Notes to the Editor

Effect of polystyrene matrix on decolouration reaction of coloured spiropyran

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INTRODUCTION

The effect of a polymer matrix of the photochromism of 6'-chloro-8'-nitro- and 6'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzospiropyran was studied by Gardlund[1]. He reported that kinetics of the coloured to colourless transformation of the spiropyran in poly(methyl methacrylate) film at 300K could be resolved into two simultaneous first order reactions. However, more complex kinetics were observed in our study of the decolouration of the coloured 1,3,3-trimethylindolinonaphthospiropyran in polystyrene matrix. The kinetics of the decolouration were found to be markedly affected by irradiation time. In this paper we report the results of our study on the photochromism of the naphthospiropyran in polystyrene matrix.
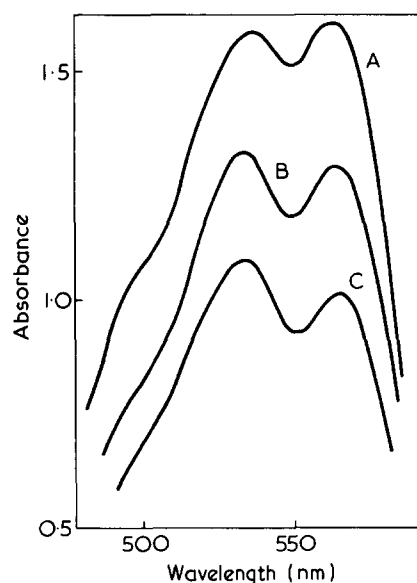

Figure 1 Change in the visible absorption spectrum of the coloured naphthospiropyran with irradiation time at 201K; naphthospiropyran content, 0.5%. A, 300 sec; B, 60 sec; C, 30 sec

RESULTS AND DISCUSSION

The visible absorption spectra of coloured naphthospiropyran in polystyrene matrix showed two absorption maxima at 535 and 565 nm as shown in Figure 1. The relative absorption at the longer wavelength increased with increasing irradiation time. The visible absorption spectra of the naphthospiropyran in solution are affected by the polarity of the solvent[2]. In an alcoholic solution the peak at the longer wavelength is higher than that at the shorter wavelength. In non-polar solvents the peak at the shorter wavelength is higher. These phenomena were interpreted by Fischer and coworkers as follows[2]: there are several isomers of coloured naphthospiropyran, and the relative amounts of these isomers depend on the nature of the solvent as well as on the temperature. The visible spectra, shown in Figure 1, indicate that the relative amounts of the coloured isomers in polystyrene matrix are also affected by irradiation time.

Plotting the disappearance of the absorption maximum at 565 nm in the dark against time gives the results illustrated in Figure 2. The data have been plotted as a first order reaction with the absorbance observed. With a short irradiation time, i.e. 5 sec, the absorbance decreased very rapidly, and the kinetics could be resolved into two simultaneous first order reactions, one faster and the other slower. With increasing irradiation time, another decolouration reaction of the slowest rate appeared, and the kinetics could be considered to be a superposition of three first order reactions. When the irradiation time was increased to 240 sec, the first order reaction of the fastest rate disappeared, and the kinetics became a superposition of the two slower first order reactions. Irradiation over 240 sec did not give further change in
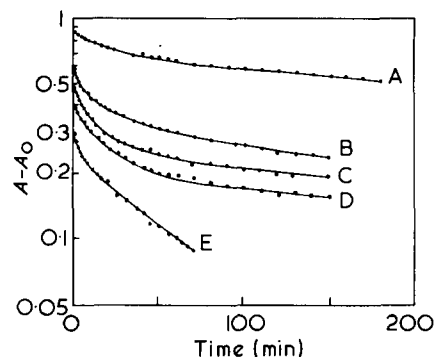
Figure 2 Decreases in the absorption maximum at 565 nm for the coloured naphthospiropyran irradiated for different times at 211K; A, absorbance; A_0, absorbance before irradiation; naphthospiropyran content, 0.2%. A, 240 sec; B, 120 sec; C, 60 sec; D, 30 sec; E, 5 sec
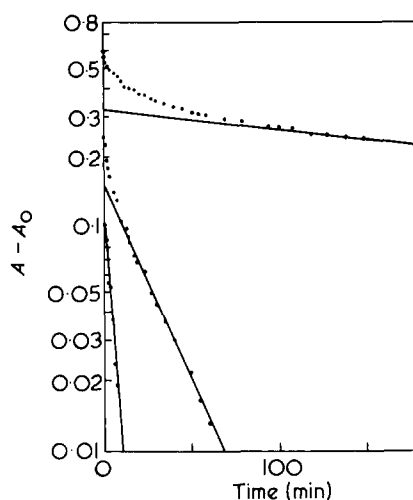
Figure 3 First order rate plots for the decolouration of the coloured naphthospiropyran at 211K: irradiation time, 120 sec

the decolouration curve.

Figure 3 illustrates how the decolouration is resolved into three separate first order reactions. The rate constants observed were shown in Table 1. We designate the rate constants of the fastest, the intermediate and the slowest reactions as k_α, k_β and k_γ, respectively. Similar values for k_α, k_β and k_γ were observed as seen in the Table. However, the value obtained from the sample of 5 sec irra-

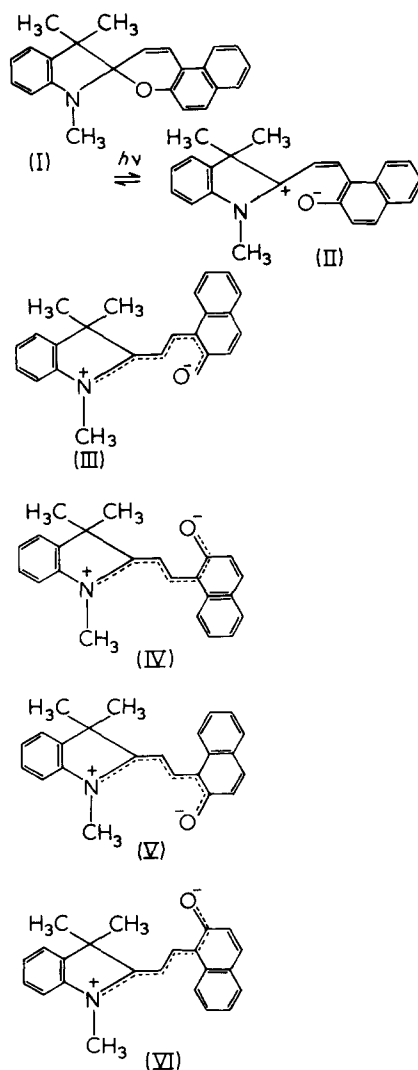*Table 1* First order rate constants of de-colouration at 211K

Irradiation time (sec)	Rate constants $(\times 10^{-4}\ sec^{-1})$		
	k_α	k_β	k_γ
5	28	2.1	—
30	20	6.7	0.25
60	29	6.1	0.26
120	37	6.7	0.36
240	—	9.7	0.26

diation was lower and that obtained from the 260 sec irradiation higher than those of the other samples. This discrepancy must come from the fact that either k_α or k_γ is neglected for these samples. The values for k_β so obtained indicate that all three reactions, in fact, occur simultaneously for these samples.

The effect of the irradiation time might be considered by formation of stable dimeric coloured forms due to increase of the concentration of monomeric coloured forms. *Figure 4* shows decolouration curves of two samples; one was irradiated with a high intensity u.v. light for short time and the other with a low intensity u.v. light for long time, but both samples showed the same absorbance at 565 nm. As can be seen from this Figure, the irradiation times have a predominant effect on the kinetics of decolouration rather than the concentration of coloured forms. Therefore, the phenomenon in *Figure 2* is not responsible for the formation of stable dimeric coloured forms.

Ultra-violet irradiation causes cleavage of the carbon—oxygen bond of the spiropyran linkage, and the resulting unstable intermediate (II) then undergoes a series of rearrangements involving the methine bridge and leading to coloured forms. Probable structures

Figure 4 Decreases in the absorption maximum at 565 nm for the coloured naphthospiropyran: A, irradiation with a high intensity u.v. light for 5 sec; B, irradiation with a low intensity u.v. light for 23 min; A, absorbance; A_0, absorbance before irradiation; naphthospiropyran content, 0.2%

of the isomeric coloured forms were estimated to be III, IV, V and VI[2].

In a rigid polymer matrix the rate of ring closure will be slower because of restriction of rotation within the coloured forms. Due to these restrictions, the isomeric coloured forms may experience varying degrees of difficulty in achieving the necessary conformation for ring closure. Thus they may have different life times. *Figure 5* illustrates the formation and decaying scheme of three isomeric coloured forms of the naphthospiropyran in polystyrene matrix. S denotes the naphthospiropyran; M_α, M_β and M_γ, isomeric coloured forms whose life times increase in this order; and X, an intermediate. Since the transformation of X to S is assumed to be very rapid compared with that of M to X, the rate-determining step of the decay process of the coloured species is the transformation of M to X. If k_α', k_β' and k_γ' decrease in this order, M_α and M_β are predominantly produced, and their decay at relative faster rates (k_α and k_β) is observed. With increasing
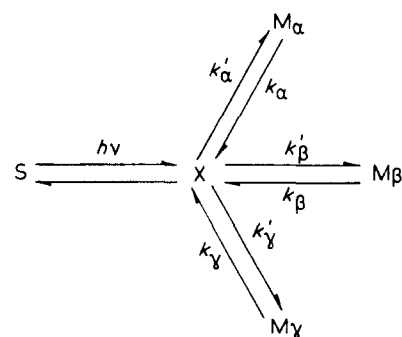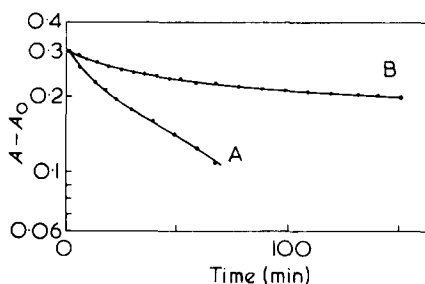
Figure 5

irradiation time, M_γ, the longest lifetime species, accumulates, and simultaneous decays of M_α, M_β and M_γ are observed. When the irradiation time is extended over ~240 sec the steady state is reached. M_α, the shortest life time species, decreases to negligible concentration, and M_γ plays the main role in the decolouration.

EXPERIMENTAL

1,3,3-Trimethylindolinonaphthospiropyran was prepared by the method reported by Fischer and coworkers[3], and recrystallized from ligroin twice, m.p. $182^\circ-183^\circ C$. Polystyrene, product from Mitsubishi Monsanto Co., was purified by reprecipitation from toluene solution into methanol, and dried *in vacuo*; $\bar{M}_v{}^4$, 1.93×10^5. A benzene solution containing the naphthospiropyran and the polystyrene was poured on a surface of a purified mercury, and solvent evaporated. The film thus obtained was dried *in vacuo* for 48 h to remove traces of solvent from the film. The thickness of the film was 0.2 mm. The film was set on an inner surface of an optical quartz cell, which was filled with n-hexane. The optical cell was placed in a Dewar vessel having optical windows. The vessel was filled with methanol, which was regulated to constant temperature within $\pm 1^\circ C$. The film was irradiated with u.v. from a 500 W ultra-high pressure mercury lamp through the window of the Dewar vessel. Kinetic runs were measured in the dark with a Hitachi 139 type spectrophotometer.

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