492. *Kinetic Studies of the Fluorene Series. Part I. The Acid-catalysed Solvolysis of 9-Diazofluorene.*

By Keith D. Warren.

The reaction has been studied in ethanol and in ethanol–water mixtures. Hydrochloric, perchloric, and picric acids were used as catalysts, and the effect of added salts was determined. Experiments with picric acid–lithium picrate buffers, and with a partially deuterated solvent, indicated that the reaction was general acid-catalysed.

A reaction mechanism is suggested in which attack of the solvated proton on the substrate is rate-determining and the fluorenyl carbonium ion is the active intermediate.

This work is preliminary to an investigation of the influence of substituents in the benzenoid rings on the rate of cleavage of the diazo-group from the 9-position of fluorene. Solvolysis of 9-diazofluorene in aqueous ethanol proves to be general acid-catalysed as is that of the closely related diphenyldiazomethane,[1] and contrasts with the specific acid-catalysed hydrolysis of diazoacetic ester.[2]

Order of Reaction.—The reaction in 93·8% (w/w) ethanol–water, with hydrochloric or perchloric acid as catalyst, is of first order with respect to 9-diazofluorene for at least 80% of its course. For values of [HCl] below 0·05M, the first-order rate constant, k_1, varies linearly with the stoicheiometric concentration of acid. With perchloric acid as catalyst, k_1 varies similarly. The specific rate constant, k_s (slope of the plot of k_1 against [$HClO_4$]) differs negligibly from the corresponding value for hydrochloric acid (Table 1). Both plots show a small zero-intercept on the acid-concentration axis, possibly associated with an irregular rate variation at very low acid concentrations (cf. diphenyldiazomethane [1]).

Table 1. *Solvolysis of* 9-*diazofluorene in* 93·8% (w/w) *ethanol–water at* 25·00°.

Catalyst: HCl. k_s = 3·93 (min.$^{-1}$ mole^{-1} l.)

$10^2[C_{13}H_8N_2]$ (M)	1·00	1·00	0·50	1·00	0·50	1·00	1·00	0·50
10^2[HCl] (M)	0·48	0·96	0·96	1·49	1·49	1·99	2·47	2·47
10^2k_1 (min.$^{-1}$)	1·50	3·05	3·20	5·05	5·20	6·65	8·53	8·40
$10^2[C_{13}H_8N_2]$ (M)	1·00	1·33	0·50	0·50	0·50	0·50	0·50	
10^2[HCl] (M)	2·95	3·55	4·18	8·25	13·53	16·90	21·65	
10^2k_1 (min.$^{-1}$)	10·4	13·3	15·3	37·6	70·5	90·0	124	

Catalyst: $HClO_4$. $[C_{13}H_8N_2]$ = 0·0050M, k_s = 4·00 (min.$^{-1}$ mole^{-1} l.)

$10^2[HClO_4]$ (M)	0·59	1·48	2·47	3·60	5·00	10·05	15·11	20·15
10^2k_1 (min.$^{-1}$)	1·93	5·56	9·30	14·3	20·5	49·4	93·0	134

Table 2. *Variation of rate with solvent composition.*

Catalyst: HCl; Temp.: 25·00°

% EtOH (w/w)	100	98·5	93·8	87·8	81·75	76·9
k_s (min.$^{-1}$ mole^{-1} l.)	45·6	12·2	3·93	4·03	4·10	4·44

Above 0·05M the value of k_s increases progressively with acid concentration, rather more so for perchloric acid than for hydrochloric acid. Since, below about 0·4M, the Hammett acidity function, h_0, varies linearly with acid concentration,[3] this is probably due to a primary salt effect, the addition of comparable amounts of electrolytes producing similar increases (Table 3).

Dependence of Rate on Solvent Composition.—When the water content of the solvent is increased from zero, k_s initially falls sharply, showing later a much smaller gradual rise (Table 2). This effect closely parallels the variation of the acidity function with solvent

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[1] Roberts and Watanabe, *J. Amer. Chem. Soc.*, 1950, **72**, 4869.

[2] Gross, Steiner, and Krauss, *Trans. Faraday Soc.*, 1936, **32**, 877.

[3] Baines and Eaborn, *J.*, 1956, 1436.

composition,[4] although the initial inhibition of the reaction can be ascribed simply to the replacement of the reactive ethoxonium ions by the less active hydroxonium ions.

Salt Effects.—The reaction, catalysed by hydrochloric or perchloric acid, shows a large positive salt effect. With about 0·02M-acid, the progressive addition of lithium chloride or lithium perchlorate, up to 0·20M, results in a regular increase in the rate, the latter being somewhat more effective (Table 3). A plot of $\log_e (k_c/k_0)$ against [Added Salt] (k_c and k_0 being the first-order rates with and without added salt, respectively) is reasonably linear, as expected for a reaction between an ion and a neutral molecule.

TABLE 3. *Salt effects.*

[HCl] = 0·0210M; Solvent and temp. as in Table 1

Added Salt	LiCl	LiCl	LiCl	LiCl	LiCl	$LiClO_4$	$LiClO_4$	$LiClO_4$	$LiClO_4$	$LiClO_4$
10^2[Added Salt] (M)	2·41	5·56	8·45	11·70	19·45	2·43	5·66	8·89	12·30	19·80
$\log_e k_c/k_0$	0·080	0·165	0·218	0·257	0·430	0·050	0·254	0·308	0·458	0·628

$[HClO_4]$ = 0·0215M

Added Salt	$LiClO_4$	$LiClO_4$	$LiClO_4$	$LiClO_4$	LiCl	LiCl	LiCl	LiCl
10^2[Added Salt] (M)	3·70	9·04	14·20	19·35	4·10	9·45	14·68	19·85
$\log_e k_c/k_0$	0·070	0·214	0·372	0·583	0·040	0·166	0·305	0·500

No measurable reaction was observed between 9-diazofluorene and either lithium salt in the absence of an acid catalyst. Since the salt effect of lithium perchlorate exceeds that of lithium chloride, and perchlorate ion is not involved in the solvolysis (see p. 2563), it is most improbable that chloride ions take part in the rate-determining stage, or that the salts act otherwise than by increasing the dielectric constant of the medium.

Similar large salt effects occur in the solvolysis of diphenyldiazomethane.[1]

Energy of Activation.—The values of the Arrhenius energies of activation, E_A, relating to each catalyst, agree well for both temperature intervals (Table 4), suggesting that in each case catalysis is due to oxonium ions. Hydrochloric acid is completely dissociated[5] in 93·8% (w/w) ethanol–water, and complete dissociation would be expected for perchloric acid. In this solvent the hydroxonium ion probably predominates over the ethoxonium ion, and the temperature variation of E_A is insufficient to imply a composite catalysis. The entropy of activation, $\Delta S^\ddagger$, is consistent with rate-determining proton transfer.

TABLE 4. *Variation of rate with temperature.*

Solvent: 93·8% (w/w) ethanol–water

	Catalyst: HCl			Catalyst: $HClO_4$		
Temp.	25·00	35·00	45·00	25·00	35·00	45·00
k_s (min.$^{-1}$ mole^{-1} l.)	3·93	10·9	26·7	4·00	10·6	26·0

E_A (25—35°) = 18,150 ± 600 cal., $\log_{10} A = 13·72 \pm 0·70$, $\Delta S^\ddagger = -4·85 \pm 1·5$ e.u. E_A (35—45°) = 17,450 ± 600 cal.

Catalysis by Picric Acid.—With picric acid alone as catalyst, the plot of k_1 against the stoicheiometric concentration of acid shows increasingly large upward deviations from linearity. For 0·04M-acid, k_s is already 30% greater than the value at infinite dilution (which approximates to k_s for hydrochloric and perchloric acids and represents oxonium ion catalysis only) whilst for hydrochloric and for perchloric acid deviations are negligible (Tables 1 and 5).

In the solvent used picric acid is considerably dissociated: extrapolations from literature data[6] give values of 1·62 and 2·08 for pK_a. General acid catalysis could not therefore be detected in the normal manner, but for four concentrations of picric acid the effect of added lithium picrate has been studied. The value of the ionic strength at each acid concentration was kept constant by adding lithium perchlorate; salt effects were thus largely

[4] Braude and Stern, *J.*, 1948, 1976, 1982.

[5] Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330.

[6] Goldschmidt, *Z. phys. Chem.*, 1928, **132**, 257; Gross, Jamock, and Patat, *Monatsh.*, 1933, **63**, 124

eliminated, but the rate increase caused by lithium picrate was never less than three times that due to lithium perchlorate (Table 5). Lithium picrate alone had no catalytic action.

Since this former rate increase seems too great to constitute a salt effect, catalysis by undissociated picric acid is indicated, with a catalytic constant $k_{s(\text{H Picr})}$, slightly greater than that, $k_{s(\text{H}_3\text{O}^+)}$, of the oxonium ion. The abnormal increase in rate with increasing acid concentration, or the addition of lithium picrate, results from the rising concentration of undissociated picric acid. This surprising result ($k_{s(\text{H Picr})} > k_{s(\text{H}_3\text{O}^+)}$) was also reached[1] for the diphenyldiazomethane solvolysis: it may be significant that in 93·8% (w/w) ethanol–water the hydroxonium ion is the simple H_3O^+, a much weaker proton donor[4] than the highly solvated $H^+,4H_2O$ present in mainly aqueous solutions.

TABLE 5. *Catalysis by picric acid.*

Solvent and temp. as in Table 1.

10^2[picric acid] (M)	1·00	1·25	1·25	2·01	2·50	2·50	2·50	2·50	2·50
10^2[Li picrate] (M)	—	5·00	—	—	—	—	1·67	3·33	5·00
10^2[$LiClO_4$] (M)	—	—	5·00	—	—	5·00	3·33	1·67	—
10^2k_1 (min.$^{-1}$)	4·12	6·05	8·25	8·70	11·1	13·0	13·9	15·3	17·8
10^2[picric acid] (M)	3·02	3·50	3·50	4·02	5·05	5·05	5·05	5·05	5·05
10^2[Li picrate] (M)	—	—	5·00	—	—	—	1·67	3·33	5·00
10^2[$LiClO_4$] (M)	—	5·00	—	—	—	5·00	3·33	1·67	—
10^2k_1 (min.$^{-1}$)	14·2	19·2	25·6	20·5	28·4	31·6	34·0	36·0	37·0

Isotope Effect.—Partial deuteration of the aqueous ethanol used as solvent leads to rapid isotopic exchange with the catalysing acid. For the solvent composition chosen (hydrochloric acid catalyst), the specific rate was reduced to 73% of its former value (Table 6), consistent with rate-determining proton transfer and general acid catalysis.

TABLE 6. *Isotope effect.*

Temp.: 25·00° Catalyst: HCl

	Solvent: 87 8% (w/w) $EtOH-H_2O$				Solvent: 87·8% (w/w) $EtOH-D_2O$			
10^2[HCl] (M)	1·91	2·89	3·69	4·58	1·91	2·89	3·69	4·58
10^2k_1 (min.$^{-1}$)	7·10	10·6	13·9	17·4	5·90	8·20	10·5	12·8

$k_s(D_2O)/k_s(H_2O) = 0{\cdot}73$

Reaction Products.—The reaction, catalysed by hydrochloric acid, produced appreciable amounts of 9-chlorofluorene (Table 7): in the product-determining step chloride ion competes more effectively with ethanol than with the more nucleophilic water. When chloride ion is added as lithium chloride the production of 9-chlorofluorene is favoured, possibly owing to the effective removal of water in solvating the lithium ion. With perchloric or picric acid, or their salts, present in the reaction mixture, *in the absence of chloride ion*, no loss of acid, due to the participation of the anion in the product-determining stage, is observed.

TABLE 7. *Side-product formation.*

Temp.: 25·00°. [$C_{13}H_8N_2$] = 0·005M

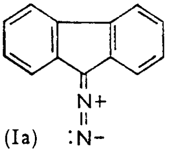
	Solvent: 100% ethanol				Solvent: 98·5% (w/w) ethanol–water		
10^2[HCl] (M)	1·15	1·90	2·49	3·80	1·14	2·47	3·76
% conversion of substrate into 9-chlorofluorene	44	43	45	46	26	29	36

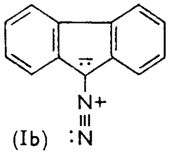
	Solvent 93·8% (w/w) ethanol–water							
10^2[HCl] (M)	8·25	13·53	16·90	2·10	2·10	2·10	2·10	2·10
10^2[LiCl] (M)	—	—	—	2·41	5·56	8·45	11·70	19·45
% conversion of substrate into 9-chlorofluorene	14	19	22	19	27	29	33	39

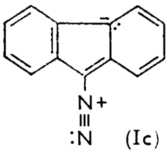
Product runs, with perchloric acid as catalyst, in 93·8% (w/w) ethanol–water, gave 9-ethoxyfluorene and 9-hydroxyfluorene, in ratio 5 : 3, and a small amount of unidentified red gum. Similar runs, with hydrochloric acid, gave, in addition, 9-chlorofluorene, which was also found, with about equal amounts of 9-ethoxyfluorene, when ethanol was used as solvent.

Mechanism of Reaction.—The solvolysis shows general acid catalysis and proton transfer from the general acid, HA,(H_3O^+, $EtOH_2^+$, or picric acid) to the substrate is therefore rate-determining. The residue whence the proton is detached (H_2O, EtOH, or picrate ion) is thus involved in the transition state (II).

9-Diazofluorene may be considered as a resonance hybrid of the contributing canonical forms (Ia) and (Ib). The former is stabilised by conjugation of the diazo-group with both benzenoid rings, and the latter by the predisposition of cyclopentadiene systems[7] to contribute structures such as (Ic), the formal negative charge being distributed over the ring. It is postulated that the solvolysis is initiated by attack of the solvated proton (or other general acid) on the 9-carbon atom, the substrate being represented as structure (Ib).


(Ia)


(Ib)

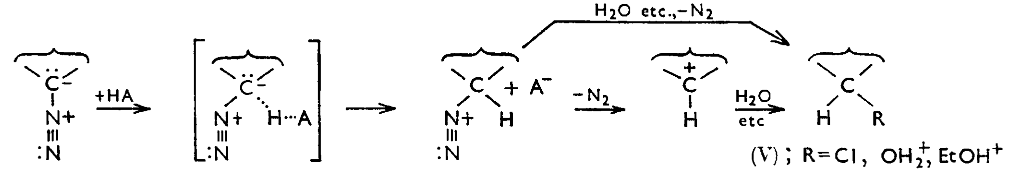

(Ic)

Confirmatory evidence from the rate-dependence in the region wherein h_0 and the hydrogen-ion concentration diverge, was unobtainable because of the rapidity of the reaction. Melander and Myhre[8] have, however, concluded that it should not thus be possible to distinguish between an $A S_E 2$ reaction and one involving a fast pre-equilibrium. The expected rate dependence for $A S_E 2$ processes remains uncertain.[9]

Previously investigated $A S_E 2$ reactions have involved subsequent rapid reaction of the protonated substrate with water or another base, Y. An alternative possibility (not distinguishable by kinetic form) is rapid decomposition of the protonated substrate to a further intermediate, X^+, which then reacts rapidly with a base. (The reaction sequence resembles the *A*-1 mechanism, but the first step is rate-determining.) It is proposed to call this mechanism $A S_E 2'$.

$$A S_E 2 \begin{cases} S + HA \longrightarrow SH^+ + A^- \text{ (slow)} \\ SH^+ + Y \longrightarrow \text{Products (fast)} \end{cases} \qquad A S_E 2' \begin{cases} S + HA \longrightarrow SH^+ + A^- & \text{(slow)} \\ SH^+ \longrightarrow X^+ & \text{(fast)} \\ X^+ + Y \longrightarrow \text{Products} & \text{(fast)} \end{cases}$$

There arises then the question whether the fluorenyldiazonium ion (III), first formed, decomposes unimolecularly ($A S_E 2'$), yielding the fluorenyl carbonium ion (IV) (which would then react with water or ethanol), or loses nitrogen simultaneously with the attack of the nucleophile in a bimolecular step ($A S_E 2$). Since these alternatives arise after the rate-determining step, kinetic evidence is inapplicable, but the following considerations suggest that the reaction proceeds *via* the carbonium ion (IV).



(Ib) (II) (III) (IV) (V); R=Cl, OH_2^+, $EtOH^+$ (VI); R=OH, OEt

(i) Participation of chloride ion in the initiating step is excluded. Its appearance in the products must then be due to attack on either the diazonium ion (III) or the carbonium

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[7] Wheland, " Resonance in Organic Chemistry," John Wiley and Co., New York, 1955, pp. 136, 347.

[8] Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507.

[9] Gold, *Ann. Reports*, 1959, **56**, 46.

ion (IV). Since the nucleophilic strength of chloride ions in processes of similar charge-type appears much greater than that of ethanol or water,[10] bimolecular reaction of the diazonium ion should lead mainly to 9-chlorofluorene, which is stable under reaction conditions. Production of this as a *minor* component thus suggests that chloride ion competes with water and ethanol for the carbonium ion. Perchlorate ion is less nucleophilic than ethanol [10] and would be expected not to intervene in this stage.

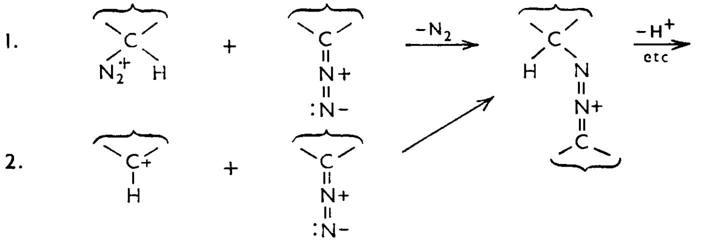
(ii) The relatively high proportion of 9-hydroxyfluorene formed (chloride ion absent) in 93·8% solvent, probably originates in the greater nucleophilic strength of water (as compared with ethanol) in such media. The appreciable production of 9-chlorofluorene (chloride ion present) is paralleled in the S_N1 solvolysis of *pp*′-dimethyldiphenylmethyl chloride in aqueous acetone [11] (small additions of sodium azide produce considerable amounts of *pp*′-dimethyldiphenylmethyl azide).

(iii) The products of reactions involving comparable diazonium ions necessitate loss of nitrogen and carbonium-ion formation, *e.g.* the Demjanov rearrangement and the action of nitrous acid on primary amines [12] to produce some branched-chain products.

(iv) Although some 9-substituted fluorenes undergo S_N2 attack, *e.g.* 9-bromofluorene with iodide ion in acetone,[13] in more polar solvents steric factors should favour S_N1 reaction. Coplanarity (favoured for the bimolecular transition complex) of the bonds attached to the 9-carbon atom, is inhibited by the rigidity of the tricyclic fluorene framework. Nucleophilic attack thus more probably involves the planar carbonium ion.

Furthermore, resonance stabilisation of the diazonium ion (III) is meagre, but the carbonium ion (IV) should be stabilised by conjugative mesomerism with the aromatic rings (cf. benzyl carbonium ion). The carbonium ion, which is about as stable as the diphenylmethyl ion and more stable than the benzyl ion,[14] is the postulated intermediate [15] in the conversion of 9-hydroxyfluorene and sodium azide into phenanthridine by strong acids.

(v) Staudinger and Kupfer,[16] using a large excess of 9-diazofluorene in about 80% (w/w) ethanol–water with hydrochloric acid as catalyst, found small amounts of fluorenone ketazine in the products. Either of the schemes shown could explain this. Mechanism (1) requires attack of 9-diazofluorene on the diazonium ion at a point remote from the carbon–nitrogen bond. This implies improbably close approach of the two fluorene residues, whereas scheme (2) is not thus hindered.



Interpolation from the present results shows that the hydrogen-ion catalysed solvolysis of 9-diazofluorene in 93·8% ethanol–water is about twelve times slower than that of diphenyldiazomethane. This difference probably originates in the electron affinity of cyclopentadiene systems whereby somewhat greater resonance stabilisation [*e.g.* structure

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[10] Hughes, Ingold, and Pocker, *Chem. and Ind.*, 1959, 1282; Swain and Kaiser, *J. Amer. Chem. Soc.*, 1958, **80**, 4089.

[11] Bateman, Hughes, and Ingold, *J.*, 1940, 974.

[12] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 486.

[13] Dickinson and Eaborn, *J.*, 1959, 3547.

[14] Deno, Jaruselski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 155.

[15] Arcus and Evans, *J.*, 1958, 789.

[16] Staudinger and Kupfer, *Ber.*, 1911, **44**, 2197.

(Ic)] is derived than is possible for diphenyldiazomethane. This accords with the comparably greater reactivity [17] of fluorenone, as compared with benzophenone, in oximation, which requires electron accession to the 9-position.

Diazoacetic ester which shows specific acid catalysis [2] in hydrolysis contrasts with the fluorene and diphenylmethane derivatives. This difference may be due to the low resonance stabilisation of diazoacetic ester itself and the rather small difference between those of the diazonium and carbonium ions thence derived. This should facilitate proton transfer and either retard the heterolysis of the diazonium ion (*A*–1) or result in a slow bimolecular substitution (*A*–2.)

EXPERIMENTAL

Reagents.—Solutions of 9-diazofluorene [18] were freshly prepared for each run. Stock solvents were prepared by the addition of the requisite volumes of water to absolute ethanol,[19] and stock hydrochloric acid by passing dry hydrogen chloride into the appropriate solvent. The 93·8% (w/w) solvent had d_4^{20} 0·8077. Stock perchloric acid was obtained from the 72% product by its addition to absolute ethanol so as to yield a solution of the acid in 93·8% (w/w) ethanol–water. Anhydrous lithium chloride was prepared by heating reagent-grade material at 120° for 3 hr., and anhydrous lithium perchlorate and lithium picrate according to Roberts and Watanabe.[1]

Products.—The reaction products [in 93·8% (w/w) ethanol–water; perchloric acid as catalyst] were fractionally crystallised from light petroleum, the first crop yielding 9-hydroxyfluorene as white needles, m. p. 156—157° (corr.), and the residues yielding 9-ethoxyfluorene as white needles (from aqueous alcohol), m. p. 53° (corr.). With hydrochloric acid as catalyst the products contained, in addition to the above, 9-chlorofluorene, produced also (with 9-ethoxyfluorene) when absolute ethanol was used as solvent. Isolation proved unsatisfactory for its estimation which was done by back titration of the reaction mixture, giving chloride ion loss during a run. 9-Chlorofluorene was shown to be negligibly solvolysed thereby.

Kinetic Runs.—These were carried out in a twin-limbed vessel held in a mechanical shaker. This was connected to a manometer consisting of a pair of microburettes, and the nitrogen evolved was measured at constant pressure. The reaction vessel was immersed in a thermostat tank, maintained at 25·00°, 35·00°, or 45·00° ± 0·03°, heating being controlled by a conventional mercury–toluene regulator. The reaction system was allowed 20 min. to equilibrate before each run was started, thus minimising corrections for evolution of solvent vapour.

The first-order rate constants were calculated by using the usual equation and were reproducible to within ±3% (±5% for $k_1 > 0{\cdot}5$). The energies of activation are believed to be correct to within ±0·6 kcal.

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

[18] Nenitzescu and Solomonica, *Org. Synth.*, Coll. Vol. II, p. 496.

[19] Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1104.