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## Photochromic behavior of hexacyanoferrate (ii) in *o*-cresolphthalein system

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**Abstract** The photo chromic behavior of Hexacyanoferrate in phthalein system was observed spectrophotometrically. Hexacyanoferrate (II) ejects electrons, which abstracts  $H^+$  from indicator molecule and this molecule of the indicator changes into their quinonoid form which is coloured.

**Keywords** Photochromism, *o*-cresolphthalein, Phthalein

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### Introduction

Photochromism is a light induced reversible change of colour. Markwald [1] observed Photochromism in solution and in the solid state, which may be due to intramolecular changes. Derivatives of malachite green luconitrile carrying a benzo -15crown -5moiety to control metal ion complexation of its crown ether moiety by photo ionization of its photochromic moiety has been used by Kimura *et al* [2]. Influence of polymer polarity on naphthodipyran which are doped in different polymeric matrix has been studied by Zhao *et al* [3]. Synthesis, kinetics and application recording of a new asymmetrical photochromic diarylethene was studied by Wang *et al* [4]. Diarylethene bearing a pyrrole unit show photochromic behavior and its synthesis and holographic optical recording studied by Liliu *et al* [5]. Use of photochromic dyes in textile industries in which establishment of a methodology for evaluation of photochromic textile during traditional colour measurement instrumentation explained in a book of coloration technology [6].

### Materials and methods

A stock solution of *o*-cresolphthalein was prepared by dissolving 0.0346 g in 100.0 mL ethyl alcohol, so that the concentration of indicator solution was  $1.0 \times 10^{-3}$  M. A stock solution of  $K_4[Fe(CN)_6]$  was prepared by dissolving 21.1100 g in 100.0 mL doubly distilled water, so that the concentration of stock solution was 0.5 M. 4.5 mL of 0.5 M solution of  $K_4[Fe(CN)_6]$  was taken and 17.0 mL doubly distilled water and 3.0 mL solution of *o*-cresolphthalein was added to it dropwise. Then the mixture was exposed to light. A 200 W tungsten lamp (Philips; light intensity =  $60.0 \text{ mWcm}^{-2}$ ) was used for irradiation purpose. The absorbance of the solution was measured at  $\lambda_{\text{max}}$  570 nm at regular time intervals (using UV-visible spectrophotometer Systronics Model 106). It was observed that the solution become red coloured with the passage.

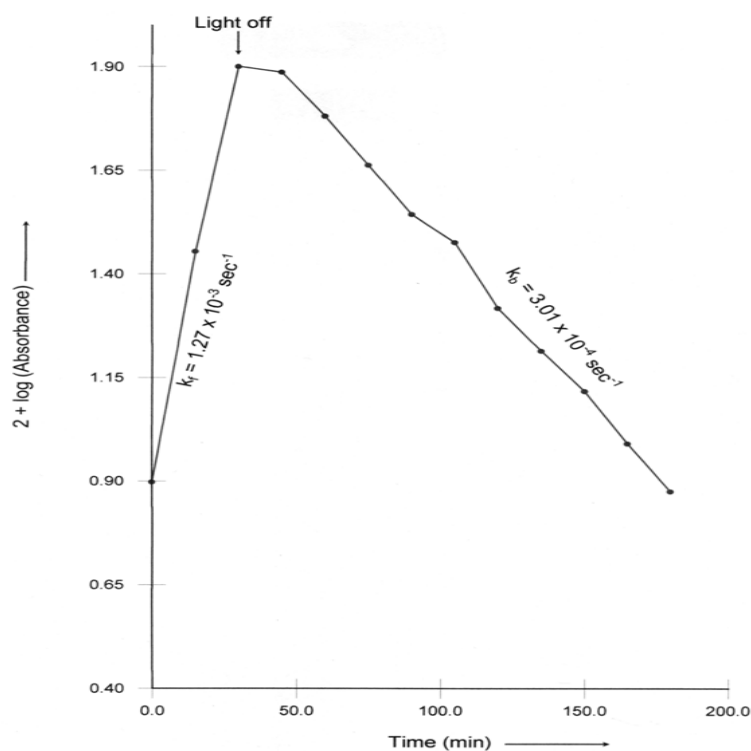


**Table 1:** A Typical Run

[ <i>o</i> -cresolphthalein]	=	$1.40 \times 10^{-4}$ M
[Pot. hexacyanoferrate (II)]	=	$9.00 \times 10^{-2}$ M
Intensity	=	$60.0 \text{ mWcm}^{-2}$
pH	=	7.5

Time (minutes)	Absorbance	2+log (Absorbance)
0.0	0.079	0.8976
15.0	0.285	1.4548
30.0	0.795	1.9003
<b>Light off</b>	-	-
45.0	0.770	1.8864
60.0	0.604	1.7810
75.0	0.460	1.6627
90.0	0.350	1.5440
105.0	0.300	1.4771
120.0	0.208	1.3180
135.0	0.164	1.2148
150.0	0.131	1.1172
165.0	0.098	0.9912
180.0	0.075	0.8750

$$k_f = 1.27 \times 10^{-3} \text{ sec}^{-1}; k_b = 3.01 \times 10^{-4} \text{ sec}^{-1}$$

**Figure 1:** A Typical Run

A graph between 2+ log (Absorbance) and time was plotted, which was linear. After reaching on optimum value, the absorbance remains constant. Thereafter, the light source was cut off. It was observed that the reaction reverts back, which is evident from the decreasing value of absorbance. The plot of log of (Absorbance) v/s time for this



backward reaction was also found to be linear. This behaviour indicates that the forward and backward reaction; both, followed pseudo-first order kinetics. The rate constant was determined by the expression:

$$k = 2.303 \times \text{slope}$$

### Result and Discussion

A graph between  $2 + \log(\text{absorbance})$  and time for forward reaction was plotted, which was linear, after reaching on optimum value, the absorbance remain constant. Thereafter, the light source was cut off. It was observed that the reaction revert back, which is evident from the decreasing value of absorbance. The plot of  $\log(\text{absorbance})$  v/s time for this backward reaction was also found to be linear.

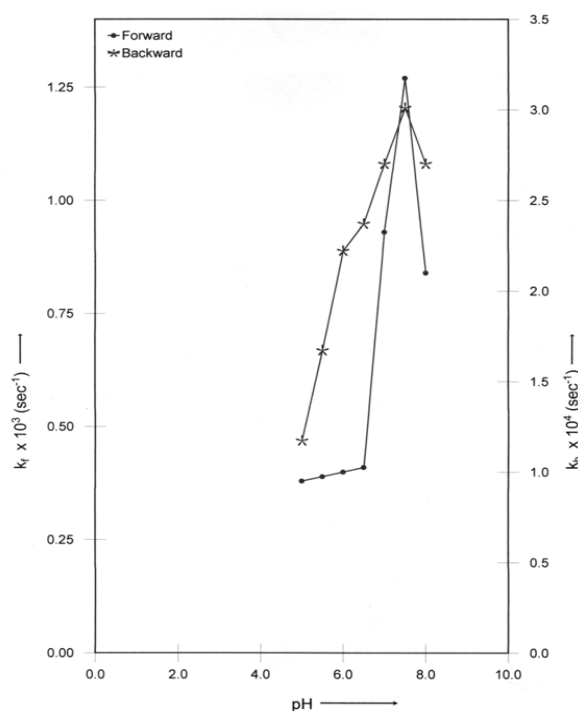
### Effect of pH

The effect of pH on generation and disappearance of colour was observed in the pH range 5.0 to 8.0 keeping all other factors identical. The results are shown in Table 2.

**Table 2:** Effect of pH

[*o*-cresolphthalein] =  $1.40 \times 10^{-4}$  M  
 [Pot. hexacyanoferrate (II)] =  $9.00 \times 10^{-2}$  M  
 Intensity =  $60.0 \text{ mWcm}^{-2}$

pH	$k_f \times 10^3 \text{ (s}^{-1}\text{)}$	$k_b \times 10^4 \text{ (s}^{-1}\text{)}$
5.0	0.38	1.17
5.5	0.39	1.67
6.0	0.40	2.22
6.5	0.41	2.37
7.0	0.93	2.70
7.5	1.27	3.01
8.0	0.84	2.70



**Figure 2:** Effect of pH



The effect of pH on reaction rate was observed in the pH range 5.5 to 8.0. The rate of the forward and backward reactions both increase with increasing pH. The rate of the reaction reaches maxima at pH 7.5 but on further increase in pH above 7.5, the reaction rate is retarded. It may be attributed to the fact that the rate of reaction increases above pH 5.0 as the abstraction of proton from *o*-cresolphthalein molecule is facile; thus converting it into its quinonoid form while the majority of *o*-cresolphthalein molecules will remain in its anionic form above pH 7.5. This anionic form will have the little tendency to interact with photo-electron generated by potassium hexacyanoferrate (II) on exposure.

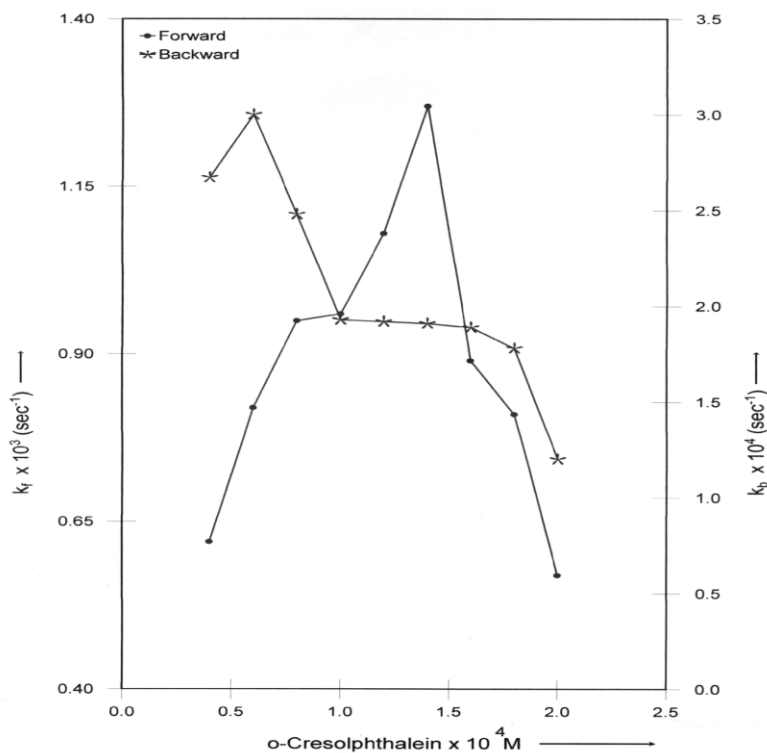
### Effect of *o*-cresolphthalein concentration

The effect of concentration of *o*-cresolphthalein on the rate of forward and backward reaction of the system was observed and the results are summarised in Table 3.

**Table 3:** Effect of *o*-cresolphthalein concentration

[Pot. hexacyanoferrate (II)]	=	9.00 x 10 <sup>-2</sup> M
Intensity of light	=	60.0 mWcm <sup>-2</sup>
pH	=	7.5

[ <i>o</i> -cresolphthalein] x 10 <sup>4</sup> M	k <sub>f</sub> x 10 <sup>3</sup> (s <sup>-1</sup> )	k <sub>b</sub> x 10 <sup>4</sup> (s <sup>-1</sup> )
0.40	0.62	2.67
0.60	0.82	3.00
0.80	0.95	2.48
1.00	0.96	1.93
1.20	1.08	1.92
1.40	1.27	1.99
1.60	0.89	1.89
1.80	0.81	1.78
2.00	0.57	1.20



**Figure 3:** Effect of *o*-cresolphthalein concentration



It is clear from the table that as the concentration of *o*-cresolphthalein was increased; the reaction rate also increases due to increase in number of molecules participating in the reaction. But the retardation in the rate of reaction above concentration  $1.40 \times 10^{-4}$  M may be due to hindrance caused by *o*-cresolphthalein in its own movements towards excited state of potassium hexacyanoferrate in a desired time limit.

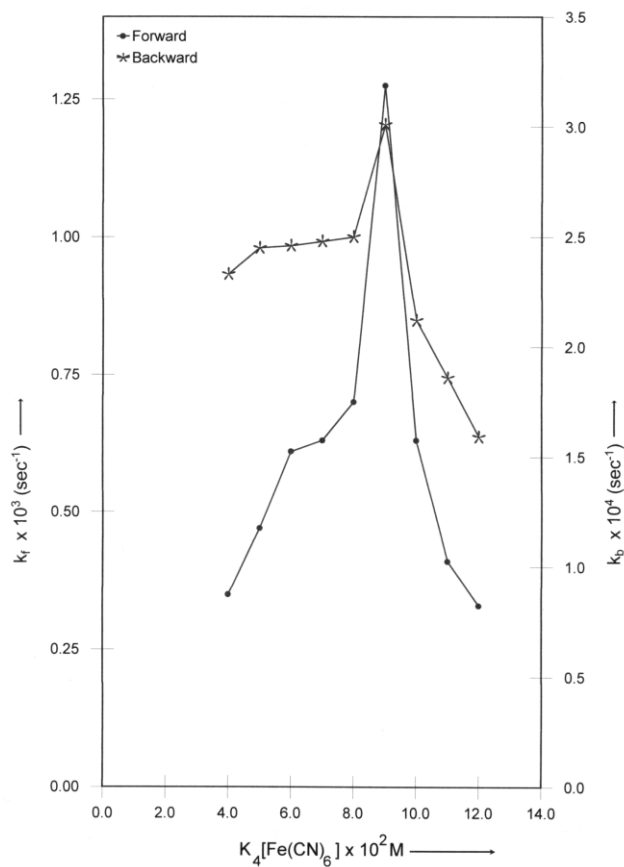
#### Effect of Potassium hexacyanoferrate (ii) concentration

The effect of concentration of potassium hexacyanoferrate (II) on the rate of both the step of this photochromic system has been observed and the results are reported in Table 4.

**Table 4:** Effect of potassium hexacyanoferrate (II) concentration

[*o*-cresolphthalein] =  $1.40 \times 10^{-4}$  M  
Intensity of light =  $60.0 \text{ mWcm}^{-2}$   
pH = 7.5

[Pot. hexacyanoferrate(II)] x $10^2$ M	$k_f \times 10^3$ (s $^{-1}$ )	$k_b \times 10^4$ (s $^{-1}$ )
4.00	0.35	2.33
5.00	0.47	2.45
6.00	0.61	2.46
7.00	0.63	2.48
8.00	0.70	2.50
9.00	1.27	3.01
10.00	0.63	2.12
11.00	0.41	1.36
12.00	0.33	1.59



**Figure 4:** Effect of potassium hexacyanoferrate (II) concentration



It was observed that the rate of reaction increases on increasing the concentration of  $K_4[Fe(CN)_6]$  as more molecules of  $K_4[Fe(CN)_6]$  are available for ejection of photoelectron. But a decrease in the rate of reaction was also observed on increasing the concentration of potassium hexacyanoferrate (II) above a particular concentration i.e.,  $9.00 \times 10^{-2}$  M. It may be explained that concentration will decrease the intensity of light in the bulk in the solution by acting as an internal filter, which in turn will result into retardation of the reaction rate.

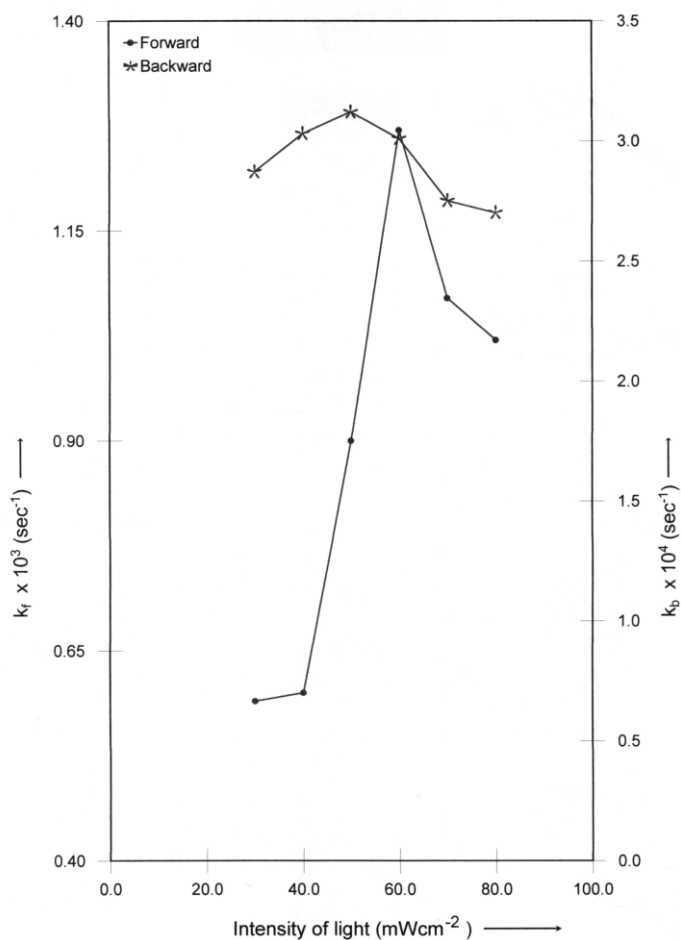
### Effect of Light Intensity

The effect of intensity of light was also observed on this photo chromic system. The results are reported in Table 5.

**Table 5:** Effect of Light Intensity

[ <i>o</i> -cresolphthalein]	=	$1.40 \times 10^{-4}$ M
[Pot. hexacyanoferrate (II)]	=	$9.00 \times 10^{-2}$ M
pH	=	7.5

Intensity ( $mWcm^{-2}$ )	$k_f \times 10^3 (s^{-1})$	$k_b \times 10^4 (s^{-1})$
30.0	0.59	2.87
40.0	0.60	3.03
50.0	0.90	3.12
60.0	1.27	3.01
70.0	1.07	2.75
80.0	1.02	2.70



**Figure 5:** Effect of Light Intensity



It was observed that the rate of reaction increases on increasing the intensity of light up to 60.0 mWcm<sup>-2</sup> and thereafter, a decrease was observed on increasing the intensity further. It may be explained on the basis that as the light intensity was increased, the number of photons per unit area also increased, resulting into a higher rate. On the other hand, adverse effect was observed above 60.0 mWcm<sup>-2</sup>, which it may be due to the side thermal reactions.

### Mechanism

On the basis of the observed data, the tentative mechanism may be proposed for this photo chromic system. The primary photochemical ejection of electron from Fe(CN)<sub>6</sub><sup>4-</sup>, and in secondary thermal reaction, the ejected solvated electron abstracts H<sup>+</sup> from o-cresolphthalein molecule, and o-cresolphthalein molecule changes into its quinonoid form, which is pink red in colour and reaction reverts back in dark.

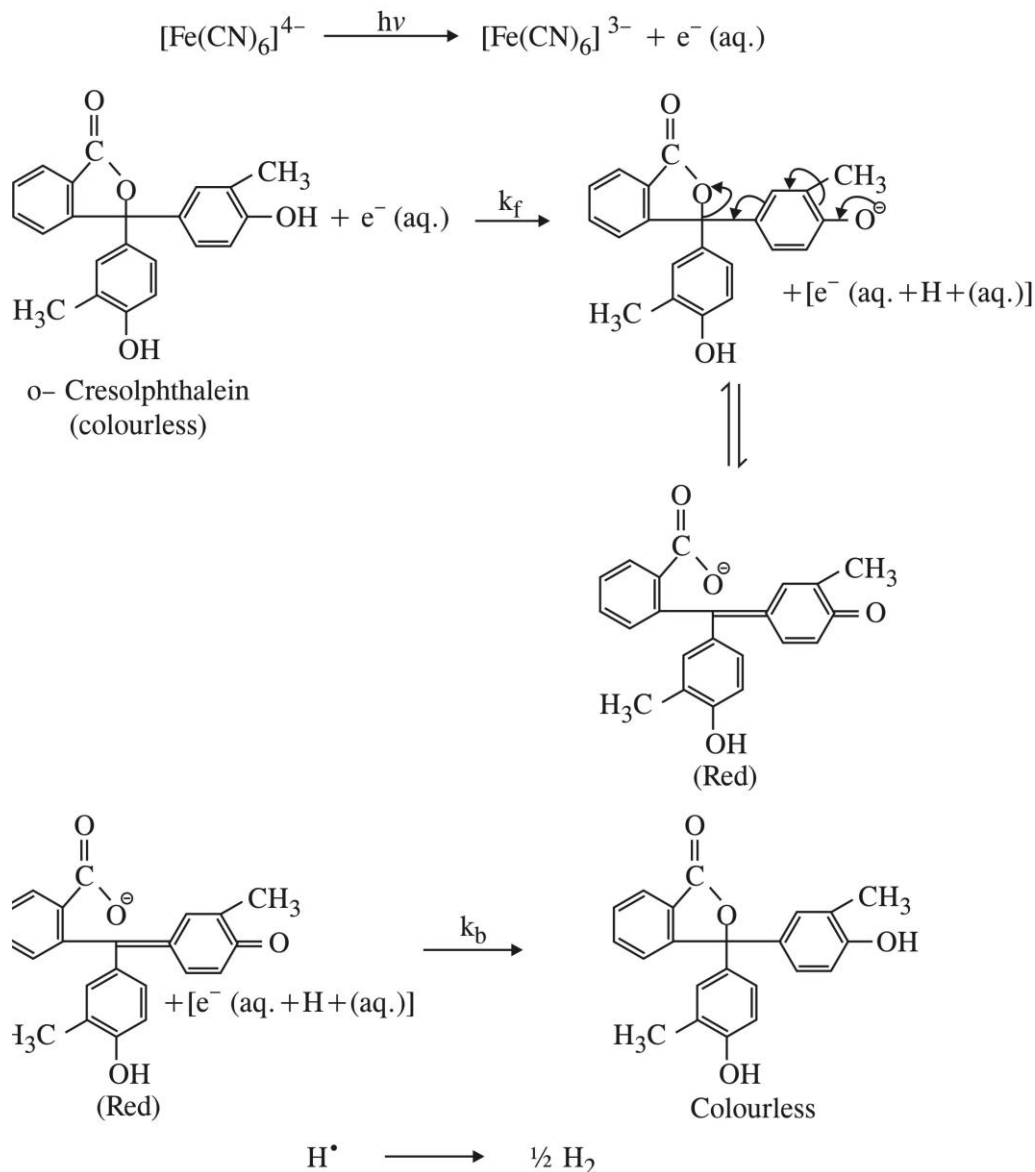


Figure 6: Mechanism



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