

# Kinetic Studies of the Oxidation of Coumarin-540 Laser Dye

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**Summary.** 3-(2-Benzothiazolyl)-7-diethylaminocoumarin (C-540) has been irradiated at 254 nm in halomethane solvents, and the first order rate constant of the photo-oxidation reaction was determined. The hydrogen bond donation of the solvents plays a substantial role in controlling the rate of formation of the photoproduct. The linearity of the isokinetic relationship supports the similarity of the mechanism in all solvents and emphasizes that the activation process is controlled by diffusion of dye into the solvent cage. Moreover, the chemical oxidation of C-540 with peroxodisulfate anion catalyzed by  $\text{Ag}^+$  ions has been studied. The reaction follows second-order kinetics, first order for each individual reactant.

**Keywords.** Solvent effect; Oxidation; Hydrogen bonds; Kinetics; Electron transfer; Dyes; Charge transfer; Catalysis.

## Introduction

Coumarin derivatives constitute a class of compounds of high significance. Their most important applications include seed germination, the growth of photosynthetic alga [1], and photomutagenic reaction with DNA bases [2, 3]. Aminocoumarins are used as laser dyes in the blue-green region [4]. Continuous and *quasi*-continuous operation of laser dyes has been achieved with dyes under different conditions [5–7].

Coumarin-540 is considered as a laser dye for tunable pulsed operation from 510 to 570 nm [8]. The effect of molecular structure of coumarin derivatives with an amino group in position 7 and the nature of the solvent on the solute/solvent interactions have attracted much attention [5, 9, 10]. The formation of specific hydrogen bonds between coumarin dyes and protic solvents has been considered to explain spectral shifts and internal conversion process [7, 11, 12].

Although the photochemical aspects of C-540 have been thoroughly investigated, information upon its photo- and chemical stability seems to be lacking. Thus, the present paper aims at studying the photochemical reactivity of C-540 in halomethane solvents owing to their physicochemical properties. Furthermore, the oxidation kinetics of this dye with peroxodisulfate anions has been investigated, providing insight into its stability.

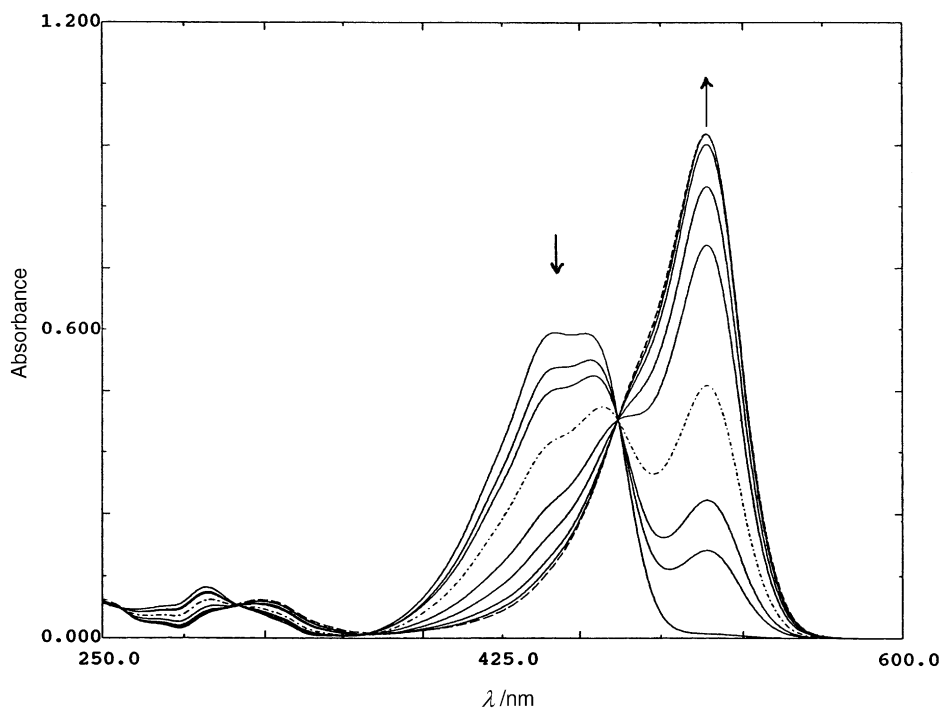
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## Results and Discussion

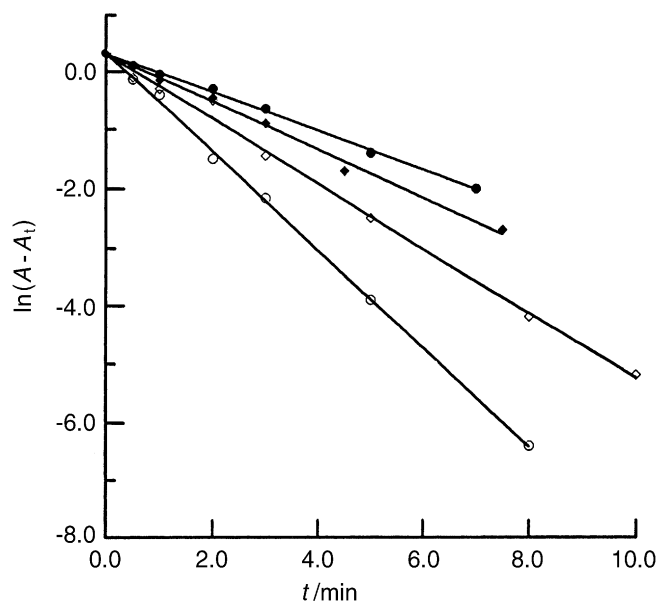
### *Photochemical oxidation*

Upon irradiation at 254 nm in chloromethane solvents of the general formula  $\text{CH}_n\text{Cl}_{4-n}$  coumarin-540 undergoes a photochemical reaction. The decrease in the absorbance at  $\lambda_{\text{max}} = 462/449, 458,$  and  $456/433$  nm in  $\text{CHCl}_3, \text{CH}_2\text{Cl}_2,$  and  $\text{CCl}_4,$  respectively, is accompanied by the appearance of new bands at  $\lambda_{\text{max}} = 515, 514,$  and  $500$  nm. The intensity of these new bands increases with increasing irradiation time as shown in Fig. 1. Furthermore their intensity depends on the type of solvent and follows the order  $\text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2.$

Figure 2 shows a plot of  $\ln(A_\infty - A_t)$  vs. time at different temperatures, from which the first-order rate constants were calculated (Table 1). The values of the rate constants were introduced in *Arrhenius* plots (Fig. 3) and the activation energies were computed and tabulated (Table 1). From Table 1 it is obvious that the rate constants in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  decrease as the temperature increases. This can be explained on the basis that the photoreaction proceeds *via* fast formation of a pre-equilibrium intermediate (exciplex formation) which is thermodynamically unstable. The excited state of aromatic molecules is expected to be involved in a charge transfer interaction with chloromethanes through exciplex formation [13, 14]. Moreover, the negative values of the activation energy in both solvents confirm the instability of the intermediate upon increasing the temperature [15]. In contrast,



**Fig. 1.** Variation of the absorption spectra of C-540 upon irradiation at 254 nm in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ ; irradiation times: 0.0, 0.25, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, and 10 min in the direction of increasing the absorbances at 514 nm



**Fig. 2.** First-order plot for the irradiation of C-540 in  $\text{CH}_2\text{Cl}_2$  at different temperatures; [C-540]:  $1.2 \times 10^{-5} \text{ M}$ ;  $\circ$ : 20°C,  $\diamond$ : 25°C,  $\blacklozenge$ : 30°C,  $\bullet$ : 35°C

**Table 1.** Rate constants and activation parameters for the photooxidation of C-540 in halomethanes at different temperatures; [C-540] =  $1.2 \times 10^{-5} \text{ M}$

Solvent	$T$ (°C)	$k \times 10^2$ ( $\text{s}^{-1}$ )	$E^\#$ (kJ/mol)	$\Delta H^\#$ (kJ/mol)	$\Delta G^\#$ (kJ/mol)	$\Delta S^\#$ (J/mol · K)
$\text{CH}_3\text{Cl}$	20	1.52				
	25	2.01	34.25	31.77	71.33	-140
	30	2.46	( $\pm 0.02$ )			
	35	3.11				
$\text{CH}_2\text{Cl}_2$	20	1.42				
	25	0.91	-56.30	-58.78	73.07	-450
	30	0.62	( $\pm 0.09$ )			
	35	0.52				
$\text{CCl}_4$	20	1.23				
	25	0.74	-80.80	-83.27	74.07	-530
	30	0.38	( $\pm 0.05$ )			
	35	0.21				

the increasing rate constant with rising temperature in the case of  $\text{CHCl}_3$  indicates the formation of a thermodynamically stable intermediate.

The other activation parameters ( $\Delta H^\#$ ,  $\Delta G^\#$ , and  $\Delta S^\#$ ) were calculated according to Eqs. (1)–(3) [15].

$$\Delta H^\# = E^\# - RT \quad (1)$$

$$k = (k_B T/h) \exp(-\Delta G^\# / RT) \quad (2)$$

$$\Delta G^\# = \Delta H^\# - T \Delta S^\# \quad (3)$$

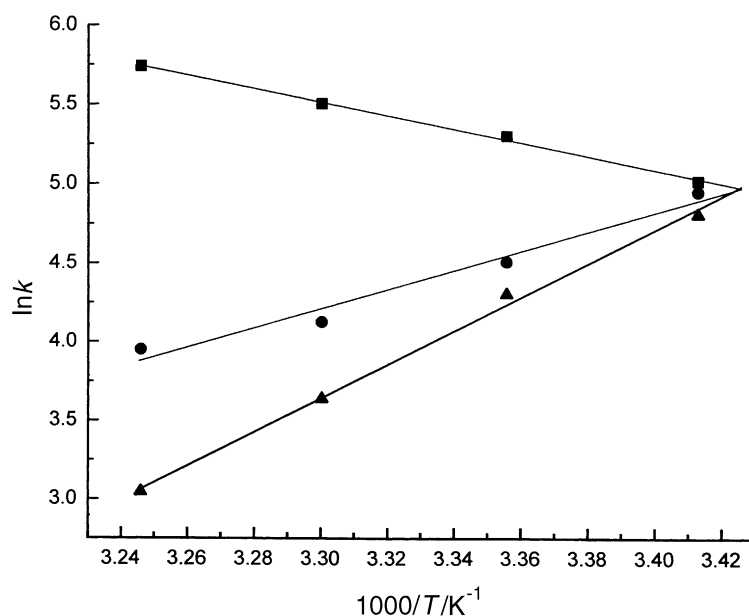


Fig. 3. *Arhenius* plot for the irradiation of C-540 in halomethanes;  $\blacktriangle$ : CH<sub>3</sub>Cl,  $\bullet$ : CH<sub>2</sub>Cl<sub>2</sub>,  $\blacksquare$ : CCl<sub>4</sub>

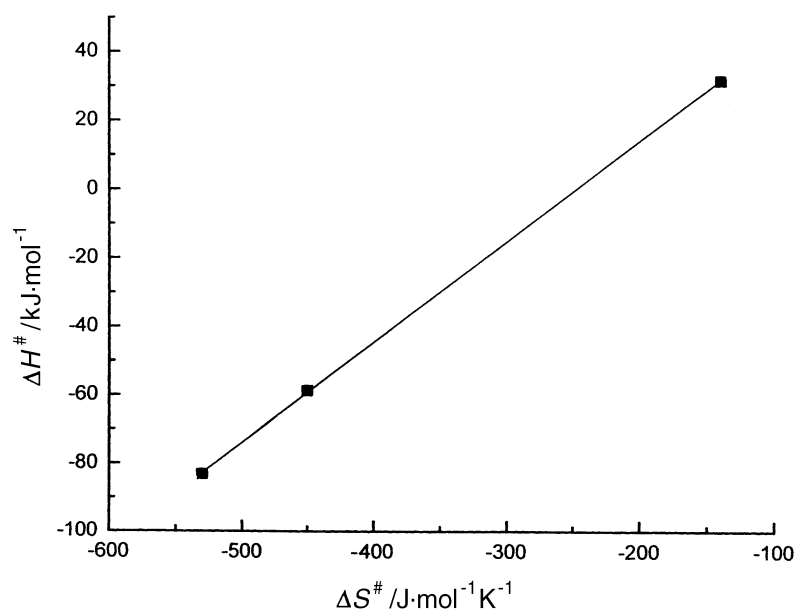


Fig. 4. Isokinetic relationship for the irradiation of C-540 in halomethanes

The high negative values of  $\Delta S^\ddagger$  indicate that the photoreaction of C-540 in halomethane solvents proceeds *via* a charge transfer complex, which is likely to be the exciplex, as an intermediate [16]. The isokinetic relationship ( $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$ ) is depicted in Fig. 4; from its slope the isokinetic temperature was calculated to 294 K. The isokinetic temperature is the temperature at which the photoreactions in the different solvents have the same rate constant. Within experimental error ( $\pm 3\%$ ), this value is equal to the average of the experimental temperature (300.5 K). Moreover, the

intersection point in Fig. 3 at  $T=291$  K confirms the hypothesis of isokinetic relationship. Thus, it can be concluded that the photoreaction is controlled by the diffusion of excited C-540 into the solvent cage and not by chemical reaction (electron transfer step) [17].

It has been reported that the degree of interaction between halomethane solvents and several electron donors follows the order of electron affinity ( $E_A = 1.36, 1.75,$  and  $2.1$  eV for  $\text{CH}_2\text{Cl}_2, \text{CHCl}_3,$  and  $\text{CCl}_4,$  respectively) [13, 18–20]. This suggested that we should obtain rate constants following the order  $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$ . However, our results reveal a decrease in the rate constant on going from  $\text{CHCl}_3$  to  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  as shown in Table 1. Thus, it seems that the electron affinity of these solvents is not the factor that controls the rate of the photoreaction of C-540. This behavior can be explained on the basis of specific interactions between the solvent molecules and the dye. It is well known that  $\text{CHCl}_3$  is a relatively strong hydrogen bond donor (HBD) and forms hydrogen bonds with tertiary amines [21]. The HBD ability of halomethanes, expressed as the solvent parameter  $\alpha$  as introduced by *Kamlet* and *Taft* [11, 22], decrease on going from  $\text{CHCl}_3$  to  $\text{CCl}_4$  ( $\alpha = 0.2, 0.13,$  and  $0.0$  for  $\text{CHCl}_3, \text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4,$  respectively). Thus, the anomalous behaviour in  $\text{CHCl}_3$  can be attributed to hydrogen bond formation with the dye molecules, which becomes stronger in the excited state due to increasing the basicity of the excited dye. The formation of hydrogen bonds may lead to stabilization of the charge transfer intermediate responsible for the formation of the photoproduct. The fluorescence quenching of 3-(*N,N*-dimethylamino)-2*H*-benzopyran-2-one by halomethane solvents in cyclohexane has been studied, and it was found that  $\text{CHCl}_3$  exhibits a different quenching effect. This behavior was explained by hydrogen bond formation of the solvent with the organic molecule [23]. Figure 5

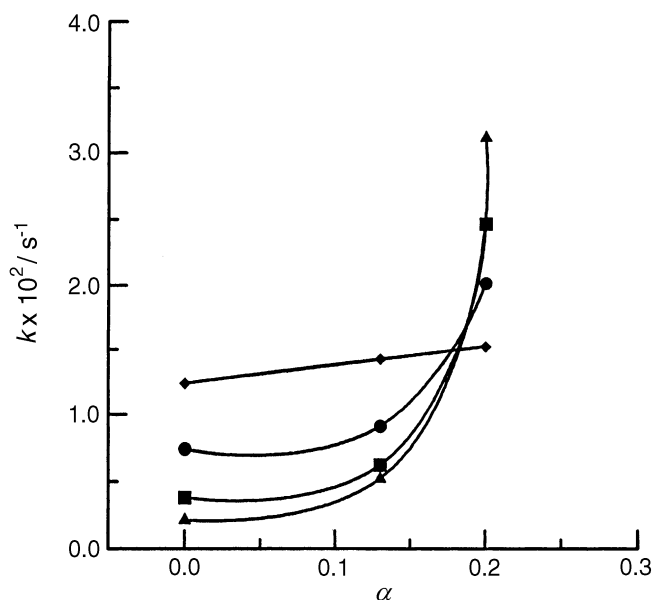
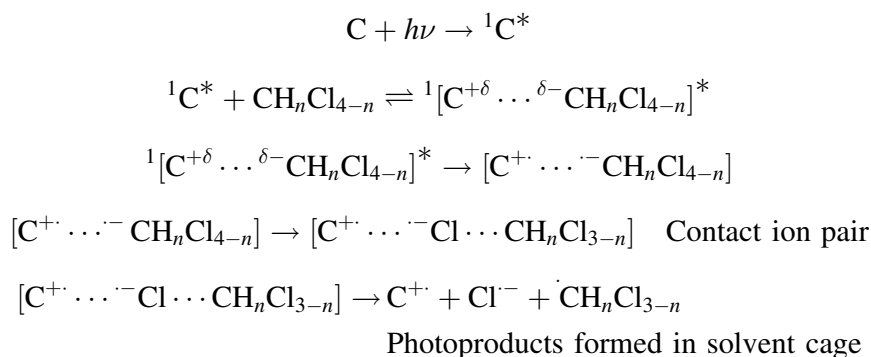


Fig. 5. Correlation between the hydrogen bond donation ( $\alpha$ ) of the solvents and the rate constants at different temperatures;  $\blacklozenge$ : 20°C,  $\bullet$ : 25°C,  $\blacktriangle$ : 30°C,  $\blacksquare$ : 35°C

shows the correlation between the rate constants and  $\alpha$  at different temperatures. As can be seen, increasing HBD enhances the rate constant remarkably.

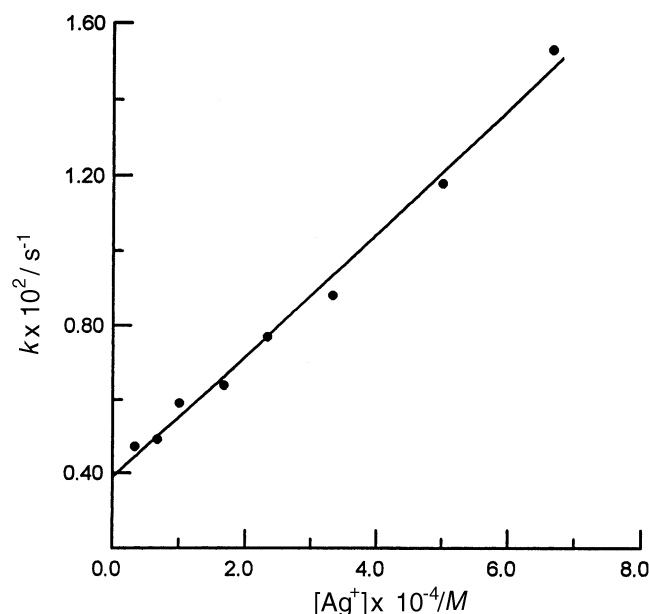
As the excited state of C-540 is more basic than the ground state [24–28], it is involved in charge transfer interactions with chloromethanes through exciplex formation. The lower energy of the C-Cl bond and the low activation energy of the dissociative process of electron attachment promote the chemical reactivity of chloromethanes [6]. Thus, the following reaction scheme can be proposed to explain the photoreactivity of C-540 in chloromethanes:



According to this scheme, an initial diffusion of the excited singlet C-540 ( ${}^1\text{C}^*$ ) into the solvent cage forming a transient exciplex, is proposed. The involvement of the excited state charge transfer exciplex in the reaction is supported by the higher negative values of  $\Delta S^\ddagger$  as mentioned previously. This is followed by formation of an ion pair, which finally gives a C-540 radical cation and chloride ion. The formation of  $\text{Cl}^-$  was confirmed by appearance of a white precipitate when an ethanolic  $\text{AgNO}_3$  solution was added to the irradiated dye solution. Thus, it can be concluded that C-540 undergoes photo-oxidation upon irradiation at 254 nm in halomethane solvents. The photo-oxidation of some aromatic and aliphatic amines in  $\text{CHCl}_3$  has also been reported [18]. A similar scheme was proposed to account for the photoreaction of carbolines in  $\text{CHCl}_3$  and  $\text{CCl}_4$  [19].

#### Chemical oxidation

To obtain further information about the chemical stability of C-540, its oxidation by peroxodisulfate anions has been studied. The oxidation reaction was carried out under *pseudo*-first-order conditions with a large excess of  $[\text{S}_2\text{O}_8^{2-}]$ . The decrease in the absorbance at  $\lambda_{\text{max}} = 468 \text{ nm}$  with time was found to be very slow (data not shown). It has been reported that the oxidation of some aromatic secondary and tertiary amines using  $\text{S}_2\text{O}_8^{2-}$  is slow unless a suitable catalyst is present. The standard catalysts are transition metal ions such as  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  [29–34]; therefore,  $\text{Ag}^+$  ions were incorporated in the reaction mixture. The effect of  $[\text{Ag}^+]$  was examined at constant concentrations of the substrate and the oxidant, and the kinetics of the catalyzed reaction were investigated. The reaction followed a *pseudo*-first-order law; the absorbance *vs.* time data were introduced in the first-order plot, and the rate constants were calculated. A plot of the *pseudo*-first-order rate constant *vs.*  $[\text{Ag}^+]$  is shown in Fig. 6. The linear relation between the *pseudo*-first order rate constant and  $[\text{Ag}^+]$  indicates first-order dependence on its



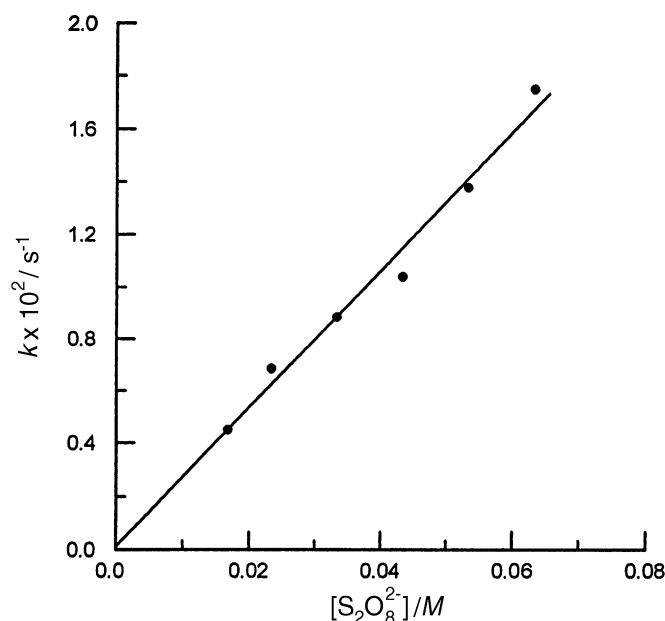
**Fig. 6.** Variation of the rate constant as a function of  $[\text{Ag}^+]$ ;  $[\text{C-540}] = 3.3 \times 10^{-5} \text{ M}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-2} \text{ M}$ ,  $T = 30^\circ\text{C}$

concentration. The ordinate intercept represents the rate constant of the uncatalyzed reaction ( $k_0$ ) that takes place simultaneously with the catalyzed one. The plot thus obeys the relation  $k = k_0 + k_c \cdot [\text{Ag}^+]$  where  $k_c$  is the second-order rate constant for the catalyzed path and represents the slope of the plot. Introducing the values of catalyzed and uncatalyzed rate constants into the above relation affords  $k = 0.004 + 16.8 \cdot [\text{Ag}^+]$ . Although both terms contribute to the rate constants, the larger contribution is due to the term  $k_c \cdot [\text{Ag}^+]$ , which proves the weakness of the oxidation process observed in the absence of the catalyst.

The effect of temperature on the reaction rate has been investigated in the 30–50°C range, and it is safe to infer that the spontaneous decomposition of the peroxodisulfate within this range was undetectable. The activation energy was determined from an *Arrhenius* plot. The other activation parameters were calculated using Eqs. (1)–(3) and are summarized in Table 2.

**Table 2.** Rate constants and activation parameters for the oxidation of C-540 by peroxodisulfate anions;  $[\text{C-540}] = 3.3 \times 10^{-5} \text{ M}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 3.3 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^+] = 1.67 \times 10^{-4} \text{ M}$

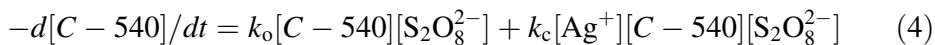
$T$ (°C)	$k \times 10^2$ (s <sup>-1</sup> )	$E^\ddagger$ (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol · K)
30	0.65				
35	1.13	122.1	119.67	86.13	–100
40	2.90	(±0.11)			
45	6.10				
50	11.90				



**Fig. 7.** Variation of the rate constant as a function of peroxodisulfate concentration;  $[C-540] = 3.3 \times 10^{-5} M$ ,  $[Ag^+] = 3.3 \times 10^{-4} M$ ,  $T = 30^\circ C$

The order with respect to  $[S_2O_8^{2-}]$  was determined at constant concentrations of the dye and the catalyst, while the concentration of  $S_2O_8^{2-}$  was varied. The plot of the *pseudo*-first-order rate constant ( $k_{obs}$ ) vs.  $[S_2O_8^{2-}]_0$  is linear which is a good evidence for the first-order kinetics with respect to  $[S_2O_8^{2-}]$  (Fig. 7). The slope is considered as the second-order rate constant and equals  $0.27 M^{-1} \cdot \text{min}^{-1}$  at  $30^\circ C$ .

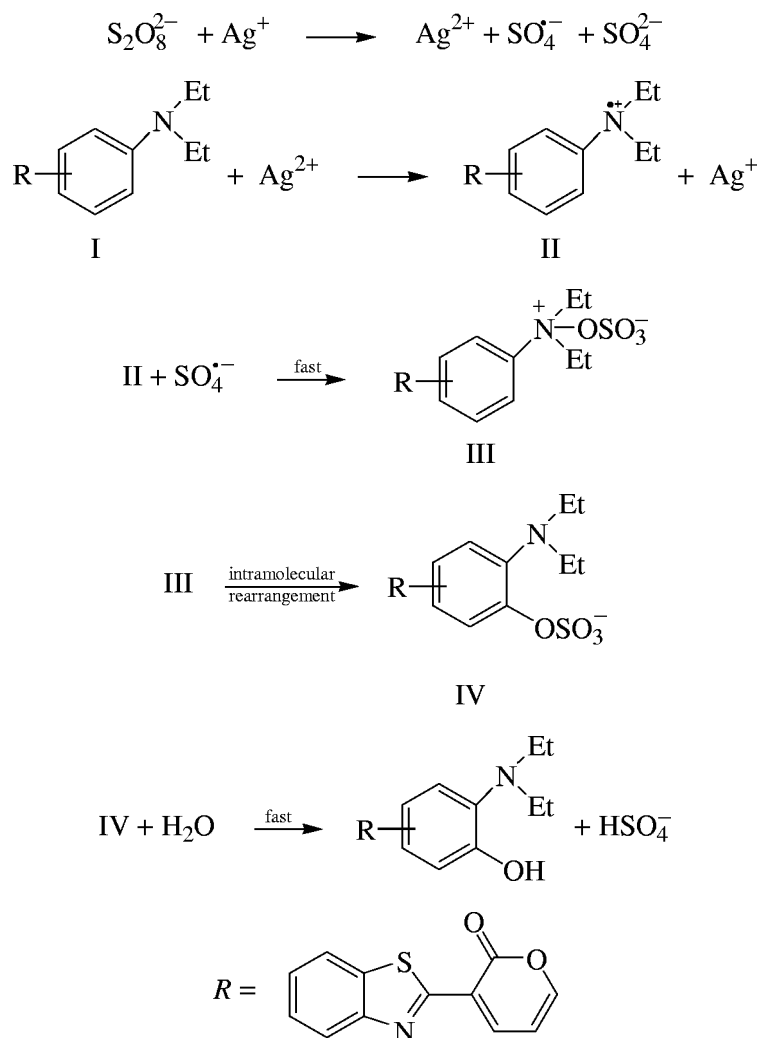
In view of these findings, the current oxidation reaction may proceed *via* two parallel pathways according to the following equation:



This kinetic behavior is supported by several analogous rate laws reported for the oxidation of organic substrates with this oxidant [29–32].

Since the non-catalyzed oxidation of C-540 dye has not been considered in detail, only an overall mechanism accounting for the catalyzed reaction can be suggested. Numerous data have been accumulated [30–32] which confirm the accelerating effect of  $Ag^+$  and give insight into the mechanism of the catalytic activity of this ion. Based on the above results it is concluded that the first step in the oxidation process involves the reaction between  $S_2O_8^{2-}$  and  $Ag^+$ , whereby  $SO_4^{\cdot -}$  and  $Ag^{2+}$  are formed. An electron transfer follows between  $Ag^{2+}$  and the  $-N-(Et)_2$  moiety of the substrate to yield the  $-N^+(Et)_2$  radical as an intermediate. This intermediate is then further oxidized and undergoes an intramolecular rearrangement to give the final product. The mechanistic scheme shown below can thus be envisaged to be similar with that reported in Refs. [30, 33]. Also, the mechanism is consistent with the fact that the reaction is first-order with respect to the concentrations of the substrate and the oxidant.





## Experimental

### Materials

Coumarin-540 (Aldrich) was used as received. Chloromethanes and acetonitrile were purified as described in the literature and kept in the dark over a molecular sieve [35]. Water of low conductivity was used. Potassium peroxodisulfate (Merck) was recrystallized twice from distilled water and then dried in vacuum over  $\text{P}_2\text{O}_5$ . Fresh solutions of peroxodisulfate were prepared when required in order to avoid self-decomposition. The solution of dye used for chemical oxidation was prepared in a 25% (v/v) acetonitrile/water mixture due to solubility requirements, and its concentration was less than  $5 \times 10^{-5} \text{ mol/dm}^3$  to avoid molecular aggregation [36]. Other chemicals were of analytical grade quality; their solutions were prepared with double distilled water immediately prior to measurements.

### Photochemical oxidation

Steady state irradiation of coumarin solution ( $1.2 \times 10^{-5} \text{ mol/dm}^3$ ) at 254 nm in halomethane solvents was performed in a thermostatted  $3 \text{ cm}^3$  stoppered quartz cell using a 30 W medium

pressure Hg-lamp (DESAGA). The irradiated cell was transferred to the thermostatted cell holder of a spectrophotometer where the absorption spectra were recorded. Kinetic runs were performed by monitoring the absorbance of the photoproducts at  $\lambda_{\max} = 515, 514,$  and  $500$  nm in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CCl}_4$ , respectively. The absorption spectra were recorded on a Shimadzu UV-3101 PC spectrophotometer operating with a Shimadzu data acquisition system. A Shimadzu electronic temperature controller kept the reaction temperature constant within  $\pm 0.1^\circ\text{C}$ .

The reactions were carried out under *pseudo*-first-order conditions with an excess of halomethanes. *Pseudo*-first-order rate constants were obtained from the slopes of linear regression plots according to Eq. (5)

$$\ln(A_\infty - A_t) = \ln A_\infty - kt \quad (5)$$

$A_\infty$  is the maximum absorbance obtained at reproducible irradiation times, and  $A_t$  is the absorbance of the photoproducts at different irradiation times  $t$ .

#### Chemical oxidation

Kinetic runs were followed spectrophotometrically by monitoring the absorbance of the non-reacting C-540 in the reaction mixture at 468 nm with time. Uncatalyzed reaction carried out under *pseudo*-first-order conditions in solutions containing an excess of  $\text{S}_2\text{O}_8^{2-}$  ( $[\text{S}_2\text{O}_8^{2-}] = 1000 \times [\text{dye}]$ ) was slow (data not shown). In order to accelerate the reaction,  $\text{Ag}^+$  ions were added as a catalyst, and the *pseudo*-first-order rate constant of the catalyzed reaction ( $k_{\text{obs}}$ ) was obtained from Eq. (6).

$$\ln(A_0 - A_t) = \ln A_0 - k_{\text{obs}}t \quad (6)$$

Rate constants obtained from duplicate runs were reproducible within  $\pm 3\%$ .

## References

- [1] Graber OR, Grimes MW, Haury A (1969) *J Chem Phys* **50**: 4
- [2] Song PS, Gordon WH (1970) *J Phys Chem* **74**: 24
- [3] Hammond GS, Stout CA, Lamola AA (1964) *J Am Chem Soc* **86**: 3103
- [4] Drexhage KH (1973) In: Schafer FD (ed) *Dye Laser*. Springer, New York, p 144
- [5] Reynolds GA, Drexhage KH (1975) *Opt Commun* **13**: 222
- [6] Tuccio SA, Drexhage KH, Reynolds GA (1973) *Opt Commun* **7**: 248
- [7] Masilamani V, Sivaram BM (1982) *J Lumin* **27**: 137
- [8] Johnston TF, Brady RH, Proffitt W (1982) *Appl Optics* **21**: (13) 2307
- [9] Kubin RF, Flecher AN (1983) *Chem Phys Lett* **99**: 49
- [10] Jones GI, Jackson WR, Choi C, Bergmark WR (1985) *J Phys Chem* **89**: 294
- [11] Kamlet MJ, Dickinson C, Taft RW (1981) *Chem Phys Lett* **77**: 69
- [12] Lopez Arbeloa T, Lopez Arbeloa F, Topia MJ, Lopez Arbeloa I (1993) *J Phys Chem* **97**: 4704
- [13] Azim SA, El-Daly HA, El-Daly SA, Zeid KA, Ebeid EM, Heldt JK (1996) *J Chem Soc Faraday Trans* **92** (15): 2685
- [14] El-Daly SA (1999) *Spectrochimica Acta, Part A* **55**: 143
- [15] Espenson JH (1995) *Chemical Kinetics and Reaction Mechanisms*, 2nd edn. McGraw-Hill, chapter 7
- [16] Dwivedi PC, Rao CNR (1972) *J Chem Soc Perkin Trans II*, 238
- [17] Zaki AB, El-Sheikh MY, Evans J, El-Safty SA (2000) *J Colloid Interface Sci* (in press)
- [18] Bard AJ, Ledwith A, Shine HJ (1976) *Adv Phys Org Chem* **12**: 155
- [19] Biondic MC, Erra-Balsella R (1990) *J Photochem Photobiol A: Chem* **15**: 341; Biondic MC, Erra-Balsella R (1994) *J Photochem Photobiol A: Chem* **77**: 149
- [20] Mattay J (1991) *Photoinduced Electron Transfer*, part I, vol 156, and part III, vol 159
- [21] Lucas JP, Guibe L (1970) *Mol Phys* **19**: 85
- [22] Marcus Y (1993) *Chem Soc Rev* 409

- [23] Boszezyk W, Latowski T (1989) *Z Naturforsch B* **44**: 1585
- [24] Jones GI, Jackson WR, Choi C, Bergmark WR (1985) *J Phys Chem* **89**: 294
- [25] Abel-Mottaleb MS, Antonious MS, Abo-Aly MM, Ismaiel LM, El-Sayed BA, Sherief AMK (1989) *J Photochem Photobiol A: Chem* **50**: 259
- [26] Chu G, Yangbo F (1987) *J Chem Soc Faraday Trans* **1**: 83, 2533
- [27] Ramalingam A, Palanisamy PK, Masilamani V, Siravam BM (1989) *J Photochem Photobiol A: Chem* **49**: 89
- [28] Van Grompel JA, Schuster GB (1989) *J Phys Chem* **93**: 1292
- [29] El-Sheikh MY, Salem MA, Ismail AA, Zaki AB (1993) *J Phys Org Chem* **6**: 609
- [30] Salem MA, El-Sheikh AY, Ismail AA, Zaki AB (1993) *J Chim Phys* **90**: 1201
- [31] Jonnalagadda SB, Choudary C, Battacharag AK (1983) *J Chem Soc Perkin Trans II*, 849
- [32] Salem MA, Zaki AB, Ismail AA, El-Sheikh MY (1995) *Z Phys Chem* **192**: 87
- [33] Salem MA, Gemeay AH, *Monatsh Chem* (in press)
- [34] Kislenco VN, Berlin AA, Litovchenko NV (1997) *Kinetic and Catalysis* **38**: 3, 359–364
- [35] Perrin DD, Armarego WLF (1988) *Purification of Laboratory Chemicals*. Pergamon, New York
- [36] Mohan D, Taneja L, Gaur A, Sharma AK, Singh RD (1991) *J Lumin* **50**: 127

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