The Hydrolysis of Brilliant Green and Some Derivatives. Part 2.[1] The Kinetics of the Hydrolysis of 3- and 4-Substituted Derivatives of Brilliant Green

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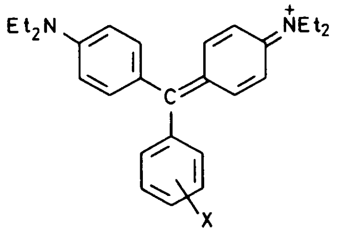
Rate constants have been measured for the reactions of hydroxide ion with the following derivatives of Brilliant Green in aqueous solution: 3-X (X = Cl, OMe, CF_3, Me, NO_2, NMe_2, or OH); 4-X (X = Cl, OMe, CF_3, Me, NO_2, or NMe_2). The substituents affect the rate of hydrolysis to an extent linearly related to the appropriate Hammett substituent constant. Thermodynamic parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been obtained for each dye and the reaction is shown to be under entropy control.

In Part 1 [1] we investigated the reactions of water molecules and hydroxide ions with Brilliant Green (I). We now discuss the hydrolysis of a range of 3- and 4-substituted derivatives of Brilliant Green. Although there are several reports in the literature of the reactions of triphenylmethane dyes with hydroxide ion,[2-6] no systematic study of the influence of substituents on the course of the reaction has been reported.



(I)

We have studied the reactions of the 3-X (X = Cl, OMe, CF_3, Me, NO_2, NMe_2, or OH) and 4-X (X = Cl, OMe, CF_3, Me, NO_2, or NMe_2) derivatives of Brilliant Green perchlorate with aqueous sodium hydroxide. The reactions were monitored spectrophotometrically at the wavelengths of maximum absorption of each dye. Aqueous solutions of the dye perchlorates absorbed at a slightly lower wavelength than solutions of the dye base or their methyl ethers in 98% acetic acid.[7] Hydroxide ion was in large enough excess to ensure pseudo-first-order kinetics. Beer's law was shown to be obeyed at concentrations below 2.0×10^{-6} mol dm^{-3} for each of the dyes and the pseudo-first-order rate constant k' was independent of the initial dye concentration. All the plots of $\log_e$(absorbance) *versus* time were linear until at least 75% completion of the reaction and the rate law (1) deduced [1] for the parent compound, BG, was shown

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

to be applicable to each derivative, since the k' *versus* $[\text{OH}^-]$ plots were linear at each of five temperatures. The values of k' are given in Supplementary Publication No. SUP 23312 (15 pp.).*

A least-squares computer program was used to give the best values for k_1 and k_2, which are shown together with their standard errors (s.e.) at each of the five temperatures in Table 1. Since k_1 is very small and is calculated from the intercept of the k' *versus* $[\text{OH}^-]$ plots, it is prone to large s.e. values. The negative values are obviously a result of these errors and are included only to give a complete summary of the results. Not surprisingly, no systematic trend in these values can be observed between the different derivatives. However, the k_2 values, which show much smaller s.e. values since they are obtained from the slopes of the graphs, show a definite dependence on the electronic properties of the substituent.

The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$, which were obtained for each dye from the application of a weighted least-squares computer program [8] to the linear plot of $\log_e k_2$ *versus* $1/T$, are given in Table 2. These data are considered to apply to reaction (2).

$$\text{BG}^+ + \text{OH}^- \rightleftharpoons \text{BGOH} \qquad (2)$$

Following the procedures suggested by Fuchs and Lewis [9] and by Wells,[10] the log k_2 values and the Hammett substituent constant, σ, for the parent compound and the 3-Cl, 3-CF_3, 3-Me, and 3-NO_2 derivatives were used to establish a Hammett line. The plot obtained from the data for twelve of the dyes studied had the same slope, within s.e. limits, as the established line. The 4-NMe_2 and 3-OH derivatives did not fit the line. In the former case, mesomeric interaction of the substituent with the reaction centre can be envisaged, although a similar situation would be anticipated for the 4-OCH_3 dye. The substituent constant for the hydroxy-group is known to show a strong dependence on solvent.[11,12] Under the basic conditions used in the present study, the phenolic moiety is expected to be converted into a phenoxide ion and the normal σ_{OH} value is not appropriate. Substituent constants for O^- are not well documented, though Hine [13] quotes a σ^+ value of -2.3 for *m*-O^-. However, the view is expressed [13] that substituent constants for electrically charged groups are relatively unreliable, depending both on the substrate and the reaction under consideration. In the present study, a value of -1.10 ± 0.05 is obtained for the *m*-O^- group, consistent with the strongly electron-releasing properties of the substituent.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

TABLE 1

The effect of temperature on the rate constants k_1 and k_2

	$10^7 k_1$/dm^3 mol^{-1} s^{-1}					k_2/dm^3 mol^{-1} s^{-1}				
Substituent	288.2 K	293.2 K	298.2 K	303.2 K	308.2 K	288.2 K	293.2 K	298.2 K	303.2 K	308.2 K
H	2.4	3.5	5.5	20	40	0.304	0.465	0.72	1.00	1.59
	±3.6	±3.6	±6.5	±14	±22	±0.006	±0.006	±0.01	±0.02	±0.04
m-Cl	−2.7[a]	0.5	21	13	34	0.42	0.65	1.03	1.67	2.4
	±8.2	±7.5	±21	±27	±93	±0.01	±0.01	±0.03	±0.04	±0.2
m-OCH$_3$	4.3	5.4	8	29	50	0.273	0.429	0.70	1.00	1.6
	±1.0	±5.3	±11	±8	±70	±0.002	±0.009	±0.02	±0.01	±0.1
m-CF$_3$	7.4	20	18	39	63	0.546	0.82	1.26	1.93	3.0
	±2.8	±15	±21	±20	±65	±0.005	±0.03	±0.04	±0.03	±0.1
m-CH$_3$	2.4	3.6	8.3	16	56	0.27	0.42	0.62	0.98	1.44
	±3.5	±9.7	±6.5	±9	±28	±0.01	±0.02	±0.01	±0.02	±0.05
m-NO$_2$	3.6	−3[a]	19	37	20	0.81	1.29	1.94	2.93	4.4
	±7.1	±40	±7	±28	±150	±0.01	±0.06	±0.01	±0.05	±0.2
m-N(CH$_3$)$_2$	4.2	5.1	12	22	31	0.224	0.346	0.52	0.75	1.16
	±2.5	±2.6	±8	±16	±15	±0.004	±0.004	±0.01	±0.03	±0.03
m-OH	2.7	2.5	11	15	25	0.064	0.103	0.150	0.22	0.33
	±0.6	±3.4	±1	±7	±8	±0.001	±0.006	±0.002	±0.01	±0.01
p-Cl	1.7	8	4	25	66	0.411	0.66	1.03	1.50	2.20
	±0.6	±11	±16	±13	±55	±0.001	±0.02	±0.03	±0.02	±0.09
p-OCH$_3$	−0.7[a]	−6.0[a]	15	3	12	0.214	0.36	0.47	0.77	1.16
	±1.9	±9.5	±9	±10	±9	±0.003	±0.02	±0.02	±0.02	±0.01
p-CF$_3$	2	10	20	19	15	0.61	0.87	1.37	2.06	3.17
	±12	±37	±26	±52	±38	±0.02	±0.06	±0.04	±0.09	±0.06
p-CH$_3$	0.1	12	12	22	29	0.233	0.378	0.56	0.86	1.37
	±2.0	±4	±9	±24	±25	±0.003	±0.006	±0.02	±0.04	±0.04
p-NO$_2$	−3[a]	5	20	2	30	0.86	1.26	1.85	2.86	4.23
	±34	±13	±15	±28	±36	±0.06	±0.02	±0.03	±0.05	±0.06
p-N(CH$_3$)$_2$	1.7	2.0	3.4	4.8	11	0.037	0.056	0.090	0.128	0.177
	±0.9	±1.0	±2.5	±3.3	±6	±0.001	±0.002	±0.004	±0.005	±0.009

[a] Negative values discussed in text.

A weighted least-squares computer program was used to obtain values for the reaction constant, ρ, from the Hammett relationship at each temperature. The value of 0.60 ± 0.02 at 298.2 K is indicative that the reaction is accelerated by electron-withdrawing substituents. This is to be expected since a cationic species such as Brilliant Green will be destabilised by electron withdrawal. This value is not dissimilar from the ρ value of 0.57 reported for the alkaline hydrolysis of a series of substituted derivatives of Malachite Green.[14] It is also of interest to compare the present result with the value of 0.65 reported for the reaction of some substituted Malachite Greens with cyanide ion at 303.2 K.[15]

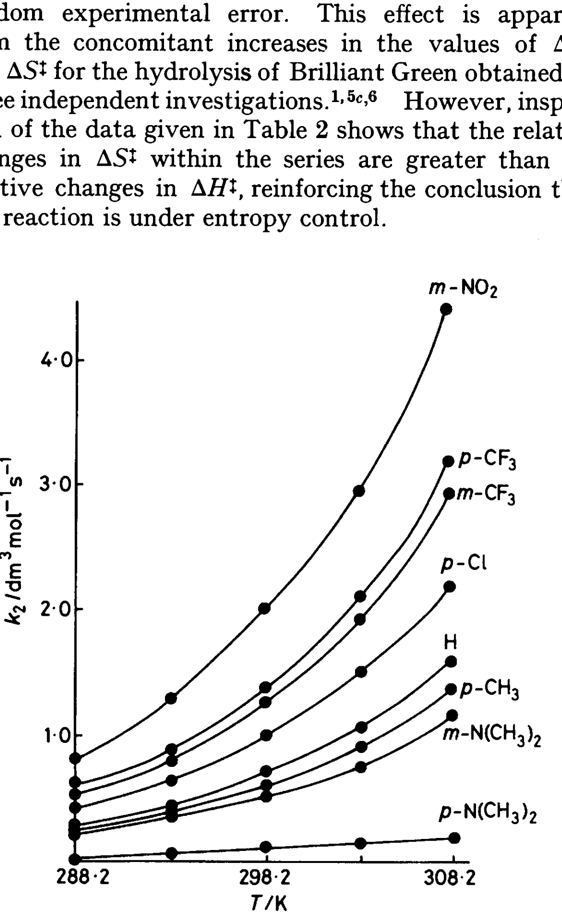
Plots of k_2 for each dye against temperature (Figure) indicate that the reactions under consideration are entropy controlled in the temperature range investigated.[16] Using the results from Table 2 and the weighted least-squares computer program, the slope of the plot of $\Delta H^\ddagger$ *versus* $\Delta S^\ddagger$ gave an isokinetic temperature, β, of 130 ± 32 K. In addition to the isokinetic temperature being prone to a large statistical error, there is the possibility that an isokinetic relationship is invalidated by changes in $\Delta H^\ddagger$ over the large temperature range involved, since β is clearly demonstrated to be well below the experimental temperatures. Further, the procedure of plotting $\Delta H^\ddagger$ against $\Delta S^\ddagger$ has been criticised by several workers.[17-20] The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ quoted in Table 2 are mutually dependent because of the manner of

TABLE 2

Thermodynamic activation parameters for the reaction between hydroxide ion and dye cations

	Experimental values		Calculated values incorporating the isokinetic temperature	
Substituent	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
H	58.9 ± 0.5	−50 ± 2	58.8 ± 0.4	−50 ± 1
m-Cl	64.0 ± 1.4	−30 ± 5	62.1 ± 1.5	−36 ± 5
m-OCH$_3$	60.7 ± 0.9	−45 ± 3	60.5 ± 0.8	−45 ± 3
m-CF$_3$	58.8 ± 0.7	−46 ± 2	59.0 ± 0.6	−45 ± 2
m-CH$_3$	59.8 ± 1.5	−48 ± 5	59.5 ± 1.2	−49 ± 4
m-NO$_2$	60.0 ± 0.3	−38 ± 1	60.2 ± 0.3	−37 ± 1
m-N(CH$_3$)$_2$	57.9 ± 0.7	−56 ± 2	57.9 ± 0.5	−56 ± 2
m-OH	58.0 ± 0.6	−66 ± 2	57.4 ± 0.6	−68 ± 2
p-Cl	60.8 ± 0.9	−41 ± 3	60.6 ± 0.6	−42 ± 2
p-OCH$_3$	60.0 ± 1.2	−49 ± 4	59.8 ± 1.0	−50 ± 3
p-CF$_3$	59.2 ± 1.2	−44 ± 4	59.5 ± 0.8	−42 ± 3
p-CH$_3$	62.4 ± 1.2	−40 ± 4	61.4 ± 1.2	−44 ± 4
p-NO$_2$	58.6 ± 1.3	−43 ± 4	59.1 ± 1.1	−41 ± 4
p-N(CH$_3$)$_2$	56.2 ± 2.0	−77 ± 7	55.5 ± 1.2	−79 ± 4

their calculation from the experimental results. Linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can arise simply from random experimental error. This effect is apparent from the concomitant increases in the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the hydrolysis of Brilliant Green obtained by three independent investigations.[1,5c,6] However, inspection of the data given in Table 2 shows that the relative changes in $\Delta S^{\ddagger}$ within the series are greater than the relative changes in $\Delta H^{\ddagger}$, reinforcing the conclusion that the reaction is under entropy control.



k_2 *versus* temperature for a number of substituted dyes. Dyes omitted in the interest of clarity show the same trend

As further proof of the existence of an isokinetic relationship,[20] the use of the average values of the calculated rate constant at the isokinetic temperature, β, as an extra point in the $\log_e k_2$ against $1/T$ plots had only a very small effect on the statistical measure of fit for the graphs (Table 2). It thus appears that each compound in the Brilliant Green series undergoes hydrolysis by the same mechanism.[21]

It is of interest to speculate on the implications of entropy control of the alkaline hydrolysis of the dyes. Some structural reorganisation must be involved during the rate-determining step. The crowded nature of the carbonium ion will be accentuated by solvation, making access to the central carbon atom difficult. As the attacking hydroxide ion approaches the dye cation, further distortion from the planar state occurs which culminates in a change of hybridisation of the central carbon atom from sp^2 to sp^3. During this process, considerable reorganisation of the solvent molecules can be envisaged. The greater the electron-withdrawing nature of the substituent in the phenyl ring, the larger will be the sphere of solvent interaction and hence the effect will be more pronounced.

The magnitude of $\Delta S^{\ddagger}$ provides useful information on a reaction mechanism in solution,[22] since it reflects the difference in the number and character of the translational and rotational degrees of freedom between the reactants and the transition state. Although translational and rotational entropy per species in solution cannot be evaluated except in a most approximate fashion, certain regularities in the entropies of activation of reactions involving gaseous species have been noted.[23] Entropy changes in solution are more variable, but empirical relationships lead to ranges for $\Delta S^{\ddagger}$ for reactions of different order.[22] The values of $\Delta S^{\ddagger}$ for most of the derivatives of Brilliant Green (Table 2) lie near to the second-order reaction range of -63 to -84 J K^{-1} mol^{-1}. The somewhat less negative values may result from the greater solvation of the charged reactants than the uncharged transition state. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the 4-NMe$_2$ derivative of Brilliant Green are similar to those obtained by Sinha and Katiyar[24] for Ethyl Violet, the 4-NEt$_2$-substituted Brilliant Green.

The results of variation in ionic strength on the rates of hydrolysis are listed in Table 3. In the range of ionic strengths 0.01—0.10 mol dm^{-3}, the Brönsted–Bjerrum relationship was found to be applicable. It is evident that there is a decrease in the rate of the reaction as the ionic strength increases, indicating the involvement of oppositely charged species in the rate-determining step. However, all the Z_AZ_B values (Table 3) are less negative than the value of -1.0 expected for a reaction between species carrying unit charges, though the value of $-(0.83 \pm 0.01)$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ for the parent dye is in good agreement with that of -0.82 reported by Katiyar.[5b] Nevertheless, too much significance cannot be attached to the Z_AZ_B values because of the considerable scatter shown for the various derivatives. However, it was stated earlier that the m-OH derivative is expected to exist as the O$^-$ species which, although electrically neutral, is dipolar. Thus a Z_AZ_B value intermediate between 0 and 1 is not unexpected. In the case of p-OH substituent, conversion into the quinonoid form, for which a Z_AZ_B value of zero would be expected, can be envisaged in alkaline solution.[25] It was not possible to purify the perchlorate of the p-hydroxy-analogue and thus this postulate could not be verified.

Using both the Hammett and the Brönsted–Bjerrum equations, the relationship (3) can be deduced,[26] in which

$$\sigma\rho = \log(k'_0/k_0) + (\mathrm{f}' - \mathrm{f})(I) \qquad (3)$$

k_0 and k'_0 are the rate constants at zero ionic strength and f(I) and f′(I) are the functions of ionic strength for the unsubstituted and a given substituted Brilliant Green, respectively. Although it can be seen from Table 3 that the values of f(I) and f′(I) are not equal, numerical comparisons show that the (f′ − f)(I) term is generally very small relative to the log (k'_0/k_0) term.

If σ is assumed to be independent of ionic strength, the constancy of ρ obtained experimentally (Table 3), within s.e. limits, is explained.

It is of interest to compare the values of $-(50 \pm 2)$

TABLE 3

Effects of variation in ionic strength at 298.2 K

Substituent	k_2/dm^3 mol^{-1} s^{-1} at given ionic strength/mol dm^{-3}							Z_AZ_B
	0.00	0.01	0.03	0.05	0.075	0.10	0.15	
H	0.875 ±0.005	0.72 ±0.01	0.62 ±0.01	0.56 ±0.01	0.52 ±0.01	0.47 ±0.01	0.45 ±0.01	−0.83 ±0.01
m-Cl	1.242 ±0.006	1.03 ±0.03	0.91 ±0.02	0.83 ±0.02	0.75 ±0.03	0.70 ±0.02	0.63 ±0.03	−0.77 ±0.01
m-OCH_3	0.841 ±0.008	0.70 ±0.02	0.61 ±0.02	0.57 ±0.02	0.51 ±0.01	0.47 ±0.01	0.43 ±0.02	−0.78 ±0.02
m-CF_3	1.48 ±0.02	1.26 ±0.04	1.11 ±0.03	1.03 ±0.03	0.95 ±0.02	0.87 ±0.02	0.80 ±0.03	−0.70 ±0.02
m-CH_3	0.745 ±0.009	0.62 ±0.01	0.55 ±0.01	0.48 ±0.02	0.45 ±0.01	0.42 ±0.02	0.368 ±0.009	−0.79 ±0.03
m-NO_2	2.41 ±0.01	1.94 ±0.01	1.65 ±0.02	1.48 ±0.02	1.33 ±0.02	1.21 ±0.03	1.16 ±0.02	−0.93 ±0.01
m-$N(CH_3)_2$	0.619 ±0.003	0.52 ±0.01	0.45 ±0.02	0.41 ±0.01	0.37 ±0.02	0.345 ±0.009	0.31 ±0.01	−0.79 ±0.01
m-OH	0.160 ±0.001	0.150 ±0.002	0.142 ±0.005	0.137 ±0.004	0.132 ±0.003	0.130 ±0.004	0.125 ±0.004	−0.29 ±0.01
p-Cl	1.19 ±0.01	1.03 ±0.03	0.91 ±0.02	0.86 ±0.03	0.79 ±0.03	0.74 ±0.02	0.67 ±0.02	−0.65 ±0.02
p-OCH_3	0.57 ±0.03	0.47 ±0.02	0.46 ±0.02	0.38 ±0.01	0.35 ±0.01	0.33 ±0.01	0.30 ±0.02	−0.75 ±0.09
p-CF_3	1.63 ±0.02	1.37 ±0.04	1.23 ±0.02	1.12 ±0.02	1.03 ±0.03	1.00 ±0.04	0.93 ±0.03	−0.71 ±0.03
p-CH_3	0.674 ±0.005	0.57 ±0.02	0.49 ±0.03	0.45 ±0.03	0.41 ±0.02	0.39 ±0.02	0.35 ±0.03	−0.76 ±0.02
p-NO_2	2.27 ±0.01	1.85 ±0.03	1.59 ±0.03	1.43 ±0.03	1.29 ±0.02	1.24 ±0.03	1.16 ±0.03	−0.88 ±0.01
p-$N(CH_3)_2$	0.106 ±0.002	0.090 ±0.004	0.079 ±0.004	0.075 ±0.007	0.068 ±0.004	0.062 ±0.003	0.053 ±0.004	−0.72 ±0.04
Reaction constant ρ at given ionic strength	0.60 ±0.03	0.60 ±0.02	0.60 ±0.04	0.60 ±0.03	0.61 ±0.03	0.58 ±0.05	0.62 ±0.03	

TABLE 4

Analytical and spectroscopic data for dye perchlorates

X in (1)	Method of preparation	Formula	Found (%) *				$\lambda_{max.}$/nm
			C	H	N	F	
H	1	$C_{27}H_{33}ClN_2O_4$	66.5 (66.9)	7.0 (6.9)	5.7 (5.8)		628
3-Cl	1	$C_{27}H_{32}Cl_2N_2O_4$	62.7 (62.4)	6.1 (6.2)	5.0 (5.4)		636
3-OMe	1	$C_{28}H_{35}ClN_2O_5$	65.3 (65.3)	6.7 (6.9)	5.3 (5.4)		629
3-CF_3	1	$C_{28}H_{32}ClF_3N_2O_4$	60.5 (60.8)	5.8 (5.8)	5.1 (5.1)	10.5 (10.3)	637
3-Me	2	$C_{28}H_{35}ClN_2O_4$	67.0 (67.4)	7.0 (7.0)	5.5 (5.6)		626.5
3-NO_2	1	$C_{27}H_{32}ClN_3O_6$	61.0 (61.2)	6.1 (6.0)	7.9 (7.9)		642
3-NMe_2	2	$C_{29}H_{38}ClN_3O_4$	65.8 (66.0)	7.4 (7.2)	7.9 (8.0)		626
3-OH	1	$C_{27}H_{33}ClN_2O_5$	64.4 (64.7)	6.7 (6.6)	5.4 (5.6)		627.5
4-Cl	1	$C_{27}H_{32}Cl_2N_2O_4$	61.9 (62.4)	6.1 (6.2)	5.1 (5.4)		633
4-OMe	1	$C_{28}H_{35}ClN_2O_5$	64.9 (65.3)	6.9 (6.8)	5.2 (5.4)		618
4-CF_3	1	$C_{28}H_{32}ClF_3N_2O_4$	60.8 (60.8)	5.8 (5.8)	4.9 (5.1)	10.6 (10.3)	641
4-Me	2	$C_{28}H_{35}ClN_2O_4$	67.2 (67.4)	7.1 (7.0)	5.4 (5.6)		623
4-NO_2	1	$C_{27}H_{32}ClN_3O_6$	61.1 (61.2)	6.0 (6.0)	7.9 (7.9)		651
4-NMe_2	2	$C_{29}H_{38}ClN_3O_4$	66.0 (66.0)	7.3 (7.2)	7.7 (8.0)		592

* Calculated values in parentheses.

J K^{-1} mol^{-1} for $\Delta S^{\ddagger}$ for the parent dye with the value of $\Delta S^{\ominus}$ for the overall reaction calculated from the data of Fox *et al.*[1] Using an average value of $(1.08 \pm 0.18) \times 10^6$ dm^3 mol^{-1} for the equilibrium constant at 298.2 K for the reaction step $BG^+ + OH^- \rightleftharpoons BGOH$, a value of $-(34.4 \pm 0.4)$ kJ mol^{-1} is obtained for $\Delta G^{\ominus}$, leading to a value of (25 ± 13) J K^{-1} mol^{-1} for $\Delta S^{\ominus}$. 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.

EXPERIMENTAL

The dye perchlorates were prepared either by the chloranil oxidation of the leuco-base of the dye and subsequent reaction of the dye solution with aqueous sodium perchlorate (method 1) or by dissolution of the dye base in acetic acid followed by precipitation of the perchlorate (method 2). Typical procedures are described below and data for the compounds used in this study are presented in Table 4. The kinetic results were obtained by the method previously described.[1] The rate constants at various temperatures are listed in SUP 23312.

*4′,4′′-Bisdiethylamino-*3*-hydroxytriphenylmethane*.—A mixture of 3-hydroxybenzaldehyde (0.1 mol), purified *NN*-diethylaniline [27] (0.3 mol), hydrochloric acid (32%; 0.2 mol), and ethanol (75 cm^3) was boiled under reflux for 24 h. The resulting solution was basified with ethanolic ammonia solution (1 : 3), distilled in steam, and the residue was reduced in volume and treated with acetone. On cooling, crystals separated which were recrystallised from ethanol and from acetone to yield the *leuco-base dihydrochloride* (58%), m.p. 227 °C (Found: C, 67.9; H, 7.6; Cl, 15.0; N, 5.8. $C_{27}H_{36}Cl_2N_2O$ requires C, 68.2; H, 7.6; Cl, 15.0; N, 5.9%).

The oil obtained on basification of the hydrochloride was dissolved in methanol and boiled with chloranil for 6 h. The hot solution was filtered into a saturated aqueous solution of potassium perchlorate. The *dye perchlorate* was collected, purified by repeated precipitation from an acetone solution with ether, and dried at 100 °C at 1 mmHg for 24 h.

*4′,4′′-Bisdiethylamino-*3*-dimethylaminotriphenylmethanol*.—An ethereal solution of 3-dimethylaminophenyl-lithium [prepared from 3-bromodimethylaniline [28] (0.02 mol) and lithium metal (0.04 mol)] was added to a slurry of 4,4′-bisdiethylaminobenzophenone (0.016 mol) in ether. After 2 h, the mixture was hydrolysed, and the product was isolated in the usual way and recrystallised from light petroleum (b.p. 60—80 °C) to yield the *dye-base* (68%), m.p. 124 °C (Found: C, 78.5; H, 8.6; N, 9.8. $C_{29}H_{39}N_3O$ requires C, 78.2; H, 8.8; N, 9.4%).

The *dye perchlorate*, obtained by adding a solution of the dye base in acetic acid to saturated aqueous potassium perchlorate, was purified as above.

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