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A kinetic study of the hydrolysis of crystal violet and some terminal and bridged analogues

Steven F. Beach [a,*], John D. Hepworth [b], Donald Mason [a],
Elizabeth A. Swarbrick [a]

[a] Department of Chemistry, University of Central Lancashire, Preston PR1 2HE, UK
[b] Department of Chemistry, The University of Hull, Hull HU6 7RX, UK

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Dedicated to Dr Geoff Hallas on his 65th birthday in appreciation of his friendship, guidance and inspiration.

Abstract

Rate constants have been measured for the reaction of hydroxide ions with Crystal Violet, Ethyl Violet, Pyrrolidine Violet and the 2,2′-isopropyl and oxygen bridged analogues of Crystal Violet. The rates of hydrolysis of Ethyl and Pyrrolidine Violets are similar to each other but are slower than Crystal Violet in accord with the electron releasing nature of the terminal groups. Bridging groups also stabilise the dye system. Thermodynamic parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ have been obtained for each dye. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Our earlier studies of the hydrolysis of triphenylmethane (TPM) dyes have centred on the behaviour of analogues of Malachite Green towards hydroxide ions and water molecules [1]. The hydrolysis of Crystal Violet (CV) **1** has also been studied [2]. In all of these cases, the dye is converted completely into the colourless dye base in alkaline solution and the process is readily reversed by the addition of acid.

In order to extend our knowledge of the hydrolysis of this important dye system, which is noted for its bright colours but only poor to moderate fastness to washing, we have studied the response to changes in the basic terminal groups in Crystal Violet. Additionally, the consequences of conferring some rigidity on the TPM dye by linking the 2- and 2′-positions with an isopropyl group and with an oxygen atom are discussed.

2. Experimental

The kinetic studies were carried out using the procedures described previously [3]. The Pye-Unicam SP8-100 UV-visible spectrophotometer used was fitted with equipment to ensure temperature control of the reaction mixture. The applicability of the Beer–Lambert law to the dyes studied in aqueous solution was established. Stock solutions of the dye, potassium chloride (used to maintain constant ionic strength), standardised carbonate-free

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* Corresponding author. Tel.: +44-1772-893593; fax: +44-1772-892926; e-mail: d.mason@uclan.ac.uk

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sodium hydroxide solution and water were kept under nitrogen and were temperature-equilibrated for 30 min in a water bath prior to use. The required volume of hydroxide was added to the reaction mixture (zero time) and after thorough mixing was transferred to the spectrophotometer. The absorbance of the solution was measured as a function of time at the λ_{max} appropriate to each dye. The dependence of the reaction rate on hydroxide ion concentration was observed over the temperature range 293.2–313.2 K. The effect of variation in initial dye concentration was also investigated, but in general the concentration used in the kinetic experiments was in the range 1×10^{-6}–5.5×10^{-6} mol dm^{-3}.

2.1. 2,7-Bisdimethylamino-9,9′-dimethyl-10-(4-dimethylaminophenyl)-9,10-dihydroanthracene

A solution of 4,4′,4″-trisdimethylamino-2-isopropenyl-triphenylmethane (4.1 g) in concentrated sulphuric acid (45 cm^3) was maintained at 20°C for 12 h. The reaction mixture was basified by careful addition to an aqueous solution of ammonia, ensuring the temperature remained below 40°C by the addition of crushed ice. The dark blue solid was collected, dried and eluted from an alumina column with toluene. After removal of the solvent, the purified product was recrystallised twice from ethanol:benzene (2:1) to give 2,7-bisdimethylamino-9,9′-dimethyl-10-(4-dimethylaminophenyl)-9,10-dihydroanthracene (2.9 g; 70%) as colourless crystals, m.p. 165–166°C [lit. [4] m.p. 167–168°C].

2.2. 3,6-Bisdimethylamino-9-(4-dimethylaminophenyl)xanthen-9-ol

A solution of 3,6-bisdimethylaminoxanthen-9-one (0.75 g) in toluene (40 cm^3) was added dropwise to a refluxing solution of 4-dimethylaminophenyllithium [prepared from 4-bromodimethylaniline (2.00 g)] [5], in ether (40 cm^3). After 1 h, the usual work-up gave a dark pink crystalline residue which was washed thoroughly with hot light petroleum (bp 60–80°C) to yield the xanthenol (64%), mp 185.4°C (DTA) as pale mauve crystals (Found: C, 74,4; H, 7.3; N, 10.3. $C_{25}H_{29}N_3O_2$ requires C, 74.5; H, 7.2; N, 10.4%).

2.3. General method of preparation of dye perchlorates

A solution of the dye base (0.2 g) in glacial acetic acid (ca. 5 cm^3) was filtered into a saturated aqueous solution of sodium perchlorate. The solid which formed was collected, washed thoroughly with water, dissolved in acetone and diethyl ether added to precipitate the dye perchlorate. The dissolution–reprecipitation sequence was repeated until the pure dye perchlorate was obtained or the dye salt was repeatedly crystallised. The following dye perchlorates were obtained by these protocols:

(a) 4,4′,4″-Trisdimethylaminotriphenylmethyl perchlorate, lustrous metallic-green crystals (Found: C, 63.3; H, 6.4; Cl, 7.3; N, 8.5. $C_{25}H_{30}ClN_3O_4$ requires C, 63.6; H, 6.4; Cl, 7.5; N, 8.9%).

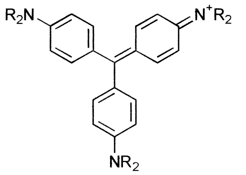
(b) 4,4′,4″-Trisdiethylaminotriphenylmethyl perchlorate, lustrous green crystals (Found: C, 67.0; H, 7.6; Cl, 6.6; N, 7.5. $C_{31}H_{42}ClN_3O_4$ requires C, 67.0; H, 7.6; Cl, 6.4; N, 7.6%).

(c) 4,4′,4″-Trispyrrolidinotriphenylmethyl perchlorate, lustrous green platelets (Found: C, 67.0; H, 6.6; Cl, 6.1; N, 7.5. $C_{31}H_{36}ClN_3O_4$ requires C, 67.7; H, 6.6; Cl, 6.4; N, 7.6%).

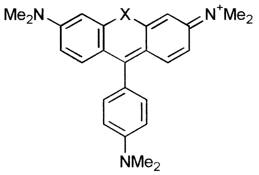
(d) 3,6-Bisdimethylamino-9-(4-dimethylaminophenyl)xanthyl perchlorate, bright metallic-green needles from acetone (Found: C, 61.4; H, 5.8; Cl, 7.3; N, 8.5. $C_{25}H_{30}ClN_3O_4$ requires C, 61.8; H, 5.8; Cl, 7.3; N, 8.7%).

2.4. 4,4′,4″-Trisdimethylamino-2,2′-isopropylidene-triphenylmethyl perchlorate

A mixture of 2,7-bisdimethylamino-9,9′-dimethyl-10-(4-dimethylaminophenyl)-9,10-dihydroanthracene (1.0 g), chloranil (0.59 g) and methanol (15 cm^3) was heated under reflux for 6 h. The resulting hot mixture was filtered into a saturated aqueous solution of sodium perchlorate. The resulting precipitate was collected and purified by reprecipitation from acetone with diethyl ether to give the perchlorate as lustrous green crystals (Found: C, 65.4; H, 6.8; Cl, 7.1; N, 7.9. $C_{28}H_{34}ClN_3O_4$ requires C, 65.7; H, 6.6; Cl, 6.9; N, 8.2%).



1 R = Me
2 R = Et
3 R = -(CH$_2$)$_4$-



4 X = CMe$_2$
5 X = O

3. Results and discussion

3.1. Synthesis

The dye bases of Crystal Violet and Ethyl Violet (EV) **2** [6] were prepared by reaction of the appropriate 4-dialkylaminophenyllithium with diethyl carbonate, whilst that of Pyrrolidine Violet (PV) **3** was obtained through reaction of 4-pyrrolidinophenyllithium [6] with 4,4′-dipyrrolidinobenzophenone [7].

The 2,2′-isopropylidene bridged analogue of leuco CV was obtained in ca. 25% overall yield from methyl 3-dimethylaminobenzoate, prepared from the acid by heating with BF_3 in methanol [8]. Reaction with methyl magnesium iodide and dehydration of the resulting 2-(3-dimethylaminophenyl)propan-2-ol yielded 2-(3-dimethylaminophenyl)-propene, which was alkylated with Michler's hydrol under acidic conditions. The resulting triarylmethane underwent an intramolecular alkylation in concentrated sulfuric acid to produce the leuco base of the bridged dye (IPCV) **4** (Scheme 1) [4].

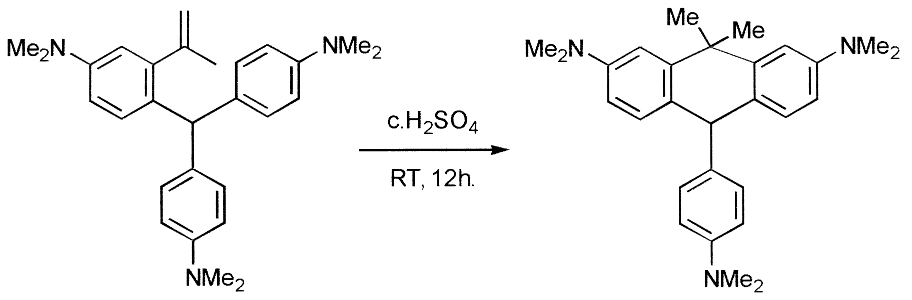
The dye base of the oxygen bridged analogue of CV, referred to as Xanthene Violet (XV) **5**, was derived from 3-dimethylaminophenol in ca. 20% overall yield by reaction with aqueous formaldehyde and cyclisation of the di-(2-hydroxyphenyl)methane so produced [9]. Oxidation of the resulting light sensitive xanthene with sulfur and hydrolysis of the thioketone was followed by reaction of the 3,6-bisdimethylaminoxanthen-9-one [10] with 4-dimethylaminophenyllithium [5] (Scheme 2). The dye cations were obtained from the dye bases by dissolution in glacial acetic acid and from the leuco base by oxidation with chloranil. The dye perchlorates were precipated when solutions of the dye were added to a saturated aqueous solution of sodium perchlorate and were purified by repeated precipitation from dry acetone solution by the addition of dry diethyl ether or by recrystallisation.

3.2. Kinetic studies

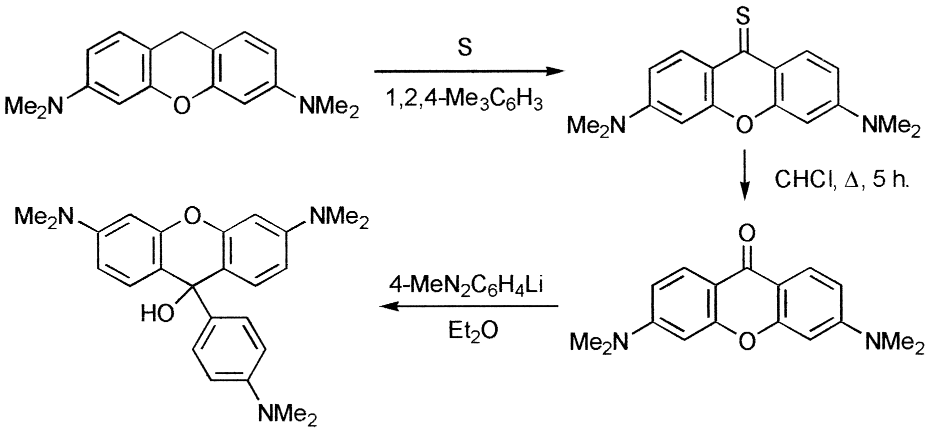
The kinetics of the hydrolysis of the dyes studied exhibited two distinct patterns of behaviour which necessitated two different methods of data treatment. CV, EV, PV and IPCV reacted with aqueous sodium hydroxide in a manner typical of a wide range of TPM dyes. However, the xanthene analogue was not completely converted to the colourless carbinol on reaction with hydroxide and this dye is considered separately.

3.2.1. Crystal Violet **1** and its analogues **2**, **3** and **4**

The reaction of the dye with the hydroxide ion brings about fading of the colour of the dye and results in the formation of the colourless carbinol. The reversibility of the reaction was confirmed for



Scheme 1.



Scheme 2.

each of the dyes. Under the basic conditions used in these kinetic experiments, the equilibrium shifts exclusively towards the product and the significance of the back reactions is minimised. As a large excess of hydroxide ion was used, the rate law can be written

$$\text{Rate} = -\mathrm{d}[D^+]/\mathrm{d}t = k_1[\mathrm{H_2O}] + k_2[D^+][\mathrm{OH^-}]$$

where D represents the dye

$$\text{Rate} = k'[D^+]$$

where

$$k' = k_1[\mathrm{H_2O}] + k_2[\mathrm{OH^-}]$$

The linearity of the ln Absorbance vs time plots established that pseudo first order kinetics applied and in each experiment the plots were observed to be linear for at least 75% of the reaction. The pseudo first order nature of the reaction was further confirmed by the observation that variation in the initial concentration of the dye did not alter the observed rate constant.

The pseudo first order rate constant k' was obtained from the ln Absorbance vs time plots using a least squares computer programme. Values of k' were obtained for a number of different hydroxide concentrations at several temperatures in the range 293.2–313.2 K and the linearity of the k' vs hydroxide concentration plots support the above rate law for all four dyes. From the k' values, the rate constants k_1 and k_2 were calculated using a least squares programme. The results for k_2 are shown in Table 1. Since k_1 is small and is determined from the intercept of the k' vs hydroxide concentration plot, it is prone to large relative errors, but despite being small, k_1 is not considered to be negligible. As a consequence, the procedure of obtaining k_2 from the expression $k_2 = k'[\mathrm{OH^-}]$, which has been adopted by a number of other workers [11] during their studies of the hydrolysis of related triphenylmethane dyes, could not be followed. Nevertheless, the values obtained for k_1 are considered to indicate no more than an order of magnitude (of about 10^{-7} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) and are not included.

In view of the decreased rate of reaction of EV relative to CV, the kinetic data for IPCV **4** were obtained at a higher concentration of hydroxide, resulting in a change of ionic strength of the experimental solutions to 0.10 mol $\mathrm{dm^{-3}}$. In order that a comparison of all the k_2 data is meaningful, k_2 values for IPCV were calculated at an ionic strength of 0.01 mol $\mathrm{dm^{-3}}$ using the Debye–Huckel–Bronsted–Davis equation and these are shown, together with the experimental values, in Table 1.

The dependency of k_2 on temperature enabled a least squares program based on the Margerison equations [12] to be applied to the linear ln k_2 vs 1/T graphs, culminating in the calculation of the

Table 1
Values of the rate constant k_2 for a series of Crystal Violet analogues

	I (mol dm^{-3})	k_2 (dm^3 mol^{-1} s^{-1}) at quoted temperatures				
Dye		293.2 K	298.2 K	303.2 K	308.2 K	313.2 K
Crystal Violet	0.01	0.122 ± 0.001	0.194 ± 0.002	0.297 ± 0.004	0.424 ± 0.006	0.64 ± 0.01
Ethyl Violet	0.01	0.035 ± 0.001	0.060 ± 0.001	0.093 ± 0.001	0.151 ± 0.003	0.224 ± 0.001
Pyrrolidine Violet	0.01	0.035 ± 0.001	0.050 ± 0.001	0.079 ± 0.005	0.122 ± 0.003	0.176 ± 0.004
Isopropylidene bridged Crystal Violet	0.10	0.046 ± 0.001	0.058 ± 0.002	0.090 ± 0.002	0.119 ± 0.003	
	0.01^{a}	0.068 ± 0.002	0.086 ± 0.003	0.133 ± 0.003	0.176 ± 0.005	
Xanthene Violet	0.20	0.0061 ± 0.0004	0.0105 ± 0.0003	0.013 ± 0.001	0.0252 ± 0.0004	
	0.01^{a}	0.0109 ± 0.0008	0.0189 ± 0.0005	0.023 ± 0.002	0.0455 ± 0.0007	

^{a}Calculated values.

activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ for the dyes (Table 2).

The observed trend in k_2 values shows that the rate of hydrolysis increases in the order:

$$\text{Pyrrolidine Violet} \leqslant \text{Ethyl Violet} \leqslant \text{IPCV} < \text{Crystal Violet}$$

The greater inductive electron release by NEt_2 compared with NMe_2 is well established [6] and is reflected in the appreciably different k_2 values for EV and CV. The cationic charge is delocalised more effectively in ethyl violet than in crystal violet and the former is more resistant to hydrolysis.

The k_2 values for PV and EV are very similar, signifying that the electron donating properties of diethylamino and pyrrolidino groups are of the same order. Nash and Maciel [13] have reported the close similarity in the ^{13}C chemical shifts of *N,N*-diethylaniline and pyrrolidinobenzene, from which it was deduced that the electron distribution in the aromatic rings of the two compounds is very nearly the same. However, a study of analogues of CV containing various terminal groups indicated that a pyrrolidino group has a slightly more stabilising influence on the TPM dye than that of a diethylamino group [6], as is marginally suggested in the present work.

The typical propeller-like shape of a TPM cation [14] is altered when the 2- and 2′-positions of CV are joined through a bridging group, with two of the dimethylaminophenyl rings becoming more coplanar. This is manifest in the increase in (ε_{max} for the main absorption band of IPCV, whilst an appreciable decrease in ε_{max}(y) indicates significant deconjugation of the non-bridged aryl ring. The similarity in the spectra of IPCV and Michler's Hydrol Blue supports this picture. The kinetic data show a similar rate of hydrolysis for EV and IPCV and it would appear therefore that the destabilising effect of the change in terminal group from NEt_2 to NMe_2 is balanced by the stabilising influences of the electron donor properties of the isopropyl group and the steric consequences of linking the two rings together.

Values for $\Delta H^{\#}$ and $\Delta S^{\#}$ (Table 2) are of the same order as those reported for other TPM dyes [1–3,7,11,15] with the exception of IPCV. The more negative value of $\Delta S^{\#}$ indicates a greater loss

Table 2
Kinetic and thermodynamic data for Crystal Violet and some analogues at an ionic strength of 0.01 mol dm^{-3} and 298.2 K

DYE	10 k_2 (dm^3 mol^{-1} s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})
Crystal Violet	1.94 ∓0.02	61 ± 1	−55 ± 4
Ethyl Violet	0.60 ± 0.01	68 ± 1	−42 ± 2
Pyrrolidine Violet	0.50 ± 0.01	60 ± 2	−67 ± 6
Isopropylidene Bridged Crystal Violet	0.86 ± 0.03	46 ± 3	−110 ± 10
Xanthene Violet	0.19 ± 0.01	67 ± 5	−54 ± 16

of freedom on forming the transition state, suggesting some structural change with this dye. Nonetheless, the value for $\Delta S^{\#}$ for all the dyes lies near to the proposed second order reaction range [16] of -63 to $-84\,\mathrm{JK^{-1}\,mol^{-1}}$.

3.2.2. *Xanthene Violet* **5**

Unlike the above four dyes, XV was not completely converted to the colourless carbinol on reaction with hydroxide ion under the prevailing reaction conditions. The absorbance values decreased until a steady value was reached, suggesting that the equilibrium between the dye cation and carbinol lies more towards the former than is the case for the other four dyes studied. Plots of ln absorbance vs time were not linear and consequently the equilibrium absorbance (A_e) had to be taken into account; this was determined for each kinetic run. Ln(A–A_e) vs time graphs were plotted and a linear relationship established. However, small errors in the value of A_e led to unacceptably large errors in k' and consequently the initial rate method was used as an alternative and gave reproducible k' values.

The approach of neglecting the back reactions is no longer valid for this dye. The reaction of the dye cation with water molecules has been shown to be of minor significance relative to the reaction with hydroxide ion and consequently it seems reasonable to ignore the terms k_1 and k_{-1} because of the more influential effect of the back reaction k_{-2} on the rate of reaction. This produces the simplified rate law:

$$\text{Rate} = -\mathrm{d}[D^+]/\mathrm{d}t = k_2[D^+][\mathrm{OH^-}] - k_{-2}[\mathrm{DOH}]$$

corresponding to the equilibrium

$$D^+ + \mathrm{OH^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{DOH}$$

According to Beers law, $[D^+] \equiv A$ and $[\mathrm{DOH}] \equiv A_o - A$ where A_o = absorbance at zero time and since a large excess of hydroxide ions are used, the rate law can be simplified to:

$$-\mathrm{d}A/\mathrm{d}t = k'(A - A_e)$$

where

$$k' = k_2[\mathrm{OH^-}] + k_{-2}$$

Satisfactory plots of k' vs $[\mathrm{OH^-}]$ were obtained using the initial rate method, in which the main assumption is that the rate of reaction is measured at the start of the reaction when any back reaction is insignificant. The rate constant, k_2, is obtained from the gradient of the k' vs hydroxide ion concentration plot. Values for the pseudo rate constant, k', were obtained for a number of hydroxide ion concentrations over the temperature range 293.2–308.2 K.

To allow for satisfactory performance of the kinetic runs, it was necessary to increase the hydroxide ion concentration and the corresponding ionic strength used for this dye was $0.20\,\mathrm{mol\,dm^{-3}}$. These k_2 values, and those at $0.01\,\mathrm{mol\,dm^{-3}}$ calculated as described previously, are given in Table 1 and the activation parameters as shown in Table 2.

Molecular models indicate that introduction of the oxygen bridge confers greater rigidity on the system than does an isopropylidene bridging group and that the bridged aryl rings are more coplanar. This latter aspect is reflected in the greater fluorescence exhibited by XV compared to IPCV. Furthermore, the oxygen heteroatom is a more efficient electron donor than isopropyl and is able to stabilise the cationic charge mesomerically. The blue shift in $\lambda_{\max}$(x) of 44 nm is in accord with Dewar's rules [17] and once again the non-bridged ring appears to be effectively deconjugated. The rate of hydrolysis of XV is appreciably slower than that of the other four dyes studied; in particular, the influence of the oxygen bridge is much more marked than that of the isopropyl unit and overwhelms the effects of the terminal group.

In conclusion, the rates of hydrolysis of dyes of the Crystal Violet type are appreciably slower than those of the analogous Malchite Green dyes in accord with the additional stabilisation of the cation provided by the third terminal amino function. Whilst a 2,2′-isopropylidene bridging group has little effect on the rate of hydrolysis, an oxygen bridge significantly retards the reaction.

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