

**548.** *The Rates of Solvolysis of Certain Arylmethyl Chlorides, and a Simple Molecular-orbital Treatment of This and Similar Reactions.*

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The rates of solvolysis in moist formic acid of a number of arylmethyl chlorides have been measured at 25°. The rates are satisfactorily interpreted in terms of a molecular-orbital treatment, despite several simplifying assumptions.

The experimental rates run closely parallel to those recently reported by Fierens, Hannaert, Van Rysselberge, and Martin<sup>1</sup> \* for the solvolyses in the ternary mixture water-formic acid-dioxan.

A similar molecular-orbital treatment accounts satisfactorily for the  $S_N2$  exchange rates of the same compounds reported by Fierens *et al.*

We have found the reactions in formic acid to be reversible. As well as the first-order rate constants for the forward reactions, the second-order rate constants for the reverse reactions and the corresponding equilibrium constants are reported.

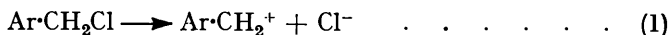
PROGRESS in theoretical organic chemistry is hampered by the lack of data on reactions which can be interpreted quantitatively in terms of current theories. The requirements are that the reaction should have a transition state of clearly defined structure, and that the relative energies of the reactants and of the transition states should be easily calculable. It seemed to us that the solvolysis of arylmethyl chlorides,  $\text{Ar}\cdot\text{CH}_2\text{Cl}$ , might meet these requirements sufficiently. In the first place the solvolysis of such a chloride in a strongly ionizing solvent is likely to be a "limiting" process,<sup>2</sup> and the transition state an ion-pair  $\text{ArCH}_2^+\text{Cl}^-$  without significant covalent bonding between the ions, having the organic fragment  $\text{Ar}\cdot\text{CH}_2^+$  in a definite and known configuration. The relative energy difference between  $\text{Ar}\cdot\text{CH}_2\text{Cl}$  and  $\text{Ar}\cdot\text{CH}_2^+$  will depend upon the  $\pi$ -energy difference between Ar and  $\text{Ar}\cdot\text{CH}_2^+$ ; since these are both alternant hydrocarbons the  $\pi$ -energy difference may be calculated very simply, in terms of a single parameter, by using perturbation theory. Accordingly we have studied the solvolyses of a number of compounds of this type and have compared experimental rates with those predicted.

\* This work was described at the XIVth International Congress of Pure and Applied Chemistry at Zurich in July, 1955. We are grateful to Dr. P. H. Gore for drawing our attention to it, and to Professor R. H. Martin for sending us a manuscript copy of the paper before its publication.

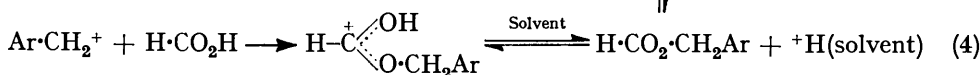
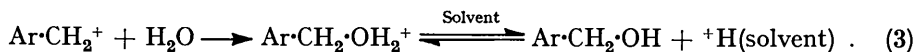
<sup>1</sup> Fierens, Hannaert, Van Rysselberge, and Martin, *Helv. Chim. Acta*, 1955, **38**, 2009.

<sup>2</sup> Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.

*The Nature of the Reaction.*—It being assumed that the solvolysis of arylmethyl chlorides in moist formic acid is a limiting or pure  $S_N1$  process, the rate-determining step is the heterolytic fission:



The carbonium ion so formed may then suffer any one of a number of fates:



where  $\text{Ar}'\text{H}$  is any of the aromatic compounds present.

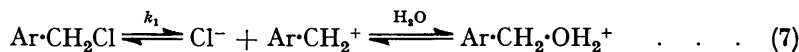
At room temperature and at the concentrations used, the reactions (5) appeared to be much slower than the initial heterolysis, no turbidity being visible until 15—20 half-lives for reaction (1) had passed. Hence the course of the initial heterolysis could be followed without interference from this source.

If the possibility of the formation of the formate, reaction (4) or (3a), is ignored there should exist an equilibrium between arylmethyl chloride and arylmethanol, with an equilibrium constant  $K$  given by:

$$K = [\text{Ar}\cdot\text{CH}_2\text{Cl}][\text{H}_2\text{O}]/[\text{Ar}\cdot\text{CH}_2\cdot\text{OH}][\text{HCl}] \quad . \quad . \quad . \quad (6)$$

For the more reactive compounds this equilibrium appeared to be reached whether the alcohol and gaseous hydrogen chloride, or the arylmethyl chloride, was dissolved in the formic acid.  $K$  was approximately constant even when the magnitude of the water concentration was increased three-fold. It thus appears that the reactions producing formate are relatively slow, or that the alcohol-formate equilibrium strongly favours the alcohol.

Only the initial reaction rates of the less reactive compounds were measured, but there is no reason to suppose that their reactions and equilibria differ in type from those of the more reactive compounds. Accordingly, for simplicity, all the reactions studied may be represented in the following way:



All the kinetic measurements fitted in well with this reaction scheme.

#### EXPERIMENTAL

For chromatography, Peter Spence alumina (type "H") was used. Microanalyses were carried out by the Organic Microanalytical Laboratory, Imperial College of Science and Technology, London, S.W.7.

*Solvents.*—"AnalaR" 98—100% formic acid was used. The water content was determined from the magnitude of the electrical conductance. A calibration curve was constructed by measuring the resistances of samples of formic acid to which weighed proportions of water had been added. The original low water content of the acid used in the calibration was determined by the Karl Fischer method, 1 ml. of the acid being diluted before titration with 5 ml. of methyl alcohol whose small water content was determined separately.

*Starting Materials.*—1-Naphthylmethanol. Lithium aluminium hydride (2.5 g.) was stirred with anhydrous ether (300 ml.) for 15 min., and then methyl 1-naphthoate (21 g.), suspended in anhydrous ether, was slowly added. Stirring was continued for another 15 min. and the excess

of hydride decomposed by moist ether. The solid alkoxides were decomposed by 5*N*-hydrochloric acid (100 ml.). The ether layer was washed with more hydrochloric acid, and then with water. Evaporation under reduced pressure left an almost quantitative yield of nearly pure 1-naphthylmethanol, which recrystallized from benzene and light petroleum (b. p. 40–60°) in needles, m. p. 60.5–61° (lit., 59.5–60°) (Found: C, 83.3; H, 6.5. Calc. for C<sub>11</sub>H<sub>10</sub>O: C, 83.5; H, 6.4%).

The other alcohols described in this paper were prepared from the corresponding esters in the same way. In each case reduction was smooth, and the yield almost quantitative.

**1-Chloromethylnaphthalene.** The alcohol was converted into chloride by Gilman's method.<sup>3</sup> Recrystallization from light petroleum (b. p. 40–60°) gave prisms, m. p. 33° (lit., 32°, 34°) (Found: C, 74.6; H, 5.4; Cl, 19.8. Calc. for C<sub>11</sub>H<sub>9</sub>Cl: C, 74.8; H, 5.1; Cl, 20.1%).

**2-Naphthylmethanol.** The material obtained by reduction of methyl 2-naphthoate recrystallized from light petroleum (60–80°) in plates, m. p. 82° (lit., 80–80.5°) (Found: C, 83.4; H, 6.5%). It gave the chloride by Campbell's method;<sup>4</sup> recrystallized from light petroleum (b. p. 40–60°) this gave plates, m. p. 47.5–48.5° (lit., 47°, 48°) (Found: C, 74.6; H, 5.2; Cl, 20.0%).

**1-Phenanthrylmethanol.** The oxime of 1-benzoylphenanthrene (14 g.) was subjected to the Beckmann rearrangement with phosphorus pentachloride.<sup>5</sup> The resultant mixture of 1-phenanthranilide and 1-benzamidophenanthrene was refluxed for 4 hr. with ethylene glycol (140 g.) and potassium hydroxide (35 g.). After cooling, the mixture was stirred into a large quantity of water, and the aqueous solution extracted with carbon tetrachloride. The aqueous layer was heated to boiling and acidified with 2*N*-hydrochloric acid. The precipitated 1-phenanthroic acid was filtered off and dried (yield, 6.6 g., 60% based on crude oxime).

It recrystallized from acetic acid as needles, m. p. 232–235° (lit., 232–233°). Esterification by the Fischer-Speier method gave methyl 1-phenanthroate (excellent yield), which recrystallized from methanol in needles, m. p. 56.5–57° (lit., 57°). This was reduced in the same way as methyl 1-naphthoate, giving 1-phenanthrylmethanol which recrystallized from benzene in needles, m. p. 165° (lit., 165°) (Found: C, 86.7; H, 5.9. Calc. for C<sub>15</sub>H<sub>12</sub>O: C, 86.5; H, 5.8%).

**1-Chloromethylphenanthrene.** 1-Phenanthrylmethanol (1 g.) was treated in hot benzene (50 ml.) with thionyl chloride (1.6 ml.) dropwise and refluxed for 2 hr. The recovered product was passed in anhydrous carbon tetrachloride through alumina (2 × 2 cm.). The solvent was distilled off and 1-chloromethylphenanthrene was obtained as plates, m. p. 90.5–91° (lit., 89–90°), from absolute alcohol (Found: C, 79.3; H, 5.1; Cl, 15.3. Calc. for C<sub>15</sub>H<sub>11</sub>Cl: C, 79.5; H, 4.9; Cl, 15.6%).

**2-Phenanthrylmethanol.** 2-Phenanthroic acid,<sup>6</sup> needles (from acetic acid), m. p. 259–262° (lit., 258–260°), gave the methyl ester, needles (from methanol), m. p. 97° (lit., 96–96.5°), and thence 2-phenanthrylmethanol, needles [from benzene and light petroleum (b. p. 80–100°)], m. p. 125–125.5° (lit., 125–125.5°) (Found: C, 86.7; H, 5.9%), and 2-chloromethylphenanthrene, plates [from anhydrous benzene and light petroleum (b. p. 60–80°)], m. p. 98–98.5° (lit.,<sup>7</sup> m. p. 98°) (Found: C, 79.6; H, 5.2; Cl, 15.6%).

**3-Chloromethylphenanthrene.** 3-Phenanthrylmethanol (7 g.) in benzene (50 ml.) with thionyl chloride (10 ml.), as above, gave 3-chloromethylphenanthrene, which distilled (yield, 2.5 g.; b. p. 185–195°/0.5 mm.) with considerable polymerization. Recrystallization from benzene-light petroleum (b. p. 60–80°) gave needles, m. p. 87.5° (Fierens *et al.*<sup>7</sup> record m. p. 81–82°) (Found: C, 79.5; H, 5.0; Cl, 15.8%).

**9-Phenanthrylmethanol.** Phenanthrene was brominated<sup>8</sup> and then converted into 9-phenanthryl cyanide;<sup>9</sup> this (20 g.) and potassium hydroxide (5 g.), in hot ethanol (300 ml.), were treated with hydrogen peroxide (100-vol., 30 ml.). Most of the solvent was removed, yielding 9-phenanthramide. Recrystallization from ethanol gave needles, m. p. 222–224° (lit., 226°) (Found: C, 81.4; H, 5.0; N, 6.3. Calc. for C<sub>15</sub>H<sub>11</sub>ON: C, 81.4; H, 5.0; N, 6.3%). The crude amide was refluxed with ethylene glycol (200 ml.) containing potassium hydroxide (50 g.) for 3 hr. After cooling, the mixture was added to water (2 l.) and filtered. The filtrate was treated with excess of 5*N*-hydrochloric acid, and the precipitated 9-phenanthroic acid filtered off

<sup>3</sup> Gilman, *J. Amer. Chem. Soc.*, 1929, **51**, 3475.

<sup>4</sup> Campbell, *J.*, 1940, 820.

<sup>5</sup> (a) Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 555; (b) Bachmann and Boatner, *ibid.*, 1936, **58**, 2097.

<sup>6</sup> (a) Mosettig and Van de Kamp, *ibid.*, 1930, **52**, 3704; (b) 1933, **55**, 2995.

<sup>7</sup> Fierens, Martin, and Van Rysselberge, *Helv. Chim. Acta*, 1955, **38**, 2005.

<sup>8</sup> May and Mosettig, *J. Org. Chem.*, 1946, **11**, 15.

<sup>9</sup> Mosettig, *J. Amer. Chem. Soc.*, 1932, **54**, 3328.

and dried. Recrystallization from acetic acid gave needles, m. p. 249—253° (lit., 250—252°). Methyl 9-phenanthroate and 9-phenanthrylmethanol (Found : C, 86.3; H, 6.0%), prepared as above, and 9-chloromethylphenanthrene, prepared as described by Badger<sup>10</sup> or Campbell<sup>4</sup> (as for 2-chloromethylnaphthalene) (Found : C, 79.6; H, 5.1; Cl, 15.6%), had the properties previously reported.

*Kinetics.*—The reactions were followed conductometrically. The cell was of conventional design with bright platinum electrodes. The bridge was that described by Archer and Hudson,<sup>11</sup> modified by the inclusion of a 100-ohm resistor which, when desired, could be switched in instead of one of the 1000-ohm ratio arms, thus enabling resistances up to ten times that of the fourth arm to be measured. The oscillator and headphone detector were those described by Archer and Hudson,<sup>11</sup> the first being adjusted to produce a sinusoidal signal of 2 v r.m.s. at 1000 cycles/sec. All measurements were made at 25.0°. An oil-thermostat maintaining a temperature constant within  $\pm 0.01^\circ$  was used.

In a run a portion of the material was weighed into a 25 ml. graduated flask, which was then filled up to the mark with the solvent and shaken to achieve dissolution. Concentrations of about  $4 \times 10^{-3}\text{M}$  were generally used, but insolubility of certain of the compounds, *e.g.*, 2-chloromethylphenanthrene, necessitated the use of concentrations down to  $10^{-3}\text{M}$ . The cell was filled with the solution and put into the thermostat. The first resistance measurement was not made until at least 20 min. after the cell was immersed (in static experiments it was found that the resistance became constant after about 15 minutes' immersion).

Calibration curves for the conductance of hydrogen chloride in the solvents used were made by bubbling dry hydrogen chloride into the solvent until the chloride concentration was about 0.05N, as determined by the Volhard procedure. These solutions were then diluted 1 : 10 with the solvent. By mixing suitable volumes of this solution and the solvent, solutions were prepared whose resistances enabled a calibration curve relating conductance and concentration of hydrogen chloride (from 0 to  $5 \times 10^{-3}\text{M}$ ) to be constructed.

The reactions of the more reactive compounds (Ar = 1-naphthyl, 1- and 9-phenanthryl) were followed to equilibrium. The forward rate constants,  $k_1$ , were calculated by the use of the integrated form of the equation for a reaction which is of the first order forwards and of the second backwards :

$$k_1 t = \left( \frac{x_e}{2a - x_e} \right) \ln \frac{ax_e + x(a - x_e)}{a(x_e - x)} \dots \dots \dots (8)$$

where  $a$  = initial concentration of  $\text{Ar}\cdot\text{CH}_2\text{Cl}$ ,  $x$  = concentration of HCl at time  $t$ , and  $x_e$  = concentration of HCl at infinite time.

The values of  $k_2$  were found from the initial rates of removal of hydrogen chloride.

A check on  $k_1$  was made by using the data from the runs starting with  $\text{Ar}\cdot\text{CH}_2\cdot\text{OH} + \text{HCl}$ . In these the concentration of acid removed in reaching equilibrium was small compared with that initially present (about  $5 \times 10^{-3}\text{M}$ ). Hence the process



in any given run was of zero order in acid, giving the appearance of an equilibrium between two first-order processes. For such a system the approach to equilibrium is itself of the first order, of rate constant  $k$ , where :

$$k = k_1 + k_2[\text{HCl}] \dots \dots \dots (10)$$

$k$  was found by the usual first-order law :

$$kt = \ln [a/(a - x)] \dots \dots \dots (11)$$

where  $a$  = concentration of acid removed in attaining equilibrium, and  $x$  = that at time  $t$ . Since  $k$  and  $k_2$  (calculated from the initial rate of removal of acid) were both known,  $k_1$  could be obtained from eqn. (10). The method gave results in satisfactory agreement with those described above.

For the faster-reacting compounds the equilibrium constants,  $K$ , were calculated from the concentrations at equilibrium of the various species.

<sup>10</sup> Badger, *J.*, 1949, 169.

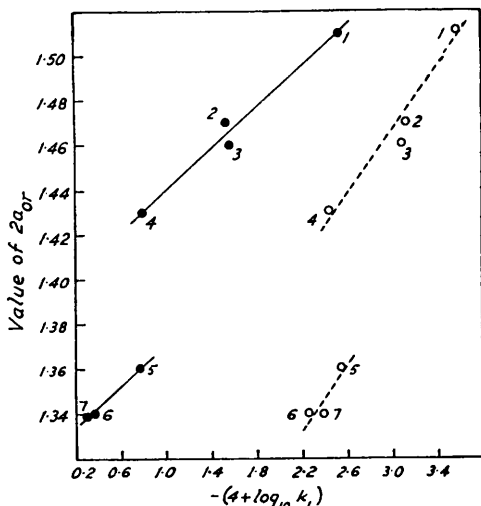
<sup>11</sup> Archer and Hudson, *J.*, 1950, 3259.





resulting from this interference. For the solvolysis in moist formic acid the vertical distance between the lines is  $0.07\beta$ , and so the strain-energy is approximately 2 kcal.

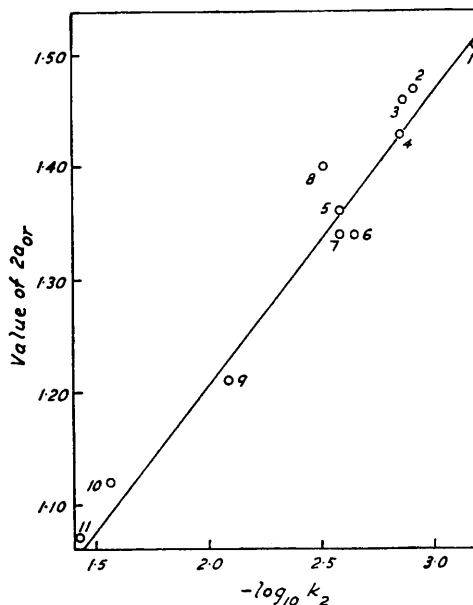
FIG. 1. The relation between the logarithms of the solvolysis rates and the value of  $2a_{or}$ .



● Solvolysis in moist formic acid (solvent III).  
○ Solvolysis in water-formic acid-dioxan (solvent I) (ref. 1).

Ar: 1, Ph; 2, 2-phenanthryl; 3, 2-naphthyl; 4, 3-phenanthryl; 5, 1-phenanthryl; 6, 1-naphthyl; 7, 9-phenanthryl.

FIG. 2. The Relation between the logarithm of the  $S_N2$  exchange rates and the value of  $2a_{or}$ .



Ar: 1-7, as for Fig. 1; 8, 4-phenanthryl; 9, 3-pyrenyl; 10, 1:2-benz-10-anthryl; 11, 9-anthryl.

For the solvolysis in the water-formic acid-dioxan mixture the value obtained for  $\beta$  is 20 kcal., and the strain-energy of the ion is about 1.5 kcal.

In the Table both our results and those of Fierens *et al.*<sup>1</sup> are collected. The value of the

Rates \* and equilibrium constants at 25°.

Ar	$2a_{or}$	$10^5 k_1$		$10^5 k_2$		K		$10^7 k_1 \dagger$	$k_1 \dagger$	$10^5 k_2 \dagger$
		Solvent III	Solvent IV	Solvent III	Solvent IV	Solvent III	Solvent IV	Solvent I	Solvent II	$S_N2$ exchange
Phenyl	1.51	0.029 <sup>a</sup>	—	—	—	—	—	0.25	—	0.51
2-Phenanthryl	1.47	0.28	0.32	4.3	1.7	5.9	6.2	0.75	—	1.2
2-Naphthyl	1.46	0.26	0.29	3.9	1.5	5.7	6.1	0.81	—	1.4
3-Phenanthryl	1.43	1.6	1.9	26	8.3	6.1	5.2	3.5	—	1.4
4-Phenanthryl	1.40	—	—	—	—	—	—	17	—	3.1
1-Phenanthryl	1.36	1.7	1.8	27	9.5	6.1	6.3	2.8	$3.2 \times 10^{-8}$	2.6
1-Naphthyl	1.34	4.4	4.8	61	21	5.3	5.1	5.5	$4.9 \times 10^{-8}$	2.3
9-Phenanthryl	1.34	4.9	5.2	77	25	6.0	5.3	4.2	$4.4 \times 10^{-8}$	2.6
3-Pyrenyl	1.21	—	—	—	—	—	—	—	$3.5 \times 10^{-5}$	8.4
1:2-Benz-10-anthryl	1.12	—	—	—	—	—	—	—	$4.5 \times 10^{-5}$	27
9-Anthryl	1.07	—	—	—	—	—	—	—	$6.9 \times 10^{-3}$	38

\* First-order rate constants  $k_1$  are expressed in  $\text{sec}^{-1}$ ; second-order rate constants  $k_2$  are expressed in  $\text{mole}^{-1} \text{l. sec}^{-1}$ . Rate constants are considered to be accurate to  $\pm 5\%$ , and equilibrium constants to  $\pm 10\%$ .

Solvent III: Moist formic acid (0.38M-water).

Solvent IV: Moist formic acid (1.2M-water).

Solvent I: Water, 6.1%; formic acid, 54.1%; dioxan, 39.8%.

Solvent II: Water, 5.8%; formic acid, 34.0%; dioxan, 60.2%.

The rate-constants  $k_2$  for  $S_N2$  exchange refer to substitution by iodide ion in anhydrous acetone.

<sup>a</sup> This value is taken from Evans and Hamann (*Trans. Faraday Soc.*, 1951, **47**, 25). It refers to solvent "almost absolute formic acid" (m. p. 8.2°).

<sup>†</sup> These rate constants are from Fierens *et al.*

equilibrium constant  $K$  is seen to vary but little with water concentration, and its constancy for all the compounds suggests that there is no additional strain effect in the molecule  $\text{Ar}\cdot\text{CH}_2\text{Cl}$  when a *peri*-hydrogen atom is present.

In Fig. 2 the values of  $\log k_2$  obtained by Fierens, Hannaert, Van Rysselberge, and Martin<sup>1</sup> for the  $S_N2$  exchange of  $\text{Ar}\cdot\text{CH}_2\text{Cl}$  with iodide ion in anhydrous acetone are plotted against  $2a_{or}$ . The points all fall close to a line without differentiation between "benzene," "1-naphthalene," or "9-anthracene" positions, although 4-chloromethylphenanthrene is anomalous. Fierens, Hannaert, Van Rysselberge, and Martin<sup>1</sup> have discussed this anomaly in steric terms. In the most likely transition state for  $S_N2$  exchange the carbon atom of the side-chain is only partly conjugated with Ar, for the groups I and Cl are covalently attached to it. The value  $\beta = 5$  kcal. obtained from the slope of the line is in full agreement with this idea. Since in the most probable transition state for this reaction the extracyclic carbon atom is in only slight conjugation with Ar there will be much less shortening of the Ar-C bond than in the ion  $\text{Ar}\cdot\text{CH}_2^+$ , and so the steric strain met with in the latter will not be important here. This accounts for the single line of Fig. 2.

The uniformity of mechanism throughout the series of compounds studied in the  $S_N2$  exchange reaction is confirmed by the linear relation between  $2a_{or}$  and  $\log k_2$ . Any change in mechanism would presumably lead to the potential conjugative ability's being used to a varied extent, and thus to a curve rather than a straight line. Uniformity of mechanism for the solvolysis reaction in moist formic acid and in the water-formic acid-dioxan mixture seems probable for the same reason.

The changes in the value obtained for  $\beta$  for these substitutions in varied environments are of great interest. For some time it has been appreciated that, although for the most part nucleophilic substitution reactions fall clearly into two kinetic classes ( $S_N1$  and  $S_N2$ ), there is no clear mechanistic classification.<sup>2,16</sup> Gleave, Hughes, and Ingold<sup>16</sup> have said that the pure  $S_N1$  and  $S_N2$  mechanisms are "extremes of a graded range," and "there must be *degrees* of collaboration by the reagent." The more nearly complete the formation of an ion of the type  $\text{Ar}\cdot\text{CH}_2^+$ , the greater will be the conjugation of the portion Ar with the extracyclic carbon atom, and the greater will be the value obtained for  $\beta$ . By carrying out the series of reactions in a number of different environments the nucleophilicity of those environments may be correlated with the value of  $\beta$ ; the greater  $\beta$ , the lower is the nucleophilicity.

In slightly moist formic acid it appears that the mechanism approaches closely to "limiting," for the rates when the water concentration is 1.2M show an almost negligible increase over those when it is 0.38M, and so the value of  $\beta$  is the same in both cases. However in the solvent used by Fierens, Hannaert, Van Rysselberge, and Martin<sup>1</sup> (water 6%, formic acid 54%, and dioxan 40%) the value of  $\beta$  falls from 30 to 20 kcal., showing some measure of participation by water in the transition state. When the substitution is carried out in anhydrous acetone with iodide ion,  $\beta$  falls to 5 kcal., indicating strong participation by the nucleophilic reagent.

A further example of a diagnostic use of the value for  $\beta$  has recently arisen in connection with the electrophilic substitution of aromatic hydrocarbons. For such reactions Wheland<sup>17</sup> postulated a transition state in which the carbon atom undergoing substitution adopts an  $sp^3$  tetrahedral configuration, being thereby removed from conjugation with the rest of the aromatic ring system, which bears the positive charge. Bavin, Warford, and Mole in this Laboratory find that the relative rates of nitration can be correlated with a simple molecular-orbital treatment of the Wheland postulate, provided that  $\beta$  is assigned the value of about 6 kcal. The most reasonable interpretation of this value for  $\beta$  is that the carbon atom undergoing substitution is only partly removed from conjugation in the transition state.

It seems that  $\beta$  is most usefully regarded as a parameter whose value for a given reaction may permit deduction of information about the transition state of that reaction.

*The Significance of Experimental Activation Energies.*—We have shown that if the entropy of activation is regarded as constant, a remarkable correlation between theory and

<sup>16</sup> Gleave, Hughes, and Ingold, *J.*, 1935, 236.

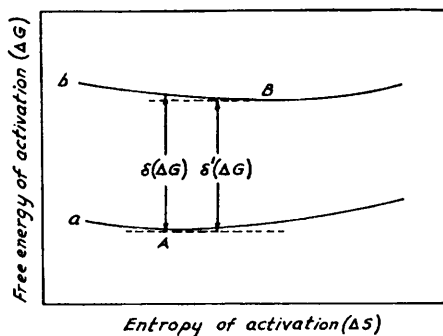
<sup>17</sup> Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.



rate exists in some substitution reactions. Fierens, Hannaert, Van Rysselberge, and Martin<sup>1</sup> have however determined the entropies of activation for the solvolysis of  $\text{Ar}\cdot\text{CH}_2\text{Cl}$  in water-dioxan-formic acid and they are far from constant, there being no obvious correlation between the experimental and calculated activation-energy differences. Similar cases occur in the literature.

Some time ago Evans and Polanyi<sup>18</sup> gave reasons for believing that it would be more correct to correlate calculated activation energies with observed rates of reaction rather than with observed activation energies. The following argument shows in a simple manner how such a situation could arise for reactions in solution. Consider a reaction in solution which can take place by any of a continuously variable set of paths, and plot the entropy of activation ( $\Delta S$ ) for each possible path against the corresponding free-energy of activation ( $\Delta G$ ). The main factor influencing the entropy of activation will be the solvation of the

FIG. 3.



reactants and transition state. Any increase in solvation in passing from the reactants to the transition state will decrease the entropy of activation and will also decrease the heat of activation. The former effect will decrease the free energy of activation, and the latter effect will increase it. Consequently the effects will tend to compensate each other, and the free energy of activation may be relatively insensitive to the reaction path ( $a$  in Fig. 3). The path actually followed will be that which minimises the free energy of activation ( $A$  in Fig. 3). Consider now the corresponding reaction of a related compound (point  $B$  on curve  $b$  in Fig. 3). The actual difference in free energy of activation is  $\delta'(\Delta G)$ , and that deduced on the assumption of a constant entropy of activation (e.g., both reactions constrained to the path which is actually taken by  $A$ ) is  $\delta(\Delta G)$ . Since the curves are flat, the calculated value of the free energy of activation approximates closely to the actual value; in other words, the neglect of entropy effects will be satisfactory so long as predicted activation energies are compared with observed rates of reaction rather than with observed activation energies.

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<sup>18</sup> Evans and Polanyi, *Trans Faraday Soc.*, 1936, **32**, 1333.