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Oxidation Kinetics and Fluorescence Quenching of Coumarin-1 Laser Dye with Peroxodisulfate

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Summary. The fluorescence of coumarin-1 laser dye (*C1*; 7-diethylamino-4-methyl-coumarin) proved to be sensitive to the presence of peroxodisulfate ($S_2O_8^{2-}$). The emission intensity decreases with increasing in peroxodisulfate concentration. The decrease is assigned to a quenching process connected with a ground state peroxodisulfate oxidation of the dye. The kinetics of the reaction have been investigated spectrophotometrically at 382 nm. The reaction follows second order kinetics, being first order for each reactant. The reaction rate is *pH* dependent; higher rates are observed in alkaline media. Addition of sodium dodecyl sulfate (*SDS*) retards the oxidation process remarkably.

Keywords. Coumarin-1; Peroxodisulfate; Oxidation kinetics; Fluorescence quenching.

Kinetik der Oxidation und Fluoreszenzlöschung des Laserpigments Coumarin-1 mit Peroxodisulfat

Zusammenfassung. Die Fluoreszenz des Laserpigments Coumarin-1 (*C1*; 7-Diethylamino-4-methyl-coumarin) reagiert auf die Anwesenheit von Peroxodisulfat ($S_2O_8^{2-}$). Die Emissionsintensität nimmt mit steigender Peroxodisulfatkonzentration ab. Die Abnahme wird einem Löschvorgang zugeschrieben, der mit einer Oxidation des Grundzustands durch Peroxodisulfat verbunden ist. Die Kinetik der Reaktion wurde bei 382 nm spektrophotometrisch untersucht. Sie verläuft nach zweiter Ordnung (nach erster Ordnung bezüglich jedes Reaktanden). Die Reaktionsgeschwindigkeit ist *pH*-abhängig; in alkalischen Medien werden höhere Geschwindigkeitskonstanten gefunden. Zusatz von Natriumdodecylsulfat (*SDS*) hemmt die Oxidation beträchtlich.

Introduction

Coumarin-1 (*C1*, 7-diethylamino-4-methyl-coumarin) is a laser dye in the blue region [1] and has received wide applications in the field of spectroscopy, photochemistry, and isotope separation. Continuous and quasicontinuous operation of dye lasers have been achieved with the *C1* dye under different conditions [2, 3]. The photodegradation of *C1* has been studied by several workers. *Antonov* and *Hohla* investigated its photostability under excimer laser pumping [4]. *Fletcher* and coworkers reported the effect of medium and temperature on the dye photodegradation [5–7]. *Winters et al.* identified two irreversible pathways for the photodegradation process which led to the formation of five photoproducts [8]. *Jones et al.*

proposed a mechanism for the self quenching photodegradation reaction [9, 10], and *Moorthy et al.* studied the photodegradation of *C1* using monochromatic 350 nm radiation [11].

Although the photochemical aspects of the present dye have been thoroughly studied, information upon its thermaly induced oxidation seems to be lacking. The interest in the present reaction, therefore, emanated from a desire to investigate the oxidation kinetics of the dye with peroxodisulfate. The results obtained are embodied in this paper.

Results and discussion

Fluorescence quenching

The fluorescence quenching of *C1* with peroxodisulfate as an acceptor was investigated monitoring the changes of the steady-state emission upon $S_2O_8^{2-}$ addition. The measurements were normally made twenty four hours after the addition of peroxodisulfate to the dye solution. Fig. 1 shows the decrease in the emission intensity of *C1* with the increasing acceptor concentration. Applying the *Stern-Volmer* relation ($I_0/I = 1 + k_a\tau[Q]$) resulted in the graph given in Fig. 2. I_0 and I are the emission intensity of the dye in the absence and in the presence of the quencher Q whose concentration is $[Q]$. k_a is the second order quenching rate constant, and τ is the lifetime of the excited singlet state. The variation of the fluorescence quenching efficiency (I_0/I) with the concentration of $S_2O_8^{2-}$ is nonlinear, indicating a ground state interaction [12] between the dye molecule and the quencher ion. Such

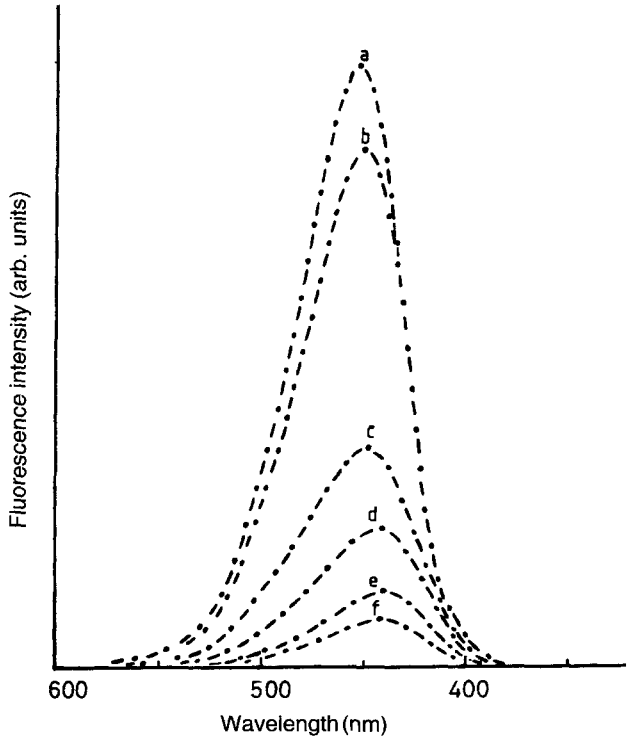


Fig. 1. Decrease in emission intensity of *C1* as a function of concentration of peroxodisulfate; (a) $[S_2O_8^{2-}] = 0$, (b) 1.6×10^{-3}, (c) 3.3×10^{-3}, (d) 6.6×10^{-3}, (e) 1.3×10^{-2}, (f) 2×10^{-2} mol·dm^{-3}; $[C1] = 1 \times 10^{-5}$ mol·dm^{-3}; $T = 25$ °C; $\lambda_{ex} = 365$ nm

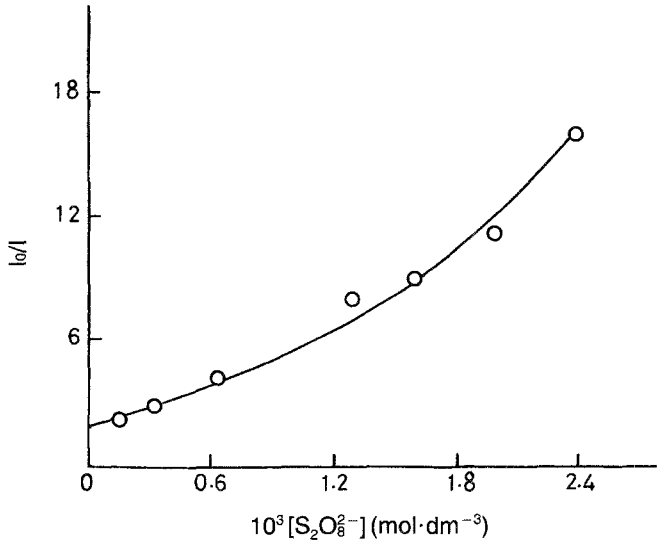


Fig. 2. *Stern-Volmer* plot of the fluorescence quenching of *C1* with peroxodisulfate; $[C1] = 1 \times 10^{-5}$ mol·dm^{-3}; $\lambda_{ex} = 365$ nm

an interaction is further confirmed by the fact that no other emission signal due to exciplex formation appears in Fig. 1. The indicated interaction must therefore be a chemical oxidation of the dye with $S_2O_8^{2-}$.

Kinetic studies

When peroxodisulfate was added to the *C1* solution, the absorbance of *C1* decreased with time (Fig. 3). On plotting the logarithm of the absorbance *vs.* time, Fig. 4 was obtained. It indicates clean pseudo-first-order kinetics for the consumption of *C1*. The slope is the observed first order rate constant, k_{obs}, at the corresponding temperature. The second order rate constant at each temperature was calculated using the equation $k = k_{obs}/[S_2O_8^{2-}]$. From the temperature dependence given in Fig. 5 the activation parameters were calculated; the data are listed in Table 1.

The relationship between k_{obs} and the concentration of peroxodisulfate is shown in Fig. 6. Since the plot is linear and passes through the origin, it indicates a first order dependence of the rate upon the $S_2O_8^{2-}$ concentration. The plot obeys the relation $k_{obs} = 3.36\,[S_2O_8^{2-}]$. The slope is the second order rate constant. According to these results, the reaction follows the overall second order rate law $-\mathrm{d}[\textit{coumarin-1}]/\mathrm{dt} = k[\textit{coumarin-1}][S_2O_8^{2-}]$.

To get a better insight into the reaction mechanism, the effect of allyl acetate as a radical trap on the reaction rate was examined [13]. Addition of this reagent to the reaction system had no detectable effect of k_{obs}. This indicates that the reaction is not likely to involve the generation of sulfate radical species ($SO_4^{\cdot -}$).

Universal buffer was employed to study the *pH* dependence of the reaction rate. In a typical experiment, the observed rate constant had the values 0.0025, 0.005, and 0.0085 min^{-1} in solutions of *pH* 2.27, 4.6, and 8.6, respectively. This may be interpreted on the basis that $S_2O_8^{2-}$ favours the reaction with the unprotonated rather than the protonated form of the dye molecule [14–17].

The effect of sodium dodecyl sulfate (*SDS*) upon the reaction rate was investigated at fixed concentrations of both *C1* and $S_2O_8^{2-}$ but at variable concentration

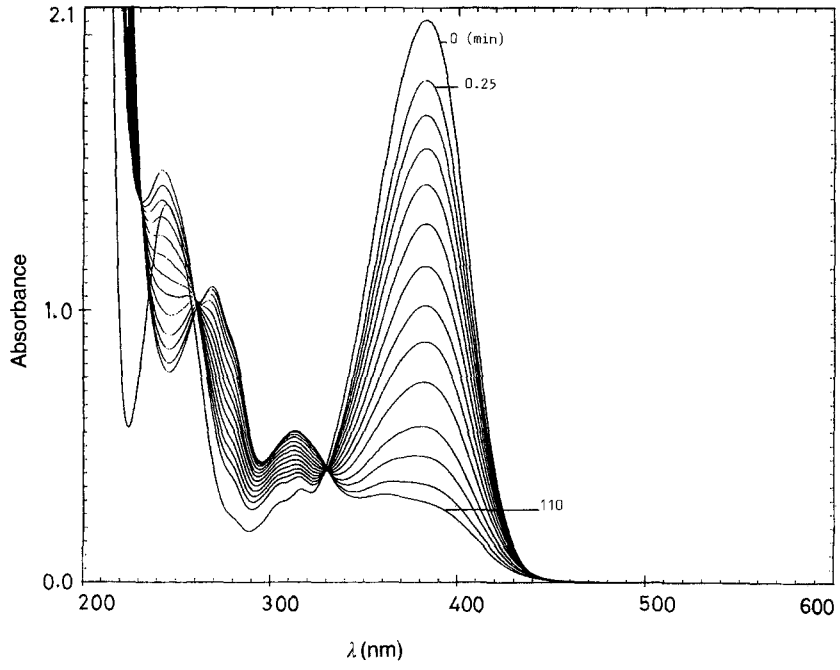


Fig. 3. Decrease of absorbance with time during the reaction of *C1* with $S_2O_8^{2-}$; $[S_2O_8^{2-}] = 6.67 \times 10^{-3}$ mol·dm^{-3}; $[C1] = 6.67 \times 10^{-5}$ mol·dm^{-3}; $T = 25$ °C

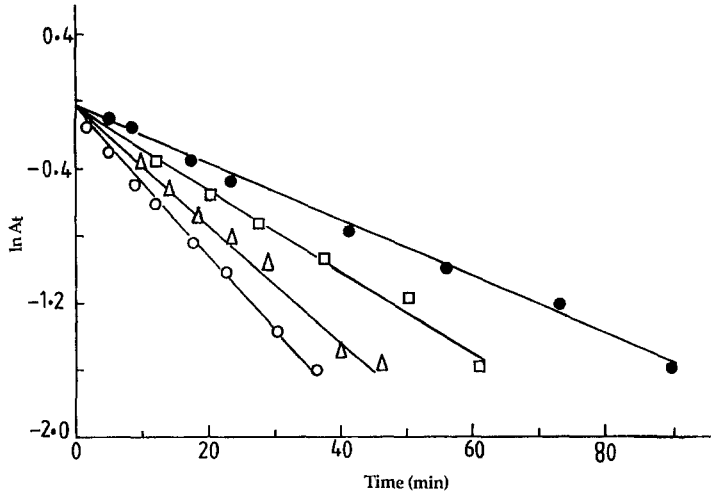


Fig. 4. First order plot for the oxidation of *C1* with $S_2O_8^{2-}$ at various temperatures; $[C1] = 3.33 \times 10^{-5}$ mol·dm^{-3}; $[S_2O_8^{2-}] = 6.67 \times 10^{-3}$ mol·dm^{-3}; ●: 20 °C; □: 25 °C; △: 30 °C; ○: 35 °C

of *SDS*. Fig. 7 depicts the decrease of the observed rate constant as a function of *SDS* concentration. This phenomenon may be atributed to the formation of *SDS* dimers, timers, *etc.* [18]. These aggretates grow in solution, and the growth continues as long as more *SDS* monomers are present. At certain concentration of *SDS* (critical micelle concentration, CMC), complete micelles are formed. The *C1* molecules are taken up

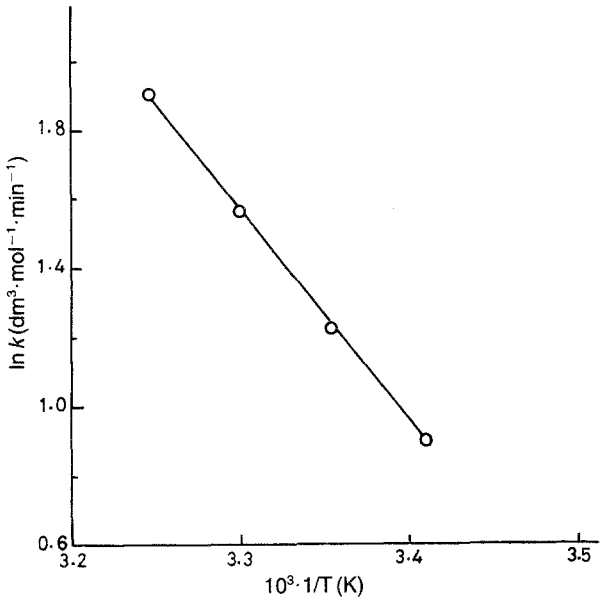


Fig. 5. *Arrhenius* plot derived from Fig. 3 for the oxidation of *C1* with $S_2O_8^{2-}$

Table 1. Kinetic parameters for the oxidation of *C1* with $S_2O_8^{2-}$; $[C1] = 3.3 \times 10^{-5}$ mol·dm^{-3}; $[S_2O_8^{2-}] = 6.66 \times 10^{-3}$ mol·dm^{-3}

Temp. (°C)	k (dm^3·mol^{-1}·min^{-1})	E (kJ·mol^{-1})	$\Delta H^{\#}$ (kJ·mol^{-1})	$\Delta G^{\#}$ (kJ·mol^{-1})	$\Delta S^{\#}$ (J·mol^{-1}·K^{-1})
20	2.58				
25	3.36	48.14	45.64	73.15	−91.54
30	4.75				
35	6.75				

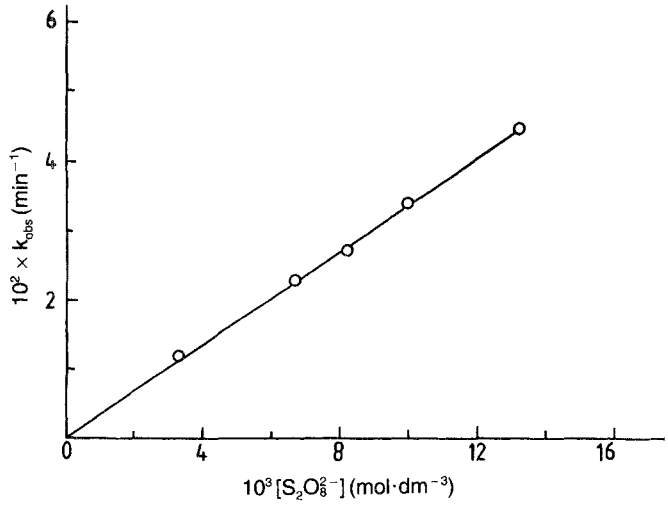


Fig. 6. Variation of the observed rate constant with the $S_2O_8^{2-}$ concentration; $[C1] = 3.33 \times 10^{-5}$ mol·dm^{-3}; $T = 25$ °C

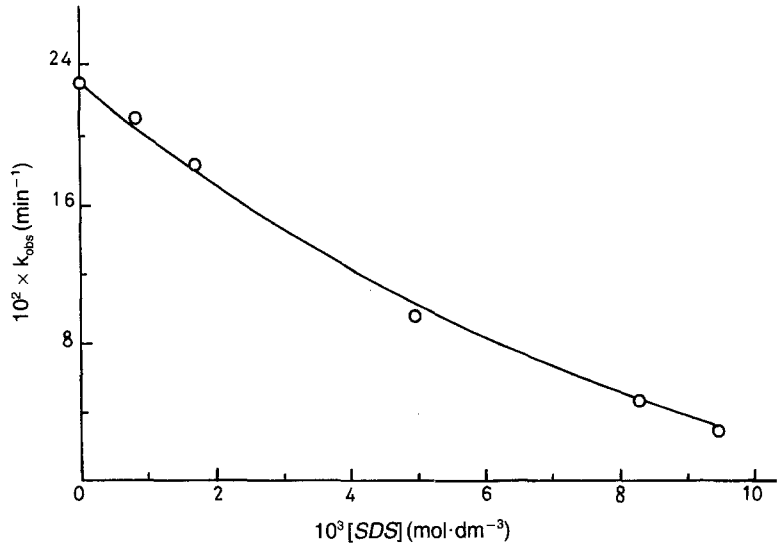


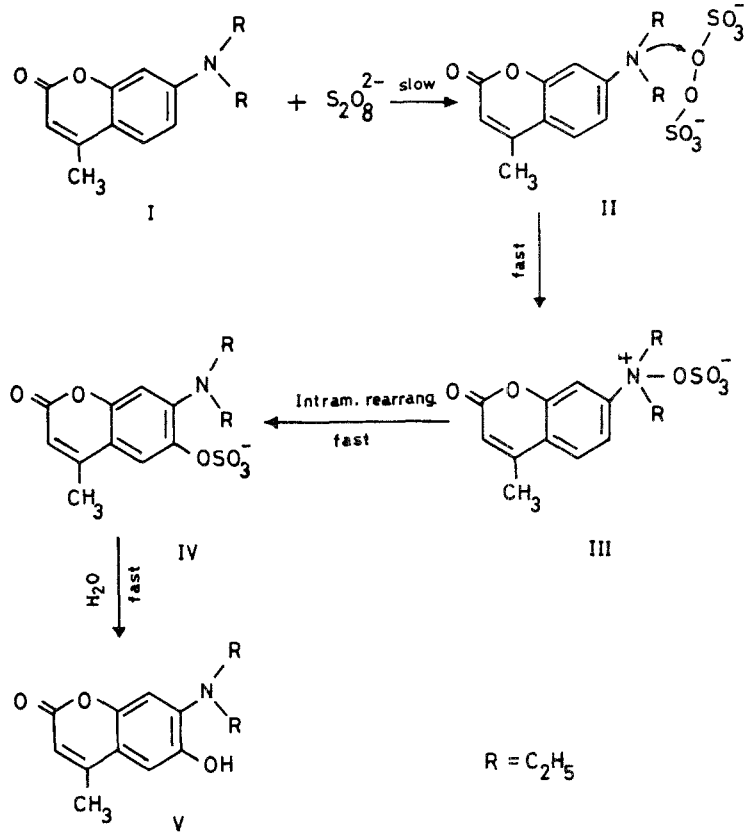
Fig. 7. Rate constant dependence upon *SDS* concentration; $[C1] = 3.33 \times 10^{-5}$ mol·dm^{-3}; $[S_2O_8^{2-}] = 4.66 \times 10^{-3}$ mol·dm^{-3}; $T = 30\,^{\circ}C$

into the micelle core and then become less exposed to the attack by $S_2O_8^{2-}$. A further interpretation may come from the increase in medium viscosity [19] associated with the building up of large micelles and different micelle shapes. These effects are expected to lower the mobility of reacting species, and consequently the reaction rate is retarded.

Mechanism

The data given in Table 1 reveal that the energy and entropy of activation determined in this study are substantially different from those reported earlier [20] for the decomposition of $S_2O_8^{2-}$ in the absence of any reducing organic substrate. For example, the energy of activation is remarkably lower than that found for the $S_2O_8^{2-}$ decomposition (110–120 kJ·mol^{-1}). It also evident from Table 1 that the entropy of activation has a negative value with respect to that observed for the first order self-decomposition of peroxodisulfate (104.6 J·mol^{-1} K^{-1}, [20]). The negative entropy indicates a greater organization of the transition state in the present coumarin/$S_2O_8^{2-}$ interaction. In view of the low activation energy and the negative entropy of activation we have found, it is expected that the oxidation process proceeds *via* a bimolecular reaction between the substrate molecule and the oxidant ion rather than *via* spontaneous dissociation of the oxidant ion (Scheme 1).

The nucleophilicity of *C1* dye facilitates its attack by the electron deficient centre of the $S_2O_8^{2-}$ ion. Such behaviour leads to the formation of a transition state intermediate (**II**). The reactive complex undergoes a fast dissociation to give the charged species **III**, followed by a rapid intramolecular rearrangement [13] into the derivative **IV**, which yields 6-hydroxy-7-diethylamino-4-methyl-coumarin (**V**). Formation of **V** supports this mechanism; it is in accordance with that reported for the peroxodisulfate oxidation of a large number of other coumarin dyes [21].



Scheme 1

Experimental

Coumarin-1 (Aldrich) was used as received. Potassium peroxodisulfate (Merck) was recrystallized twice from distilled water at 25 °C and then dried in vacuum over P_2O_5. Its stock solution was prepared fresh when required in order to avoid self-decomposition. Other chemicals were of analytical grade quality; their solutions were prepared in double distilled water immediately prior to the measurements.

The fluorescence emission spectra were recorded on a Shimadzu RF-510 spectrofluorophotometer with $\lambda_{ex} = 365$ nm and a band width of 10 nm. The instrument was connected to a circulating water thermostat (Julabo F10) of ± 0.1 °C temperature precision. Absorption spectra were recorded on a Shimadzu UV/Vis spectrophotometer (Model 2100 S) operating with a Shimadzu data acquisition system. The reaction temperature was controlled in the cell holder of the spectrophotometer by a Shimadzu electronic temperature control unit with an accuracy better than ± 0.1 °C.

Kinetic runs were carried out under pseudo-first-order conditions in solutions containing a 200-fold excess of peroxodisulfate. The reaction progress was followed monitoring the decrease of absorbance with time for the remaining dye species using quartz cells (path length: 1 cm). The measurements were performed at 382 nm in ethanol/water (3:7 v/v). Pseudo-first-order rate constants (k_{obs}) were obtained from the slopes of linear regression plots of $\ln A_t$ *vs.* time.

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