95. *Kinetic Studies of the Fluorene Series. Part II.*[1] *The Acid-catalysed Solvolysis of 2-Substituted 9-Diazofluorenes.*

By Keith D. Warren.

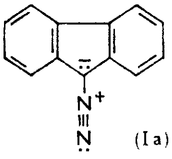
The rates of perchloric acid-catalysed solvolysis of some 2-substituted 9-diazofluorenes in 93·8% (w/w) ethanol–water have been determined. As expected, solvolysis is facilitated by electron-releasing groups and retarded by electron-withdrawing groups, but variations in both Arrhenius parameters are involved. Factors influencing the energies and entropies of activation, in this and other reactions of fluorene derivatives, are considered.

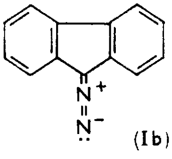
Attempts to fit the results to Hammett-type equations suggest the operation of appreciable *T* effects from the 2-position: the possible transmission of such effects to the 9-carbon atom *via* the unsubstituted ring is discussed.

The mechanism of the acid-catalysed solvolysis of 9-diazofluorene has been previously considered.[1] The influence of a wide range of 2-substituents on the rate of solvolysis is now reported. The reaction was studied in 93·8% (w/w) ethanol–water and the same range of concentrations of perchloric acid (0·01—0·05M) used for each compound. This allowed direct comparison of rates, and minimised errors due to salt effects which, for 9-diazofluorene, were appreciable at greater acidities.

The Table shows the results expressed as specific rates, k_s (slope of k_1, first-order constant, against [$HClO_4$]), the reaction being of first order with respect to diazo-compound. Except for the 2-amino-compound, k_1 varied linearly with [$HClO_4$], and energies of activation were calculated from the k_s values at 25·00° and 35·00°.

For the 2-amino-compound E_A could not be satisfactorily obtained since k_s was derived by the following approximation; pK_a for 2-aminofluorene in " 70% ethanol " at 25·0° is[2] 4·30, and 2-amino-9-diazofluorene was assumed to be of comparable base strength under reaction conditions [the diazo-group is probably slightly electron supplying (Ia) but this may be offset by the decrease in base strength shown by amines in more ethanolic media]. At acid concentrations between 0·02 and 0·05M, for 0·005M-amine, the amount of free base should vary from 0·01% to 0·38%. The values of k_s (k_1 divided by concentration of acid available for catalysis) fall slightly with increasing acid concentration, suggesting that a mainly protonated base reacts relatively slowly whilst a small amount of free amine reacts rapidly. By plotting k_s against [free base], k_s(2-NH_2) is obtained from the slope, and k_s(2-NH_3^+) from the intercept on the k_s axis. The latter value is relatively insensitive to the chosen value of pK_a and is probably correct within ±10%, but the uncertainty in k_s(2-NH_2) is unlikely to be less than ±35%.


(Ia)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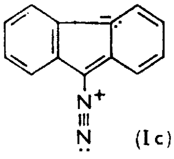
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The effects of 2- and 3-substituents on reactions at the 9-position of fluorene have been studied by Eaborn and his co-workers[3-5] in three series of derivatives: (1) 9-bromofluorenes[3] (reaction with iodide ion in acetone), (2) fluorenones[4] (oxime formation in

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[1] Part I, Warren, *J.*, 1961, 2561.

[2] Grantham, Weisburger, and Weisburger, *J. Org. Chem.*, 1961, **26**, 1008.

[3] Dickinson and Eaborn, *J.*, 1959, 3574.

[4] Dickinson and Eaborn, *J.*, 1959, 3641.

[5] Eaborn, Golesworthy, and Lilly, *J.*, 1961, 3052.

aqueous methanol), and (3) 9-chloro-9-phenylfluorenes [5] (hydrolysis in aqueous acetone). The broad pattern of substituent effects resembles that of the benzenoid series but certain anomalies were detected.

In reaction (1) electron-withdrawing groups increased E_A; this was paralleled by the expected increase in $\log_{10} k_{rel}$, but predominant non-constant entropy terms determined the order of reactivities. Variable entropy terms occurred also in reaction (2) but the dependence of E_A on $\log_{10} k_{rel}$ was erratic. In reaction (1) the 2-methoxy-group deactivated, and tautomeric electron release *via* the unsubstituted ring was suggested (II). In the other two cases, though, this group behaved normally.

The present work is designed to investigate further the energy–entropy relationships for reactions of fluorene derivatives at the 9-position, to provide more evidence about the possible transmission of T effects through the unsubstituted ring, and to assess the factors responsible for such a process.

Energy–Entropy Relationships.—The tabulated data show the following points of interest: (i) The expected order of relative rates is qualitatively observed: solvolysis is facilitated by electron supply to, and hindered by electron withdrawal from, the 9-carbon atom. (ii) $\log_{10} k_{rel}$ varies normally with E_A: the activation energy increases as k_{rel} decreases. (iii) The entropy of activation is not constant but closely parallels E_A: $-\Delta S^{\ddagger}$ falls as E_A increases. The experimental error in E_A (0·7 kcal.) introduces some uncertainty into the interpretation of this result but the plots of E_A against $\Delta S^{\ddagger}$ and $\log_{10} k_{rel}$ against E_A show regular trends rather than random scatters, encouraging the belief that these parallels are significant.

The reaction scheme suggested [1] for 9-diazofluorene should be applicable to its 2-substituted derivatives: the regular trend of substituent effects renders a mechanistic dichotomy unlikely and is consistent with rate-determining proton transfer to C-9. Any attempt to correlate these effects by a Hammett-type equation is not however justified without consideration of the E_A–$\Delta S^{\ddagger}$ relationship.

The original form of the Hammett equation [6] was an attempt to correlate substituent effects in a reaction series by identifying their polar effects with changes in the potential-energy of activation ($\Delta E_p^{\ddagger}$). Much subsequent discussion centred on whether $\Delta G^{\ddagger}$ (and therefore the relative rate) or $\Delta H^{\ddagger}$ was a better measure of changes in $\Delta E_p^{\ddagger}$. In general, $\Delta H^{\ddagger}$ appeared better to reflect changes in $\Delta E_p^{\ddagger}$ for reactions carried out without solvent or in weakly solvating media.[7]

In many reactions of *m*- and *p*-substituted benzene derivatives rate changes arise from $\Delta E_p^{\ddagger}$ variations only ($\Delta S^{\ddagger}$ constant), but the Hammett equation can be applied [7] to reaction series wherein kinetic-energy terms are significant if these contributions are directly proportional to $\Delta E_p^{\ddagger}$ changes. The dissociation constants of substituted benzoic acids, the basis of the equation, are largely dependent on ΔS° terms,[8] and parallels between E_A and $\Delta S^{\ddagger}$ are often found [7] for reactions in which solvation changes between reactants and transition state may be important.

For the present reaction, the introduction of electron-withdrawing 2-substituents into 9-diazofluorene should increase $\Delta E_p^{\ddagger}$ by increasing the repulsion between the solvated proton and C-9. No opposing trend, due to increased stability of the C–N bond, would be expected since the bond is broken to produce a neutral molecule not a positively charged entity. Furthermore, the energy required for nitrogen cleavage from a diazonium cation [9] is only 4 kcal. Variations therein are probably insignificant, but such ions can have a discrete existence, loss of nitrogen following the formation of the C–H bond.

The increase in $\Delta S^{\ddagger}$ with E_A suggests that electron withdrawal from the 9-position is

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[6] Hammett, *Chem. Rev.*, 1935, **17**, 125; *J. Amer. Chem. Soc.*, 1937, **59**, 96.

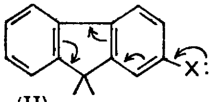
[7] Taft, in " Steric Effects in Organic Chemistry," ed. Newman, Wiley, New York, 1956, Ch. 13.

[8] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 83.

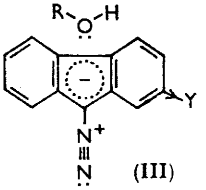
[9] Streitwieser, *J. Org. Chem.*, 1957, **22**, 861; Streitwieser and Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 2888.

accompanied either by increased solvation of the reactants or decreased solvation of the transition state. The canonical form (Ia) should contribute appreciably to the structure of 9-diazofluorene since the negative charge may be delocalised over the five-membered ring. Resonance stabilisation, *e.g.*, (Ic), resembles that of the cyclopentadienyl anion. A tendency to withdraw electrons from the 9-position would reduce this stabilisation but could be counterbalanced by solvation of the five-membered ring by water or ethanol molecules, any electron deficiency being rectified by partial co-ordination with the oxygen lone pairs (III). In the transition complex, partial localisation of electrons at the 9-carbon atom, due to the approaching solvated proton, would destroy this stabilisation. Solvation of the transition state should, then, be less than that of the reactants and virtually independent of the nature of the 2-substituent. Increase of E_{A} would thus produce more positive values of $\Delta S^{\ddagger}$. This hypothesis is similar to that of Clarke and Rothwell[10] concerning the Menschutkin reaction of substituted pyridines in nitromethane. Decreasing solvation of the base (by the weakly acidic solvent) was postulated to explain the decrease in $\Delta S^{\ddagger}$ with increasing E_{A}.

A decrease in solvation between reactants and transition state could account for the results obtained for the reaction of 9-bromofluorenes, in acetone, with iodide ion.[3] Electron withdrawal from the 9-position would reduce stabilisation by structures resembling the fluorenyl anion, but could be nullified by increasing solvation of the central ring *via* the carbonyl lone pairs of the acetone. Since E_{A} increases with increased electron withdrawal, its variation with $\Delta S^{\ddagger}$ would resemble that of the 9-diazofluorene series.



(II)



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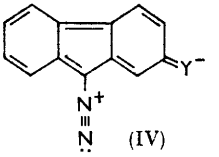

(IV)

The anomalous dependence of E_{A} on substituent is similarly understandable. The expulsion of bromine as a negative ion would be more than normally hindered by electron withdrawal and the simultaneous repulsion of the nucleophile may be less important (owing to the diffuseness of charge on the large iodide ion and the partial delocalisation of negative charge over the five-membered ring).[11]

The application of a Hammett-type equation to the results in the 9-bromofluorene and 9-diazofluorene series can be justified by the interdependence of E_{A} and $\Delta S^{\ddagger}$ discussed above. Although the fluorenone series exhibits a similar E_{A}–$\Delta S^{\ddagger}$ relationship, recent results[12] indicate that, in oxime and semicarbazone formation, depending on pH, both addition and dehydration steps may be rate-controlling. Substituent effects operate therein in opposite directions, and the very low Hammett slope (σ_m constants being used) found for the fluorenone series is thus explicable; a slight discontinuity between the 2-bromo- and 2-cyano-substituents coincides with a break in the E_{A}–$\log_{10} k_{\text{rel}}$ plot and suggests a change of rate-determining step. Under these conditions the Hammett equation could not correlate the whole range of substituent effects.

Application of the Hammett Equation to Reactions of Fluorene Derivatives.—In reactions of fluorene derivatives involving the 9-carbon atom, the effects due to 2-substituents might be expected to resemble those of *m*-substituents in toluene or its analogues. The slight distortion from regularity[13] of the benzenoid rings in the molecule is unlikely to lead to

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[10] Clarke and Rothwell, *J.*, 1960, 1885.

[11] Hinshelwood, Laidler, and Timm, *J.*, 1938, 848; Remick, " Electronic Interpretations of Organic Chemistry," Wiley, New York, 1949, p. 204.

[12] Anderson and Jencks, *J. Amer. Chem. Soc.*, 1960, **82**, 1773.

[13] Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139; Burns and Iball, *Nature*, 1954, **173**, 635.

major differences, but the possible transmission of *T* effects to the 9-position *via* the unsubstituted ring (II) may be important. One postulated example was earlier cited, and the formation [14] of 22% of the 2,5-derivative in the nitration of 2-nitrofluorene can be similarly explained. On the other hand, the effect is inoperative in the hydrolysis of 9-chloro-9-phenylfluorenes,[5] and need not be invoked to account for the acid-catalysed rearrangement products of 9-azidofluorenes.[15]

If, then, such transmission of *T* effects is real, it must vary from reaction to reaction, and 2-substituents in fluorene should show therein different amounts of *meta* as well as *para* character. It is therefore profitable to compare the correlations obtained by thus regarding 2-substituents with those resulting from their treatment as purely *meta*-groupings. Two modifications of Hammett's original equation are useful for this purpose: (*a*) Taft's treatment.[16] This divides the substituent constant σ into inductive, σ_I, and resonance, σ_R, contributions. The latter includes the effect of resonance of the substituent with the ring and with the functional group, and may vary (with reaction type) from the standard values based on the ionisation of benzoic acids. In general, an equation of the form $\sigma = \sigma_I + q\sigma_R$ is applicable and for 2-substituted fluorenes the alternative expressions result:

$$\log_{10} k_{\text{rel}} = \rho(\sigma_I + a\sigma_R m + b\sigma_R p) \qquad (1a)$$

and

$$\log_{10} k_{\text{rel}} = \rho(\sigma_I + a\sigma_R m) \qquad (2a)$$

(*b*) Alternative, but complementary, is the approach of Brown and his co-workers.[17] A series of σ^+ constants were suggested (based on the solvolysis of $\alpha\alpha$-dimethylbenzyl chlorides) which took account of the changes in resonance conjugation, between reactants and transition state, in electrophilic reactions. Recently Yukawa and Tsuno [18] showed that $(\sigma^+ - \sigma)$ should be proportional to the standard σ_R of Taft's treatment, and that the equation $\log_{10} k_{\text{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$ was widely valid. The constant, *r*, indicates the magnitude and direction of conjugational changes. Thus, for 2-substituents, there may be written:

$$\log_{10} k_{\text{rel}} = \rho[\sigma_m + \alpha(\sigma_m{}^+ - \sigma_m) + \beta(\sigma_p{}^+ - \sigma_p)] \qquad (1b)$$

and

$$\log_{10} k_{\text{rel}} = \rho[\sigma_m + \alpha(\sigma_m{}^+ - \sigma_m)] \qquad (2b)$$

van Bekkum, Verkade, and Wepster [19] have shown that the standard σ constant series makes insufficient allowance for the varying extents of conjugation of different substituents with the functional centre. The σ_G constants used by Norman and his co-workers [20] take account of this, and of resonance of the functional group with the aromatic system. The use of parameters representing reaction type and substituent polarisability gave a relationship akin to the Yukawa–Tsuno equation. Sufficient accurate data were not, unfortunately, available to apply to the present series, but correlations substantially similar to those of equations (1) and (2) were obtained with the constants of van Bekkum *et al.*

The best correlations resulted from the use of both *meta* and *para* constants (values taken from refs. 7, 17, and 24). Eqn. (1a): $\rho = -1{\cdot}63$, $a = 0{\cdot}266$, $b = 0{\cdot}523$, $\bar{r}$ (correlation coefficient) $= 0{\cdot}981$, *s* (standard deviation) $= 0{\cdot}094$. Eqn. (1b): $\rho = -1{\cdot}68$, $\alpha = 0{\cdot}509$, $\beta = 0{\cdot}393$, $\bar{r} = 0{\cdot}966$, $s = 0{\cdot}129$. Eqn. (2a): $\rho = -1{\cdot}59$, $a = 1{\cdot}84$, $\bar{r} = 0{\cdot}918$, $s = 0{\cdot}118$.

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[14] Anantakrishnan and Hughes, *J.*, 1935, 1607.

[15] Arcus and Coombs, *J.*, 1954, 4319.

[16] Taft and Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436.

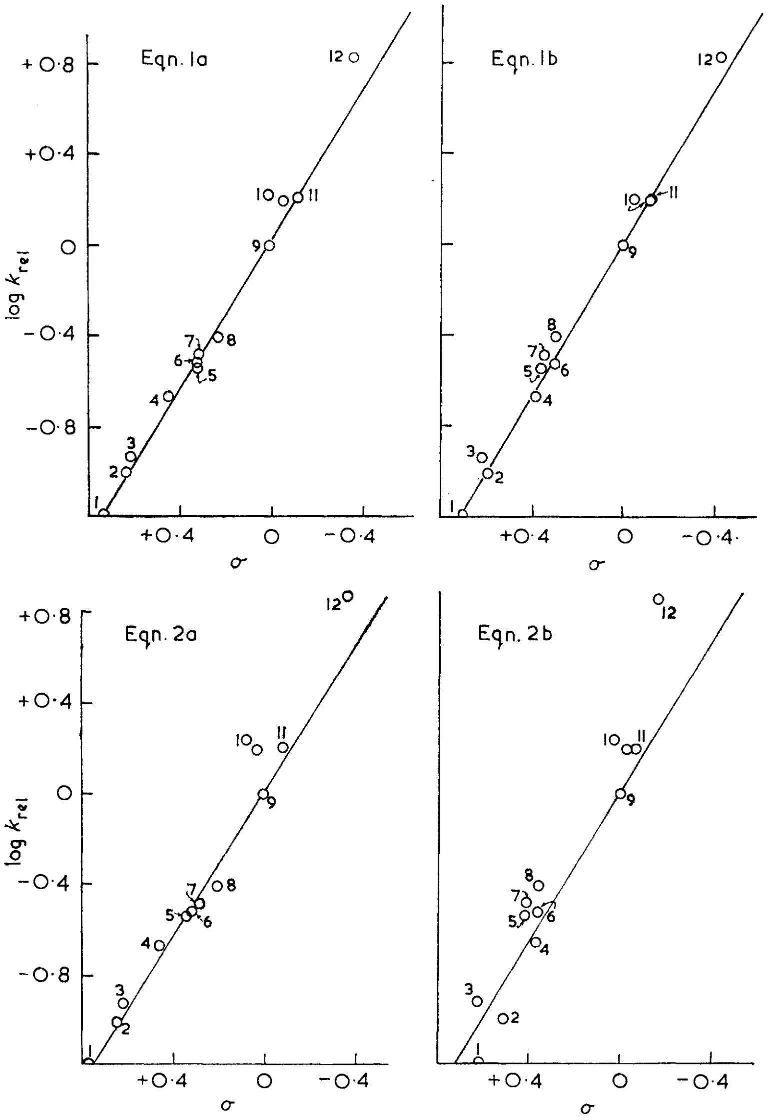
[17] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4969; Okamoto and Brown, *J. Org. Chem.*, 1957, **22**, 485.

[18] (*a*) Tsuno, Ibata, and Yukawa, *Bull. Chem. Soc. Japan*, 1959, **32**, 960; (*b*) Yukawa and Tsuno, *ibid.*, 1959, **32**, 965, 971.

[19] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[20] Norman, Radda, Brimacombe, Ralph, and Smith, *J.*, 1961, 3247; Knowles, Norman, and Radda, *ibid.*, 1960, 4885.

Eqn. (2b): $\rho = -1{\cdot}69$, $\alpha = 1{\cdot}96$, $\bar{r} = 0{\cdot}952$, $s = 0{\cdot}153$. The resulting plots are shown in the Figures. The values of σ_{I} and σ_{R} given by Taft[7] for ethoxycarbonyl groups were used for the methoxycarbonyl compound and σm-CN taken[21] as $+0{\cdot}615$.



Relationships between substituent constants and relative rates of solvolysis of 2-substituted 9-diazofluorenes.

2-Substituents: 1, NO_2; 2, CN; 3, NH_3^+; 4, CO·OMe; 5, Br; 6, I; 7, Cl; 8, F; 9, H; 10, OMe; 11, Me; 12, NH_2.

The essential agreement of the results from eqns. (1) and (2) is not surprising: tautomeric effects of *meta*-substituents arise by a secondary relay from positions conjugated with the functional group, and a rough quantitative relationship exists[7] between the resonance components of *meta*- and *para*-substituents.

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[21] Fickling, Fischer, Mann, Packer, and Vaughan, *J. Amer. Chem. Soc.*, 1959, **81**, 4226.

On the basis of a purely *meta*-type 2-position, the values of a and α [eqn. (2)] imply abnormally high resonance contributions to the observed value of σ. The transmission of T effects of 2-substituents *via* adjacent positions is unlikely to be so efficient, and the probable mechanism of solvolysis discounts any large increase in conjugation in the transition state. (Stabilisation of a complex resembling the fluorenyl diazonium ion is slight and probably insensitive to substituents.)

In contrast, the correlation of eqn. (1a) suggests a more normal resonance effect ($a + b = 0{\cdot}79$) [likewise more consistent is the value of $\alpha + \beta$ (0·90) of eqn. (1b)], and the reaction of diphenyldiazomethanes with benzoic acid in toluene[22] (also involving rate-determining proton transfer) gives results satisfactorily correlated by the standard values. Arguments based on the numerical values of these parameters are, however, necessarily tenuous and it is hoped that the study of 3-substituted derivatives now in progress will further clarify this point.

Yukawa and Tsuno have stressed[18] that a small r factor (operation of resonance potential) need not be related to low ρ values (showing general electron-demand at the reaction site). The values of ρ for the solvolysis of 9-diazofluorenes (—1·66) and for the diphenyldiazomethane reaction (—1·57) are almost identical, although solvolysis involves the stronger electrophile and a smaller ρ might be expected; this may arise from the superior resonance stabilisation of 9-diazofluorene. (Smaller ρ values are recorded for the decomposition of ω-diazoacetophenones,[18a] but this is probably an A-1 process.)

It is noteworthy that the present results and those for the 9-bromofluorene–iodide ion reaction yield a good linear free-energy plot, suggesting that resonance terms in the latter series are also nearly normal. Eqns. (1a) and (1b) are successful here too, although the σ^- function[23] might be more appropriate in eqn. (1b).

The individual results in the Table show some interesting points:

(i) The order of reactivity 2-OEt > 2-OMe is apparently anomalous (the more negative value of σ and σ^+p-OMe is well established[17,24,25] but no result exists for σ^+m-OEt, and that for σ m-OEt is uncertain[19]). Similar irregular behaviour of alkoxy-groups has occasionally been reported,[26] differences in solvation being held responsible.[24]

Perchloric acid-catalysed solvolysis of 2-substituted 9-diazofluorenes in 93·8% (w/w) ethanol–water.

Substituent	H	F	Cl	Br	I	CN	NO_2
k_s (min.$^{-1}$ mole^{-1} l.) (25·00°)	4·00	1·57	1·31	1·16	1·21	0·399	0·256
k_s (min.$^{-1}$ mole^{-1} l.) (35·00°)	10·55	4·09	3·59	3·35	3·45	1·16	0·788
E_A (kcal.)	17·7	17·5	18·4	19·3	19·2	19·5	20·4
$\log_{10} A$	13·52	13·02	13·67	14·27	14·19	13·95	14·32
$-\Delta S^‡$ (e.u.)	6·4	9·0	6·2	3·6	3·7	5·0	2,9

Substituent	Me	OMe	OEt	CO·OMe	NH_2	NH_3^+
k_s (min.$^{-1}$ mole^{-1} l.) (25·00°)	6·32	6·28	6·93	0·870	27·0	0·47
k_s (min.$^{-1}$ mole^{-1} l.) (35·00°)	16·43	16·16	17·88	2·62	—	—
E_A (kcal.)	17·4	17·3	17·2	20·0	—	—
$\log_{10} A$	13·57	13·47	13·50	14·62	—	—
$-\Delta S^‡$ (e.u.)	6·6	6·9	7·1	1·9	—	—

(ii) Of the halogen substituents, fluorine shows the greatest deviation from the regression line. The rather large $-\Delta S^‡$ value is not statistically significant, and the discrepancy more probably arises in the uncertainty about the best figure for σp-F. The moderate fit of the 2-methoxy-compound may result likewise.

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[22] Hancock, Gilby, and Westmoreland, *J. Amer. Chem. Soc.*, 1957, **79**, 1917.

[23] Bordwell and Andersen, *J. Amer. Chem. Soc.*, 1953, **75**, 6019.

[24] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[25] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

[26] Berliner and Monack, cited by Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

(iii) The resultant σ values calculated [eqn. (1)] for strongly $-T$ groups resemble the standard quantities rather than the " dual " constants[6,7,21,23] used for phenols and anilinium ions. Resonance with the diazo-group (*via* the unsubstituted ring) removing the negative charge from the central ring (IV) cannot then be significant. Dipole-moment data show[27] that the diazo-group structure is normally intermediate between the canonical forms (Ia) and (Ib). Structure (Ia) is stabilised by delocalisation of the negative charge over the five-membered ring; its location on the substituent is therefore improbable.

(iv) The values of k_s for the 2-NH_2 and 2-NH_3^+ groups are approximate. Although NMe_3^+ groups have been correlated by the Yukawa–Tsuno equation, this may be fortuitous. (Anomalous entropies of activation have been found[17] for groups bearing a full formal charge, and ascribed to solvation differences of the ion-dipole type.) The approximate fit of the 2-NH_3^+ point (Jaffé's σ_m value being used)[24] is of doubtful significance. The 2-NH_2 derivative shows a noticeably better fit to eqn. (1) than to eqn. (2), but neither point was used to obtain the correlation constants.

Investigation of the factors governing the production of partial *para*-character in 2-substituted fluorene derivatives is hindered by a paucity of kinetic data. It is clear that this is not an electromeric process, as normally understood, since its operation can lead to deactivation.[3] However, the location of a full or partial negative charge at the 9-position permits stabilisation by contributing forms such as the fluorenyl anion. For processes in which the rate-controlling step is bimolecular, this transmission of T effects should influence the charge distribution over the central ring and be reflected in the relative rates. Accordingly, the 2-methoxy-group activates in the 9-diazofluorene series and deactivates in the 9-bromofluorene–iodide ion reaction.

A unimolecular step is rate-determining in the S_N1 hydrolysis of 9-chloro-9-phenylfluorenes; electron supply by the 2-methoxy-group could activate only by facilitating chloride-ion ejection, which would involve removal of electrons from the cyclopentadiene ring. Such activation is not therefore found.

In oxime formation, addition and dehydration steps are oppositely affected by substituents. This renders nugatory any interpretation of the small activating action of the 2-methoxy-group in the fluorenone series.

Abnormal T effects appear then to operate to stabilise fluorenyl anion type structures (*e.g.*, Pauling's equation[28] indicates 11% double-bond character for the $C_{(4a)}$–$C_{(5a)}$ bond in fluorene itself) but not to assist the scission of negative ions from the 9-position. Further elucidation may result from the study of other reactions at the 9-position.

EXPERIMENTAL

Reagents.—Stock solvent [93·8% (w/w) ethanol–water] and standard perchloric acid solutions were made up as before.[1] Freshly prepared solutions of diazo-compounds, whose preparation has been described previously,[29] were used for each run. Two new 2-substituted 9-diazofluorenes (and the corresponding hydrazones) were prepared.

Hydrazones. 2-*Methoxycarbonyl*, m. p. 138—139° (decomp.) (Found: C, 71·5; H, 5·3; N, 11·6. $C_{15}H_{12}N_2O_2$ requires C, 71·4; H, 4·8; N, 11·1%); 2-*methyl*, m. p. 162—164° (decomp.) (Found: C, 80·4; H, 6·0; N, 13·2. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%).

Diazo-compounds. 2-*Methoxycarbonyl*, m. p. 112—113·5° (Found: C, 72·2; H, 4·0; N, 11·3. $C_{15}H_{10}N_2O_2$ requires C, 72·0; H, 4·0; N, 11·2%); 2-*methyl*, m. p. 105—106° (Found: C, 81·9; H, 4·9; N, 13·5. $C_{14}H_{10}N_2$ requires C, 81·5; H, 4·9; N, 13·6%).

Kinetic Runs.—The reaction was studied by the manometric method used before.[1] Apart from the 2-amino-compound (for which k_1 was derived from the first 30% of reaction), the first-order equation was obeyed for at least the first 80% of the reaction, and nitrogen evolution was always almost quantitative. Solutions of the diazo-compound were, with two exceptions,

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[27] Sidgwick, Sutton, and Thomas, *J.*, 1933, 406.
[28] Pauling, " Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, p. 239.
[29] Warren, *J.*, 1961, 1412.

approximately 0·005M at the start of the reaction: the first-order rate constants were reproducible within ±3% and the activation energies are probably correct within ±0·6 kcal. Limited solubility necessitated the use of more dilute solutions of the 2-iodo- and 2-nitroderivatives, and here rate-constant reproducibility was ±4% and the uncertainty in the energy of activation, ±0·8 kcal. The recorded values of $\Delta S^{\ddagger}$ have an estimated error of ±2·0 e.u.

The author thanks Mr. J. M. L. Cameron for microanalyses.

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[*Received, April* 11*th*, 1962.]