Oxidation of a Cyanine Dye with o-Cl-Dibenzoyle Peroxide and Peroxydisulphate

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The oxidation of the cyanine dye 1-methyl-4-N-dimethylamine-γ-stilbazolium iodide with o-Cl dibenzoyl peroxide and peroxydisulphate ion is kinetically investigated. In both cases the oxidation process obeys second order kinetics, being first order in the oxidant molecule and first order in the cyanine dye. The thermodynamic parameters evaluated for the reaction between the dye and o-Cl-DBP are $E_a = 45.6$ kJ mol^{-1}m, $\Delta H^* = 43.09$ kJ mol^{-1}, and $\Delta S^* = -115.7$ J deg^{-1} mol^{-1}. The corresponding values of E_a, ΔH, and ΔS^* obtained for the dye/$S_2O_8^{-2}$ system are 58.01 kJ mol^{-1}, 55.5 kJ mol^{-1}, and -147.8 J deg^{-1} mol^{-1}. Proposed mechanisms are discussed.

Key words: Oxidation of cyanine dyes, peroxydisulphate and organic peroxides.

Introduction

Merocyanine and cyanine dyes are photoreactive compounds whose solvatochromism is interesting as to colour and constitution [1–3]. The solvents play a great role in the behaviour of the charge transfer absorption bands. Thus, such acts are ideal solvent-indicators. The ground and excited states of some merocyanine dyes and their photosensitization have been investigated [4]. However information about the thermally induced oxidation of cyanine dyes seems to be lacking. This prompted us to study such oxidation reactions using o-Cl-dibenzoyl peroxide and peroxydisulphate ion as oxidizing agents in neutral media.

Experimental

The cyanine dye (l-methyl-4-N-dimethylamine-γ-stilbazolium iodide) was prepared by mixing p-N-dimethylamino benzaldehyde with N-methyl picolinium iodide in the presence of piperidine as catalyst in a way similar to the method described by Minch and Shah [5]. o-Cl-dibenzoyl peroxide prepared and purified according to the method described by Price and Krobs [6]. All other chemical reagents were analytical grade substances and used as received.

The kinetics were studied with two methods. In the first, method the order of the reaction of the cyanine dye was determined. This was done spectrophotometrically under an at least tenfold excess of the oxidant (i.e. under pseudo-first order conditions). The two solutions were mixed and the rate of the decrease in the absorbance of the dye (at 450 nm) was recorded with a uv/vis Pye Unicam SP 8000 spectrophotometer. The solvent was ethanol in case of syanine/o-Cl-DBP and water in case of cyanine/$S_2O_8^{2-}$. The second method was used for the evaluation of the kinetic order for the oxidants. This was done iodometrically following the procedure reported by Kolthoff and Carr [7].

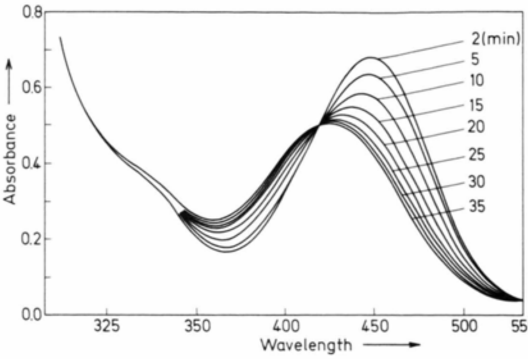

Fig. 1. The change in the absorbance of cyanine dye during the reaction with o-Cl-DBP at 50 °C in ethanol.

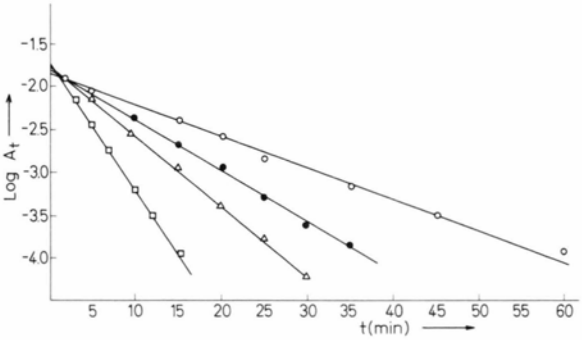

Fig. 2. Logarithm of the absorbance of the cyanine dye vs. time at four temperatures: (○) 45 °C; (●) 50 °C; (△) 55 °C; (□) 60 °C.

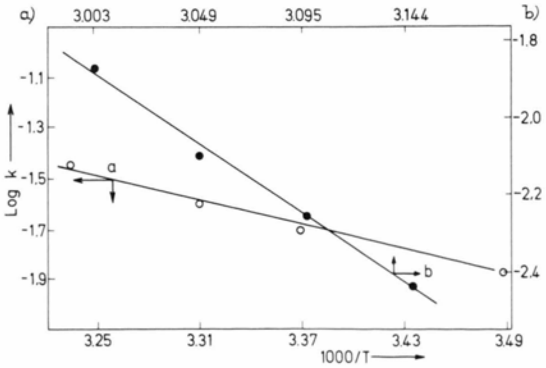

Fig. 3. Arrhenius plots for the oxidation of cyanine dye with: (●) o-Cl-DBP; and (○) $S_2O_8^{2-}$.

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Table 1. Thermodynamic parameters obtained for the oxidation reaction of cyanine/o-Cl-DBP and cyanine/$S_2O_8^{2-}$ systems

Substrate	T/C°	$k \times 10^3$ mol l^{-1} min^{-1}	E_a [kJ mol^{-1}]	ΔG^* [kJ mol^{-1}]	ΔH^* [kJ mol^{-1}]	ΔS^* [J deg^{-1} mol^{-1}]
Cyanine/o-Cl-DBP	45	3.6	58.01	103.62	55.5	−147.8
	50	5.8				
	55	8.3				
	60	15.0				
Cyanine/$S_2O_8^{2-}$	15	12.0	45.6	77.29	43.1	−115.7
	24	17.6				
	29	24.0				
	34	37.0				

Results and Discussion

The absorbance of the cyanine dye in the presence of o-Cl-DBP changed with time as shown in Figure 1. On plotting the logarithm of the absorbance of unreacted cyanine vs. time, straight lines were obtained (Fig. 2), indicating a first order reaction with respect to the dye molecule. The plot obeys the equation

$$\log A_t = \log A_0 - \frac{k' t}{2.303} .$$

k' equals k [P] where k is the true rate constant and [P] the initial concentration of the o-Cl-DBP. The measurements were repeatedly taken at various temperatures in the range 45–60 °C. At temperatures below 65 °C spontaneous thermal decomposition of the peroxide was undetectable. When the peroxydisulphate ion was substituted for the organic peroxide and the kinetic runs were carried out in the temperature range 15–34 °C, a first order reaction for the dye was again observed. Also in the iodometric measurements, where the molar ratio of the dye and either of the oxidizing agents was held as high as 10:1, the reaction was found to be of first order. Thus, the overall reaction between the cyanine dye and o-Cl-DBP or $S_2O_8^{2-}$-ion follows second order kinetics according to the equation

$$\text{rate} = k_2 \,[\text{oxidant}]\,[\text{cyanine}],$$

where k_2 is the second order rate constant. Linear relationships were obtained when plotting log k_2 vs. 1/T (Figure 3). The derived activation parameters are summarized in Table 1.

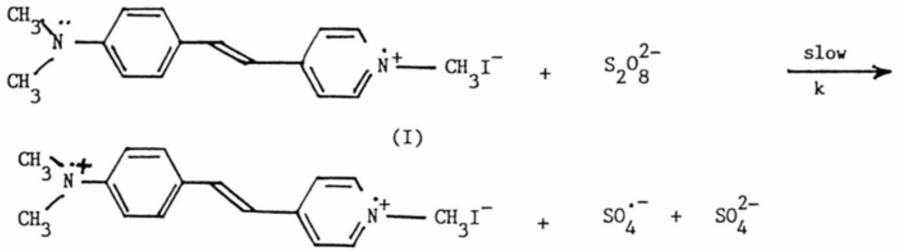
Mechanism

a) Oxidation with o-Cl-DBP

The mechanism resembles that reported by Tokumaru and Simamura [8]. The donating property of the solvent is important for this type of oxidation reactions. Thus, with donating solvents the reaction proceeds more rapidly compared with less donating ones [8, 9].

b) Oxidation with $S_2O_8^{2-}$

Since the reaction of cyanine dye with peroxydisulphate followed first-order kinetics in both the dye and the $S_2O_8^{2-}$-ion, and this is in good agreement with the results reported by Choudary et al. [10] on the aromatic amines/$S_2O_8^{2-}$ reactions, the mechanism may be as follows:



(I)

(II)

$$(I) + SO_4^{\bullet -} \xrightarrow{\text{fast}} (II) + SO_4^{2-}$$

Inspection of Table 1 shows that the energy of activation of the cyanine/$S_2O_8^{2-}$ reaction is lower than that of the cyanine/o-Cl-DBP reaction. This may be due to several factors, viz, steric effects, molecular sizes, diffusion coefficients and bond dissociation energies. The O-O-bond dissociation energies characteristic of the peroxydisulphate [11] ion and peroxide [12] molecule are 110–120 and 130 kJ mol^{-1}, respectively. This would explain the faster oxidation rate observed in the presence of $S_2O_8^{2-}$-ion than in the presence of the peroxide.

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