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The Hydrolysis of Brilliant Green and some Derivatives. Part 3: The Kinetics of the Hydrolysis of some 2-Substituted Derivatives of Brilliant Green

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ABSTRACT

Rate constants have been measured for the reactions of hydroxide ion with the 2-OMe, 2-Me, 2-Cl, 2-Br, 2-CF_3, 2-NO_2 and 2-OH derivatives of Brilliant Green. The rates of hydrolysis, which are generally slower than those of the correspondingly 3- and 4-substituted derivatives, are influenced primarily by steric factors. Thermodynamic parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been obtained for each dye and an isokinetic relationship has been established. The 2-hydroxy derivative of Brilliant Green showed anomalous behaviour for which an explanation is offered.

1 INTRODUCTION

In our earlier studies of the hydrolysis of triphenylmethane dyes, the reactions of water molecules and hydroxide ions with Brilliant Green[1] (I, X = H) and a range of its 3- and 4-substituted derivatives were investigated.[2] In alkaline solution, complete conversion into the dye base occurs and rate constants and activation parameters for the hydrolysis were obtained. The substituents 3-X (X = NMe_2, OMe, Me, Cl, CF_3 or NO_2) and

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4-X (X = OMe, Me, Cl, CF_3 or NO_2) were shown to affect the rate of hydrolysis to an extent linearly related to the appropriate Hammett substituent constant. In this paper, the hydrolysis of a range of 2-X derivatives of Brilliant Green (BG) (X = OMe, Me, Cl, Br, CF_3, NO_2 or OH) is discussed. The 2-hydroxy derivative was found to behave differently from the other dyes and is discussed separately below.

2 EXPERIMENTAL

The kinetic studies were carried out using the procedures described previously.[2] Spectrophotometric measurements were made at the wavelength of maximum absorption relevant to each dye using a Hilger-Watts H700 spectrophotometer.

The dye perchlorates were prepared by methods analogous to those described earlier.[3,4] The perchlorate of the 2-trifluoromethyl derivative was prepared from the dye base, itself prepared by the reaction of 2-trifluoromethylphenyl-lithium with 4,4′-bisdiethylaminobenzophenone, by dissolution of acetic acid and treatment with a saturated solution of sodium perchlorate. All other perchlorates were derived from the leuco-bases, prepared from the 2-substituted benzaldehyde and diethylaniline, by oxidation with chloranil and reaction with sodium perchlorate solution.

3 RESULTS AND DISCUSSION

Beer's Law was shown to be obeyed at concentrations below $2{\cdot}0 \times 10^{-6}$ mol dm^{-3} for all of the dyes and the pseudo-first order rate constant, k', was independent of the initial dye concentration. Some typical values of k' are given in Table 1. The rate law (1) was established by the usual procedures:[1,2]

$$\text{Rate} = k_1[\text{BG}][\text{H}_2\text{O}] + k_2[\text{BG}][\text{OH}^-] \qquad (1)$$

The values of k_1 are prone to large standard error values and are not considered to be worthy of tabulation, but the values of k_2, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, derived as described previously,[1,2] are given in Table 2. These data are considered to apply to the reaction $BG^+ + OH^- \rightarrow BGOH$.

The values of k_2 obtained for the *ortho*-substituted dyes are much lower than the reported values for the dyes containing the corresponding substituents in the *meta*- and *para*-positions.[2] This observation is consistent with attack at the central carbon atom being sterically hindered by the 2-substituent. Since no simple relationship between the rate constant and the electronic properties of the substituent is apparent, it would seem that steric

TABLE 1

The Effect of Hydroxide Ion Concentration on k' at 293·2 K for some 2-Substituted Derivatives of Brilliant Green ($10^4 k'(\mathrm{s}^{-1})$)

Substituent *10^3 [OH$^-$) mol dm^{-3}*	*H*	*2-Me*	*2-OMe*	*2-Cl*	*2-Br*	*2-CF$_3$*	*2-NO$_2$*	*2-OH*
2·000	8·653	0·2083	0·8583	0·3450	0·2150	0·02567	0·4667	53·83
4·000	18·52	0·3950	1·583	0·6867	0·4317	0·05467	1·007	52·33
6·000	26·67	0·5483	2·358	1·078	0·6667	0·08650	1·508	52·17
8·000	36·50	0·7683	3·140	1·400	0·8933	0·1135	2·017	52·17
10·00	44·17	0·9700	3·967	1·717	1·028	0·1423	2·408	52·83

factors outweigh the electronic influences. The dependence of the rate of hydrolysis on the *ortho*-substituent was investigated by the application of multiple linear regression analysis (MLRA) to the extended form of the Hammett equation (2):

$$\log k = h + \phi v + \alpha\sigma_{\mathrm{I}} + \beta\sigma_{\mathrm{R}} \qquad (2)$$

The parameters used for this study were those developed by Taft & Lewis[5] for inductive and resonance effects (σ_{I} and σ_{R}, respectively) and by Aslam *et al.*[6] for steric effects (v). Following the procedures adopted by Aslam *et al.*,[6] MLRA of $\log k_2$ at 293·2 K on σ_{I}, σ_{R} and v for the 2-X substituents, where X = H, Me, Cl, Br and CF_3, gave eqn (3), which is presented with the various relevant statistical parameters. These include the standard error of each regression coefficient; the number of sets of data, n; the multiple regression coefficient, R; the standard error of the estimate, s; and the value of F used to determine the significance level of the regression:

$$\begin{aligned} \log k_2 &= -0{\cdot}359 - 3{\cdot}120v + 0{\cdot}854\sigma_{\mathrm{I}} + 0{\cdot}180\sigma_{\mathrm{R}} \\ &\qquad (\pm 0{\cdot}142)(\pm 0{\cdot}195)\ (\pm 0{\cdot}220) \\ n = 5 \quad & R = 0{\cdot}999 \quad s = 0{\cdot}066 \quad F = 248 \qquad (3) \end{aligned}$$

The positive regression coefficients of σ_{I} and σ_{R} arise because electron releasing groups retard the reaction and electron withdrawing groups accelerate it.[2,7] On the other hand, the negative regression coefficient for the steric term arises because the reaction is subject to steric hindrance by *ortho*-substituents. Stepwise examination of the results as the variables were successively entered into the regression indicated that the value of the rate constant is overwhelmingly dependent on the steric factor and that the electronic factors are of minor importance.

The methoxy group does not fulfil the requirements suggested by Aslam *et al.*,[6] since it exhibits an appreciable resonance effect, and it was excluded

TABLE 2

Effect of Temperature on k_2, together with Thermodynamic Activation Parameters for the Reaction between Dye Cations and Hydroxide Ions

Substituent	$10^3\,k_2/dm^3\,mol^{-1}\,s^{-1}$						
	283·2 K	*293·2 K*	*303·2 K*	*313·2 K*	*323·2 K*	$\Delta H^{\neq}/kJ\,mol^{-1}$	$\Delta S^{\neq}/JK^{-1}\,mol^{-1}$
H	194 ± 3	450 ± 10	1 090 ± 50	2 310 ± 50	4 500 ± 100	57·8 ± 0·7	−54 ± 2
2-OMe	17·1 ± 0·5	38·9 ± 0·5	90 ± 3	200 ± 7	424 ± 2	59 ± 1	−70 ± 3
2-Me	3·32 ± 0·02	9·5 ± 0·3	23·3 ± 0·5	56·2 ± 0·8	135 ± 1	68 ± 3	−52 ± 1
2-Cl	7·2 ± 0·2	17·3 ± 0·4	41·3 ± 0·6	106 ± 1	240 ± 5	66 ± 2	−55 ± 6
2-Br	4·5 ± 0·1	10·4 ± 0·1	26·6 ± 0·3	70 ± 1	155 ± 2	68 ± 1	−51 ± 4
$2\text{-}CF_3$	0·538 ± 0·009	1·46 ± 0·02	3·84 ± 0·02	9·3 ± 0·3	23·7 ± 0·6	69 ± 1	−64 ± 3
$2\text{-}NO_2$	10·1 ± 0·2	24·5 ± 0·8	56 ± 2	148 ± 5	304 ± 8	63 ± 1	−62 ± 4

from the initial analysis. Its inclusion in the substituent set for regression analysis resulted in eqn (4):

$$\log k_2 = -0{\cdot}354 - 3{\cdot}121\nu + 0{\cdot}872\sigma_I + 0{\cdot}290\sigma_R$$
$$(\pm 0{\cdot}119)(\pm 0{\cdot}162)\ (\pm 0{\cdot}116)$$
$$n = 6 \qquad R = 0{\cdot}999 \qquad s = 0{\cdot}056 \qquad F = 364 \qquad (4)$$

Equations (2) and (3) were used to obtain values for ν (0·59) and σ_R (0·02) for the nitro-group. Comparison with Charton's conformation dependent values[8] leads to the conclusion that the nitro-group is disposed between its orthogonal and coplanar extremes. Space-filling molecular models of the 2-nitro-derivative of Brilliant Green reinforce this conclusion.

The correlation intercept term, h, obtained by excluding the parent compound from the substituent set, was lower than the measured value. This result is in line with, though not as pronounced as, the findings of Aslam *et al.*,[6] who reported an apparent 'retardatory effect connected with the replacement of an *ortho*-H by any substituent, whatever its polarity'.

Correlation equations comparable to eqn (4) were derived at each temperature. An increase in temperature was accompanied by an overall decrease in the regression coefficient of the steric factor, suggesting that over the rather small temperature range studied steric features become less important relative to the electronic effects at higher temperatures.

The functional dependence of the enthalpy–entropy data given in Table 2 was examined using the methods of Krug *et al.*[9] Their null hypothesis test, a least squares regression analysis of $\Delta H^{\neq}$ on $\Delta S^{\neq}$, is used to ascertain whether an observed compensation effect results from a statistical pattern generated by random errors or arises from a genuine chemical effect. If the data are sufficiently removed from the statistical compensation line, the estimate of the isokinetic temperature, β, will be significantly different from the harmonic mean of the experimental temperature, T_{hm}, suggesting the presence of a detectable chemical compensation.

Visible inspection of the data in Table 2 indicated that the values for Brilliant Green and its 2-trifluoromethyl derivative did not fit the best line representing the isokinetic relationship. Application of a weighted least squares computer program to the data for the other dyes in Table 2 gave an isokinetic temperature of 480 ± 50 K, suggesting the existence of an isokinetic relationship. Unfortunately, the isokinetic temperature is not attainable experimentally and Exner[10] has suggested that in such cases it should be viewed as the product of an extrapolation without any real physical meaning. More importantly, the existence of an isokinetic relationship can help to define a reaction series and can be considered as a condition of a common reaction mechanism. The failure of Brilliant Green and its 2-CF_3 derivative to conform to the isokinetic plot does not of necessity imply their exclusion from the common reaction mechanism, but rather that unexplained factors may obtain in each case. For instance, in many series[11,12] the parent compound does not conform for unknown reasons, although solvation has been considered a possible cause for some systems.[12] The kinetic data for the dyes used to calculate $\beta = 480 \pm 50$ K cover a narrow numerical range (of about 5:1), whereas Brilliant Green itself reacts some 20 times faster than the mean of this range. Conversely, the 2-CF_3 derivative reacts about 20 times slower and this dye could be subject to exceptional conformational strain in the transition state.

The effect of k_2 of varying the ionic strength, I, of the solution in the range 2·0–10·0 mmol dm^{-3} was investigated at 303·2 K. In every case, a plot of $\log k_2$ against $\sqrt{I}$ was linear, in agreement with the Bronsted–Bjerrum relationship. Values for k_0 and $z_A z_B$ derived from these plots are presented in Table 3. The results are consistent with those from previous investigations on triphenylmethane dyes[2,13–15] and are in accord with theoretical predictions for a reaction between ions of opposite unit charge. Such a reaction would be expected to give a $z_A z_B$ value of −1·0. The variations in $z_A z_B$ values and the deviations from the theoretical value are not considered significant in view of the small effect of the ionic strength on the value of k_2.

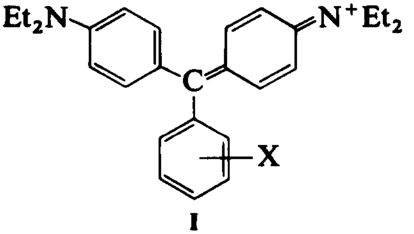
In contrast to the decreased rate shown by all the other *ortho*-substituted dyes, the observed reaction rate for the 2-OH derivative is even faster than that of the parent dye. Furthermore, at the concentrations used for the kinetic studies, the reaction is zero order with respect to hydroxide ion (see Table 1 for data at 293·2 K). At lower hydroxide concentrations, however, the reaction was neither zero nor first order and proceeded to an equilibrium absorbance, the value of which was dependent on the hydroxide ion concentration. These observations indicate that a different mechanism is operative for the hydrolysis of this dye. Since the closely related 2-methoxy BG behaves normally, the anomalous behaviour of the 2-hydroxy derivative is presumably associated with the acidic hydrogen. The 2-OH derivative is

TABLE 3

Values of k_0 and $z_A z_B$ from Plots of $\log k_2$ v. $\sqrt{I}$

Substituent	$10^3 k_0/dm^3 mol^{-1} s^{-1}$	$z_A z_B$
H	1 290 ± 20	−0·70 ± 0·08
2-OMe	109 ± 2	−0·77 ± 0·12
2-NO_2	66 ± 2	−0·82 ± 0·12
2-Cl	49 ± 1	−0·67 ± 0·12
2-Br	35 ± 1	−1·04 ± 0·11
2-Me	31 ± 1	−1·05 ± 0·15
2-CF_3	4086 ± 0·02	−0·95 ± 0·02

capable of reacting with hydroxide ion at both the carbocation centre and at the phenolic site. The *ortho*-hydroxy group must assist rather than hinder the reaction at the central carbon atom. It is postulated that an extremely rapid reversible reaction occurs between hydroxide ion and the 2-hydroxy derivative of Brilliant Green and that the kinetic studies refer to the hydrolysis of the resulting zwitterion (**II**). This initial reaction is followed by a rate determining association with a solvent molecule, leading to an intermediate species in which the water is optimally located for attack at the cationic centre. The final reaction is promoted by abstraction of a proton by hydroxide ion (Scheme 1).



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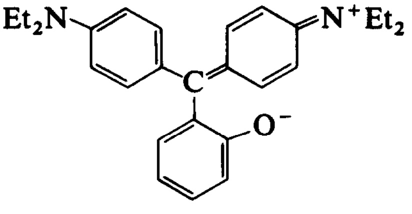
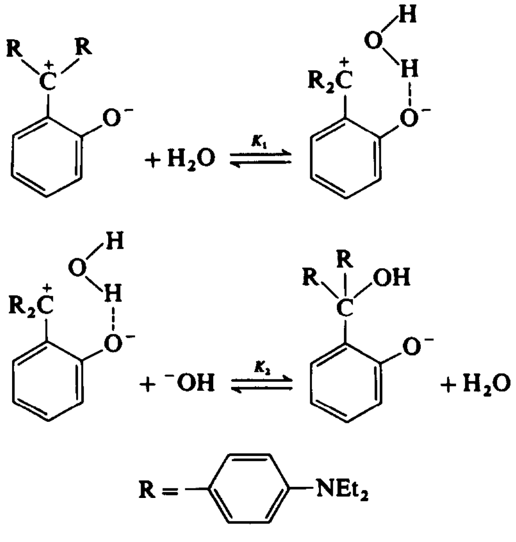


II

This reaction scheme leads to the rate equation:

$$\text{Rate} = \frac{k_1 k_2 [\text{PhO}^-][\text{H}_2\text{O}][\text{OH}^-]}{k_{-1} + k_2[\text{OH}^-]} \qquad (5)$$

where k_1, k_{-1} and k_2 are the appropriate rate constants for the reactions characterised by the equilibrium constants K_1 and K_2 (Scheme 1) and



Scheme 1

$[PhO^-]$ represents the phenoxide. At higher hydroxide concentration, eqn (5) reduces to

$$\text{Rate} = k_1[PhO^-][H_2O] \qquad (6)$$

which agrees with both the experimentally observed first order dependence of rate on the phenoxide ion and with the independence of k (observed) on the hydroxide ion concentration. The mean value of k_1 was found to be $(9{\cdot}5 \pm 0{\cdot}2) \times 10^{-5}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ at 293·2 K. If conditions can prevail such that $k_{-1} \gg k_2[OH^-]$ and $[OH^-] \gg [PhO^-]$, the rate equation reduces to

$$\text{Rate} = \frac{k_1 k_2 [H_2O][OH^-]}{k_{-1}} \qquad (7)$$

This predicted dependence of k (observed) on $[OH^-]$ was noted but was not quantified because the associated errors in this concentration range were prohibitive, since eqn (7) only applies during the early stages of the reaction, well before equilibrium is approached.

The proposed Scheme 1 also leads to the expression

$$\log[(A_0 - A_e)/A_e] = \log(K_1 K_2 [H_2O] K_w) + \text{pH} \qquad (8)$$

where K_1 and K_2 are the appropriate equilibrium constants, K_w is the ionic product of water, and A_0 and A_e are the initial and equilibrium absorbances, respectively. A plot of $\log(A_0 - A_e)/A_e$ against pH was linear, but the difference between the slope (0·78 ± 0·07) and the expected value (1·0) from eqn (8) suggests that further refinement of the reaction scheme may be required.

A value of $(1{\cdot}3 \pm 0{\cdot}3) \times 10^5\,\text{dm}^3\,\text{mol}^{-1}$ was determined for $K_1 K_2 [H_2O]$ from the intercept of the graph. Since this value refers to the overall reaction

$$PhO^- + OH^- \rightarrow \text{product}$$

it can be compared with the value of $(1{\cdot}51 \pm 0{\cdot}26) \times 10^6\,\text{dm}^3\,\text{mol}^{-1}$ for the corresponding equilibrium reaction of Brilliant Green.[1] It follows that, despite the faster rate, the hydrolysis of the 2-hydroxy derivative is thermodynamically less favourable than that of the parent dye.

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