368.   *Kinetics of Solvolysis of* 9-*Aryl*-9-*chlorofluorenes and Related Compounds in Ethanol–Acetone, in Ethanol, or in Methanol.*

By R. Bolton, N. B. Chapman, and J. Shorter.

The preparation of a series of 9-(substituted phenyl)fluoren-9-ols, and of the corresponding chloro- and ethoxy-compounds is described. We have measured first-order rate coefficients for the solvolysis of these chloro-compounds, of 9-bromo(or chloro)-9-phenylfluorene, and of triphenylmethyl and diphenylmethyl bromide and chloride in ethanol–acetone (9 : 1 v/v) at several temperatures; we have also studied the solvolysis of 9-bromo(or chloro)fluorene and of the corresponding diphenylmethyl halides in methanol and in ethanol. Arrhenius parameters and the related magnitudes of transition-state theory have been calculated.

The results for the reactions of the triphenylmethyl, 9-phenyl-9-fluorenyl and diphenylmethyl halides are discussed in terms of differences in the changes in unsaturation energy, steric compression energy, and solvation energy on forming the transition state; it is concluded that release of steric compression contributes to the high reactivity of triphenylmethyl halides. The closeness of the structure of the transition state to the tetrahedral lies in the order $Ph_3CCl > 9\text{-}Ph\text{-}C_{13}H_8Cl > Ph_2CHCl$. On the basis of the ideas mentioned, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values can be rationally interpreted.

The results for the solvolyses of the 9-chloro-9-(substituted phenyl)-fluorenes are discussed in terms of the appropriate σ or σ⁺ values of *meta*- or *para*-substituents, of steric and enhanced polar effects of the *ortho*-substituents, and of Dewar's relative activation energies, or the partial charge on the side-chain carbon atom of ions of the type $ArCH_2^+$ for the phenyl, 3(or 4)-biphenylyl, 9-phenanthryl, and 2(or 1)-naphthyl groups in the 9-position, with the additional complication of a steric effect in the last case.

The solvolysis of 9-bromo(or chloro)fluorene and of the corresponding diphenylmethyl compounds in methanol and in ethanol is briefly examined, and so is the effect of change of solvent from ethanol–acetone (9 : 1 v/v) to 100% ethanol on the solvolysis of 9-chloro-9-(1-naphthyl)fluorene.

THE reactivity of 9-bromo(or chloro)fluorene has been frequently exploited in preparative work; the derived 9-aryl compounds are known [1] to be more reactive still. When this investigation was begun, the only report of kinetic work in this field was that of Bartlett and Cohen,[2] who studied the kinetics of ethanolysis of 9-bromo-9-methylfluorene, but during the course of our work Eaborn and his co-workers [3a,b] published kinetic studies of the reactions of 2-substituted 9-bromofluorenes with potassium iodide in acetone, and of the hydrolysis in 90 or 95% aqueous acetone of 9-chloro-9-phenylfluorene and its derivatives having substituents in the *meta*- or *para*-position of the phenyl group or in the 2- or 3-position of the fluorenyl group. Further work on the solvolysis of 9-bromofluorene and its 1- and 4-methoxycarbonyl derivatives has recently been reported.[4] We now report the results of a kinetic study of the solvolysis in ethanol–acetone (9 : 1 v/v) of a wide range of substituted 9-chloro-9-phenylfluorenes with substituents in the *ortho-*, *meta-*, or *para*-position of the phenyl group, and of the corresponding 9-(1- or 2-naphthyl), 9-(9-phenanthryl), and 9-(3- or 4-biphenylyl) derivatives. The reactions of 9-bromo(or chloro)-9-phenylfluorene and of triphenylmethyl and diphenylmethyl bromide and chloride have been similarly studied for comparison. The kinetics of ethanolysis of 9-bromo(or chloro)-fluorene and diphenylmethyl bromide, and of methanolysis of 9-bromo(or chloro)fluorene and diphenylmethyl bromide and chloride have also been studied.

[1] Kliegl, Wünsch, and Weigele, *Ber.*, 1926, **59**, 631.
[2] Bartlett and Cohen, *J. Amer. Chem. Soc.*, 1940, **62**, 1183.
[3] (*a*) Dickinson and Eaborn, *J.*, 1959, 3574; (*b*) Eaborn, Golesworthy, and Lilly, *J.*, 1961, 3052.
[4] Lovins, Andrews, and Keefer, *J. Amer. Chem. Soc.*, 1962, **84**, 3959.

EXPERIMENTAL

Materials.—9-Arylfluoren-9-ols were prepared by the action of the appropriate Grignard reagent (obtained by the action of magnesium on an ethereal solution of an aryl bromide or iodide) on fluorenone, m. p. 83—84°, prepared by Huntress, Hershberg, and Cliff's method.[5] Occasionally lithium aryls were used in place of arylmagnesium halides. The required aryl halides, if not available commercially, were prepared by standard methods and purified by distillation under reduced pressure, by recrystallisation, or by chromatography on alumina from light petroleum (b. p. 40—60°). Solid aryl halides had m. p.s in accord with those in the literature. The 9-arylfluoren-9-ols were purified, when possible, by crystallisation to constant m. p. from benzene–light petroleum (b. p. 40—60°). Usually, however, the oily products were freed from unchanged aryl halide and fluorenone by heating at ~100°/15 mm. for 6 hr., and chromatographed on alumina from light petroleum (b. p. 40—60°). It was often very difficult to induce crystallisation of the purified oil. Details of the 9-arylfluoren-9-ols so prepared are given in Table 1. Diphenylmethanol and fluoren-9-ol were prepared by reducing the corresponding ketones with zinc dust and ethanolic sodium hydroxide.

TABLE 1.

9-(Substituted phenyl)fluoren-9-ols and related compounds.

Substituent	M. p.	Lit. m. p.	Ref.	Formula	Found (%) C	Found (%) H	Reqd. or calc. (%) C	Reqd. or calc. (%) H
H	85°	85°	a	$C_{19}H_{14}O$	—	—	—	—
o-Me	121—121·5	121—123	b	$C_{20}H_{16}O$	—	—	—	—
m-Me	82—83	81·5—82·5	c	$C_{20}H_{16}O$	88·2	5·9	88·2	5·9
p-Me	86—87	85·5—86·5	c	$C_{20}H_{16}O$	—	—	—	—
o-Cl	141—141·5	140—141	d	$C_{19}H_{13}ClO$	—	—	—	—
m-Cl	90—91	81—82	c	$C_{19}H_{13}ClO$	77·9	4·4	78·0	4·5
p-Cl	93—94	91—92	c	$C_{19}H_{13}ClO$	78·0	4·4	78·0	4·5
m-F	64—65	—	new	$C_{19}H_{13}FO$	82·4	4·7	82·6	4·7
p-F...............	110—110·5	—	new	$C_{19}H_{13}FO$	82·6	4·6	82·6	4·7
p-Br	99—100	—	new	$C_{19}H_{13}BrO$	68·0	4·1	67·7	3·9
o-OMe	109—110	—	new	$C_{20}H_{16}O_2$	83·1	5·6	83·3	5·6
m-OMe	Oil	89—90	c	$C_{20}H_{16}O_2$	—	—	—	—
p-OMe	Oil	130—132; 87—88	c, g	$C_{20}H_{16}O_2$	—	—	—	—
p-SMe	86—87	—	new	$C_{20}H_{16}OS$	79·0	5·1	78·9	5·3
m-Ph	148	—	new	$C_{25}H_{18}O$	90·0	5·5	89·8	5·4
p-Ph	141—142	—	new	$C_{25}H_{18}O$	89·7	5·5	89·8	5·4
1-Naphthyl ...	151—152	151·5	e	$C_{23}H_{16}O$	—	—	—	—
2-Naphthyl ...	177—178	—	new	$C_{23}H_{16}O$	89·6	5·2	89·6	5·2
9-Phenanthryl	190—191	189	f	$C_{27}H_{18}O$	90·1	5·1	90·3	5·1

a Arcus and Coombs, *J.*, 1954, 3978. *b* Weiss and Knapp, *Monatsh.*, 1932, **61**, 61. *c* Eaborn, Golesworthy, and Lilly, *J.*, 1961, 3052. *d* Campbell and Marks, *J.*, 1951, 2941. *e* Ullmann and von Wurstemberger, *Ber.*, 1905, **38**, 4105. *f* Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363. *g* Gomberg and Buchler, *J. Amer. Chem. Soc.*, 1923, **45**, 207.

The 9-arylfluoren-9-ols were converted into the corresponding chlorides by heating under reflux with acetyl chloride in a dry atmosphere for 1 hr. Unchanged acetyl chloride and other volatile impurities were removed by distillation at 760 mm., then at 15 mm. The crude product was recrystallised from light petroleum (b. p. 40—60°) (charcoal), light petroleum (b. p. 40—60°) containing 5% of acetyl chloride, and finally from " dry " acetone (0·02% water) at —70°. Details of the compounds so prepared are given in Table 2. The identity and purity of the compounds were determined by titrimetric determination of the chloride ion and hydrogen ion produced on complete hydrolysis. In Table 2 these results are expressed as observed values of the molecular weight. On the whole the observed m. p.s agreed with those recorded in the literature, and where this is not so, the purity of the chloro-compound is attested by analysis as mentioned above.

9-Bromo-9-phenylfluorene was prepared by the action of acetyl bromide on the corresponding carbinol and purified by many recrystallisations from benzene–light petroleum (b. p. 40—60°), then finally from " dry " acetone at —70°. It had m. p. 99° (lit.,[6] 99°). Diphenylmethyl

[5] Huntress, Hershberg, and Cliff, *J. Amer. Chem. Soc.*, 1931, **53**, 2720.
[6] Kliegl, *Ber.*, 1905, **38**, 284.

chloride and bromide, 9-bromo(or chloro)fluorene, triphenylmethyl chloride and bromide, and 9-chloro-9-phenylfluorene were prepared by standard methods and had m. p.s in accord with those previously reported, except for diphenylmethyl chloride which had m. p. 18·4° (lit.,[7a-d] 14, 12—14, 18, 20·5°) and b. p. 171—172°/19 mm. (lit.,[7a] 170°/18 mm.).

TABLE 2.

9-Chloro-9-(substituted phenyl)fluorenes and related compounds.

Substituent	M. p.	Lit. m. p.	Ref.	Formula	M (Cl⁻ titration)	M (H⁺ titration)	Reqd. or calc., M
H	79°	78—79°	a	$C_{19}H_{13}Cl$	—	—	—
o-Me	114—115	—	new	$C_{20}H_{15}Cl$	290·7	291·0	290·8
m-Me	70—71	83·5—84·5	b	$C_{20}H_{15}Cl$	290·9	290·8	290·8
p-Me	99—100	97; 96—97	b, c	$C_{20}H_{15}Cl$	—	—	—
o-Cl	141 *	—	new	$C_{19}H_{12}Cl_2$	311·1	310·9	311·2
m-Cl	65—66	72·5—73	b	$C_{19}H_{12}Cl_2$	311·4	311·1	311·2
p-Cl	80—81	79·5—80·5	b	$C_{19}H_{12}Cl_2$	311·3	311·4	311·2
m-F	63—64	—	new	$C_{19}H_{12}ClF$	294·6	295·0	294·8
p-F	119—120	—	new	$C_{19}H_{12}ClF$	295·0	295·0	294·8
p-Br	101—102	—	new	$C_{19}H_{12}BrCl$	356·0	355·6	355·7
o-OMe	142—143	—	new	$C_{20}H_{15}ClO$	306·4	306·8	306·8
m-OMe	113—114	108·5—109	b	$C_{20}H_{15}ClO$	306·9	307·0	306·8
p-OMe	147—148	151·5—152·5	b	$C_{20}H_{15}ClO$	—	—	—
p-SMe	107—108	—	new	$C_{20}H_{15}ClS$	322·9	322·8	322·8
m-Ph	110—111	—	new	$C_{25}H_{17}Cl$	353·0	352·8	352·9
p-Ph	135—136	—	new	$C_{25}H_{17}Cl$	353·0	352·9	352·9
1-Naphthyl ...	149—150	149—150	d	$C_{23}H_{15}Cl$	326·8	326·9	326·8
2-Naphthyl ...	130—131	—	new	$C_{23}H_{15}Cl$	327·2	326·8	326·8
9-Phenanthryl	211—212	211—212	e	$C_{27}H_{17}Cl$	—	—	—

    * Campbell and Marks (*J.*, 1951, 2941) report, m. p. 145°, for the " acetate." This compound appears to be the chloride.

    ᵃ Kliegl, *Ber.*, 1905, **38**, 284. ᵇ Eaborn, Golesworthy, and Lilly, *J.*, 1961, 3052. ᶜ Schniepp and Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 1635. ᵈ Wanscheidt and Moldavski, *Ber.*, 1930, **63**, 1362. ᵉ Bachmann and Kloetzel, *J. Org. Chem.*, 1937, **2**, 356.

Reaction Products.—These were prepared in independent experiments by boiling the chloro-compound with ethanol or acidic ethanol. They were recrystallised from ethanol to constant m. p. Details of the ethanolysis products of most of the 9-aryl-9-chlorofluorenes prepared are given in Table 3.

TABLE 3.

9-Ethoxy-9-(substituted phenyl)fluorenes and related compounds.

Substituent	M. p.	Lit. m. p.	Ref.	Formula	Found (%) C	Found (%) H	Reqd. or calc. (%) C	Reqd. or calc. (%) H
H	113—114°	113°	a	—	—	—	—	—
o-Me	116	—	new	$C_{22}H_{20}O$	87·8	6·7	88·0	6·7
m-Me	102—103	—	new	$C_{22}H_{20}O$	88·0	6·5	88·0	6·7
p-Me	123—124	123	b	—	—	—	—	—
o-Cl	136—137	—	new	$C_{21}H_{17}ClO$	78·7	5·4	78·6	5·3
p-Cl	140—141	—	new	$C_{21}H_{17}ClO$	78·3	5·4	78·6	5·3
p-F	116	—	new	$C_{21}H_{17}FO$	83·0	5·7	82·9	5·6
p-Br	147—148	—	new	$C_{21}H_{17}BrO$	69·0	4·8	69·1	4·7
o-OMe	138—139	—	new	$C_{22}H_{20}O_2$	83·4	6·5	83·5	6·4
m-OMe	66—67	—	new	$C_{22}H_{20}O_2$	83·6	6·5	83·5	6·4
p-OMe	134—135	—	new	$C_{22}H_{20}O_2$	83·5	6·4	83·5	6·4
p-SMe	134—135	—	new	$C_{22}H_{20}OS$	79·8	6·1	79·5	6·1
p-Ph	166—167	—	new	$C_{27}H_{22}O$	89·4	6·1	89·5	6·1
1-Naphthyl	136	—	new	$C_{25}H_{20}O$	89·0	5·9	89·3	6·0
2-Naphthyl	143—144	—	new	$C_{25}H_{20}O$	89·3	6·1	89·3	6·1
9-Phenanthryl	174	173—174	c	$C_{29}H_{22}O$	91·0	4·9	91·1	4·7

    ᵃ Table 2, ref. *a*. ᵇ Table 2, ref. *c*. ᶜ Table 2, ref. *e*.

    ⁷ (*a*) Engler and Bethge, *Ber.*, 1874, **7**, 1128; (*b*) Boeseken, *Rec. Trav. chim.*, 1903, **22**, 313; (*c*) Hughes, Ingold, and Taher, *J.*, 1940, 954; (*d*) Ward, *J.*, 1927, 2288.

Solvents.—Ethanol was dried by Lund and Bjerrum's method [8] and fractionally distilled, rejecting the fore-run, when it had b. p. 78·4°/760 mm., d_4^{20} 0·7893 (lit.,[9a] b. p. 78·3°, d 0·7893) and contained <0·01% of water (Karl Fischer titration).[10] Methanol, similarly purified, had b. p. 64·7°/760 mm., d_4^{25} 0·7867 (lit.,[9b] b. p. 64·5°, d 0·7867$_5$). It contained <0·01% water (Karl Fischer titration).[10] AnalaR acetone was dried for 3 months over three separate portions of anhydrous calcium sulphate, and then fractionally distilled from fresh calcium sulphate until the distillate had f. p. within one degree of the accepted value. The residual acetone was then fractionally distilled at a reflux ratio of 10 : 1, and contained 0·02% of water (Karl Fischer titration).[10] It had b. p. 56·2°/760 mm., d_4^{20} 0·7898 (lit.,[9c] b. p. 56·24°, d 0·7899$_5$).

All solvents were stored and manipulated with very careful exclusion of atmospheric moisture.

Procedure.—Conventional thermostats were used for the temperature range 0—60°, the temperature usually being controlled to ±0·05° or better. For the range −20—0°, ice–salt baths were used, and with adequate stirring could be controlled to ±0·1°; for the range −70—−20°, stirred melting organic solvents were used giving temperature control of ±0·1°, *e.g.*, pure melting ethyl benzoate gives a temperature of −34·8 ± 0·1°. For very rapid reactions at room temperature, well-stirred water in a 5-l. beaker maintained a temperature constant to ±0·1° for 30 min. For temperatures >0°, standardised thermometers (N.P.L.) were used; for temperatures <0°, thermometers were calibrated against the f. p. of purified organic solvents.

The solvolyses were usually followed by an adaptation of Swain, Esteve, jun., and Jones's [11] method for fast reactions. In a 100-ml. three-necked flask fitted with stirrer, thermometer, and 5-ml. burette containing 0·0500M-ethanolic sodium ethoxide, was placed pure ethanol (90·0 ml.) containing two drops of ethanolic Methyl Red indicator (0·1%) and the flask was then immersed in the thermostat bath. The reaction was started by adding 10·0 ml. of a 0·05—0·1M-solution of the chloride in pure acetone of accurately known concentration, which had been brought to thermostat temperature, the time of half-addition being taken as zero. A measured volume of sodium ethoxide solution, sufficient to change the colour of the indicator from red to yellow, was immediately run in from the burette, the time at which the indicator reverted to the red colour was noted, and a further measured quantity of sodium ethoxide solution was added. The solvolysis generates acid according to the stoicheiometric equation: ArX (X = Cl or Br) + ROH ⟶ Ar·OR + HX. Thus, from the ethoxide " titre," the amount of halogeno-compound consumed could be calculated for a series of time intervals. In this way the reaction could be followed to 99% completion with an accuracy greater than that given by the usual sampling technique. The method depends on the reaction pursuing the S_N1 mechanism (*i.e.*, its rate is unaffected by the added sodium ethoxide), and on keeping the total volume of titrant small in relation to the initial volume of the reaction solution. (In all the reactions the " infinity " titre gave a satisfactory check with the concentration of the solution of the chloride determined by weighing the chloride.) This method was also used for studying the solvolysis of the diphenylmethyl halides in pure ethanol or methanol, the reaction being initiated by addition of the pure molten halide to the solvent. The titrant was sodium methoxide in methanol, or ethoxide in ethanol. The experiments with 9-chloro-9-(1-naphthyl)fluorene were carried out similarly except that $(100 - y)$ ml. of ethanol were added initially and the chloride was dissolved in y ml. of acetone. In this way the percentage of acetone in the solvent could be varied as desired.

In studying the solvolysis of 9-halogenofluorenes in methanol or in ethanol, samples (10·0 ml.) of 0·0500M-solution were sealed in reaction tubes, which were immersed in the thermostat bath. The first tube was removed after 15 min., chilled in ice, opened, and the contents were washed into cold AnalaR acetone (30 ml.). The hydrogen ion liberated during solvolysis was determined by titration with sodium alkoxide solution, with Methyl Red as indicator. The reaction was timed from the removal of the first tube, and further tubes were removed and their contents were analysed at suitable intervals.

Rate coefficients were calculated from the equation, $k(t - t_0) = 2·303 \log [(a - x_0)/(a - x)]$,

[8] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[9] Weissberger, Proskauer, Riddick, and Toops, " Organic Solvents," Interscience, New York, **1955**, (*a*) p. 91; (*b*) p. 90; (*c*) p. 137.

[10] Seaman, McComas, and Allen, *Analyt. Chem.*, 1949, **21**, 510.

[11] Swain, Esteve, jun., and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 969.

TABLE 4.

Solvolysis of 9-chloro-9-(4-methylthiophenyl)fluorene (0·0100M) in ethanol–acetone
(9 : 1 v/v) at −8·0°; titrant, 0·0513M-ethanolic sodium ethoxide.

Time (sec.)	0·0 *	11·6	26·2	41·6	58·6	75·4	94·6	115·0
Vol. of titrant (ml.)	—	1·00	2·02	3·00	4·04	5·00	6·02	7·00
% Reaction	0·00	5·13	10·33	15·38	20·66	25·64	30·87	35·96
$10^3 k$ (sec.$^{-1}$)	—	(3·94)	(3·90)	3·85	3·83	3·84	3·83	3·81

Time (sec.)	137·0	161·2	187·0	216·4	250·0	266·2	286 †	
Vol. of titrant (ml.)	8·02	9·02	10·00	11·02	12·02	12·50	13·02	
% Reaction	41·13	46·26	51·26	56·51	61·64	64·10	66·77	
$10^3 k$ (sec.$^{-1}$)	3·82	3·82	3·81	3·82	3·81	3·82	3·83	

Time (sec.)	307	330	355	383	415	448	∞	
Vol. of titrant (ml.)	13·50	14·02	14·50	15·00	15·52	16·00	19·50	
% Reaction	69·23	71·90	74·36	76·92	79·59	82·05	100·07	
$10^3 k$ (sec.$^{-1}$)	3·82	3·83	3·82	3·81	3·81	3·82	—	

Mean $k = (3·82 \pm 0·01) \times 10^{-3}$ sec.$^{-1}$.

* Zero time from graph.   † At this stage, and thereafter, the colour change of the indicator takes
>0·5 sec.

Solvolysis of 9-bromo-9-phenylfluorene (0·00428M) in ethanol–acetone (9 : 1 v/v) at
29·3°; titrant, 0·0285M-ethanolic sodium ethoxide.

Time (sec.)	16·4	27·0	36·2	53·0	63·8	86·0	105·0	∞
Vol. of titrant (ml.)	6·04	8·00	10·00	12·10	13·00	13·92	14·44	15·00
% Reaction	40·27	53·33	66·67	80·67	86·67	92·80	96·27	100·00
$10^2 k$ (sec.$^{-1}$)	3·14	3·04	3·04	3·10	3·16	3·06	3·13	—

Mean $k = (3·09 \pm 0·04) \times 10^{-2}$ sec.$^{-1}$.

This reaction has a half-life of 22·4 sec. and is the fastest that can be accurately studied by the
technique employed.   Reactions with half-lives as low as ~17 sec. can be followed with some loss of
accuracy.

Solvolysis of 9-chlorofluorene (0·05M) in methanol at 86·2°; titrant, 0·1354M-
methanolic sodium methoxide.

Time (sec.)	0	230	505	720	935	1145	1500
Vol. of titrant (ml.)	0·386	0·508	0·660	0·764	0·868	0·960	1·042
% Reaction	10·45	13·75	17·87	20·68	23·50	25·99	28·21
$10^4 k$ (sec.$^{-1}$)	—	1·62	1·71	1·68	1·68	1·66	(1·47)

Mean $k = (1·67 \pm 0·02) \times 10^{-4}$ sec.$^{-1}$.

after plotting $\log (a - x)$ against t, and determining from the linear plot so obtained $\log$
$(a - x_0)$ for an arbitrary zero time.

Results.—A few typical experiments are described in Table 4, and all the measured rate-
co-efficients and Arrhenius parameters are assembled in Tables 5—8, 10, and 11.

DISCUSSION

*Solvolysis of Diphenylmethyl, 9-Phenyl-9-fluorenyl, and Triphenylmethyl Halides in
Ethanol–Acetone (9 : 1 v/v).*—First-order rate coefficients are given in Table 5, and the derived
Arrhenius parameters, together with the corresponding free energies, enthalpies, and

TABLE 5.

Rate coefficients for solvolysis of diphenylmethyl, 9-phenyl-9-fluorenyl, and triphenyl-
methyl halides in ethanol–acetone (9 : 1 v/v).

Compound	$10^4 k$ (sec.$^{-1}$); temperatures in parentheses
Ph$_2$CHCl	0·0567 (10·3), 0·211 (20·4), 0·772 (29·4), 1·13 (34·4)
9-Ph-C$_{13}$H$_8$Cl	5·75 (20·0), 14·0 (27·3), 18·6 (30·5), 35·2 (36·3), 74·6 (44·5), 133 (51·8)
Ph$_3$CCl	3·58 (−63·4), 17·1 (−51·4), 43·7 (−43·8), 77·7 (−39·2), 176 (−31·5)
Ph$_2$CHBr	6·15 (21·5), 14·4 (29·4), 41·0 (40·0)
9-Ph-C$_{13}$H$_8$Br	17·3 (0·2), 38·9 (8·2), 60·6 (13·0), 76·3 (14·5), 76·4 (14·8), 104 (17·8), 169 (22·3), 309 (29·3)

Values of k are accurate to $\pm 1\%$.

TABLE 6.

Arrhenius parameters and transition-state parameters at 0° for solvolysis of diphenyl-methyl, 9-phenyl-9-fluorenyl, and triphenylmethyl halides in ethanol–acetone (9 : 1 v/v), and some related unsaturation energies.

Compound	E (kcal. mole^{-1})	$\Delta H^{\ddagger}$	log A (sec. units)	$-\Delta S^{\ddagger}$ (e.u.)	$10^4 k_0$ (sec.$^{-1}$)	$\Delta F^{\ddagger}$ (kcal. mole^{-1})	$(U_\pi)_{\mathrm{R}^+}$ [a]	$(U_\pi)_{\mathrm{RX}}$ [b]	$(\Delta U_\pi - \alpha)\beta^{-1}$
Ph$_2$CHCl	22·1	21·6	11·8	6·4	0·0130	23·3	$13\alpha + 17{\cdot}30\beta$	$12\alpha + 16{\cdot}00\beta$	1·30
9-Ph-C$_{13}$H$_8$Cl	18·6	18·1	10·7	11·4	0·588	21·2	$19\alpha + 26{\cdot}04\beta$	$18\alpha + 24{\cdot}38\beta$	1·66
Ph$_3$CCl.........	12·3	11·8	9·4	17·3	3430	16·5	$19\alpha + 25{\cdot}79\beta$	$18\alpha + 24{\cdot}00\beta$	1·79
Ph$_2$CHBr ...	18·8	18·3	10·7	11·4	0·494	21·4	$13\alpha + 17{\cdot}30\beta$	$12\alpha + 16{\cdot}00\beta$	1·30
9-Ph-C$_{13}$H$_8$Br	16·4	15·9	10·4	12·8	16·3	19·4	$19\alpha + 26{\cdot}00\beta$	$18\alpha + 24{\cdot}38\beta$	1·66

Values of E and $\Delta H^{\ddagger}$ are usually accurate to ± 200 cal. mole^{-1}, log A to $\pm 0{\cdot}2$ unit, and $\Delta S^{\ddagger}$ to $\pm 1{\cdot}0$ e.u.

a, Unsaturation energy of the di- and tri-phenylmethyl and 9-phenyl-9-fluorenyl cations calculated by Hückel molecular orbital theory in terms of the coulomb integral, α, and the resonance integral, β. *b* Unsaturation energy of the halide similarly calculated (cf. Gold, *J.*, 1956, 3944; Streitwieser, jun., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, p. 364. A minor error in Gold's paper has been corrected).

entropies of activation in Table 6. The solvolysis of triphenylmethyl bromide was too rapid for study, even at $-65°$; at lower temperatures the solution was too viscous for efficient stirring. The solvolysis of all the above compounds pursues by the S_N1 mechanism; the main evidence is the satisfactory linearity, for the whole experiment, of the log $(a - x)$ versus t plot obtained, when the reaction is followed by the method outlined above,[11] *i.e.*, the rate of the reaction is unaffected by addition of a more powerful nucleophile (ethoxide ion) than solvent ethanol. There was a slight trend towards an increased rate coefficient beyond 70% completion of reaction; this we ascribe to the small increase, arising from the titration, in the proportion of ethanol in the solvent as the reaction proceeds. We did not observe a progressive decrease in the rate coefficient as the reaction proceeds, typical of the S_N1 process, unlike Eaborn *et al.*[3b] who observed it in the solvolysis of 9-chloro-9-phenylfluorene derivatives in 95% aqueous acetone. It appears that in our case an approximate balance between the mass law and ionic strength effects [12] is observed, possibly to be associated with a reduction in the rate of reversal of the carbon–halogen bond heterolysis because of the greater proportion of hydroxylic solvent in our reaction medium than in that of Eaborn *et al.*, with consequent stronger solvation of the ions formed in heterolysis.

In the S_N1 mechanism, the structure of the transition state in the rate-determining step tends towards that of the relevant carbonium ion. The activation parameters are to be considered in terms of the differences between the properties of this carbonium ion and that of the initial halide in each case, it being assumed that the carbonium ion is a satisfactory model of the transition state, especially when closely related reactions are compared. The major factors to be considered are unsaturation or π-electron energy, steric compression, and solvation. On this basis we may write formally, for two closely related reactions:

$$\Delta\Delta F^{\ddagger} = \Delta\Delta H_{\mathrm{U}}^{\ddagger} + \Delta\Delta H_{\mathrm{C}}^{\ddagger} + \Delta\Delta H_{\mathrm{S}}^{\ddagger} - \mathrm{T}(\Delta\Delta S_{\mathrm{U}}^{\ddagger} + \Delta\Delta S_{\mathrm{C}}^{\ddagger} + \Delta\Delta S_{\mathrm{S}}^{\ddagger})$$

where subscripts U, C, and S, refer to unsaturation, steric compression, and solvation, respectively, it being assumed that σ-bond energy changes remain more or less constant. In the following qualitative discussion we shall consider only potential energy contributions to the $\Delta H^{\ddagger}$ terms.

Table 6 shows that the rate relations for 0° are qualitatively expressible thus: Ph$_2$CHCl $<$ 9-Ph-C$_{13}$H$_8$Cl $\ll$ Ph$_3$CCl. The associated decreases in free energy of activation ($\Delta\Delta F^{\ddagger}$) arise from substantial decreases in $\Delta H^{\ddagger}$, especially as between Ph$_3$CCl and

[12] Ingold, "Structure and Mechanism in Organic Chemistry," 1st edn., G. Bell and Sons, London, 1953, p. 360.

9-Ph-$C_{13}H_8$Cl, offset by decreases in $\Delta S^{\ddagger}$. Initially we consider only $\Delta H_U^{\ddagger}$ for the 9-phenyl-9-fluorenyl and triphenylmethyl systems. The 9-phenyl-9-fluorenyl cation may be regarded as a phenyl-substituted dibenzocyclopentadienonium ion, which would be expected to be less stable than the triphenylmethyl cation because of the well-known preference of the cyclopentadiene system for the carbanionic rather than the carbonium ion form, and so our results are qualitatively understandable. The introduction of the interannular link into the triphenylmethyl cation should reduce the delocalisation of positive charge by incorporating some of the carbon atoms in a cyclopentadiene system, and thereby decrease their ability to accommodate fractional positive charges. The diphenylmethyl cation is the least stable of the three because delocalisation of positive charge occurs over two phenyl ring systems only. Gold [13] assessed quantitatively, but approximately, the $\Delta\Delta H^{\ddagger}$ term by using Hückel molecular orbital theory (see the last three columns of Table 6). Since β is a negative quantity, the values in the last column indicate the unsaturation energy excess for the carbonium ion, and likewise the related transition state, over the halide. This limited theoretical analysis accords well, qualitatively, with the kinetic results, but its limitations from the quantitative viewpoint are clear.

In the above calculation of ΔU_{π} (Table 6) it is assumed that the triphenylmethyl cation is planar. In fact this is very unlikely, as Sharpe and Sheppard [14] have shown by infrared spectroscopic studies of suitable salts of the ion, which apparently has a structure resembling a three-bladed propeller, resulting from steric repulsions between the six " *ortho* " hydrogen atoms. However, a study of scale models shows that, although a few compression-free conformations are available to the initial state, on the average, steric compression, especially between " *ortho* " hydrogen atoms, is greater in the initial state than in the propeller-like structure of the transition state. Release of steric compression energy may well contribute, therefore, to the low values of $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ observed for triphenylmethyl chloride (cf. Table 6). In the 9-phenyl-9-fluorenyl system, two of the benzene rings are necessarily coplanar in both initial and transition states. In the initial state a series of compression-free conformations of the 9-phenyl group with its plane more or less perpendicular to that of the rest of the molecule appear to be available, while the attainment of a fully coplanar transition state, corresponding to a carbonium ion structure, involves only compression between the *ortho*-hydrogens of the phenyl ring and the 1- and 8-hydrogens of the fluorene ring. Much of this compression can be relieved by a small rotation of the 9-phenyl group towards a conformation similar to the propeller-form of the triphenylmethyl cation. The release of steric compression energy in forming the transition state seems relatively unimportant in this case; indeed any effect may be in the opposite direction. In the diphenylmethyl system, steric factors appear to be of little importance as numerous compression-free conformations are available to the initial state, and in the carbonium ion the interplanar angle between the two benzene rings is small; any effect would be in the same direction as for the 9-phenyl-9-fluorenyl system.

The observed decrease in entropy on forming the transition state lies in the order Ph_2CHCl < 9-Ph-$C_{13}H_8$Cl < Ph_3CCl. Disregarding solvation for the present, it appears that, since the transition state will in each case tend toward the rigid, well-ordered carbonium ion, the " internal " entropy decrease might well lie in the order Ph_2CHCl > 9-Ph-$C_{13}H_8$Cl > Ph_3CCl, for reasons indicated above as to the conformations available to the initial state. We therefore suggest that solvation of the transition state and the attendant entropy decrease lie in the order Ph_2CHCl < 9-Ph-$C_{13}H_8$Cl < Ph_3CCl, and dominate the pattern of entropy decreases. Streitwieser jun.,[15a] proposed two postulates, concerning the structure of the transition state in the solvolysis of halides, on the basis of

[13] Gold, *J.*, 1956, 3944.
[14] Sharpe and Sheppard, *J.*, 1957, 674.
[15] (a) Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 639; (b) Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

the Hammond [15b] postulate. These are: (*a*) the greater the solvation forces " the closer the transition state structure will be to tetrahedral "; (*b*) " the greater the ability of the system internally to disperse the positive charge (*i.e.*, form the more stable carbonium ion) " the closer the transition state will be to tetrahedral. It appears that, on this basis, closeness to the tetrahedral structure for the transition state lies in the order $Ph_3CCl >$ $9\text{-}Ph\text{-}C_{13}H_8Cl > Ph_2CHCl$. This would support the conclusion reached above concerning the " internal " entropy decrease, because Ph_3CCl would have undergone the least and Ph_2CHCl the greatest change in the direction of the rigid well-ordered carbonium ion. The argument developed above concerning release of compression energy in forming the transition state would be little affected because this release is thought to arise only with Ph_3CCl and it will be greatest in the early stages of motion along the reaction co-ordinate. However, the orientational requirements for the solvating species, which affect the entropy term, would still be in the order $Ph_3CCl > 9\text{-}Ph\text{-}C_{13}H_8Cl > Ph_2CHCl$.

Solvolysis of 9-Chloro-9-(substituted phenyl)fluorenes in Ethanol–Acetone (9 : 1 v/v).— First-order rate coefficients for the solvolysis of 9-chloro-9-(substituted phenyl)fluorenes are assembled in Table 7, and the corresponding Arrhenius parameters, enthalpies, entropies, and free energies of activation are in Table 8. The mechanism of these solvolyses is believed to be the same as that of the 9-phenyl compound itself, *viz.*, S_N1, for the same reasons.

We apply the Hammett [16] equation, $\log k/k_0 = \rho\sigma$, to the effect of *meta*- and *para*-substituents in the way recommended by van Bekkum, Verkade, and Wepster.[17] The Hammett line is established by using only the σ-values of those *meta*-substituents of small

TABLE 7.

Rate coefficients, k (sec.$^{-1} \times 10^3$), for solvolysis of 9-chloro-9-(substituted phenyl)fluorenes and related compounds in ethanol–acetone (9 : 1 v/v), temperatures in parentheses.

Substituent	
o-Me	1·16 (25·2), 2·05 (30·4), 2·63 (33·7), 4·31 (37·8), 6·30 (41·8)
m-Me	2·70 (28·0), 4·48 (33·2), 5·07 (34·0), 6·43 (36·4), 7·99 (39·0), 12·4 (43·5)
p-Me	2·94 (13·0), 5·20 (17·8), 14·2 (28·0), 18·1 (30·6), 25·8 (34·0)
o-Cl	0·602 (42·6), 1·40 (51·2), 1·47 (51·6), 2·54 (57·0), 2·79 (58·0), 3·87 (61·4)
m-Cl	1·32 (55·6), 2·24 (61·6), 2·83 (64·0), 3·90 (67·4), 4·05 (68·0), 4·45 (69·5), 5·11 (71·4) *
p-Cl	0·192 (16·5), 0·554 (27·0), 1·36 (35·0), 2·44 (40·5)
m-F	1·18 (52·4), 2·40 (59·7), 3·17 (62·8), 4·42 (66·2), 5·60 (68·6), 6·63 (71·1)
p-F.............	0·582 (17·8), 1·19 (24·0), 3·02 (32·6), 4·68 (37·5), 8·12 (43·0)
p-Br	0·921 (31·2), 2·14 (40·0), 2·42 (42·0), 3·57 (45·5), 7·3 (54·6), 10·2 (58·2), 11·8 (60·4)
o-OMe	0·966 (0·2), 2·68 (9·2), 4·86 (15·0), 22·1 (29·5)
m-OMe	0·423 (16·9), 0·687 (21·0), 1·43 (28·0), 2·13 (31·6), 6·41 (42·4), 6·57 (43·2)
p-OMe	0·589 (−30·5), 0·564 (−30·0), 1·20 (−25·9), 1·34 (−25·3), 5·87 (−14·9), 7·16 (−12·8), 13·2 (−8·3)
p-SMe	2·65 (−11·2), 2·70 (−11·0), 3·82 (−8·0), 7·02 (−3·0), 10·6 (+0·6), 11·4 (+1·4), 13·6 (+3·2)
m-Ph	2·95 (30·8), 5·05 (44·2), 6·10 (46·2), 9·79 (51·8), 10·5 (52·4), 20·9 (61·2), 29·6 (65·4)
p-Ph	1·92 (14·8), 3·46 (20·4), 5·26 (24·8), 9·21 (30·0), 12·0 (32·8)
1-Naphthyl ...	1·44 (2·0), 2·64 (7·2), 4·82 (12·5), 5·53 (13·5), 6·72 (15·2), 7·35 (16·8), 11·8 (20·6)
2-Naphthyl ...	1·99 (19·0), 4·83 (27·8), 8·68 (33·6), 15·8 (40·6), 23·6 (44·8)
9-Phenanthryl	2·08 (0·5), 3·69 (5·2), 6·58 (10·0), 13·1 (16·2), 15·3 (17·4)

* Also 5·78 (73·0). Values of k are usually accurate to ±1%.

mesomeric effect; in the present work, H, F, Cl, and Me. The value of ρ for 25° is **−3·51**, and of $\log k_0$ **−2·96**, with a correlation coefficient, $r = 0.997$, and a standard deviation, $s = 0.08$. Effective σ-values (Table 9) for the *para*- and remaining *meta*-substituents can now be calculated from the equation $\sigma = (1/\rho)\log k/k_0$, by using the corresponding observed values of k.

They differ markedly from σ-values based on the dissociation constants of substituted

[16] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, pp. 184—199.
[17] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

TABLE 8.

Arrhenius parameters and transition-state parameters, at 25° for solvolysis of 9-chloro-9-(substituted phenyl)fluorenes and related compounds in ethanol–acetone (9 : 1 v/v).

Substituents	E (kcal. mole^{-1})	$\Delta H\ddagger$	$\log A$ (sec. units)	$-\Delta S\ddagger$ (e.u.)	$10^4 k_{25}$ (sec.$^{-1}$)	$\Delta F\ddagger$ (kcal. mole^{-1})
H	18·6	18·0	10·7	11·6	10·5	21·5
o-Me	18·9	18·3	10·9	10·7	11·3	21·5
m-Me	18·5	17·9	10·9	10·7	19·9	21·1
p-Me	17·8	17·2	11·1	9·7	106	20·1
o-Cl	20·8	20·2	11·2	9·3	0·842	23·0
m-Cl	19·4	18·8	10·0	14·8	0·635	23·2
p-Cl	19·2	18·6	10·7	11·6	4·77	22·1
m-F	20·9	20·3	11·1	9·7	0·599	23·2
p-F	19·0	18·4	11·1	9·7	13·1	21·3
p-Br	17·7	17·1	9·7	16·1	5·04	21·9
o-OMe	17·5	16·9	11·0	10·2	140	20·0
m-OMe	19·1	18·5	11·0	10·2	10·5	21·5
p-OMe	18·1	17·5	13·1	0·6	6360	17·7
p-SMe	16·6	16·0	11·3	8·8	1260	18·6
m-Ph	17·6	17·0	9·8	15·7	8·47	21·6
p-Ph	17·8	17·2	10·8	11·1	55·4	20·5
1-Naphthyl	18·0	17·4	11·5	7·9	185	19·8
2-Naphthyl	17·6	17·0	10·5	12·5	36·9	20·7
9-Phenanthryl	18·5	17·9	12·1	5·2	342	19·4

Values of E and $\Delta H\ddagger$ are usually accurate to ± 200 cal. mole^{-1}, $\log A$ to ± 0.2 unit, and $\Delta S\ddagger$ to ± 1.0 e.u.

TABLE 9.

The application of the Hammett equation to the solvolysis of 9-chloro-9-(substituted phenyl)fluorenes and related compounds in ethanol–acetone (9 : 1 v/v).

Substituent	$-\log k$ (25°)	σ	σ(effective) [b]	Solvolysis of 1-methyl-1-phenylethyl chlorides in 90% aqueous acetone	
				σ^+ (Brown) [a]	σ (calc.) (Wepster) [c]
H	2·98	—	—	—	—
m-Me	2·70	−0·069	—	—	—
p-Me	1·98	−0·170	−0·279	−0·311	−0·321
m-Cl	4·20	+0·373	—	—	—
p-Cl	3·32	+0·227	+0·103	+0·114	+0·107
m-F	4·22	+0·337	—	—	—
p-F	2·88	+0·062	−0·023	−0·073	−0·081
p-Br	3·30	+0·232	+0·097	+0·150	+0·143
m-OMe	2·98	+0·115	+0·006	+0·047	+0·040
p-OMe	0·20	−0·268	−0·786	−0·778	−0·792
p-SMe	0·90	0·00	−0·587	−0·604	−0·617
m-Ph	3·07	+0·06	+0·031	+0·109	+0·102
p-Ph	2·26	−0·01	−0·205	−0·179	−0·205
2-Naphthyl	2·43	+0·42	−0·151	−0·135	—

[a] σ and σ^+ values from compilation by Brown in " Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 100. [b] Present work. [c] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

benzoic acids, because of the highly electron-demanding character of the S_N1 process. However, they resemble closely the " calculated " σ-values derived by Wepster and his co-workers[17] from Brown and Okamato's results[18] for the S_N1 solvolysis of substituted 1-methyl-1-phenylethyl chlorides in 90% aqueous acetone, and the σ$^+$ values calculated by Brown himself (see Table 9). (These σ$^+$-values were based on establishment of the Hammett line with the results for *all* the *meta*-substituents, which included groups such as NH_2 or OMe unacceptable to Wepster because of their mesomeric effects. However, this procedure

[18] Brown, Okamoto, and Inuka, *J. Amer. Chem. Soc.*, 1958, **80**, 4964.

leads to $\rho = -4.54$, compared with -4.49 calculated by Wepster.) The electron-releasing conjugative effects of *p*-halogen, -methyl, -methoxyl, and -methylthio-, *m*-methoxyl, and 3,4-benzo-groups are greatly enhanced. In particular, the large conjugative effect of the *p*-methylthio-group discussed by Brown[18] is also observed here.

Turning now to the effect of *ortho*-substituents, an *o*-methyl group enhances the rate very slightly compared with a *p*-methyl group. The most likely explanation of this is steric compression in the transition state between the *o*-methyl group and the hydrogen atom at the 1- or 8-position of the fluorene ring, which almost offsets the facilitating polar influence of the methyl group as observed in the *meta*-isomer. The same steric interactions may well inhibit the hyperconjugative effect of the *o*-methyl group. The *o*-chloro-compound is substantially less reactive than the *p*-chloro-compound, and although similar steric effects probably are partly responsible, Chapman, Shorter, and Utley[19] showed that the electron-withdrawing effect of an *o*-chloro-, -bromo-, or -iodo-group may well be three times that of the corresponding *para*-group, and this must also be partly responsible for
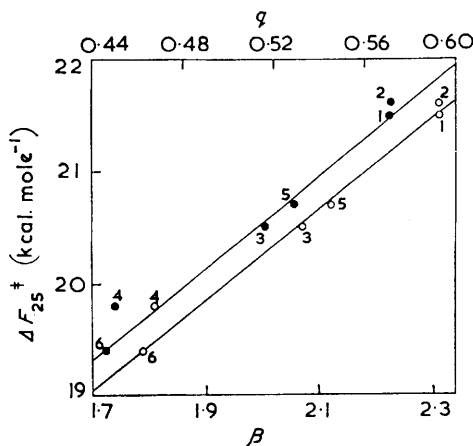

FIG. 1. Solvolysis of 9-aryl-9-chlorofluorenes in ethanol–acetone (9 : 1 v/v). $\Delta F_{25}^{\ddagger}$ against: ○ Dewar's relative activation energies (units of β); ● partial charge on side-chain carbon atoms (electron units, *q*). 9-Aryl groups: 1, phenyl; 2, 3-biphenylyl; 3, 4-biphenylyl; 4, 1-naphthyl; 5, 2-naphthyl; 6, 9-phenanthryl.
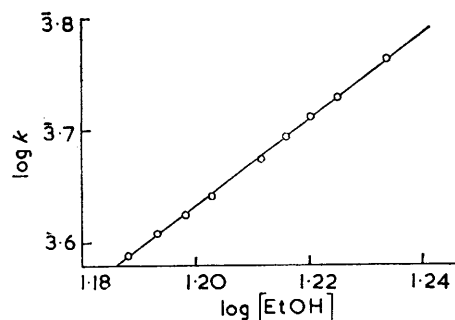
FIG. 2. Solvolysis of 9-chloro-9-(1-naphthyl)fluorene in ethanol–acetone (9 : 1 to 10 : 0 v/v), at 10°; [EtOH] in moles l.$^{-1}$.

the observed facts. The limited facilitating effect of *o*-methoxyl, compared to the *para*-group, we attribute mainly to steric inhibition of the conjugation necessary for the facilitating effect, and to steric compression in the transition state, in addition to the usual weakening of the conjugative effect from the *ortho*-position.

We now consider the effect of replacing the 9-phenyl group by 9-(3- or 4-biphenylyl), 9-(1- or 2-naphthyl), or 9-(9-phenanthryl). The electron-attracting effect of *m*-phenyl is shown in the result for the 3-biphenylyl compound. The enhanced reactivity of the remaining compounds in the series reveals the increased delocalisation of positive charge in the carbonium ion which is made possible by an extension of the conjugated ring system. All these results are usefully interpreted in terms of Dewar's[20a] relative activation energies, or in terms of the partial charge on the side-chain carbon atoms of ions of the type $ArCH_2^+$ (calculated by Longuet-Higgins[21]), as shown in Fig. 1. With the sole exception of

[19] Chapman, Shorter, and Utley, *J.*, 1962, 1824.

[20] (a) Dewar, *Progr. Org. Chem.*, 1953, **2**, 23; (b) Dewar and Sampson, *J.*, 1956, 2789; 1957, 2946, 2952.

[21] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

the 1-naphthyl group, a good linear relation is displayed between $\Delta F_{25}^{\ddagger}$ and the relative activation energy in units of β, the resonance integral, or between $\Delta F_{25}^{\ddagger}$ and q, the partial charge on $ArCH_2^+$ in electron units. Dewar calculated the approximate relative activation energies for substitution (electrophilic, nucleophilic, or free radical) at different positions of a series of aromatic hydrocarbons, by assuming that in the transition state the carbon atom undergoing attack was "localised," *i.e.*, its hybridisation was changed from sp^2 to sp^3. Application of perturbation theory to the relevant molecular orbital treatment of the problem gave the results sought. The applicability of the results of these calculations, which can be judged from Fig. 1, to the solvolyses under investigation, requires, in the limit, that the interaction between the central (carbonium) carbon of the transition state and the attached 9-aryl substituent be essentially similar in character to the localisation described above. There is an important difference insofar as, for example, C-1 in the naphthyl residue in carbonium ion (II) is still sp^2-hybridised, but it is intuitively acceptable that the lower the energy of structures of type (I) the more effective will be the conjugation between the carbonium carbon atom and the corresponding 9-aryl group in
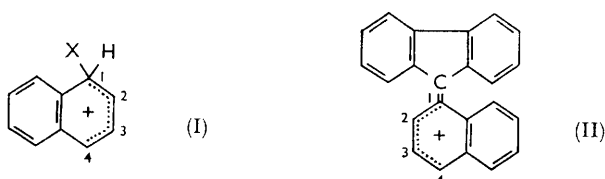
lowering the energy of ions of type (II). It also appears that the structural dependence of the partial charge mentioned above is quantitatively correlated with the difficulty of formation of the 9-aryl-9-fluorenyl cation as measured by $\Delta F_{25}^{\ddagger}$. A further implication of these correlations is that the change in solvation free energy on going from the initial to the transition state is either constant throughout the series of reactions or varies in parallel fashion with the variation of the unsaturation energy, measured by Dewar's relative activation energies, or the variation of the partial charge q. Mason[22] arrived at a conclusion similar to the second alternative, for the ionisation of triarylmethyl chlorides in liquid sulphur dioxide. The deviation from the linear relations of the result for the 1-naphthyl compound is almost certainly steric in origin. Dewar and Sampson[20b] observed similar phenomena for the 1-naphthyl group, which is effectively an *ortho*-substituted phenyl group. However, the point for 9-phenanthryl lies on the line, even though a similar steric effect would be expected.

TABLE 10.

Rate coefficients for solvolysis of 9-halogenofluorenes and diphenylmethyl halides in methanol and in ethanol.

Compound	Solvent	$10^5 k$ (sec.$^{-1}$); temperatures in parentheses
$C_{13}H_9Cl$	MeOH	7·76 (76·6), 10·3 (80·0), 12·3 (82·7), 16·7 (86·2), 19·0 (88·0)
Ph_2CHCl	MeOH	30·5 (16·9), 381 (38·6), 1130 (49·2)
$C_{13}H_9Br$	MeOH	0·814 (38·8), 2·49 (47·9), 4·32 (52·9), 9·65 (60·1)
Ph_2CHBr	MeOH	87·5 (0·5), 238 (8·5), 486 (14·5), 865 (18·9)
$C_{13}H_9Br$	EtOH	0·889 (55·0), 1·43 (60·0), 3·42 (69·2), 92·1 (80·6)
Ph_2CHBr	EtOH	43·6 (16·8), 257 (31·4), 663 (40·0)

Values of k are accurate to $\pm 1\%$.

Solvolysis of 9-Bromo(or chloro)fluorene and Diphenylmethyl Bromide or Chloride in Methanol and in Ethanol.—First-order rate coefficients are given in Table 10 and Arrhenius parameters in Table 11. The diphenylmethyl compounds react several thousand times

[22] Mason, *J.*, 1958, 808.

TABLE 11.

Arrhenius parameters and transition state parameters, at 50°, for solvolysis of
9-halogenofluorenes and of diphenylmethyl halides in methanol and in ethanol.

Compound	Solvent	E (kcal. mole^{-1})	$\Delta H^{\ddagger}$ (kcal. mole^{-1})	log A (sec. units)	$-\Delta S^{\ddagger}$ (e.u.)	$10^5 k_{50}$ (sec.$^{-1}$)	$\Delta F^{\ddagger}$ (kcal. mole^{-1})
$C_{13}H_9Cl$ ...	MeOH	19·5	18·9	8·10	23·6	0·768	26·5
Ph_2CHCl	MeOH	20·8	20·2	12·1	5·3	1230	21·9
$C_{13}H_9Br$ ...	MeOH	23·9	23·3	11·7	7·2	3·12	25·6
Ph_2CHBr	MeOH	19·6	19·0	12·6	3·0	21,900	20·0
$C_{13}H_9Br$ *	EtOH	21·1	20·5	9·0	19·5	0·535	26·8
Ph_2CHBr...	EtOH	21·1	20·5	12·6	3·0	1910	21·5

Values of E and $\Delta H^{\ddagger}$ are accurate to ± 200 cal. mole^{-1}, log A to $\pm 0·2$ unit, and $\Delta S^{\ddagger}$ to ± 1 e.u.

* Second-order reaction (bimolecular mechanism) with piperidine: $E = 14·2$ kcal. mole^{-1}, log A = 7·7, $10^4 k_{20·5} = 10·5$ l. mole^{-1} sec.$^{-1}$.

faster than the 9-fluorenyl compounds under the same conditions. · Indeed, 9-chloro-fluorene seems somewhat less reactive than benzyl chloride, for the ethanolysis of which Kohnstam and Robinson [23] found $10^5 k$ (initial) = 6·7 sec.$^{-1}$ at 80°. The results we obtained for 9-chlorofluorene are not entirely satisfactory, but $10^5 k < 1$ at 80°.

For an assessment of the results in Table 11, the mechanisms of the solvolyses must be known; for diphenylmethyl halides [24] this is S_N1, whereas benzyl halides probably react through a combination of the S_N1 and S_N2 mechanisms,[25] the exact nature of which is still in doubt. We have not been able definitely to establish the mechanism for the solvolysis of the 9-fluorenyl compounds. An attempt to establish a mass-law effect typical of the S_N1 mechanism [12] was complicated by an acid-destroying reaction of the liberated hydrogen halide with the solvent, and the apparent reversibility of the product-forming stage. Other standard tests of mechanism gave ambiguous results. The possibility that the 9-fluorenyl compounds react by a combination of the S_N2 and S_N1 mechanisms indicates that the diphenylmethyl cation is more readily formed than the 9-fluorenyl cation, which is partly to be understood in terms of Hückel molecular orbital theory, Gold [13] having calculated values of $(\Delta U_\pi - \alpha)\beta^{-1}$ (cf. Table 6) for these two of 1·30 and 1·16, respectively, and for benzyl of 0·72. However, the low relative reactivity of the 9-fluorenyl compounds is due mainly to very unfavourable log A values (Table 11), so the situation is more complicated than appears from the values of $(\Delta U_\pi - \alpha)\beta^{-1}$, which lead one to expect a much lower reactivity for benzyl halides than is observed. In view of the mechanistic uncertainties, further discussion of these points is unwarranted at present.

Solvolysis of 9-Chloro-9-(1-naphthyl)fluorene in Ethanol Containing 0—10% v/v of Acetone.—Fig. 2 shows that log k for the above solvolyses at 10° is a linear function of log [EtOH] with a slope of 3·8. The termolecular mechanism suggested by Swain [26] requires the relation, log k = const. + 2 log [EtOH], assuming that ethanol is exclusively the solvating species. Thus, while the predicted linear relation is observed, the discrepancy between the observed and predicted slopes provides evidence against the operation of the termolecular mechanism in this case.

THE UNIVERSITY, HULL. [*Received, December 4th, 1963.*]

[23] Kohnstam and Robinson, *J.*, 1957, 4970.
[24] Ref. 12, p. 325.
[25] Bensley and Kohnstam, *J.*, 1957, 4747.
[26] Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1119.