ACID EFFECT ON PHOTOCHROMISM OF SPIROPYRANS: A STUDY BY MICROSECOND AND NANOSECOND FLASH PHOTOLYSIS

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Summary

Microsecond and nanosecond flash photolysis was used to study the photochromic reactions of spiropyrans of the indoline series $1',3',3'$-trimethyl-6-nitro, 6-nitro-8-methoxy, 6-methoxyspiro[$2H$-1-benzopyran-2,2'-($2H$)-indol] in acetone in the presence of the acids HNO_3, HCl and H_2SO_4. Two relatively unstable trans isomers of spiropyran (merocyanine form) were found to be involved in the protolytic reaction. A reaction mechanism is proposed.

1. Introduction

Spiropyrans are photochromic compounds which reversibly change colour on irradiation [1 - 3]. Illumination of spiropyran solutions with UV light results in the formation of a coloured merocyanine. Irradiation of spiropyrans in the presence of acid (*e.g.* HCl, phenol or carboxylic acids) results in the production of a coloured species whose absorption spectrum differs markedly from that of the initial merocyanine. The difference in absorption spectra of solutions of spiropyrans with and without acid present, measured during UV irradiation, is associated with the formation of a complex between the merocyanine form of the spiropyran and the acid [4, 5]. However, using a UV steady-state source did not allow the mechanism of the reaction of the spiropyran intermediate with the acid to be elucidated [4, 5]. Using microsecond flash photolysis, we have previously shown [6] that the addition of HNO_3 to a solution of spiropyran in acetone resulted in a decrease in the lifetime of the intermediates produced. In this work we present the results of a microsecond and nanosecond flash photolysis study of the photochromic reactions of spiropyrans in acetone in the presence of the acids HCl, HNO_3 and H_2SO_4.

2. Experimental details

The absorption spectra and the decay kinetics of intermediates were measured using microsecond [7] and nanosecond flash photolysis apparatus. In the microsecond flash photolysis experiments, air-saturated solutions of spiropyrans were irradiated through UFS-6–BS-7 glass filters in cells of path length 1 cm and 20 cm. The flash energy was 250 J and the duration $\tau_{0.1}$ of the flash was 40 μs. Spectral measurements of transients were carried out using a point-by-point method by means of an MDR-23 monochromator. A KGM-9-75 filament lamp was used as the probing source. An FEU-97 photomultiplier was interfaced to a C8-13 storage oscilloscope. In the nanosecond laser flash photolysis experiments, spiropyran solutions were irradiated using an Nd–YAG laser (354 nm pulses; duration $\tau_{0.5} = 10$ ns; pulse energy, 0.5 mJ) in a cell of path length 1 cm. The optical set-up ensured that the beams of the monitoring light and laser pulse were almost parallel. A diaphragm of hole diameter 1 mm was placed at the front of the cell. A xenon high pressure lamp (120 W) operating in continuous mode was used as the source of the monitoring light. The lamp power source ensured that a short (about 500 μs) increase in intensity would result on pulsing the solution with the laser. The apparatus for recording the spectral changes consisted of a monochromator, FEU-84 photomultiplier (load resistance, 50 Ω; spectral range, 300 - 850 nm), and a C8-12 storage oscilloscope. The lowest change in optical density was 5×10^{-3}. The steady-state UV irradiation of solutions of spiropyrans was carried out in standard quartz cells (1 cm $\times$ 1 cm) by means of a high pressure mercury lamp (250 W) through UFS-6–BS-7 glass filters. A Unicam SP-700 spectrophotometer was used to measure the absorption spectra of the stable products of the photoreaction. Measurements were made on air-saturated solutions of spiropyrans in acetone (concentration, 1×10^{-4} M) at 20 °C. All spiropyrans were in the indoline series
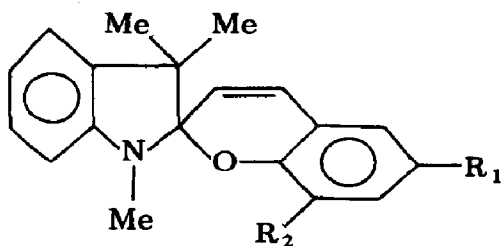
SP1: $R_1 \equiv NO_2$, $R_2 \equiv H$
SP2: $R_1 \equiv NO_2$, $R_2 \equiv OCH_3$
SP3: $R_1 \equiv OCH_3$, $R_2 \equiv H$

The acid concentrations (HCl, HNO_3 and H_2SO_4) were varied from 10^{-6} M to 10^{-2} M. Acetone was purified by the standard procedure.

3. Results and discussion

On steady-state UV irradiation of a solution of SP1 in acetone without acid, an absorption band appears in the visible range of the spectrum with

λ_{max} = 560 nm; this is caused by the formation of a merocyanine-coloured form B of SP1 from the initial colourless form A. Figure 1 shows the absorption spectra of A and B. Steady-state UV irradiation of the SP1 solution in the presence of HCl, HNO_3 or H_2SO_4 also results in the colouration of the solution, caused by absorption in the range 400 - 450 nm (Fig. 1). Figure 2 shows the differential absorption spectrum of SP1 measured after UV irradiation of the solution in the presence of HNO_3, compared with that of the non-irradiated SP1 solution containing no acid. A similar absorption spectrum was observed in the presence of HCl and H_2SO_4. It is apparent from Fig. 2 that, as the coloured form of SP1 is produced during the UV irradiation of the solution in the presence of HNO_3, a band appears with its maximum at 405 nm (form C) in the differential absorption spectrum.

A similar differential absorption spectrum was also observed after adding the acid to the irradiated SP1 solution. With SP2 and SP3, there is insignificant colouration on dissolving spiropyrans in acetone. On UV irradiation of such solutions the colouration is intensified. In the absorption spectra of irradiated SP2 and SP3 solutions, bands with peaks at 545 nm and 580 nm respectively are observed in the visible range. Irradiation of SP2 and SP3 solutions in the presence of acid also leads to colouration caused by bands with peaks at 405 nm and 450 nm respectively in the differential absorption spectrum.

On microsecond and nanosecond excitation of spiropyran solutions with and without acids, we observed changes in absorption in the range 400 - 650 nm. Figure 3 shows oscillograms of spectral changes obtained on micro-
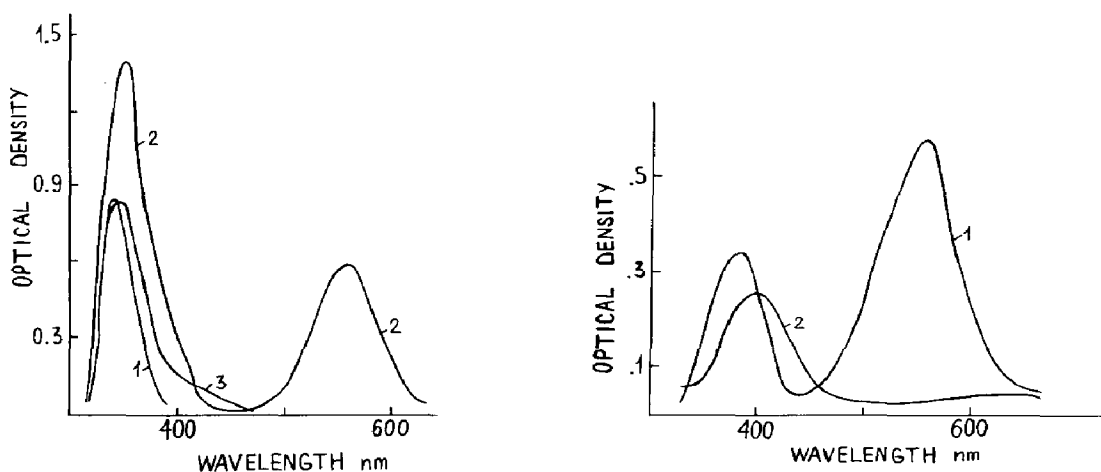

Fig. 1. Absorption spectra of SP1: colourless form in acetone, curve 1; merocyanine form, curve 2; product of reaction between SP1 and HNO_3 upon UV irradiation, curve 3; concentration of SP1 and HNO_3, 10^{-4} M.

Fig. 2. Differential absorption spectrum of SP1: merocyanine form, curve 1; product of reaction between SP1 and HNO_3 upon UV irradiation, curve 2; concentration of SP1 and HNO_3, 10^{-4} M.

second flash excitation of SP1 with and without HNO_3. Similar oscillograms were obtained in the presence of HCl and H_2SO_4.

The oscillograms were measured at the absorption wavelengths of B (Figs. 3(a) - 3(c)) and C (Figs. 3(d) - 3(f)). From the oscillograms in Figs. 3(a) and 3(d) it follows that in the absence of acid, an increase in absorption occurs in a single fast step. In the laser nanosecond photolysis this fast increase in optical density was observed within an oscilloscope sweep lasting not less than 1 μs (division)$^{-1}$. Oscillograms similar to those shown in Figs. 3(a) and 3(d) were measured in the range 400 - 650 nm, and were used to plot differential absorption spectra which were found to be similar to the absorption spectra of the merocyanine form of SP1 obtained upon steady-state UV irradiation. From the oscillograms shown in Figs. 3(b) and (c) it follows that in the presence of acid, the change in optical density occurs in three steps. The oscilloscope traces consist of regions of fast and slow changes in optical density and a region of constant optical density. Similar oscillograms were measured for SP2 and SP3. A detailed analysis of the oscillograms is presented below. Figure 4 shows the oscillograms obtained with and without HNO_3 and measured using a slow oscilloscope sweep through the absorption maximum of B. By comparing the oscillograms presented in Figs. 4(a) and 4(b) one can see the reduction in lifetime of the merocyanine when acid is present.

The lifetime of B was reduced on increasing [HNO_3] from 5 × 10^{-6} M. Figure 5 shows the oscillograms obtained on nanosecond laser excitation of SP1 solutions in the absence of acid. The oscillogram in Fig. 5(b) was measured at the wavelength of the absorption maximum of the merocyanine. From this oscillogram, it may be deduced that the merocyanine is produced
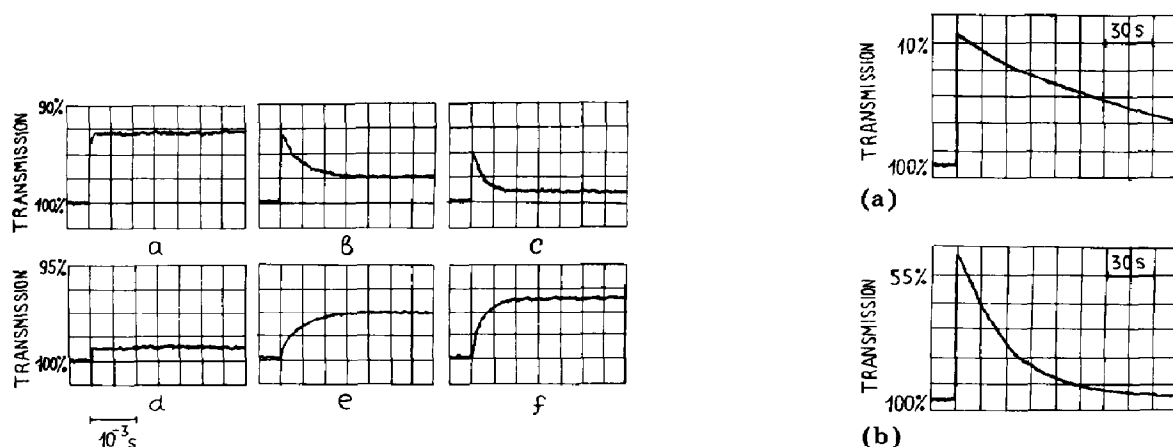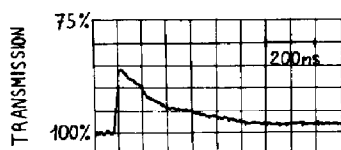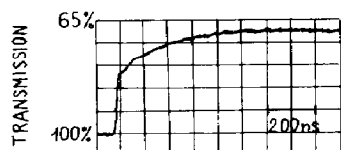

Fig. 3. Oscillograms of SP1 transient absorption: without HNO_3, curves a and d; [HNO_3] = 5 × 10^{-6} M, curves b and e; [HNO_3] = 6 × 10^{-6} M (curves c and f). ([SP1] = 10^{-4} M; curves a, b and c, λ = 560 nm; curves d, e and f, λ = 420 nm; absorption path length, 1 cm.)

Fig. 4. Oscillograms of SP1 transient absorption: (a) without HNO_3 and (b) with HNO_3. [SP1] = 10^{-4} M; [HNO_3] = 6 × 10^{-6} M; absorption path length, 20 cm; λ = 560 nm.
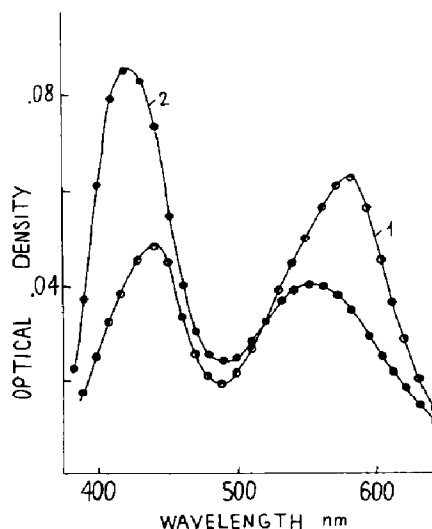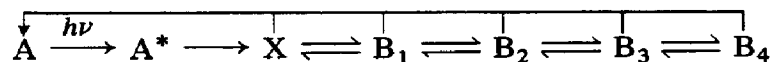
Fig. 5. Oscillograms of SP1 transient absorption: (a) $\lambda = 440$ nm and (b) $\lambda = 560$ nm. ([SP1] = 10^{-4} M; absorption path length, 1 cm.)

Fig. 6. Differential absorption spectra of SP1 (curve 1) and SP2 (curve 2). ([SP1] = [SP2] = 10^{-4} M; absorption path length, 1 cm.)

via two consecutive steps at least, *i.e.* a fast step lasting about 20 ns and a corresponding slow step lasting about 500 ns. Similar oscillograms were measured for SP2. Figure 6 shows a differential absorption spectrum measured 30 ns after a laser pulse. Acid may be present up to a concentration of 10^{-2} M before the rate of formation of the merocyanine is influenced.

As was pointed out in refs. 8 - 11, the formation of the relatively stable merocyanine is preceded by the formation of cis and several trans isomers which have different stabilities. The scheme of photochromic reactions for SP1 is as follows [12 - 14]:

$$\text{A} \xrightarrow{h\nu} \text{A}^* \longrightarrow \text{X} \rightleftharpoons \text{B}_1 \rightleftharpoons \text{B}_2 \rightleftharpoons \text{B}_3 \rightleftharpoons \text{B}_4$$

According to refs. 12 and 15, the intermediate X is a cis–cisoid isomer in a non-planar configuration with a broken pyran heterocycle C—O bond and a lifetime less than 5 ns. The intermediates B_1 - B_4 are trans isomers whose stability increases from B_1 to B_4 [16]. We could not observe the cis-cisoid isomer X because the laser pulse was longer than its lifetime. The absorption spectrum shown in Fig. 6 corresponds to that of the least stable trans isomer B_1. This assignment is supported firstly by the similarity of the absorption spectrum shown in Fig. 6 to that measured 5 ns after the picosecond laser excitation of the SP1 solution [12], and secondly by the lifetime of the intermediate assigned to B_1 being much longer than that of the cis–trans isomerization of the intermediate X [12, 15, 17] found in the present work (Fig. 5). Owing to the resemblance between the spectra of the trans isomers B_2, B_3 and B_4 [10, 18, 19] and also to the similarity of their extinction coefficients, these isomers cannot be separated in acetone. Hence

the oscillograms in Fig. 3(a) characterize the changes in absorption of all three isomers.

Figure 7 presents a schematic view of oscillograms which are similar to those presented in Fig. 3. They consist of three regions: 0 - 1 which corresponds to a fast increase ΔD_1 (or $\Delta D_1'$) in optical density; 1 - 2 which is characterized by a monotonic decrease in optical density to ΔD_2 (Figs. 7(b) and 7(c)), or by an exactly equivalent increase in optical density to $\Delta D_2'$ (Figs. 7(e) and 7(f)); 2 - 3 represents the constant optical density. Increasing the acid concentration results in both a decrease in ΔD_2 and a rise in the rate of decrease of optical density (1 - 2, Figs. 7(b) and 7(c)).

Increasing the acid concentration also enlarges $\Delta D_2'$ and accelerates the growth of the optical density (Figs. 7(e) and 7(f)). The decrease in ΔD_1 compared with ΔD_1^0 is due to the fact that the SP1 photochromic reaction which occurs in the presence of acid ($[HNO_3] \geqslant 5 \times 10^{-6}$ M) takes place during a time comparable with the duration of the flash. These results may be explained as follows. The decrease in ΔD_2 (region 2 - 3) with increasing acid concentration may be due to the most stable spiropyran trans isomer B_4 being in lower yield as a result of competition between the protonation reaction of the trans isomer B_3 ($B_3 + H^+ \rightleftharpoons B_3H^+$) and the isomer intramolecular reaction ($B_3 \rightleftharpoons B_4$). An increase in the rate of thermal bleaching of the merocyanine with acid present (Fig. 4) reveals that the most stable trans isomer B_4 is also involved in the protolytic reaction. However, it can be expected that the efficiency of the protolytic reaction that involves B_4 is considerably lower than that of the reaction involving B_3. This fact may be accounted for by the influence of steric hindrance in the protolytic reaction involving B_4 arising from changes in the geometry of the molecule in this state compared with states B_1 - B_3. The participation of B_3 in the protolytic reaction leads to the formation of C_3, accompanied by an increase in optical density at $\lambda = 420$ nm (region 1 - 2, Figs. 7(e) and 7(f)). Since the lifetime of B_2 is less than that of B_3 [9, 15], the former participates in protolytic reaction at a higher acid concentration than the latter. Thus, increasing the acid concentration further leads to the involvement of B_2 in protolytic reaction ($B_2 + H^+ \rightleftharpoons B_2H^+$). In this case, we observed a further increase in the rate
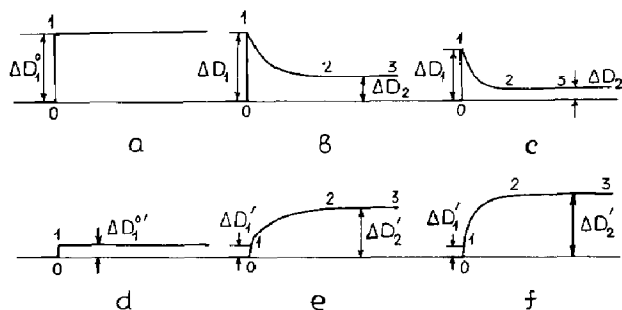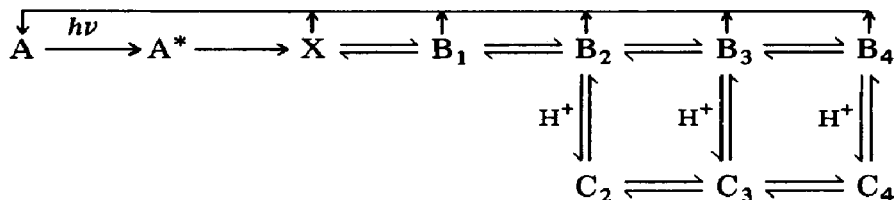

Fig. 7. Schematic oscillograms: without HNO_3, curves a and d; $[HNO_3] = 5 \times 10^{-6}$ M, curves b and e; $[HNO_3] = 6 \times 10^{-6}$ M, curves c and f. ($\lambda = 560$ nm, curves a, b and c; $\lambda = 420$ nm, curves d, e and f.)

of decrease of transient absorption and a further drop in ΔD_2 (Fig. 7(c)). From the results obtained it follows that the lifetime of the least stable trans isomer B_1 (Fig. 5) is constant even when the acid concentration is varied up to 10^{-2} M. Thus, photochromic reactions of SP1 in the presence of acid may be explained by the following:

$$A \xrightarrow{\ h\nu\ } A^* \longrightarrow X \rightleftharpoons B_1 \rightleftharpoons B_2 \rightleftharpoons B_3 \rightleftharpoons B_4$$

$$H^+ \quad\quad H^+ \quad\quad H^+$$

$$C_2 \rightleftharpoons C_3 \rightleftharpoons C_4$$

According to this mechanism, it may be anticipated that the yield of the most stable isomer B_4 would decrease linearly with higher acid concentrations because of the protolytic reaction of B_3. The decrease in the yield of B_4 on further increase of acid concentration follows a quadratic dependence, which also corresponds to the involvement of B_2 in the protolytic reaction. Figure 8 shows the experimental dependence of the relative yield of the merocyanine form B_4 of SP1 on acid concentration. As is apparent from Fig. 8, the dependence is linear for $[HNO_3] \leqslant 5 \times 10^{-6}$ M, and it becomes quadratic with increasing acid concentration. Thus, the experimental dependence is in good agreement with the mechanism cited above. From the nature of the dependence, it follows that B_2 reacts with a proton at $[acid] \geqslant 5 \times 10^{-6}$ M. Figure 9 shows the experimental dependence of the reciprocal value of the halflife of formation of trans isomers upon acid concentration.
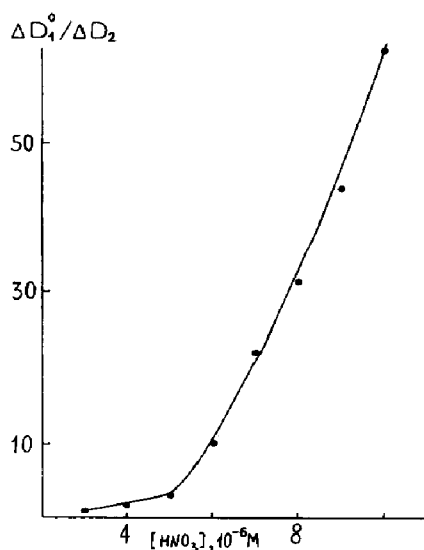

Fig. 8. Dependence of the relative change of ΔD_2 on $[HNO_3]$. ($[SP1] = 10^{-4}$ M; $\lambda = 560$ nm.)
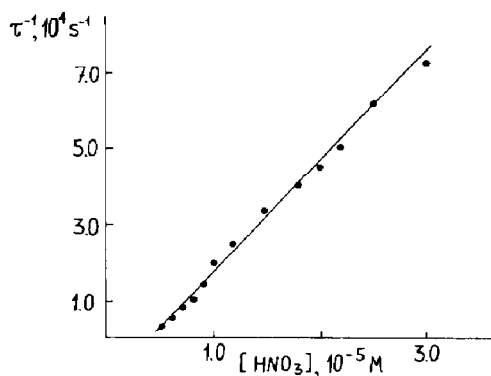
Fig. 9. Plot of reciprocal halftime of SP1 trans isomers *vs.* $[HNO_3]$. ($[SP1] = 10^{-4}$ M; $\lambda = 560$ nm.)

As is apparent from Fig. 9, this dependence is linear with a constant slope in the entire range of acid concentration. From this fact, as well as by comparing the plots presented in Figs. 8 and 9, it may be concluded that the trans isomers B_2 and B_3 are involved in the protolytic reaction, possessing similar rate constants. For SP2 and SP3, we obtained experimental dependences similar to those shown in Figs. 8 and 9, and this indicates a protolytic reaction for these spiropyrans that is similar to that of SP1.

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