A Kinetic and Equilibrium Study of the Hydrolysis of Pyrrolidine Green

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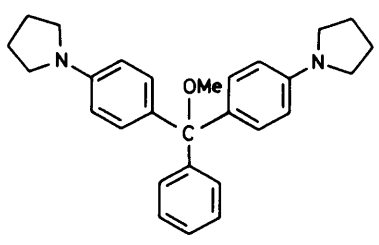
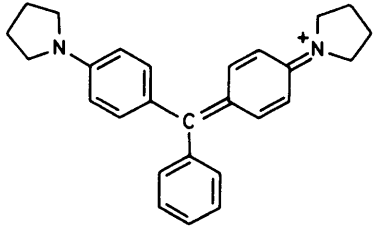
Rate constants and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been determined for the hydrolysis of Pyrrolidine Green over the pH range 10—11. The equilibria associated with the hydrolysis of the dye have been studied over the pH range 0—10 and a reaction scheme is proposed. Equilibrium studies have been extended in the pH range 6.8—7.8 and the thermodynamic parameters ΔH° and ΔS° have been obtained.

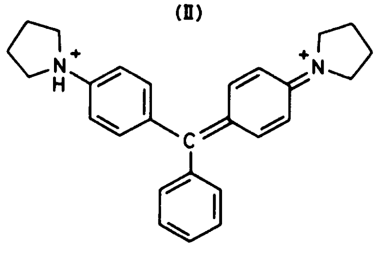
During our studies of sterically hindered basic dyes, we have examined the spectral properties of a range of substituted derivatives of Brilliant Green [1] and studied their hydrolysis under basic conditions.[2] The influence of substituents was such that it was considered of value to investigate the consequences of variation in the terminal basic groups. In this paper, the hydrolysis of Pyrrolidine Green, PG$^+$ (II), over a wide pH range and over the temperature range 293.2—313.2 K is reported.



(I)



(II)



(III)

Experimental

The kinetic and equilibrium studies were carried out using the procedures described previously.[3] Measurements were made on Pye-Unicam spectrophotometers SP6-350 and SP8-100. Beer's Law was obeyed for dye concentrations below 2.5×10^{-6} mol dm^{-3}. The need for such dilute solutions could be expected on the basis of various polymerisation studies on triphenylmethane dyes.[4-6] The equilibria were studied in the pH range 0—10 using appropriate constant ionic strength buffer solutions.[7] The vessels were wrapped in black polythene to avoid exposure of the solutions to light.

Pyrrolidinobenzene.—A mixture of 1,4-dichlorobutane (63.5 g) and aniline (93 g) was boiled under reflux for 30 min. After quenching with water, organic material was extracted into chloroform. The residue from the dried and evaporated extracts was boiled with acetic anhydride (100 cm^3) for 1 h and the mixture was then distilled under reduced pressure to yield pyrrolidinobenzene (82%), b.p. 110 °C at 0.7 mmHg (Found: C, 81.4; H, 9.1; N, 9.6. $C_{10}H_{13}N$ requires C, 81.6; H, 8.9; N, 9.5%).

4,4'-Dipyrrolidinotriphenylmethane.—A mixture of pyrrolidinobenzene (14.7 g), benzaldehyde (3.5 g), ethanol (25 cm^3), and concentrated hydrochloric acid (8 cm^3) was boiled under reflux for 24 h. The cooled solution was poured into a mixture of ethanol (30 cm^3) and concentrated ammonia solution (90 cm^3). The oil which separated was dissolved in ether and the crystals which slowly formed were recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to yield the *leuco-base* (44%), m.p. 147—148 °C (Found: C, 84.6; H, 7.9; N, 7.0. $C_{27}H_{30}N_2$ requires C, 84.8; H, 7.9; N, 7.3%).

4,4'-Dipyrrolidinotriphenylmethyl Methyl Ether.—The leuco-base (1.5 g) was boiled with chloranil (1.0 g) in methanol (15 cm^3) for 7 h. The hot mixture was filtered into a solution of sodium methoxide [from sodium (0.5 g) and methanol (20 cm^3)]. The solid which separated was crystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give green prisms of the *methyl ether*, m.p. 149 °C (Found: C, 81.3; H, 7.9; N, 6.8. $C_{28}H_{32}N_2O$ requires C, 81.5; H, 7.8; N, 6.8%).

4,4'-Dipyrrolidinotriphenylmethyl Perchlorate.—The leuco-base was oxidised with chloranil as above and the hot solution was filtered into a saturated aqueous solution of sodium perchlorate. The solid which formed was purified by dissolution in acetone and reprecipitation with ether to give the *dye perchlorate* as lustrous metallic green needles (Found: C, 66.8; H, 5.9; Cl, 7.6; N, 5.8. $C_{27}H_{29}ClN_2O_4$ requires C, 67.4; H, 6.1; Cl, 7.4; N, 5.8%).

Results and Discussion

Dissolution of the methyl ether (I) of the dye base in 98% acetic acid resulted in conversion into the blue-green dye cation, PG$^+$ (II), and the wavelength of maximum absorption (629 nm) was obtained from this solution. An aqueous solution of the dye perchlorate absorbed at a slightly lower wave-

Table 1. Effect temperature on K_1—K_3

	T/K					$\Delta H^\ominus$/ kJ mol^{-1}
	293.2	298.2	303.2	308.2	313.2	
K_1/dm^3 mol^{-1}	0.021 ±0.001	0.023 ±0.001	0.023 ±0.001	0.024 ±0.001	0.024 ±0.002	4.2 ±1.1
10^{-6} K_2/dm^3 mol^{-1}	1.99 ±0.06	1.81 ±0.04	1.77 ±0.05	1.67 ±0.05	1.56 ±0.09	−8.1 ±1.3
10^8 K_3/mol dm^{-3}	1.14 ±0.07	1.43 ±0.05	2.1 ±0.1	2.6 ±0.1	3.4 ±0.3	43 ±3

Ionic strength 0.01 mol dm^{-3}; $[PG^+]_{init}$ *ca.* 1.7 × 10^{-6} mol dm^{-3}.

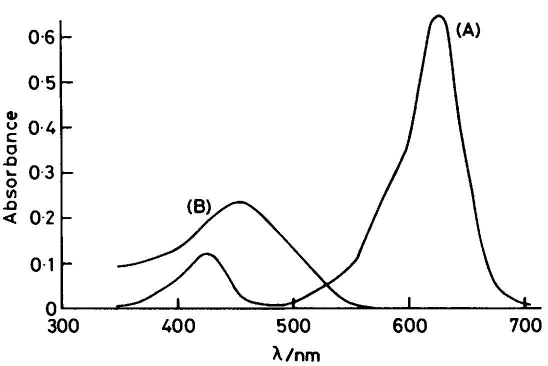


Figure 1. Visible absorption spectra of Pyrrolidine Green, PG^+ (A) and protonated Pyrrolidine Green, PGH^{2+} (B)

Table 2. Effect of pH on A_e and A_{470}

pH	A_e(expt.)	A_e(calc.)	A_{470}
0.49	0.061	0.063	0.034
0.70	0.092	0.091	0.030
0.77	0.120	0.101	0.028
1.25	0.184	0.187	0.018
1.67	0.252	0.253	0.010
1.83	0.273	0.271	
1.86	0.285	0.274	
2.42	0.305	0.308	
2.70	0.317	0.315	
4.13	0.323	0.323	
4.96	0.322	0.323	
5.99	0.320	0.320	
6.88	0.307	0.299	
7.52	0.258	0.239	
8.00	0.168	0.156	
8.40	0.098	0.088	
8.95	0.037	0.031	
9.43	0.014	0.011	
9.60	0.012	0.007	
10.00	0.009	0.003	

A_u 0.580.

length (625 nm) as has been noted for derivatives of Brilliant Green.[1] Increasing the acidity of this aqueous solution brought about a pronounced change in the spectrum (Figure 1) and in concentrations of acid >1.0 mol dm^{-3} the visible spectrum is considered to be attributable solely to the protonated species, PGH^{2+} (III), which is yellow in aqueous solution.

The reversible nature of the hydrolysis of Pyrrolidine Green was demonstrated by adding a measured quantity of aqueous sodium hydroxide to a solution of the dye. The colourless solution which resulted was treated with an amount of hydrochloric acid equivalent to the added sodium hydroxide, whereupon the dye solution was restored to the expected absorbance. The conclusion reached in the work on Brilliant Green [3] that the nature of the anion did not affect the equilibria was considered likely to apply to Pyrrolidine Green. The equilibria were initially studied in the pH range 6.8—7.8 using phosphate buffers at a constant ionic strength of 0.01 mol dm^{-3}. Plots of $1/A_e$ *versus* $[OH^-]$ were linear at each temperature studied using an initial dye concentration of 1.7 × 10^{-6} mol dm^{-3} whereas in the case of Brilliant Green [8] linearity was only achieved at initial concentrations below 1.8 × 10^{-7} mol dm^{-3}. The results are compatible with equilibria (1)—(3).

$$PG^+ + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} PGOH_2^+ \qquad (1)$$

$$PG^+ + OH^- \overset{K_2}{\rightleftharpoons} PGOH \qquad (2)$$

$$PGOH_2^+ \overset{K_3}{\rightleftharpoons} PGOH + H^+ \qquad (3)$$

A least-squares computer program was used to give the best values for K_1—K_3 as calculated from the equations given below. These values, together with their standard errors (s.e.), are given at each of five temperatures in Table 1 which also includes the appropriate ΔH° values calculated using a weighted least-squares computer program based on the equations of Margerison.[9]

The equilibrium study was extended at 298.2 K to cover the pH range 0—10 at a constant ionic strength of 0.01 mol dm^{-3}. The variation of the equilibrium absorbance, A_e, measured at 625 nm, with pH is given in Table 2. Similar variations have been reported for Malachite Green derivatives [10] and Crystal Violet.[11]

In addition to the equilibria characterised by K_1—K_3 the complete reaction scheme proposed to fit these results involves equilibria (4)—(6). Above pH 6.5 the equilibria

$$PG^+ + H^+ \overset{K_4}{\rightleftharpoons} PGH^{2+} \qquad (4)$$

$$PGH^{2+} + H_2O \overset{K_5}{\rightleftharpoons} PGOH_3^{2+} \qquad (5)$$

$$PGOH_3^{2+} \overset{K_6}{\rightleftharpoons} PGOH_2^+ + H^+ \qquad (6)$$

characterised by K_1—K_3 are expected to predominate and expressions (7) and (8) are appropriate. The values of K_1 and

$$A_0/A_e = 1 + K_1[H_2O] + K_2[OH^-] \qquad (7)$$

$$K_3 = K_2K_w/(K_1[H_2O]) \qquad (8)$$

K_2 from this work are (0.009 ± 0.004) dm^3 mol^{-1} and (1.90 ± 0.05) × 10^6 dm^3 mol^{-1} respectively. The agreement between this value of K_2 and the one quoted in Table 1 lies within s.e.

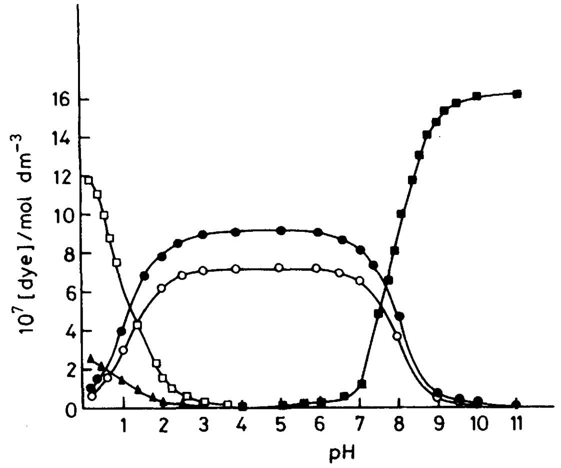


Figure 2. Distribution of the dye between the different species as a function of pH at equilibrium: ●, PG^+; ○, $PGOH_2^+$; ■, PGOH; ▲, PGH^{2+}; □, $PGOH_3^{2+}$

limits. Throughout this paper classical equilibrium constants are quoted. The K_1 values are outside the statistical s.e. limits but this is not considered to be too surprising since K_1 is calculated from the small intercept on the graph.

Below pH 2.0 the equilibria characterised by K_4—K_6 are expected to predominate and expressions (9) and (10) and

$$A_0/A_e = 1 + K_1[H_2O] + K_4[H^+](1 + K_5[H_2O]) \quad (9)$$

$$\frac{A_{470}}{A_e} = \frac{\varepsilon'_{470}}{\varepsilon_{625}} \cdot K_4[H^+] + \frac{\varepsilon_{470}}{\varepsilon_{625}} \quad (10)$$

$K_1 = K_4K_5K_6$ are appropriate. The wavelength of 470 nm was chosen because of the large difference between the ε_{470} and ε'_{470} values. ε'_{470} refers to the species PGH^{2+} whereas ε_{470} and ε_{625} refer to the PG^+ species. ε_{625} was obtained simply from the relevant A_0 value. The ratio $\varepsilon_{470}/\varepsilon_{625}$ was obtained as 0.016 from the PG^+ spectrum given in Figure 1. ε'_{470} was obtained by measuring the spectra of solutions containing increasing amounts of hydrochloric acid whereupon a steady value of $\varepsilon_{max.}$ was obtained once the concentration of the acid exceeded *ca.* 10 mol dm^{-3}. It was considered that the dehydrating nature of this concentration of hydrochloric acid ensured that the solution contained only the species PGH^{2+}. The variations of A_{470} and A_e with pH are given in Table 2. Plots of A_{470}/A_e *versus* $[H^+]$ were linear and the least-squares routine gave an intercept of 0.012 ± 0.017 in support of the above expression. K_4 was calculated to be (4.05 ± 0.22) dm^3 mol^{-1}. Plots of $1/A_e$ *versus* $[H^+]$ were also linear giving values of (0.012 ± 0.007) and (0.08 ± 0.01) dm^3 mol^{-1} for K_1 and K_5, respectively.

The equilibrium constants deduced from this work were used in expression (11) to give a computer simulation of the

$$A_e = A_0/\{1 + K_1[H_2O] + K_2[OH^-] + K_4[H^+](1 + K_5[H_2O])\} \quad (11)$$

variation of A_e with pH. The similarity between these values and the experimental results is apparent from Table 2. The various values of K_1 which have been calculated from data over different pH ranges do not quite agree within s.e. limits. Consequently K_1 was allowed to vary so as to give a best fit to the experimental results. This value of K_1 was found to be 0.014 dm^3 mol^{-1} which is within the range of values found experimentally. K_6 was calculated to be (0.043 ± 0.006) mol dm^{-3} using this value of K_1. The effect of pH on the concentration of each species could now be calculated and these results are shown in Figure 2. These curves show some similarity to those of Cigén and Ekström.[10] However, the Pyrrolidine Green curves show that the hydrated species $PGOH_3^{2+}$ and $PGOH_2^+$ exist to a much greater extent than do the corresponding species from *p*-halogeno-derivatives of Malachite Green.

Table 3. Effect of temperature on k', k_1, and k_2

$10^3[OH^-]$/ mol dm^{-3}	10^3 k'/s^{-1} at the given temperature 293.2 K	298.2 K	303.2 K	308.2 K	313.2 K
0.200				0.358	0.563
0.400	0.157	0.288	0.415	0.625	0.910
0.500				0.730	1.10
0.704				0.982	1.46
0.803	0.300	0.473	0.763		
1.000	0.377	0.580	0.925	1.37	1.99
1.407	0.527	0.828	1.30		
2.000	0.737	1.143	1.79		
10^7 k_1/ dm^3 mol^{-1} s^{-1}	2.0 ±0.4	9.5 ±2.5	12 ±1	20 ±1	37 ±1
k_2/ dm^3 mol^{-1} s^{-1}	0.364 ±0.003	0.544 ±0.015	0.862 ±0.007	1.25 ±0.02	1.78 ±0.01

Ionic strength 0.01 mol dm^{-3}; $[PG^+]_{init}$ *ca.* 1.7 × 10^{-6} mol dm^{-3}.

Under the basic conditions used in the kinetic experiments the protonation and back reactions can be neglected and the rate law (12) can be formulated. A large excess of hydroxide ion was used such that the pseudo-first-order rate law (13) was followed where equation (14) holds. Typical first-order rate

$$R = -d[PG^+]/dt = k_1[PG^+][H_2O] + k_2[PG^+][OH^-] \quad (12)$$

$$R = k'[PG^+] \quad (13)$$

$$k' = k_1[H_2O] + k_2[OH^-] \quad (14)$$

plots were obtained from experiments in which the initial concentration of Pyrrolidine Green was varied. This variation had no effect on the observed rate constant, thereby confirming the pseudo-first-order kinetics. All the plots were found to be linear until at least 75% completion of the reaction. Values of k' were obtained for several different hydroxide ion concentrations at each of five temperatures (Table 3) and the linearity of the k' *versus* $[OH^-]$ plots supported the proposed rate law. The least-squares computer program was used to give the best values of k_1 and k_2 which are included in Table 3. The weighted least-squares computer program was applied to the linear plots of $\log_e k_1$ *versus* $1/T$ and $\log_e k_2$ *versus* $1/T$ to give values of (91 ± 8) kJ mol^{-1} and (−60 ± 27) J K^{-1} mol^{-1} for $\Delta H^‡$ and $\Delta S^‡$, respectively for the reaction characterised by K_1 and (58 ± 1) kJ mol^{-1} and (−56 ± 3) J K^{-1} mol^{-1} for $\Delta H^‡$ and $\Delta S^‡$ for the reaction characterised by K_2.

Comparison with other published work [3,12-18] shows that the rate of hydrolysis of some triphenylmethane dyes increases in the order: Ethyl Violet < Crystal Violet < Pyrrolidine Green < Brilliant Green < Malachite Green. As expected, the Violets, which contain three basic terminal groups, are more stable than the Greens. The enhanced stability of Brilliant Green compared with Malachite Green may be attributed to the greater electron releasing ability of the

Table 4. Effect of ionic strength on k_2

Ionic strength (mol dm^{-3})	0.005	0.0075	0.01	0.025	0.050
k_2/dm^3 mol^{-1} s^{-1}	0.579	0.563	0.545	0.489	0.435

Temperature 298.2 K; $[PG^+]_{init}$ *ca.* 1.7×10^{-6} mol dm^{-3}.

diethylamino- relative to the dimethylamino-group. It therefore appears that a pyrrolidino-group is even more electron releasing. This conclusion is in agreement with the order found by Effenberger [19] and Nash [20] for the donor potential of the amino-group in a series of dialkylaminobenzenes. The reported values of $\Delta H^\ddagger$ are approximately constant for all of the dyes and it is likely that changes in the rate constant k_2 arise from changes in $\Delta S^\ddagger$. This suggests that the change in disorder on forming the activated state is the major factor causing the decreased rate. The conclusions reached in our work on the hydrolysis of Brilliant Green derivatives [2] appear to be further substantiated. The value of $\Delta S^\ddagger$ reported herein is consistent with the bimolecularity of the predominant step in the reaction.[21] Whilst the k_1 values cannot be compared rigorously because of the s.e. limits, the value at 298.2 K found in the present work is of the same order of magnitude as those quoted for Brilliant Green [3] and Crystal Violet [14] though somewhat less than quoted for Malachite Green.[14,18] Surprisingly the values of k_2 are larger for Pyrrolidine Green than the corresponding values for Brilliant Green [3] giving rise to conjecture about the implied increased rate for the conversion of carbinol into dye cation for the latter dye.

The effects of changes in the ionic strength of the solution were observed at constant hydroxide ion concentration by varying the concentration of sodium nitrate in the reaction mixture. The values of k_2 quoted in Table 4 were calculated from the established rate law assuming that k_1 is independent of ionic strength. The results fit the Brönsted–Bjerrum relationship (15) with values of $k^0 = (0.659 \pm 0.002)$ dm^3 mol^{-1} s^{-1} and $B = (-0.81 \pm 0.01)$ dm$^{3/2}$ mol$^{-\frac{1}{2}}$ up to an

$$\log k = \log k^0 + B\sqrt{I} \qquad (15)$$

ionic strength of 0.05 mol dm^{-3}. The value of B compares with values of -0.84 [1] and -0.85 [3] reported for Brilliant Green. These results indicate that the predominant step involves a reaction between singly charged ions of opposite sign. The possible catalytic effect of added ions was investigated by making the constant ionic strength (0.01 mol dm^{-3}) phosphate buffer at pH 7.5 and adding different electrolytes (sodium nitrate, potassium nitrate, magnesium nitrate, sodium chloride, sodium sulphate, and sodium perchlorate) to a total ionic strength of 0.02 mol dm^{-3}. The rate of hydrolysis was found to be constant within s.e. limits, suggesting that the ions do not exert any catalytic effect.[3]

Using the data in Table 1, a value of (-35.8 ± 0.1) kJ mol^{-1} for $\Delta G^\ominus$ can be calculated at 298.2 K for reaction (2). Thus $\Delta S^\ominus$ is calculated to be (93 ± 4) J K^{-1} mol^{-1}. It is of interest to compare this with the value of (-56 ± 3) J K^{-1} mol^{-1} for $\Delta S^\ddagger$. It would appear that the loss of translational and rotational degrees of freedom on forming the transition state is more than counterbalanced by the increased freedom associated with a reduction in solvation on moving from the transition state to the final state. We made a similar observation, with respect to Brilliant Green,[1] although the difference between $\Delta S^\ddagger$ and $\Delta S^\ominus$ was smaller.

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