

SYDNONES AND THEIR PHOTOCHROMIC PROPERTIES

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Properties of some photochromic sydnones have been described. A model of photochromic behaviour is discussed using measurements of optical absorption, photochromism kinetics, photoconductivity and EPR absorption.

Photochromic properties of organic compounds are now widely studied because of the possibilities of their application. A number of organic compounds are known which possess pronounced photochromic properties, including heterolytic and homolytic bond cleavage, *cis-trans* isomerization, tautomerism *etc.*, or in other words, predominantly processes of molecular nature. A special position among these compounds has been held by 3-(3-pyridyl)sydnone, for which it has been assumed up to the recent times that its photochromism is due to the formation of colour centres^{1,2}, similarly to alkali halides.

The photochromic properties of 3-(3-pyridyl)sydnone in the solid state were first observed by Tien and Hunsberger³. After irradiation with UV light the crystals of 3-(3-pyridyl)sydnone turned blue. The change was reversible: bleaching could be achieved either by irradiation with visible or infrared radiation, or thermally. The primary induced change in colour did not exhibit any EPR absorption *in vacuo*. If air was introduced at temperatures above 323 K, the intensity of blue colour decreased, while the intensity of the EPR absorption strongly increased. Mitsui and Ehara⁴, who measured radiolysis, flash photolysis and optical absorption, rule out the existence of colour centres and assume that photochromism is due to an intermolecular charge-transfer transition. Experiments carried out by Metz, Servos and Welsh⁵ (the blue form was bleached by applying e.m.f.), and by Mill, van Roggen and Wahling¹ (a considerable increase in electric current was observed in the course of thermal bleaching of coloured crystals) do not seem convincing enough to these authors⁴. Thus, it can be said that the mechanism of photochromism of sydnones remained unexplained. The effect of substituents on the photochromism of 3-(3-pyridyl)sydnone has been studied earlier^{6,7}, but none of the derivatives prepared exhibited a reversible change in colour after irradiation with UV light. Recently, a few photochromic 4-alkenyl-3-phenyl-sydnones have been prepared^{8,9}, but their properties have not been investigated in greater detail.

Since we could not observe any effects characterizing the coloured centres of the F and F' type on 3-(3-pyridyl)sydnone prepared according to the described procedure^{10,11}, we attempted to prepare some new sydnones and to study their optical,

electrical and magnetic properties in greater detail. The results are summarized in this paper.

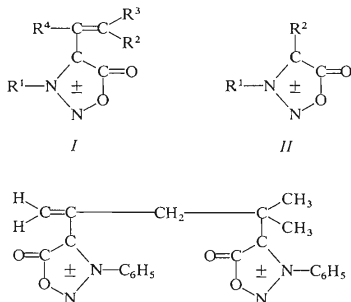
EXPERIMENTAL

The method of preparation of sydnones and their spectral characteristics have been given in our earlier paper⁹. The sydnones were purified by repeated crystallization and eventual sublimation *in vacuo* 10^{-3} Pa. Thin polycrystalline layers for optical transmission measurements were obtained by sublimation onto microscopic uviol glasses in *vacuo* 10^{-3} Pa. The absorption spectra of solutions were measured with a CF-4 Optica Milano recording photometer, spectra of thin solid layers were recorded with a Cary 14 spectrophotometer, and the kinetics of photochromism was determined by measuring the diffusion reflection with a CF-4R Optica Milano spectrophotometer. The EPR measurements were performed with a JES-3B JEOL Tokyo spectrometer. The infrared spectra were measured with a Perkin-Elmer 457 apparatus.

RESULTS

Photochromism in the Solid State

The photochromic sydnones are listed in Scheme I, their photochromic characteristics are summarized in Table I. Sydnones 4-isopropenyl-3-cyclohexylsydnone, 4-vinyl-3-phenylsydnone and its dimer were nonphotochromic.



SCHEME 1

III

A characteristic photochromic behaviour can be described as follows: immediately after irradiation with light of a wavelength shorter than λ_1 (Table I) there is a change in colour in the crystalline phase. The wavelength of the maximum of this absorption (λ_3) varies within the range $560 < \lambda_3 < 750$ nm. Compounds in which fast photo-

degradation takes place must not be irradiated with a light whose wavelength is shorter than a certain limiting λ_2 . In the case of *Ig* this fact made Greco and O'Reilly⁸ regard the sydnone as nonphotochromic. At the liquid nitrogen temperature the crystals of sydnone *Ib* and *Ig* do not become coloured when irradiated, although they are photochromic at room temperature. *Ila* and *Ilb* also do not become coloured at the liquid nitrogen temperature when irradiated, but unlike *Ib* and *Ig* an increase in temperature leads to an additional blue colouration. The photodegradation of sydnone *Ila* proceeds in a similar way: the photodegradation products are not formed in the irradiated frozen solution, but on an additional heating in the dark these products are formed without any further irradiation.

Ia: $R^1 = \text{pyridyl}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $R^4 = \text{H}$

Ib: $R^1 = \text{phenyl}$, $R^2 = \text{CH}_3$, $R^3 = \text{CH}_3$, $R^4 = \text{CH}_3$

Ic: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $R^4 = \text{CH}(\text{CH}_3)_2$

Id: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $R^4 = \text{CH}_3$

Ie: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3 = \text{CH}_3$, $R^4 = \text{CH}_3$

If: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3-R^4 = \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$

Ig: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3-R^4 = \text{CH}_2-\text{CH}_2-\text{CH}_2$

Ih: $R^1 = \text{phenyl}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $R^4 = \text{CH}_2-\text{CH}_3$

Ila: $R^1 = \text{pyridyl}$, $R^2 = \text{H}$

Ilb: $R^1 = \text{pyridyl}$, $R^2 = \text{Br}$

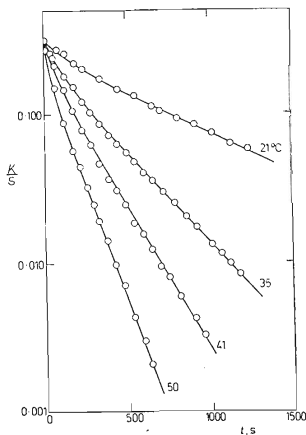


FIG. 1
Kinetics of Bleaching Process of Sydnone *Id*

The photochromic change of sydnones with the exception of *Ib* is reversible. Bleaching occurs *via* a thermal monomolecular process with a somewhat faster drop at the beginning. The characteristic course for *Id* is shown in Fig. 1. The half-time of the drop $t_{1/2}$ of the Munk-Kubelka function K/S (ref.¹²), where K is the absorption coefficient, S is the scattering coefficient, is given in Table I. "The half-time of bleaching" varies from several seconds to several thousands of seconds at room temperature depending on the type of sydnone. The rate constant is independent of the intensity of colouration of the sample, but depends on the wavelength of the colouring light: it is higher for shorter wavelengths (for *Id*: for the colouring monochromatic

TABLE I

Parameters of the Photochromism of Sydnones

Symbols are defined in the text. Samples were irradiated with colouring light, wavelength (400 ÷ 460) nm. The $t_{1/2}$ values were measured at 296 K. Column A contains data on colour change after irradiation for 20 s at liquid nitrogen temperature, column B the same data on bombarding with electrons 0.08 MeV.

Compound	λ_1 nm	λ_2 nm	λ_3 nm	$t_{1/2}^a$ s	$t_{1/2}^b$ s	E_a kJ/mol	λ_4 nm	A	B
<i>Ia</i>	450		625 ± 5	1 700	3 500	88	630	yes	yes
<i>Ib</i> ^c	410	340	640 ± 5	<5	<5		665 ± 5	no	no
<i>Ic</i>	—	—	—	—	—	—	655 ± 5	no	no
<i>Id</i>	470	—	635 ^d	650 ^d	800	50	640	yes	yes ^e
<i>Ie</i> ÷ <i>hf</i>	460	—	640				640	yes	no ^e
<i>If</i>	465	—	670 ± 10 ^g	20	25		weak	yes	no
<i>Ig</i>	460 ^h	390	670 ± 20 ^g	60 ± 10 ^d	100 ^d	84	no	no	no
<i>Ila</i>	430 ⁱ		600 ^j	5 200	6 700		no	no ^k	yes
<i>Ilb</i> ^l	470	—	560 ^m 610 675	—	—	—	no	no ^k	yes
<i>III</i>	470	—	750	<30 ⁿ	100 ^{n,p}		weak	yes	yes

^a Determined from a drop of K/S to 1/2 taking into account faster decrease at the beginning, where a deviation from the monomolecular course is observed. ^b Determined from a drop of K^0/S^0 to 1/2, where K^0/S^0 is K/S of the monomolecular course extrapolated to the beginning.

^c The compound was irradiated with "colouring" light, wavelength (300 ÷ 400) nm. ^d Measured at 294 K. ^e Blue fluorescence observed. ^f Mixture of isomers: 93% *Ie* + 7% *Ih*. ^g Estimated from reflexion spectra. ^h No colouration *in vacuo*. ⁱ Taken from ref.². ^j Ref.¹¹. ^k Additional heating in the dark leads to colouration. ^l Change in colour is irreversible. ^m Two less intensive bands with maxima at 610 nm and 675 nm are superimposed on the basic band with a maximum at 560 nm. ⁿ Measured at 283 K. ^p Monomolecular process cannot be defined.

radiation of the wavelength λ 333 nm, $k = 2 \cdot 10^{-3} \text{ s}^{-1}$, for λ 425 nm, $k = 7 \cdot 10^{-4} \text{ s}^{-1}$ at room temperature). We assume that this effect is due rather to the penetration of light into the bulk of the sample or to the diffusion of blue formations than to the process of photochromism proper. The process of thermal bleaching is thermally activated. The linear dependence $\ln k \sim T^{-1}$ was used for the determination of the activation energy, E_a , of the rate constant of bleaching, k . Its value again depends on the wavelength of the "colouring" light and increases insignificantly with increasing wavelength of light. Fast bleaching occurs if sydnone is irradiated with visible or infrared light of a wavelength longer than λ_1 .

Colour components were also formed if sydnone crystals, particularly *Ia*, *Id*, *Iib*, *III* were bombarded with electrons having an energy of 0.08 MeV. The bombarded samples exhibited an EPR signal with a g -factor ~ 2.0043 . The signal cannot be unambiguously assigned to the electrons shot into the sample, because their high energy may lead to the rupture of molecular bonds.

The photochromic fatigue of the material depends on the wavelength of the "colouring" light and on the irradiation time. There exists an optimal combination of the chosen irradiation time and the wavelength on the one hand, and of the change in light transmission and the number of cycles (*i.e.* colouration – bleaching), on the other. In addition, the fatigue strongly depends on the concrete molecular structure of the compound. Among the sydnones under investigation there were several compounds (*e.g.* *Ib*, *Id*, *If*, *III*) for which photochromic changes could still be observed after several tens of cycles, while for other compounds (*e.g.*, *Ig*) the number of these steps was very low. The number of photochromic reversible changes depends on the method of preparation and above all on the purity of the compound. The quantum yield of the colouration process decreased with increasing number of cycles; at the same time, yellow-brown degradation products were formed, all of them insoluble in acetone.

The colour change of *Iib* is not reversible. After irradiation with visible or UV light with a wavelength shorter than 470 nm the compound turns blue. Colouration also takes place if the compound is bombarded with electrons of an energy of 0.08 MeV. In the absorption spectra of the blue form we observe a band with a maximum at 560 nm, on which two less intensive bands are superimposed with maxima at λ_2 610 nm and λ_3 675 nm. The bleaching of the blue form can be carried out neither optically, *i.e.* by irradiation with visible or infrared light, nor thermally without degradation of the compound. Complete bleaching occurs if the compound is dissolved. The infrared spectra of the colourless and coloured form of sydnone *Iib* in KBr discs did not differ either in the frequencies or in the intensities of the individual bands (the coloured form was obtained by irradiation with UV light of a wavelength of 400 – 460 nm for 15 min with simultaneous grinding and stirring of the sample). Similarly, the infrared spectrum of the colourless form obtained by dissolving

the coloured form in acetone and evaporation of the solvent was identical with that of the colourless form before irradiation.

Photochromism in Organic Solid Solutions

Interesting results were obtained by measuring the optical absorption of sydnone in organic glasses at low temperatures after irradiation with UV light. This is a qualitatively different effect in the photochromism of the sydnones, so far unknown. Unlike a number of authors^{1,2,5,6}, we found that solid solutions of some sydnones were photochromic, be it frozen solutions in ethanol, methylpentane, an EPA mixture (ether-isopentane-ethyl alcohol 8 : 3 : 5) or solid solutions in polymers (*e.g.*, of poly(glycol methacrylate)) at liquid nitrogen temperature. This property was not observed with sydnones *Ig*, *Ila*, *Ilb*, which are photochromic in the solid state, but it was observed also with *Ic* which is nonphotochromic in the solid state. The wavelengths of the maxima of these absorption bands, λ_4 , are given in Table I. The character of the surrounding medium (*e.g.*, the polarity of the solvent) does not affect the position of the maximum too much. The ability to produce a reversible change in colour is not reduced even in the presence of a minor amount of acid. The coloured form can be bleached similarly to crystals by irradiation with visible or infrared light. Bleaching also takes place at the moment when the organic glass begins to soften or in the case of polymer solutions at a temperature higher than that of the liquid nitrogen. No paramagnetism of coloured solutions has been observed at low temperatures.

EPR Absorption

Let us now briefly mention the magnetic properties of sydnones, with *Id* as the representative. The EPR absorption of sydnone *Ila* described earlier² has a character completely different from the other sydnones studied by us (*e.g.*, *Id*).

Simultaneously with the formation of coloured products of sydnone in the air a weak EPR absorption is formed, consisting of a singlet line having the width ~ 14 G, $g = 2.004$. In *vacuo* 10^{-3} Pa (the sample was evacuated two hours and heated to 323 K before measurement) neither the colourless nor the coloured form exhibited the EPR absorption within the temperature range (133 \div 293) K. If air is admitted, the material after some time becomes "EPR active" on irradiation. The signal intensity depends on the duration and intensity of irradiation, but after a certain irradiation dose saturation is reached. The EPR absorption is irreversible at room temperatures and lower. Optical bleaching of the sample does not affect the signal intensity to any considerable degree either. An essential drop in the EPR absorption occurs only at elevated temperatures. Thus, it can be said that the EPR absorption is not directly related to the formation of coloured products, but only accompanies

the process. Since the EPR absorption appears only in the presence of oxygen, we assume that what is involved here are degradation radical products of the oxidation character. On the other hand, however, a purely physical mechanism of their formation cannot be ruled out, such as *e.g.* interaction of the excited state with the paramagnetic O₂ molecule.

DISCUSSION

Only a few of the wide assembly of sydnone derivatives so far in existence¹³ possess photochromic properties. The presence alone of a sydnone mesoionic ring is not a sufficient condition of photochromism in such systems. The photochromic behaviour of sydnones is very varied, and the nature of photochromism seems to depend on a number of other factors. Let us now summarize in brief the properties of sydnones under study: Sydnone (*IIa*) is photochromic at room temperatures only, but not at low temperatures, it possesses an "optical memory" reflected in the colouration of a sample heated in the dark after preceding irradiation at low temperature; it also possesses a "magnetic memory" which is characterized by an increase in the EPR signal on admission of air, if the sample had been preirradiated *in vacuo*. *Id* and *III* are photochromic both *in vacuo* and in the air at liquid nitrogen temperature and room temperature in the solid state and solid solutions at low temperatures. Sydnone *Ib* is photochromic at room temperature, but not at low temperatures. It is also photochromic in solid solutions. Its isomer *Ic*, which differs only in the position of the double bond on the carbon atom of the isopropenyl group, is nonphotochromic in the solid state, but strongly photochromic in frozen solutions at low temperatures. Sydnones *Ia*, *Ie* and *If* behave similarly to sydnone *Id*. Sydnone *Ig* is photochromic at room temperature in the air, but not *in vacuo*, and nonphotochromic at low temperatures both in the solid state and in solutions. Sydnone *Iib* has an exceptional position owing to its irreversible colour change.

According to Baker's hybrid theory¹⁴, it may be expected that the nitrogen substituted atom in the sydnone ring carries a large fractional positive charge, balanced by a corresponding negative charge located on the oxygen atom of the carboxylic group, even if the localization is only diffuse. The stabilization of the sydnone ring requires substitution in the ring. If metastable excited states greatly affect the electron structure of the molecule, a change in colour may take place. The surroundings of the molecule or the crystal lattice in the solid state can also strongly participate in the process. The effect of the forces of the crystal lattice may considerably influence the inter-ring resonance structure, which in turn may lead to the formation of coloured products in the solid state. An important role may be played by the steric inhibition of resonance. Photochromism in the solid state will in this case greatly depend on the concrete crystal structure. Judging by the properties of frozen solutions, it seems that photochromism will be primarily of molecular nature. The original assumptions

concerning the photochromism of sydnone and based on the existence of the F and F' colour centres, similarly to alkali halides, seem unlikely with respect to the results described above.

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REFERENCES

1. Mill T., Van Roggen A., Wahling C. F.: *J. Chem. Phys.* 35, 1139 (1961).
2. Gutowsky H. S., Rutledge R. L., Hunsberger I. M.: *J. Chem. Phys.* 29, 1183 (1958).
3. Tien J. M., Hunsberger I. M.: *J. Amer. Chem. Soc.* 77, 6604 (1955).
4. Mitsui A., Ehara N.: *Bull. Soc. Chem. Jap.* 46, 327 (1973).
5. Metz F. I., Servoss W. C., Welsh F. E.: *J. Phys. Chem.* 66, 2446 (1962).
6. Ohta M., Masaki M.: *Bull. Chem. Soc. Jap.* 33, 649 (1960).
7. Greco C. V., Hunsberger I. M.: *J. Heterocycl. Chem.* 7, 761 (1970).
8. Greco C. V., O'Reilly B. P.: *J. Heterocycl. Chem.* 9, 207 (1972).
9. Šorm M., Nešpůrek S.: *This Journal* 40, 3459 (1975).
10. Masaki M., Ohta M.: *Bull. Chem. Soc. Jap.* 33, 649 (1960).
11. Brown G. H.: *Photochromism*, p. 364. Wiley, New York—London—Sydney—Toronto 1971.
12. Kortym G.: *Reflexionsspektroskopie*. Springer, Berlin 1969.
13. Snyder J. P.: *Nonbenzoid Aromatics*, Vol. I. New York—London 1969.
14. Backer W., Ollis W. D., Poole V. D.: *J. Chem. Soc.* 1949, 307.

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