

MECHANISM OF THE α RUPTURE OF THE $C_{\text{spiro}}-\text{O}$ BOND IN INDOLINOSPIROPYRANS

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Summary

Spiropyrans (SPPs) appear to be heteroaromatic compounds with a multi-level electronic structure. The mutual arrangement of the lowest electronic states with various orbitals determines the efficiency of intermolecular photophysical processes. In turn, the position of the lowest electronic levels is quite sensitive to the nature of the solvent which thus influences the efficiency of the population of the photophysically active electronic state of the SPP. In the case of an SPP containing a nitro group this is found to be a triplet state of the (π, π^*) type with an electron density deficiency of the nitrogen heteroatom of the indoline cycle. The orbital nature of the photochemically active state of the spiropyran suggests that the $C_{\text{spiro}}-\text{O}$ bond in the benzopyran cycle dissociates via the α rupture mechanism.

The mechanism of α rupture clarifies the problems discussed in Section 1 and satisfactorily explains the dependence of the quantum yield of the photocolouration reaction on the structure of SPPs when both the substituents and the heterocycles are varied.

1. Introduction

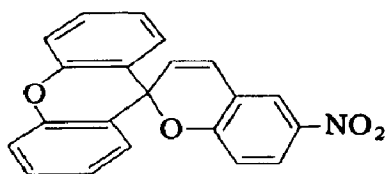
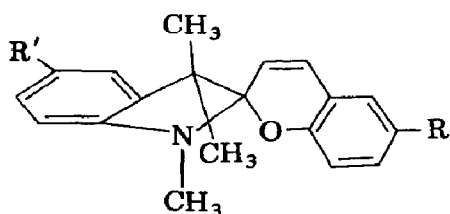
Spiropyrans (SPPs) are widely used for manufacturing non-silver photo-materials for photochromic applications and for non-reversible recording of information [1, 2]. The mechanism of the photocolouration of SPPs is based on the reversible intramolecular photochemical rupture of the $C_{\text{spiro}}-\text{O}$ bond [3, 4]. Although this reaction has been thoroughly investigated by a number of workers, the details and unusual aspects have not been completely elucidated. The following key problems still require solution: (1) the role and mechanism of the effect of the second heterocycle (indoline, xanthene or benzothiazole) upon the efficiency of the $C_{\text{spiro}}-\text{O}$ bond rupture; (2) the multiplicity and orbital nature of the photochemically active electronic state of SPPs; (3) the mechanism of the σ bond rupture upon excitation of the $\pi-\pi^*$ transition to an SPP.

The results of an investigation of the photocolouration reaction in indoline SPPs with a nitro group are summarized in this paper and the orbital

nature of the lower electronic excited states is considered. These SPPs appear to be the most typical representatives of photochromic spirochromenes. It is assumed that the photodissociation of the $C_{\text{spiro}}-O$ bond in SPPs follows the well-known α rupture mechanism.

2. Experimental details

The following SPPs were studied:



$SP_1: R' \equiv H; R \equiv NO_2$

$SP_2: R' \equiv NO_2; R \equiv OCH_3$

SP_3

Anthracene, *N,N,N',N'*-tetramethyl-*n*-phenylenediamine (TMPD), triphenylamine (TPA), triethylamine (TEA), acenaphthene and naphthalene were used as quenchers of the photocoloration reaction. Toluene was used as the solvent. Atmospheric oxygen was not removed from the solutions. The solvent and the quenchers were distilled and purified using standard techniques.

The quantum yield ϕ of the SPP photocoloration reaction was calculated for the conditions of a thin optical layer. The following values were used for the extinction coefficients of the coloured forms of the SPPs at the absorption band maxima [5, 6]: SP_1 and SP_3 , $5.2 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$; SP_2 , $3 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Light of wavelengths 365 and 405 nm from a PRK-4 mercury lamp was used for irradiation. The investigations of the quenching of the photocoloration reaction were performed using irradiation of wavelength $\lambda = 405 \text{ nm}$ which was absorbed only slightly by the quencher. The calculation of ϕ and the quantum yield ϕ_q in the presence of the quenchers was carried out under thermostatic conditions at 295 K for SP_1 and at 253 K for SP_2 and SP_3 . The error in the measurement of ϕ was 20%.

3. Results

The quantum yields ϕ_{365} and ϕ_{405} obtained under irradiation with light of wavelengths 365 nm and 405 nm respectively and the relative phosphorescence intensity I_{phos} of the SPPs in toluene at 77 K taken from ref. 7 are

given in Table 1. The Stern–Volmer dependences for quenching the photo-colouration reactions of SP₁ and SP₂ using various quenchers were linear. Figure 1 shows the dependences obtained for SP₁. The slopes $K_q\tau$ of the Stern–Volmer dependences are given in Table 1.

TABLE 1

The quantum yields and phosphorescence intensities of SPPs and the Stern–Volmer constants for quenching the photo-colouration reaction in toluene

SPP	ϕ_{365}	ϕ_{405}	I_{phosph} (o.e.)	K_q					
				Anthra- cene	TMPD	TPA	TEA	Ace- naph- thene	Naph- thal- ene
SP ₁	0.75	0.75	1	8.5	8.5	3.0	1.5	0.8	0.5
SP ₂	0.60	0.60	1	85	90	14	0.9	0.5	—
SP ₃	0.1	—	1	—	—	—	—	—	—

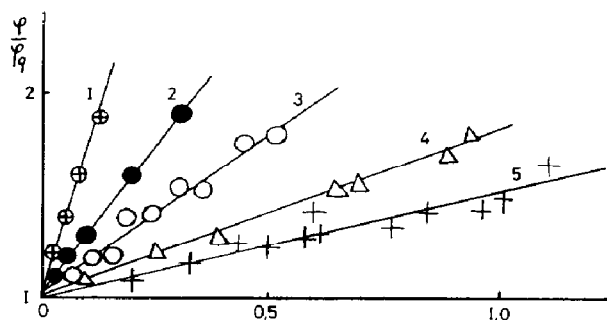


Fig. 1. Stern–Volmer dependence of the quenching of the photo-colouration reaction of SP₁ by various electron donors: curve 1, TMPD; curve 2, TPA; curve 3, TEA; curve 4, acenaphthene; curve 5, naphthalene.

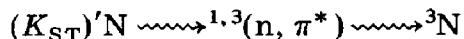
4. Discussion

Light of wavelengths 365 and 405 nm excites the first transition in SPPs containing a nitro group. On the basis of the solvatochromism theory [4–8] the transition was shown to be a π – π^* intramolecular charge transfer. The corresponding singlet excitation can be represented in the mono-electronic approximation as the linear combination [4, 9]

$$N = C_1(\pi, \pi^*) - C_2(l, \pi^*) - C_3(\pi, \pi_n^*)$$

and it can be written as ${}^1N = {}^1(\pi l, \pi_1^* \pi_n^*)$ where l is the orbital of the oxygen (SP₁ and SP₃) or nitrogen (SP₂) heteroatom symmetrically close to the orbital $2p_z$ of the carbon atom of the benzene cycle (π_n^* is the orbital of the nitro group). It has been shown [7, 10] that the low triplet state of SPPs containing a nitro group is of the ${}^3(\pi l, \pi^* \pi_n^*)$ type (the 3N type in our

notation). In addition to electronic states of the $^{1,3}\text{N}$ type, SPPs have low energy states of the $^{1,3}(\text{n}, \pi^*)$ type owing to the presence of a nitro group [10, 11]. The exact location of these states is unknown, although it has been assumed [7, 10, 11] that in slightly polar media at least one of the $^{1,3}(\text{n}, \pi^*)$ levels is located between the $^{1,3}\text{N}$ levels. Such a location of the electronic levels of SPP results in a high value of the rate constant of the intersystem crossing



and hence it can be assumed that the ^3N -type triplet state participates in the photodissociation of the $\text{C}_{\text{spiro}}-\text{O}$ bond. Indeed, SP_1 in polystyrene is completely coloured through the triplet state [12].

We now consider our results obtained for the quenching of the photo-colouration of SP_1 and SP_2 with various quenchers in the light of these data. The linearity of the Stern-Volmer dependences shows that the quenchers deactivate only one state which takes part in the photo-colouration reaction. Proceeding from the data for the location of the singlet and triplet levels of SPP and the quenchers and for their ionization potentials [3 - 8, 13, 14], we can conclude that anthracene will probably quench the triplet state of SPP via an energy transfer mechanism with the quenching constant K_q having a similar value to that of the diffusion constant K_d . In the case of the quenchers for electron donors it can be assumed that they deactivate the photochemically active state of SPP via an electron transfer mechanism [15], and it is well known that TMPD quenches the electronically-excited states of various organic compounds with K_q close to K_d [15].

Since in our case the values of $K_q\tau$ obtained upon quenching the photo-colouration reactions of SPPs with TMPD and anthracene are very similar (see Table 1), we can assume that these quenchers deactivate the lowest triplet state of the ^3N type. The lifetimes τ_T of this state for SP_1 and SP_2 can be evaluated from K_q and K_d ($1.1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ and $5.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at 295 K and 253 K respectively in toluene); they are given in Table 2. The low values of τ_T for SPP may be due to the high deactivation rate of the triplet state of the rupture of the $\text{C}_{\text{spiro}}-\text{O}$ bond.

The values of τ_T for SP_1 and SP_2 can be used to determine K_q for other electron donors whose ionization potentials are higher than those of TMPD (see Table 2). In this case the constant K_q , which can be determined experimentally, is expressed in terms of elementary constants [15, 16]:

TABLE 2

The values of τ_T and K_q for SP_1 and SP_2

SPP	$\tau_T \times 10^{10}$ (s)		$K_q \times 10^{-8}$ ($\text{l mol}^{-1} \text{ s}^{-1}$)			
	<i>Anthracene</i>	<i>TMPD</i>	<i>TPA</i>	<i>TEA</i>	<i>Acenaphthene</i>	<i>Naphthalene</i>
SP_1	7.5	7.5	40	21	10	5
SP_2	150	160	0.9	0.6	0.4	—

$$K_q = \frac{K_q^T K_d}{K_r - K_q^T} \quad (1)$$

where K_q^T is the rate constant of electron transfer in the complex (SPP-quencher)* formed by the impact [3] and K_r is the rate constant of the relaxation of the impact complex into waste products. Expression (1) can be recast as

$$\frac{K_q^T}{K_r} = \frac{K_q}{K_d - K_q} \quad (2)$$

$\log(K_q^T/K_r)$ is proportional to the change in the free energy of the electron transfer reaction in the impact complex which in turn is proportional to the ionization potential of the electron donor and the negative value of the electron affinity of the SPP in the 3N state. Indeed, we observed a linear dependence of $\ln \{K_q/(K_d - K_q)\}$ on the ionization potential of the electron donor for SP_1 and SP_2 (Fig. 2).

The values of K_q for SP_1 are more than an order of magnitude higher than the corresponding values of K_q for SP_2 . This may be due to the difference between the electron affinities of the 3N states of SP_1 and SP_2 and suggests that the electron captured by the SPP is localized on the electron-deficient l orbital of the heteroatom. The ionization potential of the l orbital of the oxygen heteroatom is greater than that of the l orbital of the nitrogen heteroatom of SP_2 [7]. Therefore the electron affinity of the 3N state of SP_1 appears to be greater than that of SP_2 . The results obtained lead to the conclusion that the 3N state of an SPP containing a nitro group, like the cor-

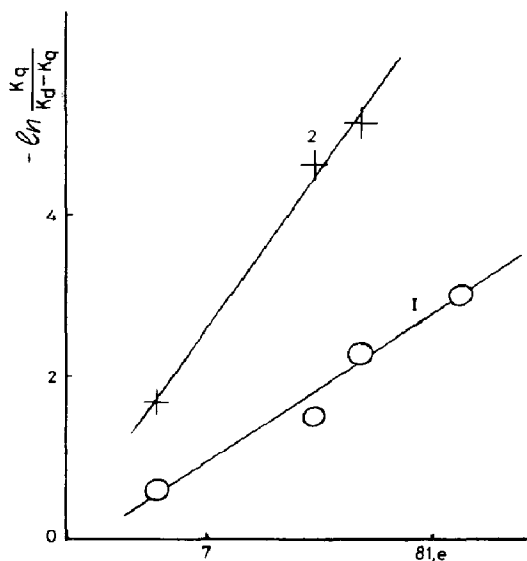


Fig. 2. Dependence of $\ln \{K_q/(K_d - K_q)\}$ on the ionization potential I of the electron donor (values taken from ref. 11): curve 1, SP_1 ; curve 2, SP_2 .

responding ^1N state [7, 8], has a considerable positive charge on the heteroatom of the fragment in which the nitro group is located.

The investigations of the quenching of the photocoloration reaction of SP_2 with anthracene show that it proceeds almost completely through an electron-excited state of the ^3N type which is localized mainly in the indoline cycle of SP_2 [5]. The high value of ϕ for SP_2 in the absence of electron excitation of the dissociating benzopyran fragment suggests that the rupture of the $\text{C}_{\text{spiro}}-\text{O}$ bond in SP_2 proceeds according to the well-known α rupture mechanism [15, 17].

The electron density deficit on the $1_{\text{N}-}$ orbital of the nitrogen heteroatom of SP_2 in the ^3N state and the similar symmetries of the $1_{\text{N}-}$ and $\sigma_{\text{C}-\text{O}}$ orbitals [7] contribute to the exchange reaction between the electrons in these orbitals [17, 18]. As a result of this interaction the $\text{C}_{\text{spiro}}-\text{O}$ bond becomes weaker and if there is sufficient vibrational excitation of the benzopyran fragment the latter opens and isomerizes.

Amine cation radicals excited by vibration dissociate according to the same mechanism [18]. It should be noted that in the case of SP_2 in the ^3N state the contribution of the electronic structure close to that of the cation radical of the tertiary amine can be pronounced [7]. The observation that substituents in the benzopyran fragment of SPP containing a nitro group in the indoline cycle have a negligible effect on ϕ , which is close to the ϕ of SP_2 [5], implies that the efficiency of the rupture of the $\text{C}_{\text{spiro}}-\text{O}$ bond in these SPPs does not depend on the electronic structure of the benzopyran cycle and is in good agreement with the assumed α rupture mechanism.

We now consider whether the photodissociation of the $\text{C}_{\text{spiro}}-\text{O}$ bond in SPP containing a nitro group in the benzopyran cycle (SP_1) occurs via the α rupture mechanism. It has often been suggested [4, 6, 9, 19 - 21] that the electron can tunnel from the indoline fragment to the benzopyran fragment in the excited state of SPPs. It has been proposed [19 - 21] that this transition in SPPs containing a nitro group in the benzopyran fragment results in the formation of an intramolecular ion radical pair (IRP) (observed using electron spin resonance (ESR)) with the distance r between the unpaired electrons equal to 2.6 Å which is almost the same as the distance between the nitrogen and oxygen heteroatoms (2.33 Å).

In view of the data obtained, we can assume that the $\text{C}_{\text{spiro}}-\text{O}$ bond in SPP containing a nitro group in the benzopyran fragment dissociates via the α rupture mechanism. This mechanism seems to account for the correlation [4, 6] observed between ϕ and the intensity of the first absorption band of a number of SPPs containing nitro groups and other substituents in the benzopyran fragment. In fact the intensity of this band determines the quantity of positive charge on the oxygen heteroatom in the ^1N state, and probably in the ^3N state, of the SPP [4]. The quantity of positive charge on the 1_0 orbital of the oxygen heteroatom in the $^1,^3\text{N}$ states of the SPPs determines the probability of electron tunnelling and thus the efficiency of the α rupture mechanism.

The above considerations are valid for low-polar aprotic solvents (toluene, heptane, dioxane, ethyl acetate etc.) in which the ϕ of an SPP con-

taining a nitro group is high and is almost independent of the solvent [3, 5, 7]. It is known [3] that in alcohol and highly polar solvents the ϕ of an SPP containing a nitro group is much less than that in the aprotic solvents listed above. The phosphorescence intensities of SP₁, SP₂ and SP₃ decrease on going from toluene to ethanol or dimethylformamide [8]. The ϕ of 5,7-dichloro-SP₁ (in acetonitrile) sensitized by the donor of the triplet colouration energy is comparable with the ϕ of this SPP in low-polar solvents [3, 22].

These results suggest that the main reason for the decrease of ϕ in polar and alcoholic solvents is a sharp decrease in the K_{ST} of the $^1N \rightsquigarrow ^3N$ transition. The influence of the medium on the efficiency of the α rupture of the C_{spiro}-O bond is almost negligible. A sharp decrease in K_{ST} can be explained by a change in the relative position of the $^{1,3}(n, \pi^*)$ states of the $^{1,3}N$ levels which undergo antibate shifts when the solvents are changed as described above [4, 8, 14, 15].

In the case of SP₃ the value of K_{ST} is comparable with that for SP₁, which is supported by the similarity of the values of I_{phosph} for these SPP. However, the ϕ of SP₃ is substantially less than the ϕ of SP₁ (see Table 1). This result can be accounted for as follows. If electron tunnelling from the xanthene cycle to the benzopyran cycle occurs upon excitation of the $^{1,3}N$ states of SPP (which is unlikely [7]), the positive charge on the xanthene fragment is either delocalized according to the π system or is far removed from the C_{spiro}-O bond. Thus the conditions do not favour the α rupture mechanism. Therefore, for this reason and because of the low efficiency of oscillatory rupture of the bond in the $^{1,3}N$ state, the value of ϕ for SP₃ is small.

It should be noted that the process of quenching the photocoloration reaction of SP₁ in solution owing to intermolecular electron transfer from the donor to SPP competes with electron tunnelling inside the SPP molecule. Such a situation appears to be similar to that observed in the low temperature photolysis of a doped single crystal of SPP with a nitro group in the 8-position [21]. In such a single crystal the competition of the two processes was observed using ESR, the intramolecular electron transition resulting in the formation of an IRP with $r = 2.6 \text{ \AA}$ and the intermolecular electron transition resulting in the formation of an IRP with $r = 4.6 \text{ \AA}$ [21].

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