Primary Photochemical Processes in the 366-nm Photolysis of 5′,7′-Dichloro-6′-nitro-1,3,3-trimethylindolinobenzopyrylospiran in Acetonitrile[1]

Helmut Bach and Jack G. Calvert

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received September 19, 1969*

Abstract: Quantum yields of the formation of the colored form (II) of the spiropyran I were determined for the direct and the sensitized photolysis in acetonitrile solutions at 366 nm and 24° in most experiments. The compounds benzophenone and 2-acetonaphthone sensitize the formation of II. Benzil has little effect either as a sensitizer or as a quencher, while 9-fluorenone quenches rather effectively a fraction of the color formation in the direct photolysis of I. From a kinetic analysis of the initial rates of formation of II in the sensitized and quenched reactions, quantitative estimates were made of the quantum yields of the primary reactions involved in the direct photolysis of I. The data suggest that in the direct photolysis at 366 nm both singlet and triplet excited states of I react to form II. Triplet-energy-transfer experiments indicate that the energy of the triplet state of I lies above the ground state by 53-57 kcal/mol; this estimate is reasonably consistent with the observed position of the 0-0 band (58 kcal/mol) in the phosphorescence spectrum of I.

The photochromism exhibited by the indolinobenzopyrylospirans (commonly called "spiropyrans") was first observed in the low-temperature matrix experiments by Fischer and Hirshberg.[2] This photochromism and the photochemical and thermal reversibility of the coloration have excited the interest of both academic and industrial research groups. Many of the features of the reactions of these compounds have been well established. There is a great variety of evidence concerning the nature of the structure and properties of the colored and the uncolored forms which has been obtained from ultraviolet, visible, infrared, esr, and nmr spectral data,[2-19] dipole moment determinations,[20] studies of the effects of substituents on the reactions,[21-23] studies of the properties of the molecules in polymeric matrices,[24-26] evaluations of kinetic, equilibrium,[4-6,10,26-36] and thermodynamic constants related to these reactions,[3,6,18,35,36] theoretical considerations of the bonding in the different structural forms,[37] and the properties of molecules adsorbed on polar and nonpolar materials.[38-41]

Reasonable extrapolation of the extensive previous work on the spiropyrans suggests the following reactions as the probable overall structural changes effected on irradiation of the compound chosen for our studies, 5′,7′-dichloro-6′-nitro-1,3,3-trimethylindolinobenzopyrylospiran (I). In the compound I the two halves of the molecule, joined at the spiro-carbon atom, lie in planes at right angles to one another. Tyer and

---

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. The authors acknowledge gratefully the support of this work through a research grant from the National Air Pollution Control Administration, U. S. Department of Health, Education, and Welfare, Public Health Service, Arlington, Va.

(2) E. Fischer and Y. Hirshberg, *J. Chem. Soc.*, 4522 (1952).

(3) O. Chaudé, P. Rumpf, and J. Cabannes, *C. R. Acad. Sci., Paris*, **236**, 697 (1953).

(4) Y. Hirshberg, E. H. Frei, and E. Fischer, *J. Chem. Soc.*, 2184 (1953).

(5) Y. Hirshberg and S. I. Weissman, *J. Chem. Phys.*, **28**, 739 (1958).

(6) O. Chaudé, *Cah. Phys.*, **50**, 17 (1954); **51**, 6 (1954); **52**, 3 (1954).

(7) Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 297 (1954); 3129 (1954).

(8) Y. Hirshberg, *J. Amer. Chem. Soc.*, **78**, 2304 (1956).

(9) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Chem. Soc.*, 156 (1961).

(10) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2465, 2470 (1962).

(11) P. Douzou and C. Wippler, *J. Chim. Phys.*, 1409 (1963).

(12) G. I. Lashkov and A. V. Shablya, *Opt. Spectrosk.*, **19**, 455 (1965).

(13) C. Schiele, G. Arnold, and A. Wilhelm, *Tetrahedron Lett.*, 5775 (1966).

(14) E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).

(15) C. Schiele and G. Arnold, *Tetrahedron Lett.*, 1191 (1967).

(16) J. Kolc and R. S. Becker, *J. Phys. Chem.*, **71**, 4045 (1967).

(17) R. S. Becker and J. Kolc, *ibid.*, **72**, 997 (1968).

(18) J. B. Flannery, Jr., *J. Amer. Chem. Soc.*, **90**, 5660 (1968).

(19) C. Schiele and G. Arnold, *Z. Naturforsch., B*, **23**, 628 (1968).

(20) E. D. Bergmann, A. Weizmann, and E. Fischer, *J. Amer. Chem. Soc.*, **72**, 5009 (1950).

(21) E. B. Knott, *J. Chem. Soc.*, 3038 (1951).

(22) C. F. Koelsch, *J. Org. Chem.*, **16**, 1362 (1951).

(23) C. F. Koelsch and W. R. Workman, *J. Amer. Chem. Soc.*, **74**, 6288 (1952).

(24) Z. G. Gardlund, *J. Polym. Sci., Part B*, **6**, 57 (1968).

(25) P. H. Vandevijer and G. Smets, *ibid., Part C*, **22**, 231 (1968).

(26) A. V. Shablya, K. B. Demidov, and Y. N. Polyakov, *Opt. Spectrosk.*, **20**, 412 (1966).

(27) E. Berman, R. E. Fox, and F. D. Thomson, *J. Amer. Chem. Soc.*, **81**, 5605 (1959).

(28) C. A. Heller, D. A. Fine, and R. A. Henry, *J. Phys. Chem.*, **65**, 1908 (1961).

(29) T. Bercovici and E. Fischer, *J. Amer. Chem. Soc.*, **86**, 5687 (1964).

(30) J.-Ch. Métras, M. Mossé, and C. Wippler, *J. Chim. Phys.*, **62**, 659 (1965).

(31) G. I. Lashkov, A. V. Shablya, and D. N. Glebovskii, *Opt. Spectrosk.*, **20**, 95 (1966).

(32) J. Arnaud, M. Mossé, and J. J. Trillat, *C. R. Acad. Sci., Paris*, **264**, 1145 (1967).

(33) J. Arnaud, C. Wippler, and F. B. d'Augeres, *J. Chim. Phys.*, **64**, 1165 (1967).

(34) R. E. Bowman, R. E. Fox, A. J. Kresch, and J. E. G. Taylor, National Cash Register Company Report to School of Aerospace Medicine, USAF Aerospace Medical Center (ATC), Brooks Air Force Base, Texas, Defense Documentation Center, No. AD427601.

(35) R. Guglielmetti, M. Mossé, J.-Ch. Métras, and J. Metzger, *J. Chim. Phys.*, **65**, 454 (1968).

(36) D. B. McQuain, A. J. Kresch, R. E. Fox, and R. E. Bowman, National Cash Register Company Report to USAF School of Aerospace Medicine, Defense Documentation Center, No. AD465855 and AD464983.

(37) O. Bloch-Chaudé and J.-L. Masse, *Bull. Soc. Chim. Fr.*, 625 (1955).

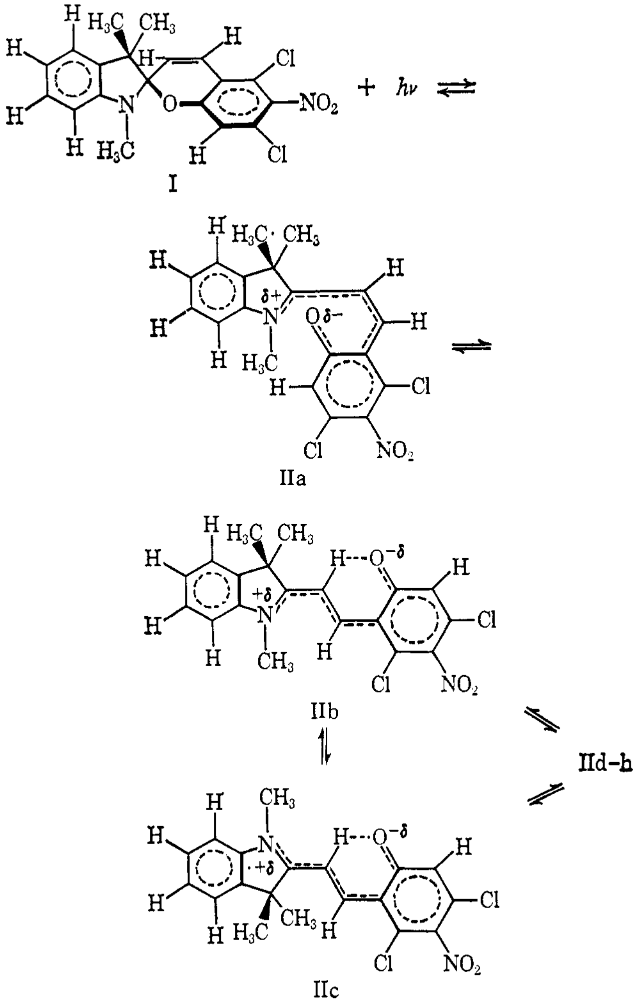
(38) A. Schönberg, A. Mustafa, and W. Asker, *J. Amer. Chem. Soc.*, **74**, 5640 (1952).

(39) G. Kortüm and G. Bayer, *Z. Phys. Chem.* (Frankfurt am Main), **33**, 254 (1962).

(40) C. Balny and P. Douzou, *C. R. Acad. Sci., Paris*, **264**, 477 (1967).

(41) (a) T. R. Evans, A. F. Toth, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**, 5060 (1967); (b) N. W. Tyer, Jr., and R. S. Becker, *ibid.*, **91**, 1289, 1295 (1970).

Becker[41b] have shown recently that the absorption and the emissions from the colorless form of the benzospiropyrans are localized or originate in a particular half of the molecule. Thus in our experiments (irradiation at 366 nm) it seems probable that excitation is localized largely in the chromene half (the right half) of the molecule I.



The structures labeled IIa-h represent the various forms of the colored product of irradiation. Presumably IIa is the first product formed from an electronically excited I molecule, or in thermal reactions from a ground state I molecule, through cleavage of the O-C bond on the spiro-carbon atom. It is theorized that the steric crowding in this molecule is released through isomerization to forms such as IIb, IIc, etc. In both IIb and IIc the bulky groups are in the *trans* configuration, and these isomers probably represent the lowest energy forms, and hence the dominant colored species at thermal equilibrium at room temperature. The five other forms of higher energy, symbolized by IId-h, include two other *trans* and three other *cis* forms. Light absorbed within the visible (or ultraviolet) absorption bands of the colored forms (IIb, IIc, . . .) may result in isomerizations and a shift of the distribution of isomers present at thermal equilibrium. Specifically form IIa and possibly other *cis* forms may be formed in part and subsequently undergo a thermal, or possibly a photochemically induced ring closure by a mechanism which is as yet ill-defined.

There is significant evidence for the involvement of a triplet excited state of the colorless 6′-nitro-substituted indolinobenzopyrylospirans in the color-forming reactions. (1) Color formation has been sensitized in certain spiropyrans through the use of triplet-energy-transfer reactions.[29,42,43] (2) Esr signals corresponding to a triplet species ($\Delta m = 2$) have been observed on irradiation of the 6′-nitro-substituted spiropyrans in a polar matrix at 77°K.[44] (3) Phosphorescence emisson from a triplet state of the nitro-; nitro-, chloro-; and nitro-, methoxy-substituted spiropyrans has been observed in rigid matrices at 77°K.[41b,42,45,46] (4) A transient absorption first observed by Windsor, Moore, and Novak[47] in the flash photolysis of the 8′-methoxy-6′-nitro-substituted spiropyran, has been attributed to a triplet-triplet absorption in experiments both at room temperature and at 77°K.[46,48a] Recently Bercovici, Heiligman-Rim, and Fischer[48b] have demonstrated the presence of an oxygen-sensitive transient in the flash photolysis of several spiropyrans; furthermore this transient seems to form the colored compound at least in part. They have concluded that there may be some involvement of the triplet spiropyrans in direct photocoloration, but that a considerable fraction of the colored form comes directly from the first excited singlet state.

Although it has been shown in the previous work that a triplet excited species can be found in certain irradiated spiropyran systems, it remains uncertain to what extent this triplet state may be involved in the color-forming reactions in the direct photolysis of the spiropyrans. For example, in the work of Lashkov, Ermolaev, and Shablya,[43] triplet energy acceptors did not inhibit the color formation of the 6′-nitro-8′-bromo-substituted spiropyran in toluene, and oxygen had little or no effect on this reaction[43] and in the photolysis of the unsubstituted spiropyran at −100°.[29] Obviously these results are not typical of reactions involving triplet molecules. In the work reported here we have delineated the extent of the involvement of both the singlet and triplet states in the mechanism of the direct photolysis of compound I at 366 nm. This has been accomplished by the determination of the quantum yields of color formation in triplet-sensitized and direct photolyses of I with and without added quenchers. Through the choice of compound I and the polar solvent acetonitrile for these studies, the reaction resulting in the thermal fading of the colored forms (reaction 12 in the sequence presented in the Discussion) has been minimized so that quantitative experiments could be performed with the conventional steady-state photochemical method in solutions at room temperature, 24°.

---

(42) R. S. Becker and J. K. Roy, *J. Phys. Chem.*, **69**, 1435 (1965).

(43) G. I. Lashkov, V. L. Ermolaev, and A. V. Shablya, *Opt. Spectrosk.*, **19**, 305 (1965).

(44) C. Balny, R. Santus, and P. Douzou, *C. R. Acad. Sci., Paris*, **262**, 1311 (1966).

(45) C. Balny and P. Douzou, *ibid.*, **262**, 1235 (1966).

(46) T. A. Shakverdov and A. B. Shablya, *Opt. Spectrosk.*, **24**, 326 (1968).

(47) M. W. Windsor, R. S. Moore, and J. R. Novak, *Spectrochim. Acta*, **18**, 1364 (1962).

(48) (a) M. Mossé and J.-Ch. Métras, *J. Chim. Phys.*, **64**, 691 (1967); (b) T. Berçovici, R. Heiligman-Rim, and E. Fischer, *Mol. Photochem.*, **1**, 23 (1969).

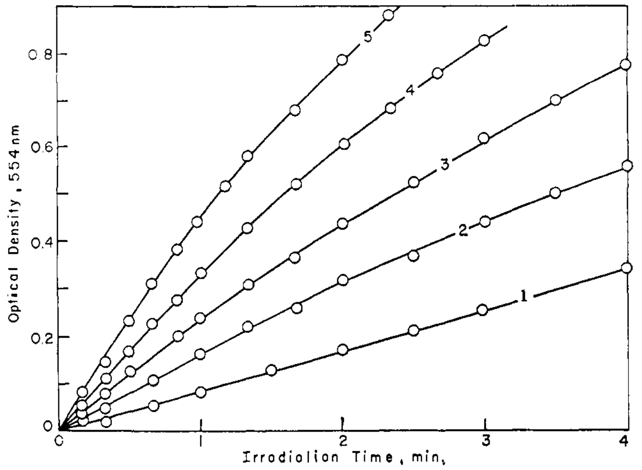


Figure 1. Benzophenone triplet-sensitized formation of the colored product II from the spiropyran I; the optical density at 554 nm as a function of time in the 366-nm irradiated solutions of the spiropyran (Sp) and benzophenone (B) in acetonitrile at 24°; [Sp] = 2.1×10^{-4} *M;* [B] $\times 10^3$ *M* = 0, 1.6, 3.3, 6.7, and 13.3 in runs labeled 1, 2, 3, 4, and 5, respectively.

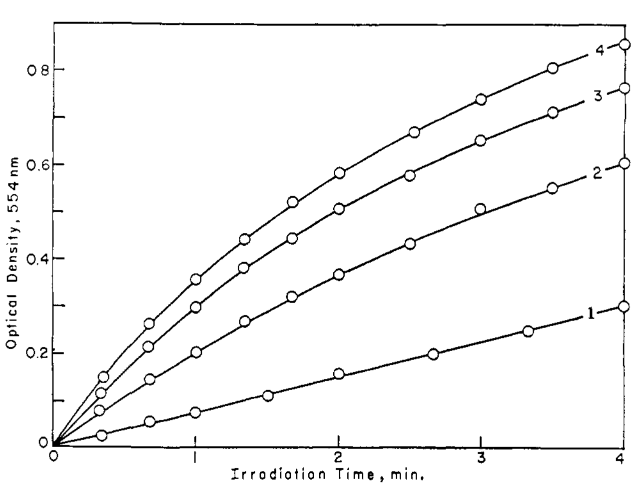


Figure 2. 2-Acetonaphthone triplet-sensitized formation of the colored product II from the spiropyran I; the optical density at 554 nm as a function of time in the 366-nm irradiated solutions of the spiropyran (Sp) and 2-acetonaphthone (B) in acetonitrile at 24°; [Sp] = 2.1×10^{-4} *M;* [B] $\times 10^3$ *M* = 0, 8, 20, and 40 in runs labeled 1, 2, 3, and 4, respectively.

Experimental Section

The photochromic compounds, the colorless spiropyran I and its colored form II, were synthesized and provided for our use by the Materials Research Department, the National Cash Register Co., Dayton, Ohio.[34] The solvent, acetonitrile (Spectrograde), and the sensitizers and quenchers, benzophenone, 2-acetonaphthone, benzil, and 9-fluorenone, used in this work were all products of the Eastman Organic Chemicals Co.

The photochemical reactions were carried out in a 1-cm path length absorption cell. The cell could be sealed off with a Fischer-Porter Teflon vacuum stopcock (5 mm). Solutions were prepared, introduced into the cell (3.00 ml), and degassed on a vacuum system (10^{-5} mm) with alternate freeze-thaw cycles (liquid nitrogen). Then the cell was placed in the holder in the light train. The light exposures were made in a collimated beam of 366-nm light derived from a medium pressure mercury lamp (Hanovia, 673A) and a glass filter system. The absorption due to the colored product was determined at intervals during the exposure by measurement at its absorption maximum in acetonitrile, 554 nm.

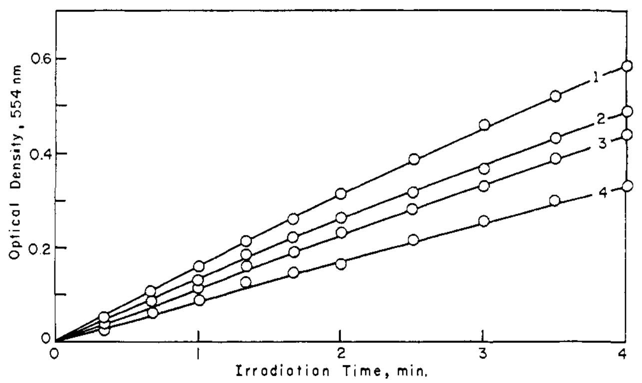


Figure 3. The benzil-quenched formation of the colored product II from the spiropyran I; optical density at 554 nm as a function of time in 366-nm irradiated solutions of the spiropyran (Sp) and benzil (Q) in acetonitrile at 24°; [Sp] = 5.1×10^{-4} *M;* [Q] $\times 10^3$ *M* = 0, 0.5, 2.0, and 5.0 in runs labeled 1, 2, 3, and 4, respectively.

The molar extinction coefficient of the colored form II (ϵ_{554} 5.0×10^4 l./(mol cm)) was determined by preparing acetonitrile solutions of the colored form from weighed samples of the pure colored compound, following the absorption at 554 nm as a function of time, and extrapolation of the data to zero time. Our measurements checked within the experimental error of the value reported by McQuain, Kresch, Fox, and Bowman.[36] The thermal fade rate of the colored form was first order with $k_{12} \cong 2.0 \times 10^{-5}$, 1.4×10^{-4}, and 1.9×10^{-3} sec^{-1} at temperatures of 2, 24, and 52°, respectively. The visible absorption spectrum and the rate constant for the thermal fade of the colored form prepared from the solution of the pure solid material were identical with these same quantities determined from the colored product formed from I photochemically. Obviously equilibration of the isomeric forms is achieved very rapidly in acetonitrile at 24°. The extinction coefficients at 366 nm in acetonitrile were determined by conventional procedures using a Bausch and Lomb Model 505 spectrometer: colorless form of the spiropyran I, 1200; benzophenone, 50; 2-acetonaphthone, 8.3; benzil, 74; 9-fluorenone, 230 l./(mol cm).

The light intensity was determined using potassium ferrioxalate actinometry.[49] The incident 366-nm light intensity was essentially constant during the entire series of runs with an average value of 1.16×10^{15} quanta/sec.

The rate of formation of II in the direct photolysis was not greatly influenced by degassing the solutions or by temperature change (2–52°). However, in the sensitized photolyses a major suppression of the sensitized coloration occurred in nondegassed solutions. In all kinetic experiments solutions were degassed.

In Figure 1 rate data from one of several series of experiments at 366 nm are shown for the formation of the colored compound II in acetonitrile solutions of pure spiropyran (curve 1) and in solutions of the spiropyran at the same concentration (2.1×10^{-4} *M*) with benzophenone at concentrations from 1.6 to 13.3×10^{-3} *M*. Note that although benzophenone acts as an internal filter and absorbs an increasing fraction of the incident light in the experiments labeled 2–5, the rate of color formation increases. Obviously the benzophenone sensitizes the color formation. The same result is evident in experiments with added acetonaphthone, Figure 2. However, the result is quite different in experiments with added benzil (Figure 3) or 9-fluorenone (Figure 4). Here suppression of the color formation occurs with the added compounds. The effect is most evident with 9-fluorenone. The rate data given in Figures 1–4 and other similar data for other concentration conditions were used to determine initial rates of color formation for each of the series of runs. From these data quantum yields of formation of the colored product II were calculated. The quantum yields from the direct photolysis of both the pure spiropyran I and for spiropyran–quencher mixtures (Φ_{dye}) were calculated from the initial slope of the plot of the optical density of the product dye-containing solutions at 554 nm *vs.* the time of the irradiation (as in Figure 3 and 4) using the following relation

$$\Phi_{\text{dye}} = \frac{\left(\frac{\mathrm{d(OD)}_{554}}{\mathrm{d}t}\right)_{t\to 0}\dfrac{(0.00300)(6.02 \times 10^{23})}{\epsilon_{\text{dye}}}}{I_0\left(\dfrac{\epsilon_{\text{Sp}}}{\epsilon_{\text{Sp}} + \epsilon_{\text{Q}}}\right)(1 - 10^{-\epsilon_{\text{Sp}}[\text{Sp}] - \epsilon_{\text{Q}}[\text{Q}]})}$$

---

(49) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

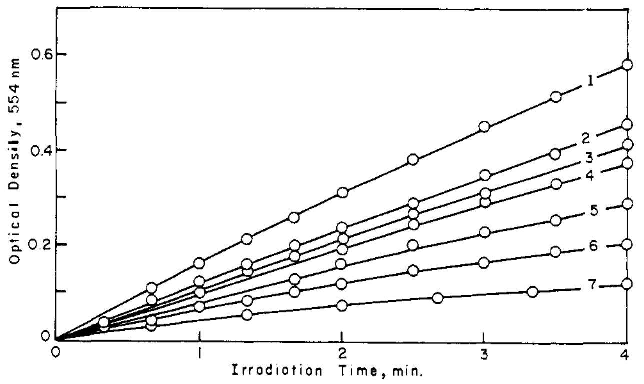


Figure 4. The 9-fluoroenone-quenched formation of the colored product II from the spiropyran I; optical density at 554 nm as a function of time in the 366-nm irradiated solutions of the spiropyran (Sp) and 9-fluorenone (Q) in acetonitrile at 24°; [Sp] = 5.1 × 10^{-4} *M;* [Q] × 10^3 *M,* = 0, 0.10, 0.25, 0.50, 1.0, 1.5, and 2.5 in runs labeled 1, 2, 3, 4, 5, 6, and 7, respectively.

where Sp and Q refer to the spiropyran I and the quencher molecule, respectively. I_0 is the light intensity in quanta/sec incident at the front face of the solution. For the experimental conditions and the method of calculation employed in most of these experiments, the correction to the observed rates of colored product formation due to the thermal reaction 12 is negligible. In a few runs at 52° a correction of about 6% was necessary to adjust the data for the rate of thermal fade of the product dye. Quantum yields of color formation calculated in this fashion for runs at several spiropyran I concentrations are summarized in Table I and for experiments with added quenchers in Table III. The sensitized quantum yields of colored product II, Φ_{sens}, were calculated in a similar fashion using the following relation

Table I. Quantum Yields of Formation of the Colored Form of the Spiropyran (Sp) in its Direct Photolysis at 366 nm in Acetonitrile Solution at 24° [a]

[Sp] × 10^4, *M*	Φ_{dye}
1.0	0.115
2.1	0.100
2.1	0.101
4.0	0.109
5.1	0.109
6.3	0.107
	Av 0.107

[a] In a series of comparative rate experiments at [Sp] = 5.0 × 10^{-4} *M* and at temperatures of 2 and 52°, the ratio of the quantum yield of dye formation, $(\Phi_{\text{dye}})_{52°}/(\Phi_{\text{dye}})_{2°}$ = 1.03 ± 0.02; thus Φ_{dye} is not sensitive to temperature change.

$$\Phi_{\text{sens}} = \frac{\left(\frac{\mathrm{d(OD)}_{554}}{\mathrm{d}t}\right)_{t\to 0}\frac{(0.00300)(6.02\times 10^{23})}{\epsilon_{\text{dye}}} - \left(\frac{I_0\Phi_{\text{dye}}\epsilon_{\text{Sp}}[\text{Sp}](1-10^{-\epsilon_{\text{Sp}}[\text{Sp}]-\epsilon_{\text{B}}[\text{B}]})}{\epsilon_{\text{Sp}}[\text{Sp}]+\epsilon_{\text{B}}[\text{B}]}\right)}{\left(\frac{I_0\epsilon_{\text{B}}[\text{B}]}{\epsilon_{\text{B}}[\text{B}]+\epsilon_{\text{Sp}}[\text{Sp}]}\right)(1-10^{-\epsilon_{\text{Sp}}[\text{Sp}]-\epsilon_{\text{B}}[\text{B}]})}$$

where B refers to the triplet sensitizer molecule. For our conditions colored product formation by direct photolysis was not inappreciable; the second term in the numerator represents this rate. In the runs with benzophenone this term varied from 10 to 38% of the first term in the runs with [Sp] = 1.00 × 10^{-4}, [B] = 8.0 × 10^{-4} *M* and [Sp] = 4.00 × 10^{-4}, [B] = 4.00 × 10^{-4} *M*, respectively. The quantum yields of benzophenone triplet-sensitized color formation calculated in this fashion are summarized in Table II. In runs with 2-acetonaphthone relatively high sensitizer concentrations were necessary to avoid near equality of the terms in the numerator of the Φ_{sens} relation. The rate data of Figure 2 gave the following estimates of Φ_{sens}: 0.61 (run 2), 0.55 (run 3), 0.48 (run 4).

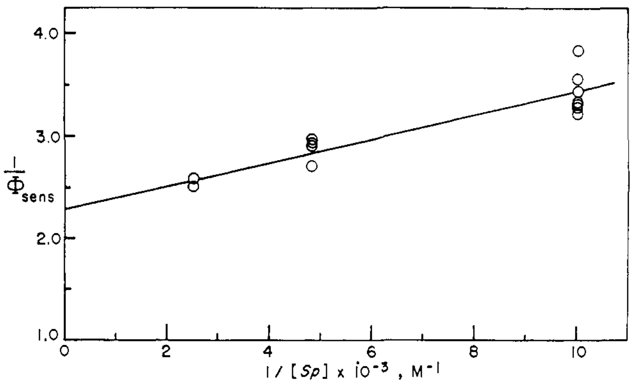


Figure 5. Plot of the reciprocal of the quantum yield of benzophenone triplet-sensitized formation of the colored product II from the spiropyran I *vs.* the reciprocal of the spiropyran concentration; data are from experiments at 366 nm in acetonitrile at 24° (Figure 1, Table II).

The trend of Φ_{sens} with acetonaphthone concentration is not expected in theory and must be an artifact related to uncertainties in the extinction coefficient data and the fraction of the incident light absorbed by the acetonaphthone. Extrapolation of these data to total light absorption by acetonaphthone and complete energy transfer to the spiropyran in these mixtures, gives the limiting value of $\Phi_{\text{sens}} \cong 0.46$; this is in reasonable agreement with the limit Φ_{sens} = 0.43 ± 0.06 derived from the benzophenone data of Figure 5.

Table II. Quantum Yields of the Benzophenone (B) Triplet-Sensitized Formation of the Colored Form of the Spiropyran (Sp) at 366 nm in Acetonitrile at 24°

[B] × 10^3, *M*	[Sp] × 10^3, *M*	$\Phi_{\text{dye, sens}}$
1.0	0.10	0.29
2.0	0.10	0.26
2.4	0.10	0.30
3.0	0.10	0.30
4.0	0.10	0.31
6.0	0.10	0.28
8.0	0.10	0.31
1.65	0.21	0.34
3.3	0.21	0.37
6.6	0.21	0.34
13.3	0.21	0.34
4.0	0.40	0.40
6.0	0.40	0.39

Phosphorescence spectra of the colorless I and the colored forms II of the spiropyran were determined on a Turner absolute spectrofluorimeter (Model 210) using an EPA matrix at 77 °K. No emission from I was observable in acetonitrile at 24°. Because of the conversion of I to II, measurements of fluorescence or phosphorescence with this system are very difficult. The time dependence of the intensity of the phosphorescence bands gave indication of the source of these bands. Bands centered at approximately 535 and 490 nm appeared to originate from the spiropyran I since these bands become less intense as the colored form II is built up. The maximum band in the emission of the colored species II is centered at 606 nm. If the shortest wavelength band in the phosphorescence of I is the 0–0 band, then the energy of the triplet of the spiropyran I above the ground state is about 58 kcal/mol. This is a reasonable check on the 53–57 kcal/mol estimate made by triplet energy transfer experiments described in the Discussion section of this work.

Discussion

The present data can be rationalized well in terms of the following reaction mechanism

$$\text{Sp} + h\nu \longrightarrow \text{Sp(S}_1) \qquad \text{(I)}$$

$$\text{Sp(S}_1) \longrightarrow \text{dye} \qquad \text{(1)}$$

$$\mathrm{Sp(S_1)} \longrightarrow \mathrm{Sp(T_1)} \tag{2}$$

$$\longrightarrow \mathrm{Sp} \tag{3}$$

$$\mathrm{Sp(T_1)} \longrightarrow \mathrm{dye} \tag{4}$$

$$\longrightarrow \mathrm{Sp} \tag{5}$$

$$\mathrm{B} + h\nu \longrightarrow \mathrm{B(S_1)} \tag{6}$$

$$\mathrm{B(S_1)} \longrightarrow \mathrm{B(T_1)} \tag{7}$$

$$\mathrm{B(T_1)} \longrightarrow \mathrm{B} \tag{8}$$

$$\mathrm{B(T_1)} + \mathrm{Sp} \longrightarrow \mathrm{B} + \mathrm{Sp(T_1)} \tag{9}$$

$$\mathrm{Sp(T_1)} + \mathrm{Q} \longrightarrow \mathrm{Sp} + \mathrm{Q(T_1)} \tag{10}$$

$$\mathrm{Sp(S_1)} + \mathrm{Q} \longrightarrow \mathrm{Sp} + \mathrm{Q(S_1)} \tag{11}$$

$$\mathrm{dye} \longrightarrow \mathrm{Sp} \tag{12}$$

$$\mathrm{B(T_1)} + \mathrm{dye} \longrightarrow \mathrm{dye(T_1)} + \mathrm{B} \tag{13}$$

$$\mathrm{dye(T_1)} \longrightarrow \mathrm{Sp} \tag{14}$$

$$\longrightarrow \mathrm{dye} \tag{15}$$

where Sp represents a molecule of the colorless form of the spiropyran I, dye indicates a molecule among the equilibrated mixture of colored product molecules II, B is a benzophenone or other molecule which acts as a triplet sensitizer, Q is a quencher molecule, and S_1 and T_1 represent electronically excited singlet and triplet states, respectively. In view of the recent spectroscopic study of Tyer and Becker,[41b] who used the 6′-nitro derivative analogous to I, the S_1 and T_1 states excited in I at 366 nm may be the lowest $n \rightarrow \pi^*$ excited states of the chromene half of the molecule.

The Direct Photolysis of the Spiropyran I. The quantum yields of formation of the colored product dye molecules II, Table I, are seen to be independent of the spiropyran concentration. From the average value of Φ_{dye} we can estimate $\phi_1 + \phi_4 = 0.107 \pm 0.013$[50] at 366 nm in acetonitrile solutions (2–52°). This estimate is about a factor of 3 lower than that reported by Bowman, Fox, Kresch, and Taylor[34] using ethanol solutions, and a factor of 5 or 6 lower than the value they observed in toluene or dioxane solutions. It is not clear what the influence of the different solvents is on Φ_{dye}. Since the quantum yield of sensitized color formation in I is found to be 0.43 ± 0.06 in this work (see the following section), the solvent-impurity quenching in this work cannot account for more than a possible factor of 2 suppression of the quantum yields reported here. Fluorescence and phosphorescence of electronically excited spiropyran I are negligible from 2–52°, so $\phi_3 + \phi_5 = 0.89 \pm 0.01$ in the direct photolysis. One cannot rule out the possibility of a rapid re-formation of I from the transient molecule of structure IIa; the number $\phi_3 + \phi_5$ may be an artifact of the time scale used in these experiments (see the discussion of this point in the summary).

Triplet-Sensitized Formation of the Colored Product Dye II. The data of Table II confirm the previous observation that a very effective sensitization of the colored product II occurs with benzophenone.[29,42,43] From the present quantitative rate data we can test the proposed reaction scheme and estimate the relative quantum efficiency of primary processes 4 and 5. From a steady-state treatment of the reaction scheme the quantum yield of sensitized colored product formation (Φ_{sens}) should be given by

$$\frac{1}{\Phi_{\mathrm{sens}}} = \frac{k_4 + k_5}{k_4} + \frac{(k_4 + k_5)k_8}{k_4 k_9[\mathrm{Sp}]} \tag{16}$$

Note from this relation that Φ_{sens} should be independent of the sensitizer concentration. The data of Table II show that this is the case. Relation 16 suggests further that $1/\Phi_{\mathrm{sens}}$ should be a linear function of $1/[\mathrm{Sp}]$. The data of Table II, plotted in Figure 5, follow the expected linear relation within the experimental error. From the least-squares fit of the data of Figure 5, we estimate

$$(\text{intercept})_{\text{Figure 5}} = (k_4 + k_5)/k_4 = 2.3 \pm 0.3$$

$$(\text{slope})_{\text{Figure 5}} = (k_4 + k_5)k_8/k_4k_9 = (1.2 \pm 0.3) \times 10^{-4}\,M$$

$$\left(\frac{\text{intercept}}{\text{slope}}\right)_{\text{Figure 5}} = k_9/k_8 = (1.9 \pm 0.5) \times 10^{4}\ \text{l./mol}$$

The value of k_8 is probably near to that estimated for this quantity for benzene solutions at 20° by Bäckström and Sandros,[51] $k_8 \cong 5.3 \times 10^5\ \mathrm{sec}^{-1}$. Accepting this, our data give $k_9 = 1.0 \pm 0.3 \times 10^{10}$ l./(mol sec). Thus k_9 is near to the value expected for a rate constant for a diffusion-controlled reaction between reactants; in acetonitrile at 24°, $k_{\mathrm{diff}} \cong 1.9 \times 10^{10}$ l./(mol sec).

From the value of the intercept of the function plotted in Figure 5 one can derive the estimate, $\phi_5/\phi_4 = 1.3 \pm 0.3$. The maximum benzophenone triplet-sensitized quantum yield of color formation from excited triplet spiropyran 1 is considerable less than unity; $\Phi_{\mathrm{sens}} = 0.43 \pm 0.06$. The previous qualitative studies of the unsubstituted spiropyran in methylcyclohexane-2-methylpentane at −100° gave a value near unity.[29] Our results with 2-acetonaphthone as sensitizer are in accord with those we found for benzophenone, although the results are much less reliable. Extrapolation of the acetonaphthone data to the condition of complete triplet energy transfer gives $\Phi_{\mathrm{sens}} \cong 0.46$, in reasonable agreement with the more reliable value from benzophenone.

The Photolysis of the Spiropyran I in the Presence of Quencher Molecules. The molecules benzophenone and 2-acetonaphthone, with triplet energies of 69 and 60 kcal/mol, respectively, sensitize effectively the color formation in the spiropyran I, so the triplet energy of the spiropyran must lie lower than 60 kcal. Previous attempts to quench the color formation in the direct photolysis of the spiropyrans have failed.[43,29] However, we employed sensitizers of decreasing triplet energy in an attempt to locate the triplet level in the spiropyran. Indeed quenching was observed with certain compounds. Benzil, with $E_{\mathrm{T}_1} \cong 57$ kcal/mol, showed no sensitization but a slight inhibition of the color formation (see the data of Table III). 9-Fluorenone, with $E_{\mathrm{T}_1} = 53$ kcal/mol, showed an effective quenching of a fraction of the colored product II in the direct photolysis of the spiropyran I. The energy levels of the excited singlet states are such that quenching of the excited singlet spiropyran I by fluorenone and by benzil may occur here as well (see Table IV). In the fluorenone case, reactions I, 1–5, 10, and 11 of the reaction mechanism should apply. A steady-state treatment of these reactions predicts the depen-

---

(50) The error limits shown throughout this work are the 95% confidence limits (twice the standard deviation) as estimated by standard statistical methods (least squares, etc.).

(51) H. L. J. Bäckström and L. Sandros, *Acta Chem. Scand.*, 14, 48 (1960).

Table III. Quantum Yields of the Colored Form of the Spiropyran (Sp) at 366 nm in Acetonitrile at 24° with Added Quencher Molecules (Q)[a]

$[Q] \times 10^3$, *M*	$\Phi_{\text{dye,quench}}$
(a) Q = Benzil	
0.00	0.109
0.50	0.097
2.00	0.090
5.00	0.084
(b) Q = 9-Fluorenone	
0.00	0.109
0.010	0.106
0.030	0.106
0.050	0.099
0.10	0.084
0.25	0.079
0.50	0.077
0.75	0.071
1.00	0.067
1.50	0.060
2.00	0.057

[a] $[\text{Sp}] = 5.1 \times 10^{-4}$ *M*.

Table IV. Approximate Energy Separations (kcal/mol) of the Excited Singlet (S_1), Triplet (T_1), and Ground-State (S_0) Molecules and the Quantum Yields of Intersystem Crossing (Φ_{ISC}) for Compounds Studied in this Work

Compound	$E_{S_1} - E_{S_0}$[a]	$E_{T_1} - E_{S_0}$	Φ_{ISC}
Benzophenone	74	69[b]	0.99[c]
2-Acetonaphthone	78	60[b]	0.84[c]
Benzil	65	57[b]	0.92[c]
9-Fluorenone	63	53[b]	0.93[c]
Spiropyran (I)	66	58 53-57	0.048

[a] These are very approximate values derived from the absorption spectra of the given compound in acetonitrile; the energy at the long wavelength limit of the absorption at ϵ 5 was chosen arbitrarily. [b] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537(1964). [c] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

dence of Φ_{dye} on quencher concentration [Q] given by

$$\frac{1}{\Phi_{\text{dye}}} = \frac{(k_1 + k_2 + k_3 + k_{11}[Q])(k_4 + k_5 + k_{10}[Q])}{k_1k_4 + k_1k_5 + k_2k_4 + k_1k_{10}[Q]} \qquad (17)$$

In Figure 6 a plot of $1/\Phi_{\text{dye}}$ *vs.* [Q] is shown for data from the upper concentration range of the quencher. There are two distinctive regions of quenching. We shall interpret the effective quenching at low quencher concentrations as due to a triplet quenching reaction. At higher [Q] values the quenching is less sensitive to [Q]. For these conditions the following inequalities hold: $k_{10}[Q] > k_4 + k_5$ and $k_1k_{10}[Q] > k_1k_4 + k_1k_5 + k_2k_4$, and relation 17 reduces to

$$\frac{1}{\Phi_{\text{dye}}} = \frac{k_1 + k_2 + k_3}{k_1} + \frac{k_{11}[Q]}{k_1} \qquad (18)$$

Extrapolation of the linear portion of the data for 9-fluorenone in Figure 6 gives

$$(\text{intercept})_{\text{Figure 6}} = (k_1 + k_2 + k_3)/k_1 = 11.8 \pm 0.4$$

$$(\text{slope})_{\text{Figure 6}} = k_{11}/k_1 = (3.0 \pm 0.3) \times 10^3\ M^{-1}$$

From the reciprocal of the intercept we estimate $\phi_1 = 0.086 \pm 0.003$. From the ratio of slope to intercept we find $k_{11}/(k_1 + k_2 + k_3) = 2.5 \pm 0.3 \times 10^2\ M^{-1}$. If the rate constant for the singlet energy transfer step 11 is of the order of 10^{11} l./(mol sec), as seems probable, then the data suggest that the lifetime of the excited singlet I is less than about 10^{-8} sec. Since the Sp(S_1) state excited in these experiments may be an n → π^* state for which the radiative lifetime may be quite long ($\sim 10^{-5}$ sec), it is not surprising that the fluorescence of this state is not detectable in our experiments.

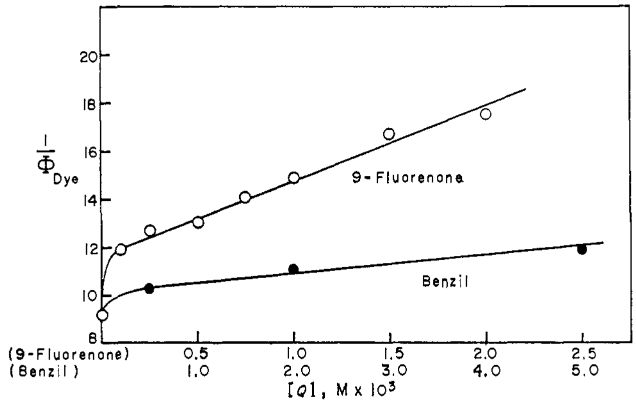


Figure 6. The quenching of the formation of the colored product II at high quencher concentrations; plot of the reciprocal of the quantum yield of colored product *vs.* quencher concentration in the 9-fluorenone- and benzil-quenched 366-nm photolysis of the spiropyran I in acetonitrile at 24°.

For the experiments at low added quencher concentrations, where singlet quenching is unimportant, function 17 reduces to

$$\frac{1}{\Phi_{\text{dye}} - \phi_1} = \frac{(k_1 + k_2 + k_3)(k_4 + k_5 + k_{10}[Q])}{k_4k_2} \qquad (19)$$

As derived above, $\phi_1 = 0.086$. The method of measurement of Φ_{dye} employed here is not sufficiently precise to allow an accurate test of function 19. However, data from the low [Q] experiments are not inconsistent with this function. A plot of the function $1/(\Phi_{\text{dye}} - \phi_1)$ *vs.* [Q] gives the slope-to-intercept ratio, $k_{10}/(k_4 + k_5) = (6.2 \pm 4.4) \times 10^5/(41 \pm 13) = (1.5 \pm 1.2) \times 10^4\ M^{-1}$. If the rate of the quenching reaction 10 is diffusion controlled ($k_{10} = 1.9 \times 10^{10}$ l./(mol sec)), then the data suggest $k_4 + k_5 = (1.3 \pm 1.0) \times 10^6$ sec^{-1}. Thus the lifetime of the triplet spiropyran I in the absence of intentionally added quencher is estimated to be $(0.8 \pm 0.6) \times 10^{-6}$ sec. This lifetime is approximately a factor of 60 smaller than the lifetime observed for the triplet of the analog of I without chlorine atom substitution; direct triplet-triplet absorption following flash excitation[48a] gave $\tau = 4.5 \times 10^{-5}$ sec for the unchlorinated analog of I in toluene solution near room temperature. Conceivably the heavy chlorine atom perturbation of the spin-orbit coupling in I may account for this difference,[52] although there is some uncertainty as to the theoretically expected influence of heavy atoms on the lifetimes of excited n → π^* triplet states.[53]

---

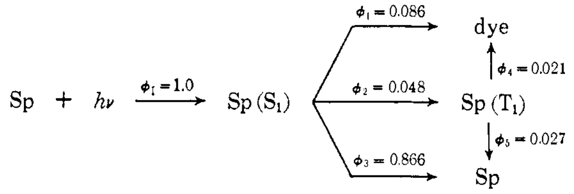
(52) D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949).

(53) For example, see S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969, p 276.

We have presented in this work the first definitive evidence that both triplet and singlet states are involved in the color-forming reaction. From the triplet energies of the sensitizers and quenchers of the spiropyran color formation it can be concluded that the energy of the spiropyran I triplet state is about 53–57 kcal/mol if there is no activation energy for reaction 4. The shortest wavelength band of the phosphorescence of Sp(T_1) in EPA at 77°K corresponds to 58 kcal/mol so that $E_4 \cong 0$.

The falloff in the rate of dye formation with time, observed in all rate experiments (see Figures 1–4), can be rationalized in terms of the several factors which must contribute: the depletion of Sp as the run progresses; light absorption by the product dye molecules and photobleaching of the dye; thermal fading of the dye by reaction 12 at long exposures; and a quenching of excited Sp and/or B species by the colored dye product by reactions 10, 11, 13, and 14. It is not possible to sort out the extent of each reaction from the data at hand, but the kinetics of the falloff of the rate with time fits the form expected from these probable reactions.

Summary of the Primary Quantum Yields in the Photolysis of the Spiropyran I in Acetonitrile Solutions. The quantum efficiencies for each of the reactions of the excited spiropyran molecule I in the direct photolysis at 366 nm in acetonitrile can be estimated from the work which has been described.



The results obtained in this work show that the dominant reaction leading to the colored dye product II in the direct photolysis of the spiropyran I in acetonitrile at 24° involves the singlet excited state. The triplet accounts for only about 20% of the color formation for these conditions. Triplet excited states formed directly by energy transfer form colored product only 43% of the time. The inefficiency of the chemical change in the direct photolysis (89% of the excited Sp is unchanged) and the triplet-sensitized photolysis (57% unchanged) may be due in part to impurity quenching in the "pure" solvent. It may be also an artifact of the time scale employed in these measurements. Cleavage of the carbon–oxygen bond on the spiro-carbon atom may occur with considerably higher efficiency than that observed as the net reaction, but a large fraction of the initially formed product dye molecules may be favorably disposed for rapid re-formation of I in a structure such as IIa. If this is the case then it is somewhat surprising that the Φ_{dye} is independent of temperature over the range 2–52°. It is possible that a direct internal conversion of the excited singlet to a vibrationally excited singlet ground state ($S_1 \rightsquigarrow S_0^v$) accounts for the inefficiency in the singlet color formation reaction; however, this mode of energy dissipation has been considered to be unimportant in the photolysis of many organic molecules in solution.[54] It is an interesting but unexplained result that the triplet excited state, once populated, is more efficient in color formation than the excited singlet state.

The spiropyran molecule I appears to offer a unique probe for the study of heavy atom effects on rates of intersystem crossing. Our studies are continuing with the determination of the effect on ϕ_2 and ϕ_5 of heavy atoms in the solvent and as substituents in the spiropyran molecule.

Acknowledgment. The authors gratefully acknowledge the gift of the photochromic compounds used in this work, and the helpful discussions with Drs. Helmut Schwab, Alan Kresch, Richard Fox, Richard Bowman, Robert Bertelson, and others of the Materials Research Division of the National Cash Register Company, Dayton, Ohio. We also thank Dr. T. Navaneeth Rao for his help with calculations and the determination of the phosphorescence spectra, Dr. David H. Slater for useful discussions and calculations related to this work, and Professor Ralph Becker for access to preprints of his unpublished work.

---

(54) For example, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 4.