its formation probably via the long-lived triplet state of form B.

References

1. V. A. Barachevsky, G. I. Lashkov and V. A. Tzekhomsky, *Photochromism i ego primeneniye* (Khimiya, Moscow, 1977).
2. E. Fischer and Y. Hirschberg, *J. Chem. Soc.* 4522, (1952).
3. G. I. Lashkov, M. V. Savostjanova, A. V. Shablya and T. A. Shakhverdov, in: *Molekulyarnaya Photonika* (Nauka, Leningrad, 1970) p. 299.
4. R. C. Bertelson, in: *Techniques of Chemistry: Photochromism*, Vol. 3, ed. G. M. Brown (Wiley-Interscience, New York, 1971) p. 45.
5. A. S. Kholmansky, A. V. Zubkov and K. M. Dyumaev, *Uspekhi Khim.* **50**, 569, (1981).
6. V. A. Murin, V. F. Mandgikov and V. A. Barachevsky, *Opt. i Spektrosk.* **37**, 1174, (1974).
7. Y. Kalisky and D. J. Williams, *Chem. Phys. Lett.* **86**, 100, (1982).
8. S. G. Kuzmin, V. F. Mandgikov, V. A. Barachevsky, E. P. Pozhidaev and E. A. Kuzmina, Abstracts of the 14th Congress of High-Speed Photography and Photonics, Moscow (1980) p. 353.
9. S. A. Krysanov and M. V. Alfimov, *Chem. Phys. Lett.* **76**, 221, (1980); *Chem. Phys. Lett.* in press.
10. H. E. Lessing and A. von Jena, *Chem. Phys. Lett.* **42**, 213, (1976).
11. T. A. Shakhverdov and A. V. Shablya, *Opt. i Spektrosk.* **24**, 619, (1968).
12. N. W. Tyler and R. S. Becker, *JACS* **92**, 1295, (1970).
13. I. L. Belaiz, T. D. Platonova and V. A. Barachevsky, *Opt. i Spektrosk.* **49**, 1125, (1980).

14. R. N. Nurmukhametov, V. G. Plotnikov and D. N. Shigorin, *Z. Fiz. Khim.* **40**, 1154, (1966).
15. T. Bercovici and E. Fischer, *JACS* **86**, 5687, (1964).
16. R. S. Becker and J. K. Roy, *J. Phys. Chem.* **69**, 1435, (1965).
17. D. A. Reeves and F. Wilkinson, *J. Chem. Soc. Faraday Trans. II* **69**, 1381, (1973).