Kinetic Study on Decolouration Process of Chelated Photomerocyanine of Spironaphthoxazine

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Photochromism is a reversible transformation of a single chemical species between two states whose absorption spectra are recongnizably different, the transformation in at least one direction being induced by electromagnetic radiation[1]. Organic photochromic compounds have attracted more and more attentions, because colour change usually accompanied with the change of molecular properties and functions[2]. Spironaphthoxazines and their derivatives are photochromic compounds analogous to spiropyrans, which occur in reversible cleavage and rebinding in the (spiro) C-O bond, and yield a color opening and a colorless closed form respectively[3]. In 1989, Tamaki et al. found that when there is a co-ordinating group such as -OMe, $-SO_3^-$ at the orthoposition of the O atom, the coloured open form can act as a chelating agent and form complexes with M(II) cations[4]. With the formation of such complex, the coloured form can be stabilized and spectra may be different to unchelated one. In the recent work of Tamaki et al. [5], such a method has been used to stablized the coloured form of spironaphthoxazine in cetain polymer matrixes. In literatures more attention has been paid to the effect of the nature of metal ions on the formation of such complexes, no systematic work has been done on the mechanism of the decoloration process of the chelated form as well as the kinetic effect of metal ions on it. In this work, we report the chelatation of $Ni(NO_3)_2$, and 1,3, 3-trimethyl indole spironaphthoxazine with a coordinating group, 5-COOMe (I) in its open form (B). The concentration effect of $Ni(NO_3)_2$ on decoloration rate of the chelated complex was investigated by UV-VIS spectroscopic method.

The compounds(A) was prepared according to literature[3]. The irradiation was done with a 500W high pressure Hg lamp and a suitable coloured glass filter. The absorption spectra and decolouration rates were measured with a diodes-array spectrophotometer(Hewlett Packard HP 8452)

The transformation of the coloured form of (I) in acetone solution is much faster than in ethanol, no reliable decoloration rate constant can be obtained with the steady

state methoed. When $Ni(NO_3)_2$ is added, the coloured form is stablized, and a slight shift of the λ_{max} can be observed. This originates from the chelation of opened form with Ni (II) ions. Fig. la is the visible spectra of 1.0×10^{-4} mol·L^{-1} (I) with 3.0×10^{-6} mol·L^{-1} $Ni(NO_3)_2$ in acetone at different time after 2 min UV irradiation. From Fig.la it can be seen that the λ_{max} of the complex is about 606 nm. The rate constant of thermal decoloration of the complex can be found by using equation[1]:

$$\ln(A_t - A_e) = -k_1 t + C \tag{1}$$

Where A_t is the absorbance at the λ_{max} of the chelated opened form at time t, A_e is the equilibrium absorbance at the λ_{max}(taken as the absorbance after 2-6h in the dark.)
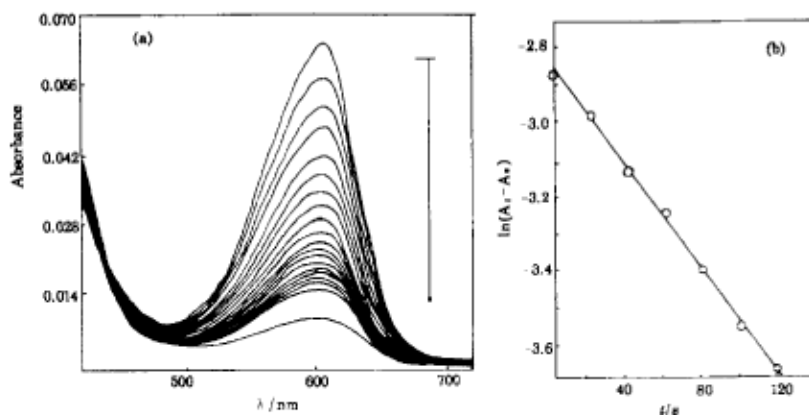

Fig.l (a) At 1.6 C, visible spectral changes of 1.0×10^{-4}mol·L^{-1}(A) with 3.0×10^{-6}mol·L^{-1} $Ni(NO_3)_2$ after 2 min UV irradiation at different times(sec.): 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 320, 340, 360, ∞ and unirradiated.
(b) first-order plot for the thermal decoloration of the chelate

Table 1 Correlation between the observed decoloration rates k_{ob} with $Ni(NO_3)_2$ concentrations

[Ni(II)]·10^6mol·L^{-1}	3.0	5.0	8.0	10.0	16.0	20.0
1/[N i(II)]·10^{-6}mol·L^{-1}	33.3	20.0	12.5	10.0	6.25	5.00
k_{ob}·10^3, (s^{-1})	6.60	4.17	2.48	2.11	1.37	1.05

Fig. 1b shows that the thermal decoloration kinetics fit eq.(1) very well. This indicates that the thermal decoloration is of first order to the chelate complex. The effect of Ni(II) concentrations on the decoloration rate in acetone solution, and the changes of the absorbance at 606 nm with time were recorded after irradiation. Fig.2a gives two examples, the concentrations of $Ni(NO_3)_2$ are of 1.0×10^{-5}mol·L^{-1} and 2.0×10^{-5}mol·L^{-1}, respectively. From Fig.2a, the rate constant plot for first-order decoloration process can be obtained(Fig.2b). They were listed in Table 1.

Discussion and Conclusion The chelate formation process can be shown in scheme 1. There are two possible routines for the transformantion of the chelate (C) to the colorless form (A). The first way is, the metal ion is dechelated and gives the metal free opened

form (B) and then to (A); the other is that it changes directly from (C) to the original colourless (A).
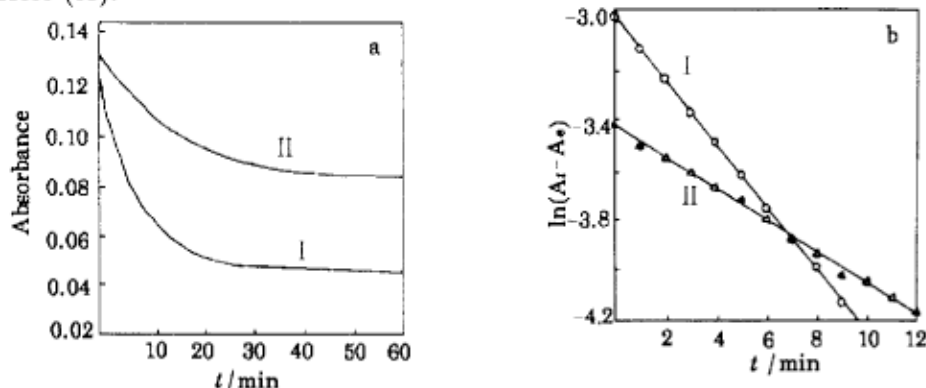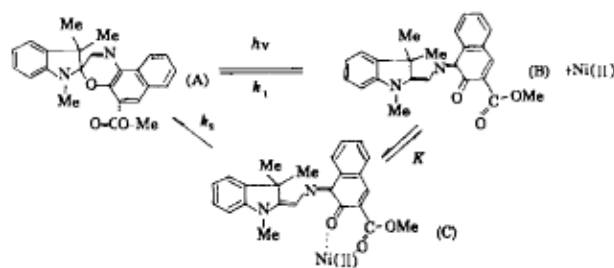

Fig.2 a: Thermal decoloration of the chelate in acetone with Ni(NO$_3$)$_2$ concentrations of 1.0×10^{-5} mol·L^{-1} (I) and 2.0×10^{-5}mol·L^{-1}(II), respectively
b: first-order plots for the thermal decoloration of the chelate. Ni(NO$_3$)$_2$ concentration: 1.0×10^{-5} mol·L^{-1} (I), 2.0×10^{-5} mol·L^{-1}(II)
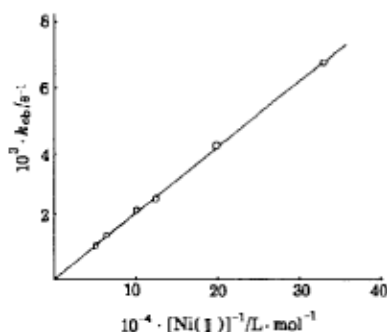

Scheme 1

Fig.3 The variation of the observed decoloration rates k_{ob} with the reciprocal of Ni (II) concetration

From scheme 1, we have

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

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

then
$$k_{Ob} = \frac{k_1}{K[\text{Ni(II)}]} + k_2 \qquad (4)$$

k_{ob}: the observed decoloration rate constant of C; k_1: the decoloration rate constant of B; K: the equilibrium constant of the chelated complex.

Fig.3 was obtained by treating experimental data with equation (4). It can be seen that $k_2=0$, $k_1/K=2.0\times10^{-8}$, this shows that the chelate complex can not be decolorated to the colourless form directly, then $k_{ob} \propto 1/[\text{Ni(II)}]$. This indicates that routine 1 is the key decoloration path and routine 2 may be negligible under our experimental conditions. Therefore we can adjust the decorolate rate by controlling the concentration of Ni(II).

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光致变色螺萘并噁嗪配合物的褪色过程动力学研究

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摘要　报导了一种带 5'-CO_2Me 取代基的螺噁嗪 (A) 的开环形式 (B) 与金属离子的配合作用. 利用紫外可见吸收光谱研究了金属离子浓度的影响，并证明了有色体配合物 (C) 的主要消色过程是先解离出金属离子生成 (B). 再褪色生成闭环无色体 (A). 未观测到由 (C) 直接褪色生成 (A) 的过程.

关键词： 光致变色，　螺萘并噁嗪，　螯合，　褪色机理