Investigation of the chelation of a photochromic spiropyran with Cu(II)

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Abstract

The formation of a Cu(II) chelate from a photochromic spiropyran in acetone in the dark and the decolouration of its coloured form and the Cu(II) chelate in tetrahydrofuran (THF) after UV irradiation were studied by UV–visible absorption spectroscopy. The results indicate that the rate-determining step of chelate formation in acetone is the formation of the coloured form. The concentration of metal ions has no effect. In THF after UV irradiation, the coloured form and its Cu(II) chelate are in equilibrium during thermal decolouration, with an equilibrium constant K of 8.9×10^4 l mol^{-1}. The decolouration rate constants of the coloured form and its Cu(II) chelate are 1.57×10^{-2} s^{-1} and 5.7×10^{-4} s^{-1} respectively. From electron spin resonance (ESR) spectra of the chelate in acetone at 77 K, the structure of the chelate is square or square pyramidal.

Keywords: Chelation; Photochromism; Spiropyran; Electron spin resonance

1. Introduction

The photochromic phenomenon involves a reversible change of a single chemical species between two states having different absorption spectra, where the change is induced in at least one direction by the action of electromagnetic radiation [1]. Photochromic compounds are of interest due to their applications in various fields, such as non-silver high-resolution photography, optical devices and variable transmission materials and photovoltaic and holographic systems. The spiropyrans are an important class of photochromic materials; their photochromic reactions are accompanied by intramolecular pericyclic reactions [2].
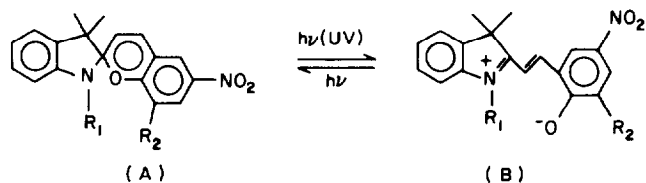
The transformation between the closed form (SP) and the open photomerocyanine form (PC) results in a colour change. However, the stability of the open coloured form is particularly important in certain applications. Thus three methods have been proposed to enhance the stability of the coloured form: (a) modify the structure of the compound (e.g. introduce suitable substituents in appropriate positions, etc.) [3]; (b) select a suitable medium (e.g. polymeric matrix) which is unfavourable for the decolouration process; (c) introduce a suitable coordinate group in the ortho position or other adjacent position to the O atom of pyran in order to form a bidentate group with the phenolate anion of the coloured form which can be chelated with a metal cation to stabilize the coloured form. Many investigations on the coordination of spiropyran have been published in recent years, but the decolouration mechanism of spiropyran complexes is still obscure [4]. The reaction equilibrium of such complex formation reactions has not been reported.

In this work, the kinetics of chelate formation in acetone and decolouration of the coloured form and its Cu(II) chelate in tetrahydrofuran (THF) were studied by UV–visible spectroscopy. The mechanisms of chelate formation in acetone and decolouration of the chelate in THF were proposed and the PC–Cu(II) chelate formation constant in THF was determined. Finally, the structure of the chelate in acetone was studied using Cu(II) as an electron spin resonance (ESR) probe.

2. Materials and apparatus

CuCl$_2$·2H$_2$O was analytically pure (AR). Acetone was dried before use, and THF was treated with Zn

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and 3 Å molecular sieves and then distilled under N_2; its collected range was 66–67 °C. Spiropyran (SP-1, $R_1 \equiv Me$, $R_2 \equiv OMe$) was synthesized according to the literature [5] and identified by conventional methods. Irradiation was performed with a 500 W high-pressure Hg lamp through a suitable filter for 90 s, with a distance of 10 cm to the sample. The absorption spectra and decolouration rates were measured with a diode-array spectrophotometer (Hewlett Packard HP8452A). ESR spectra were recorded on a Bruker 200D.

3. Experimental results and discussion

3.1. Chelation in acetone in the dark

In acetone, the chelating properties of spiropyrans with bidentate ligands can be observed by treating the coloured or colourless solutions with metal ions such as Cu(II), Ni(II), Zn(II), etc. For colourless solutions, the chelate formation rate can be accelerated by UV irradiation or reduced by lowering the temperature [3]. In the determination of the mechanism of chelate formation and dissociation, there are three possible routes: (a) $SP \rightleftharpoons PC + M(II) \rightarrow PC-M(II)$; (b) $SP + M(II) \rightarrow SP-M(II) \rightarrow PC-M(II)$; (c) $SP \rightarrow PC + M(II) \rightleftharpoons PC-M(II)$. For (a) and (b), the formation rates of the complex are proportional to the concentration of the metal ions. For (c), the coloured form (PC) reacts readily with metal ions as it is formed thermally from SP, and the formation process is the rate-determining step in the reaction sequence, with little effect of the metal ion concentration on the reaction rate.

To study the exact reaction scheme, the chelation process was investigated at different concentrations of Cu(II). Fig. 1 shows the UV–visible spectra of 6.0×10^{-5} mol l^{-1} SP-1 in the presence of 5.0×10^{-4} mol l^{-1} $CuCl_2$ at different times. It can be seen that the absorbance of the complex at 400 nm increases gradually
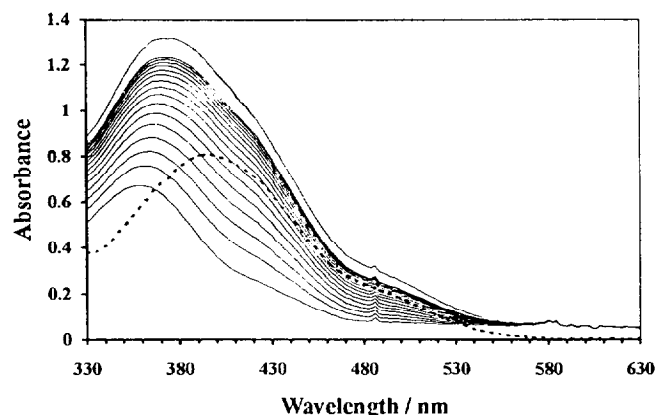
with time. By assuming that the chelation kinetics are first order, we can use [6]

$$\ln(A_e - A_t) = kt \tag{1}$$

where A_e and A_t denote the absorbance at infinite time and time t respectively. From Fig. 2, we obtain $k = 4.93 \times 10^{-4}$ s^{-1}. In a similar way, when the concentrations of Cu(II) are 1.0×10^{-3} mol l^{-1} and 2.0×10^{-3} mol l^{-1}, the k values are 4.89×10^{-4} and 5.01×10^{-4} s^{-1} respectively (Fig. 2). Obviously, the concentration of Cu(II) has no effect on the rate of complex formation. In dilute solution, thermal colouration of SP is too weak to be detected. As the concentration of SP increases, its thermal colouration process is easy to monitor, especially for a freshly prepared sample or on irradiation with visible light. Thus reaction scheme (c) occurs, consistent with the work carried out by laser flash photolysis [7].

3.2. Decolouration of photomerocyanine (PC) and its chelate with Cu(II) in THF

In THF, when the concentration of Cu(II) is sufficiently high, SP may form stable complexes with Cu(II) as observed in acetone. Unfortunately, the solubility of $CuCl_2$ in THF is strictly limited; therefore no reliable kinetic measurements can be performed for comparison of the solvent effect under the given conditions. When the Cu(II) concentration is low, SP cannot form a stable complex with Cu(II) in the dark. However, on UV irradiation, the photomerocyanine (PC) form of SP can form a chelate with Cu(II). Both PC and its chelate with Cu(II) can transform to the colourless form in the dark [4]. Fig. 3(a) shows the visible absorption spectra of 1.0×10^{-4} mol l^{-1} SP-1 in THF solution at
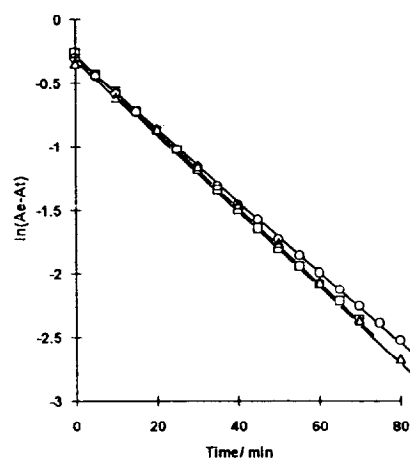

Fig. 1. Visible spectra of 6.0×10^{-5} mol l^{-1} SP-1 in acetone with 5.0×10^{-4} mol l^{-1} $CuCl_2$ at different times (min): 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, ∞.

Fig. 2. Rate plot for the first-order chelation of SP at different concentrations of Cu(II): 5.0×10^{-4} mol l^{-1} (○); 1.0×10^{-3} mol l^{-1} (△); 2.0×10^{-3} mol l^{-1} (□).
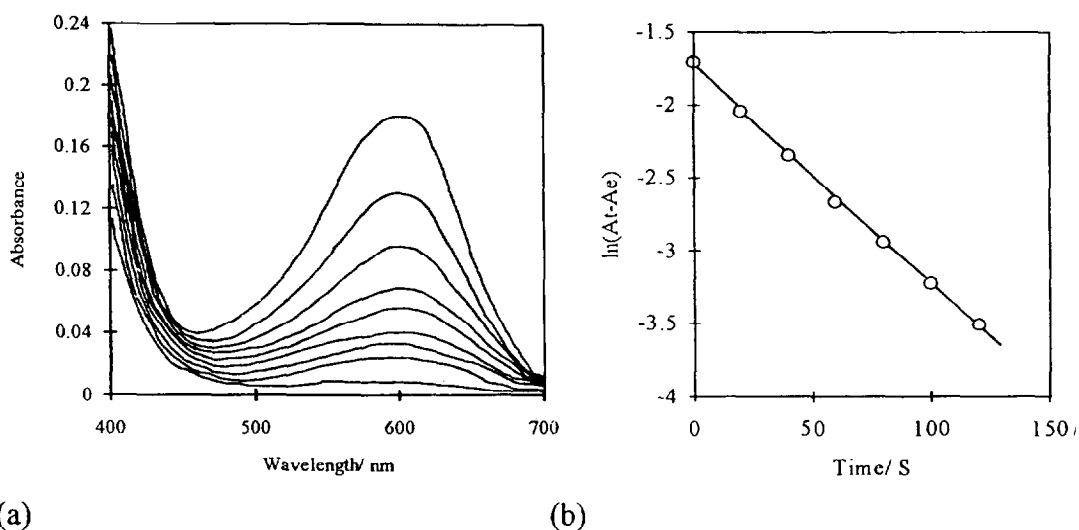
Fig. 3. (a) Visible spectra of 1.0×10^{-4} mol l^{-1} SP-1 in THF after UV irradiation from zero time to infinity at 16 °C. (b) Rate plot for the first-order decolouration process of the open coloured form (PC).

different times after UV irradiation. The absorbance of the open form at 600 nm decreases quickly. By fitting the experimental data to Eq. (1), a linear relation can be obtained (Fig. 3(b)); this means that first-order kinetics are appropriate for the decolouration process.

When $CuCl_2$ is present in the solution, a new absorption band appears at 500 nm after irradiation (Fig. 4). This band is the absorption of the chelate formed between PC and Cu(II). The difference between the λ_{max} value of this band (500 nm) and that of the complexes in acetone (400 nm) is obvious. The shift in λ_{max} may be caused either by structural differences between the complexes formed in THF and acetone or by differences between the dipole moments in the ground and excited states of the complex. In this case, we assume that the former effect is more significant.

As the concentration of $CuCl_2$ is increased, the absorption at 500 nm becomes stronger relative to that at 600 nm. From the rate constant plots at 600 nm and 500 nm (Fig. 5), it can be seen that the decolouration processes of the coloured form of SP-1 (PC) and its Cu(II) chelate can be described by first-order kinetics. The rate constants at different Cu(II) concentrations are listed in Table 1.

From Table 1 it is clear that, when the open form coexists with free Cu(II) ions, the observed rate constants of decolouration of 500 nm and 600 nm are nearly the same. This indicates that the open form and its chelate with Cu(II) are in equilibrium during the process of thermal decolouration. There are two possible paths of decolouration
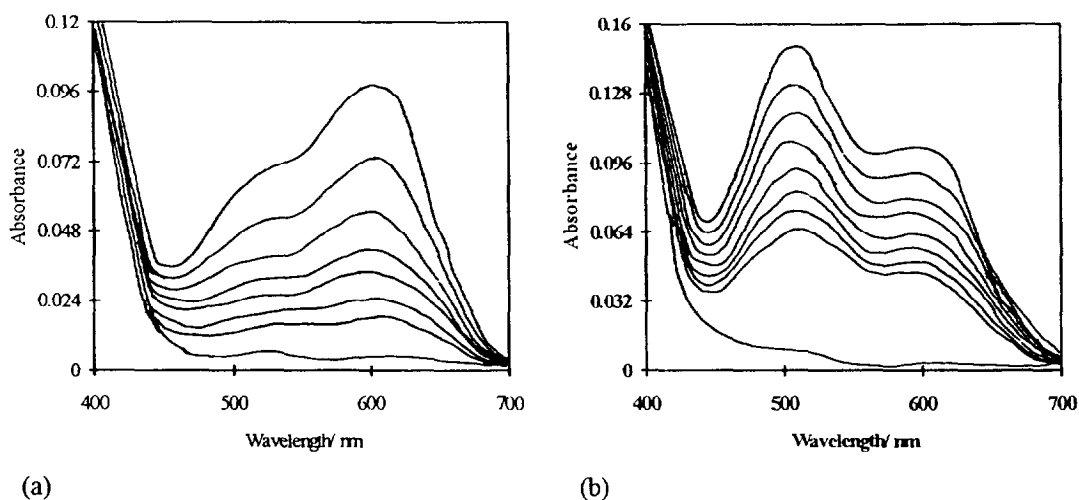

Fig. 4. Changes in the visible spectra of 1.0×10^{-4} mol l^{-1} SP-1 with time in THF with different concentrations of Cu(II) after UV irradiation. [Cu(II)] $\times 10^5$ mol l^{-1}: (a) 1.0; (b) 2.0.
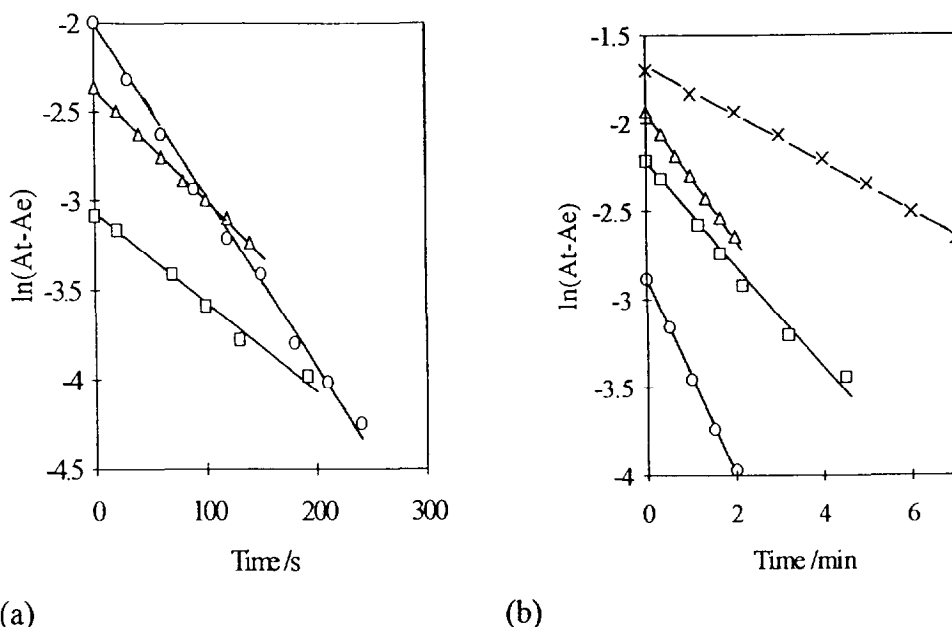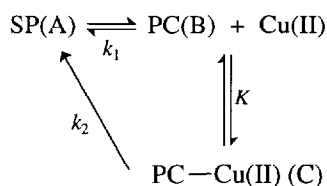
Fig. 5. Decolouration rate plots of PC (a) at 600 nm and chelate (b) at 500 nm at different Cu(II) concentrations. [Cu(II)]×10^5 mol l^{-1}: 1.0 (O); 2.0 (△); 4.0 (□); 10.0 (×).

Table 1
Correlation between the observed decolouration rate constants and Cu(II) concentration

Rate constant	[Cu(II)]×10^6 (mol l^{-1})								
	0	1.0	2.0	4.0	6.0	10.0	25.0	50.0	100
k_{ob}×10^4 (s^{-1}) (600 nm)	157	101	64	52					
k_{ob}×10^4 (s^{-1}) (500 nm)		96	61	53	35	23.2	13.2	8.23	7.4

$$SP(A) \underset{k_1}{\overset{}{\rightleftharpoons}} PC(B) + Cu(II)$$

where k_1 and k_2 are the decolouration rate constants of PC and PC–Cu(II) respectively. When the concentration of Cu(II) is high (more than 10^{-4} M), the absorption band at 600 nm disappears. This means that the concentration of PC is below the detection limit. Since

$$- \frac{d[C]}{dt} = \frac{d[A]}{dt} = \left(\frac{k_1}{K[Cu(II)]} + k_2 \right)[C] \qquad (2)$$

and

$$- \frac{d[C]}{dt} = k_{ob}[C] \qquad (3)$$

then

$$k_{ob} = \frac{k_1}{K[Cu(II)]} + k_2 \qquad (4)$$

where K is the equilibrium constant of chelate (C) formation.

Using the data in Table 1 and Eq. (4), Fig. 6 was obtained. We obtain $k_2 = 5.7 \times 10^{-4}$ s^{-1} and $k_1/K = 1.75 \times 10^{-7}$ l s^{-1} mol^{-1}. Since $k_1 = 1.57 \times 10^{-2}$ s^{-1}, we have $K = 8.9 \times 10^4$ l mol^{-1}. The observed decolouration rate constant of the chelate consists of two parts. One is $k_1/K[Cu(II)]$, which corresponds to the
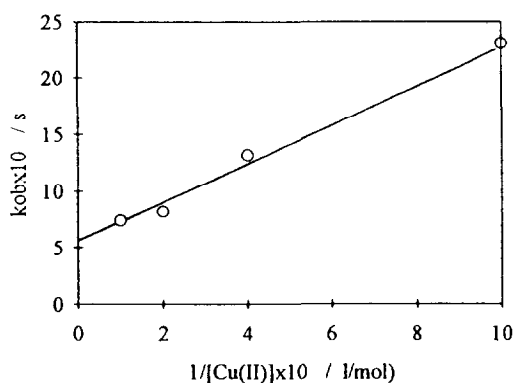

Fig. 6. Variation in the observed decolouration rate as a function of the reciprocal of [Cu(II)].

decolouration route in which the chelate is transformed to the metal-free open form initially and then the colourless closed form. The other is k_2, which correlates with the direct decolouration of the chelate form. When [Cu(II)] is low, because $k_1 \gg k_2$, the first route is the main process in the decolouration. As [Cu(II)] increases, such that $k_1/K[Cu(II)] < k_2$, the second process becomes important. Between these two extremes, both forms coexist and contribute to the decolouration in different proportions; we have

$$\frac{d[A]}{dt} = k_1[B] + k_2[C] = (k_1 + k_2 K[Cu(II)])[B]$$

$$\frac{d[A]}{dt} = -\frac{d[B]}{dt} - \frac{d[C]}{dt} = k_{ob}[B] + k_{ob}[C] \qquad (5)$$

so that

$$\frac{d[A]}{dt} = k_{ob}(1 + K[Cu(II)]) + [B] \qquad (6)$$

From Eqs. (5) and (6), we have

$$K = \frac{k_1 - k_{ob}}{k_{ob} - k_2}[Cu(II)] \qquad (7)$$

If the concentration of Cu(II) for the chelate is negligibly small, we obtain K values of 6.0×10^4, 8.2×10^4 and 5.7×10^4 for Cu(II) concentrations of 1.0×10^{-5}, 2.0×10^{-5} and 4.0×10^{-5} mol l^{-1} respectively, which are similar to the results obtained from Fig. 4.

3.3. ESR spectra

Until now, no details on the structure of the complex have been reported. For the Co(II) complex of benzothiazole merocyanine, a model compound of the PC of spiropyran, X-ray structural analysis has indicated that there are two molecules in the asymmetric unit [8]. The geometry of the coordination polyhedra of the two molecules can be described as distorted trigonal bipyramids. The complexes of Mn(II), Fe(II) and Zn(II) are isotypic but the Debye–Scherrer diagrams of copper complexes are quite different [9]. This may be caused by different crystal structures. In order to obtain more structural information on the present complexes, their ESR spectra in acetone solution were recorded at liquid nitrogen temperature. Fig. 7 shows the ESR spectrum of 2.0×10^{-3} mol l^{-1} Cu(II) complex with SP in acetone at 77 K.

The hyperfine lines due to the Cu(II) nuclei are well resolved in the low-field region: four weak peaks can be identified and $g\| = 2.3682$; the high-field region of the spectrum, which corresponds to the perpendicular lines, is broadened; from the ground line, we obtain $g_\perp = 2.0664$. The $g_\|$ and $g_\perp$ values and the spectral characteristics are in good agreement with the $d_{x^2-y^2}$ ground state of Cu(II) [10,11]. Therefore a certain
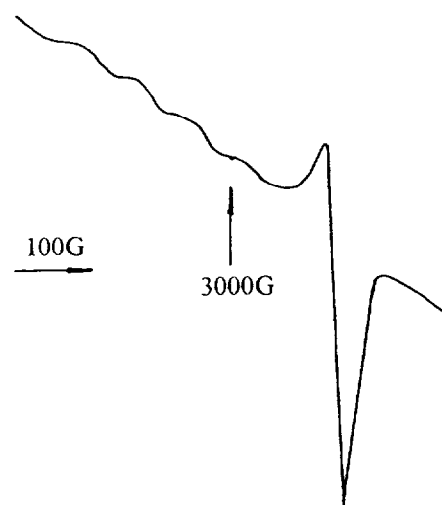

Fig. 7. ESR spectrum of Cu(II) complex with SP in acetone at 77 K.

portion of the present complex is assigned a square or square pyramidal structure rather than a trigonal bipyramid. If this is not the case, a reverse spectrum with $g_\| < g_\perp$ should be observed [12].

4. Conclusions

During the formation of the Cu(II) chelate of photochromic spiropyran in acetone in the dark, the rate-determining step is the formation of the coloured form.

During the decolouration of the coloured form and its Cu(II) chelate in THF after UV irradiation, the kinetics indicate that the coloured form and its Cu(II) chelate are in equilibrium during thermal decolouration, with an equilibrium constant K of 8.9×10^{-4} l mol^{-1}. The decolouration rate constants of the coloured form and its Cu(II) chelate are 1.57×10^{-2} s^{-1} and 5.7×10^{-4} s^{-1} respectively.

From the ESR spectrum of the Cu(II) chelate in acetone at 77 K, the structural type of the chelate is reasonably assigned to be square or square pyramidal rather than trigonal bipyramidal.

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