778. *Kinetic Studies of the Fluorene Series. Part IV.*[1] *The Acid-catalysed Solvolysis of 4-Substituted 9-Diazofluorenes*

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The rates of perchloric acid-catalysed solvolysis of some 4-substituted 9-diazofluorenes in 93·8% w/w ethanol have been determined. Solvolysis is hindered by electron-withdrawing groups, and the energies and entropies of activation are linearly related.

Treatment of the data by Hammett-type equations shows that transmission of *T* effects to the 9-position is much less effective than for 2-substituents. This could be due to the displacement of substituents from the plane of the aromatic ring, by interaction with the 5-hydrogen atom, but is also consistent with the results of simple molecular orbital calculations.

Whilst both the 2- and the 4-position in fluorene and its derivatives formally resemble *meta*-positions in toluene or its analogues, 2-substituents have been shown [2] to exert abnormally large resonance effects on the rate of acid-catalysed solvolysis of 9-diazofluorene. For comparison, the rates for thirteen 4-substituted 9-diazofluorenes, under the same reaction conditions, are now reported (Table 1).

Table 1

Perchloric acid-catalysed solvolysis of 4-substituted 9-diazofluorenes in 93·8% (w/w) ethanol–water

Substituent	H	OCH_3	CH_3	C_6H_5	SCH_3	CO_2CH_3	Cl
k_s (l. mole^{-1} min.$^{-1}$) (25·00°)	4·87	4·71	4·46	3·53	2·52	1·39	0·952
k_s (l. mole^{-1} min.$^{-1}$) (35·00°)	13·08	11·36	12·29	8·86	7·50	4·16	2·78
E_A (kcal.)	18·0	16·1	18·5	16·8	19·9	20·0	19·5
$\log_{10} A$	12·13	10·67	12·43	11·08	13·21	13·03	12·54
$-\Delta S^{\ddagger}$ (e.u.)	5·1	11·8	3·7	9·9	0·1	1·0	3·2

Substituent	I	CN	NO_2	Br	NH_2	F	NH_3^+
k_s (l. mole^{-1} min.$^{-1}$) (25·00°)	1·12	0·343	0·249	0·858	35·2	1·17	0·282
k_s (l. mole^{-1} min.$^{-1}$) (35·00°)	3·11	0·893	0·732	2·70	—	3·12	—
E_A (kcal.)	18·6	17·5	19·7	20·9	—	17·9	—
$\log_{10} A$	11·93	10·56	12·04	13·49	—	11·41	—
$-\Delta S^{\ddagger}$ (e.u.)	6·0	12·3	5·5	−1·1	—	8·4	—

The specific rates, k_s, at 25·00 and 35·00°, and the energies and entropies of activation thence derived, are shown in the Table. Using 4-amino-9-diazofluorene, values of k_s for the 4-NH_2 and 4-NH_3^+ groups were deduced as previously described; [2] the pK_a for 4-aminofluorene [3] in "70% ethanol" (3·40) was assumed for the diazo-compound, and the uncertainties in k_s(4-NH_2) and k_s(4-NH_3^+) are about ±30 and ±10%, respectively. Neither value was therefore used for the calculation of the regression line by the equation shown below. For the parent compound, slightly larger k_s values than earlier recorded [2] are found, owing possibly to the use of a different stock 72% perchloric acid, or to an improved design of the apparatus. However, E_A is negligibly different, and check runs showed k_{rel} for 2-bromo-9-diazofluorene to be unaltered.

Energy–Entropy Relationships.—Despite the expected rate-retarding effect of electron-withdrawing substituents, the normal regular increase in E_A with decreasing $\log_{10} k_{rel}$ is not observed. The familiar compensating variation [4,5] of E_A with $\Delta S^{\ddagger}$ is however found, although the scatter about the regression line is somewhat greater than for the 2-substituted series. Excluding the points for the 4-cyano- and 4-nitro-derivatives which deviate substantially, a value of 85° is obtained for the isokinetic temperatures. {Where E_A and

[1] Part III, J. A. Parry and K. D. Warren, *J.*, 1965, 4049.
[2] K. D. Warren, *J.*, 1963, 598.
[3] P. H. Grantham, E. K. Weisburger, and J. H. Weisburger, *J. Org. Chem.*, 1961, **26**, 1008.
[4] R. A. Fairclough and C. N. Hinshelwood, *J.*, 1937, 538.
[5] J. Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

$\Delta S^{\ddagger}$ are correlated by an equation of the form $\Delta S^{\ddagger} = pE_A + q$, then since $\log_{10} k_{rel} =$ const. $- E_A/\boldsymbol{R}T + \Delta S^{\ddagger}/\boldsymbol{R}$, then $\log k_{rel} =$ const. $- [q + E_A(1/T - p)]/\boldsymbol{R}$. Thus a correlation of $\log k_{rel}$ with E_A is expected unless $p \simeq 1/T$, which is actually the case here.*}

As for the 2-substituted compounds,[2] the values of $-\Delta S^{\ddagger}$ are relatively small in view of the established rate-determining proton transfer. This suggests that formation of the transition complex may be accompanied by some desolvation; a positive entropy contribution from internal rotation of the diazo-group about the C–N bond is unlikely since this would require a hybridisation of the α-nitrogen atom unfavourable to the subsequent ready loss of nitrogen.

Application of the Hammett Equation.—The data were correlated, as before, by means of the following equation based on the Taft modification [6] of the Hammett equation. The results at 25·00° gave the values (Figure 1) $\rho = -1{\cdot}836$ and $a = +1{\cdot}083$.

$$\log_{10} k_{rel} = \rho(\sigma_I + a\sigma_{m,\,R})$$

It is apparent that for 9-diazofluorenes the transmission of resonance effects is much less effective for 4-substituents than for groups in the 2-position. Indeed, for the former, the data are almost as well correlated by the standard σ_m constants as by the use of the above equation. However, examination of molecular models show that for conjugating groups,

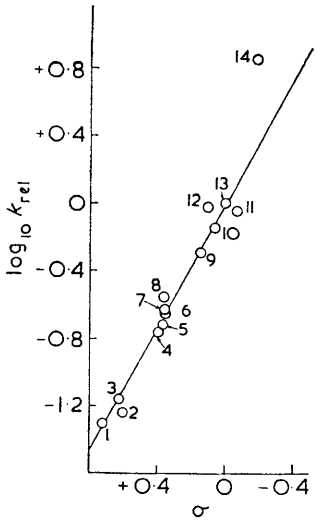

FIGURE 1. Relationship between substituent constants and relative rates of solvolylsis of 4-substituted 9-diazofluorenes.

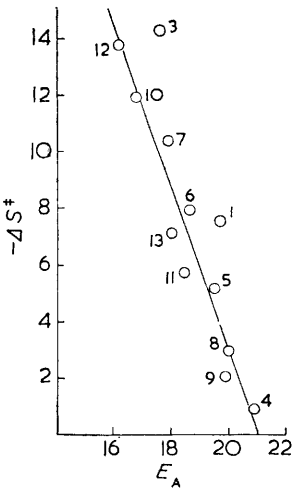

FIGURE 2. Relationship between energies and entropies of activation. (The numbers have the same meaning as in Figure 1.)

4-Substituents: 1, NO_2; 2, NH_3^+; 3, CN; 4, Br; 5, Cl; 6, I; 7, F; 8, CO_2CH_3; 9, SCH_3; 10, C_6H_5; 11, CH_3; 12, OCH_3; 13, H; 14, NH_2

such as C_6H_5, OCH_3, SCH_3, CO_2CH_3, and NO_2, in the 4-position of fluorene derivatives, there is considerable steric hindrance to coplanarity with the benzenoid ring, owing to interaction with the 5-hydrogen atom. If such substituents were actually displaced from the plane of the ring, to a greater extent than in unhindered benzene derivatives, the transmission of their T effects to the reaction site would be appreciably impaired.

Comparison of rates for the 4-OCH_3, -SCH_3, -C_6H_5, and -CO_2CH_3 derivatives with the corresponding values for 2-substituents supports this hypothesis; in the 4-position, the methoxyl, thiomethyl, and phenyl groups (all $+T$) are substantially more deactivating

* The authors thank a Referee for drawing their attention to this point.

[6] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436.

than in the 2-position, whilst the methoxycarbonyl group ($-T$) now deactivates less, and not more, than halogen substituents. The 4-methoxy-group is, however, still appreciably more electron-supplying than predicted by the standard σ_m constants, suggesting that some abnormal resonance effects still operate, and the slight deactivating effect of the 4-methyl group remains anomalous. It is important then to attempt to assess the extent to which steric hindrance is responsible for the observed effects of 4-substituents and also to consider how the effects of 2- and 4-substituents would compare in the absence of such hindrance.

The suggested prevention of coplanarity of substituents would not of itself necessarily result in an irregular E_A *vs.* log k_{rel} plot. However, although the previously observed rate-determining proton transfer and the ρ value found indicate an early transition state, some change of hybridisation of the 9-carbon atom from sp^2 towards sp^3 must accompany electrophilic attack, thus lengthening the 1a,9- and 8a,9-bonds. This could possibly be offset by some extension of the 4a,5a-bond, but the net effect would be to bring the 4-substituent and the 5-hydrogen atom closer together, the consequent increases in E_A depending on the magnitude and rotational ability of the substituent.

Detailed discussion of the observed energies and entropies of activation for the series is necessarily tentative, in view of the experimental uncertainties, but qualitative comparison of the figures for the 2- and 4-substituted series reveals the following points.

(i) The present small deactivating effect of the methyl group results from an E_A slightly greater, and a $\Delta S^\ddagger$ somewhat more negative, than in the 2-position. This accords with increased steric compression, and restriction of rotation in the transition state.

(ii) For the methoxy-group E_A is slightly smaller for the 4-substituent but $\Delta S^\ddagger$ is nearly 5 e.u. more negative, implying that restriction of rotation rather than compression is the dominant feature. For the thiomethyl group, though, both E_A and $\Delta S^\ddagger$ are substantially more positive in the 4-position, suggesting that the larger group undergoes appreciable steric strain, possibly accompanied by desolvation.

(iii) The greater deactivating effect of the phenyl group in the 4-position is due mainly to a slightly less favourable entropy; rotation of the substituent is considerably hindered in the ground state and is probably only slightly further restricted in the transition complex. For the methoxycarbonyl group, the E_A and $\Delta S^\ddagger$ values differ little for the 2- and 4-positions. Presumably rotation is similarly already substantially hindered in the ground state.

(iv) The 4-cyano- and 4-nitro-derivatives react more slowly than the 2-substituted analogues, smaller E_A values being counterbalanced by substantially more negative entropies. This is consistent with non-coplanarity of the substituents with the ring (rendering them less electron-withdrawing) and increased steric restriction in the transition state. For the cyano-compound, though, some bond angle distortion in both the substituent and the aromatic ring seems implied.

(v) The fluoro- and chloro-compounds show no significant difference in E_A and $\Delta S^\ddagger$ between the two series; for the bromo-group, however, E_A is larger and $\Delta S^\ddagger$ more positive for the 4-substituted compound. If the increased E_A is due to steric compression, the failure of the iodo-group to behave similarly is hard to understand, though experimental errors, which, for this substituent, are somewhat greater than for the rest of the series, may be responsible.

Molecular Orbital Calculations.—Comparison of E_A and $\Delta S^\ddagger$ values cannot, however, determine unequivocally whether steric hindrance to coplanarity is responsible for the markedly smaller resonance effects exhibited by 4-substituents. It is equally possible that T effects of 4-substituents in the diazofluorene system would be less effectively relayed to the 9-position in the absence of such interactions.

Molecular orbital calculations support this view; localisation energies [7] (L_r^+) for attack

[7] A. Streitwieser, jun., "Molecular Orbital Theory for Organic Chemistry," Wiley, New York, 1961, p. 335.

of an electrophile at the 9-carbon atom, obtained modelling electron-withdrawing groups by CH_2^+ and electron-releasing groups by $-CH_2^-$, are shown in Table 2. The differences, ΔL_r^+, between the values for $-CH_2^+$- and $-CH_2^-$-substituents are a measure of the susceptibilities of the systems to tautomeric effects of substituents. (Comparison with the parent compound is less reliable for simple MO treatment.) Thus, even neglecting steric contributions, the results predict greater resonance effects for substituents in the 2-position.

TABLE 2

Localisation energies (L_r^+) for substituted 9-diazofluorenes

Substituent	2-CH_2^+		2-CH_2^-	4-CH_2^+		4-CH_2
$L_r^+(\beta)$	2·006		1·938	2·028		1·968
$\Delta L_r^+(\beta)$		0·068			0·060	

Calculated by simple Hückel MO method: $\alpha_N = \alpha + 0{\cdot}5\beta$, $\beta_{CN} = 0{\cdot}8\beta$, $\beta_{NN} = \beta$

(In the related diphenyldiazomethane, ΔL_r^+ for a *meta*-substituent is zero; the small finite values for 2- and 4-substituents in 9-diazofluorene are thus consistent with the unusually large $+T$ effects found for the methoxy-group in both positions.)

It is noteworthy that similar calculations for the fluorenone system [8] (sodium borohydride reduction) predict the opposite result (*i.e.*, that T effects should be greater for 4-substituents) and that preliminary results [9] fulfil this expectation. It seems likely then, that, in the diazofluorene system, T effects would be more effectively transmitted from the 2- than from the 4-position, irrespective of steric factors, but the complex pattern of E_A and $\Delta S^\ddagger$ values strongly suggests that some interaction between the 4-substituent and the 5-hydrogen atom is involved.

EXPERIMENTAL

Reagents.—Stock solvent 93·8% (w/w) ethanol–water and standard perchloric acid solutions were made up as before,[10] and freshly prepared solutions of diazo-compounds used for each run. Details of the new 4-substituted 9-diazofluorenes (and the corresponding hydrazones), prepared as previously described,[11] are given in Tables 3 and 4.

TABLE 3

4-substituted fluorenone hydrazones

Subst.	Yield (%)	M. p.	Found (%) C	H	N	Formula	Required (%) C	H	N
OCH_3	48	189—191° (dec.)	74·5	5·6	12·5	$C_{14}H_{12}N_2O$	74·9	5·4	12·5
CH_3	92	150—151 (dec.)	80·7	5·8	13·5	$C_{14}H_{12}N_2$	80·2	5·9	13·6
C_6H_5	75	127—128 (dec.)	83·7	5·2	10·1	$C_{19}H_{14}N_2$	84·4	5·2	10·4
SCH_3	69	172—173 (dec.)	70·0	5·1	11·8	$C_{14}H_{12}N_2S$	70·0	5·0	11·8
CO_2CH_3	,,	140—141 (dec.)	71·6	,,	11·2	$C_{15}H_{13}N_2O_2$	71·5	4·8	11·1
F	84	154—155 (dec.)	73·7	4·2	13·1	$C_{13}H_9FN_2$	73·6	4·3	13·2
Cl	,,	166—167 (dec.)	68·1	4·1	12·1	$C_{13}H_9ClN_2$	68·3	3·9	12·2
I	79	165—166 (dec.)	48·8	2·9	8·9	$C_{13}H_9IN_2$	48·8	2·8	8·8
CN	83	165—166	76·4	4·1	19·4	$C_{14}H_9N_3$	76·7	4·1	19·2
CN		183—184	76·7	4·2	19·0	,,	,,	,,	,,
NO_2	80	146—147		*		$C_{13}H_9N_3O_2$	65·3	3·8	17·6
Br	55	155—162 (dec.)	57·1	3·6	10·4	$C_{13}H_9BrN_2$	57·2	3·3	10·3
NH_2	84	189—190 (dec.)		*		$C_{13}H_{11}N_3$	74·6	5·3	20·1

* Not obtained analytically pure.

The required ketones were obtained by standard methods, with the exception of the 4-iodo- and 4-thio-methyl compounds, which are new, and the 4-methyl derivative.

[8] K. D. Warren and J. R. Yandle, unpublished calculations.
[9] K. D. Warren and J. R. Yandle, unpublished results.
[10] K. D. Warren, *J.*, 1961, 2561.
[11] K. D. Warren, *J.*, 1961, 1412.

TABLE 4

4-Substituted 9-diazofluorenes

Subst.	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
OCH_3	85	96—97°	75·7	4·9	12·7	$C_{14}H_{10}N_2O$	75·7	4·5	12·6
CH_3	92	87	81·7	5·2	13·4	$C_{14}H_{10}N_2$	81·5	4·9	13·6
C_6H_5	67	90—91	85·2	4·6	10·2	$C_{19}H_{12}N_2$	85·1	4·5	10·5
SCH_3	57	94—95	70·8	4·8	11·2	$C_{14}H_{10}N_2S$	70·6	4·2	11·8
CO_2CH_3 * ...	48	57—58	72·3	4·2	11·4	$C_{15}H_{10}N_2O_2$	72·1	4·1	11·2
CO_2CH_3 * ...	,,	76—76·5	71·7	,,	11·1	,,	,,	,,	,,
F	63	69—70	74·4	3·2	13·5	$C_{13}H_7FN_2$	74·2	3·4	13·3
Cl	76	82—83	68·9	,,	12·4	$C_{13}H_7ClN_2$	68·8	3·1	12·3
I	80	95—96	49·3	2·4	8·7	$C_{13}H_7IN_2$	49·1	2·2	8·8
CN	77	151—151·5	77·6	3·7	19·5	$C_{14}H_7N_3$	77·4	3·3	19·3
NO_2	59	135—135·5	65·6	3·0	17·9	$C_{14}H_7N_3O_2$	65·8	3·0	17·7
Br	47	98—99	57·4	2·8	10·5	$C_{13}H_7BrN_2$	57·4	2·8	10·5
NH_2	71	119—119·5	75·7	4·5	20·2	$C_{13}H_9N_3$	75·3	4·4	20·3

* Two crystal forms.

4-*Iodofluorenone*. This was prepared from 4-aminofluorenone by the method of Kharasch and Bruice,[12] and the crude product chromatographed in benzene on neutral alumina. Elution with benzene–light petroleum (b. p. 40—60°) and then benzene alone, removal of solvent, and recrystallisation from ethanol gave 4-*iodofluorenone*, chrome-yellow needles (31%), m. p. 117—118° (Found: C, 51·5; H, 2·1; I, 40·7. $C_{13}H_7IO$ requires C, 51·0; H, 2·3; I, 41·5%).

4-*Thiomethylfluorenone*. This was prepared from 4-aminofluorenone using the method previously described for the 2-substituted compound.[1] 4-*Thiomethylfluorenone* was obtained as pale orange-yellow needles (37% overall) from ethanol, m. p. 111—112° (Found: C, 74·4; H, 4·4; S, 13·5. $C_{14}H_{10}OS$ requires C, 74·3; H, 4·45; S, 14·2%).

4-*Methylfluorenone*. An attempted preparation by the decarboxylation of 9-oxofluoren-4-ylacetic acid failed, and this compound was therefore obtained, *via* 4-methylfluorene, from indene and penta-1,3-diene according to Bergmann.[13] To confirm the orientation of this product, 4-methylfluorene was synthesised by an unambiguous route.

Fluorenone-4-carboxylic acid was reduced by the Wolff–Kishner procedure to fluorene-4-carboxylic acid and esterified with methanol and concentrated sulphuric acid. Reduction with lithium aluminium hydride yielded *fluoren-4-ylmethanol* (78%), white needles (from benzene–ether), m. p. 125·5—126° (Found: C, 85·5; H, 6·0. $C_{14}H_{12}O$ requires C, 85·7; H, 6·1%). Treatment with phosphorus tribromide in benzene gave putative *fluoren-4-ylmethyl bromide* (51%), white needles [from light petroleum (b. p. 80—100°)], m. p. 115—118°, which on reduction with zinc and glacial acetic acid afforded 4-methylfluorene (36%), identical with the product obtained by Bergmann.

Kinetic Runs.—The reaction was studied by the manometric method used before,[1] the apparatus being improved by a greater use of capillary tubing for connections and by circulating thermostat water through the burette jackets. For the 4-amino-compound k_1 was as before derived from the first 30% of the reaction; otherwise the process gave first-order kinetics for at least the first 80% of its course, and nitrogen evolution was almost quantitative. With two exceptions, the reaction solutions were initially about 0·005M with respect to diazo-compound; the first-order rate constants were reproducible to within ±3%, and the activation energies probably correct within ±0·6 kcal. More dilute solutions were used for the less soluble 4-iodo- and 4-nitro-compounds for which the rate constants were reproducible within ±4% and the activation energies probably correct within ±0·8 kcal. The recorded values of $\Delta S^{\ddagger}$ have an estimated error of ±2·0 e.u.

One of us (J. R. Y.) thanks the D.S.I.R. for a Maintenance Grant.

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CATHAYS PARK, CARDIFF. [*Received, December 8th*, 1964.]

[12] N. Kharasch and T. C. Bruice, *J. Amer. Chem. Soc.*, 1951, **73**, 3240.
[13] E. D. Bergmann, *Bull. Res. Council Israel*, 1956, **5***A*, 147.