312. *The Neutral Hydrolysis of Some Allyl and Benzyl Halides.*

By R. E. Robertson and J. M. W. Scott.

The rates of hydrolysis of benzyl chloride and allyl chloride, bromide, and iodide have been measured over a wide range of temperature. The derived pseudo-thermodynamic parameters for the activation process, when considered in conjunction with those derived from structurally related saturated compounds, suggest that resonance contributions to the transition state are relatively small. Evidence indicates that the transition state for these reactions in water, while being highly polar, is essentially that of a bimolecular displacement reaction.

The solvolysis of allyl and arylmethyl halides has frequently been investigated,[1-10] and more recently that of the arylmethyl halides has been used in testing aspects of theories of organic reactivity derived from the quantum theory.[2,4,11] This communication presents precise data for the hydrolysis of benzyl chloride, and allyl chloride, bromide, and iodide, representing part of a comprehensive study of the hydrolysis of simple organic halides [12] with a view to a critical examination of the current theories of nucleophilic substitution by means of the parameters $\Delta S^\ddagger$, $\Delta H^\ddagger$ and $\Delta C_p^\ddagger$ which characterize the activation process.

Experimental

Benzyl chloride (Eastman Kodak) was passed through alumina and fractionated twice with liberal rejection of initial and tail fractions; it had b. p. 51—52°/4 mm.; n_D^{23} 1·5374 (lit., 1·5375).

The allyl halides (Eastman Kodak) were fractionated twice with liberal rejection of initial and tail fractions; the chloride had b. p. 44·5—45°/760 mm. (lit., 44·6°), the bromide b. p. 69·5°/760 mm. (lit., 71·3°), and the iodide b. p. 98·0°/760 mm. (lit., 99·3°).

The reproducible Guggenheim plots obtained from the rate determinations [13] provided a very sensitive check as to the kinetic homogeneity of each compound. All samples were stored over silica gel, usually in the dark, especially allyl iodide which is very prone to decomposition; samples showing the colour of iodine gave solvolysis rates identical with those of freshly purified material. Samples not ultimately showing such a colour could not be prepared.

Solutions.—Solutions were prepared from the appropriate organic halide and a backing electrolyte (0·001M), which was prepared from deionized water and the potassium halide corresponding to the organic halide being studied. Before a run the appropriate weight or volume of organic halide was added to a suitable volume of backing electrolyte to give a solution (*ca.* 0·001M) which was then rapidly degassed and introduced into the conductance cells. For allyl chloride and bromide, where degassing subsequent to mixing might seriously alter the concentration of the solute, the technique was modified. A suitable quantity of organic halide was frozen in a side arm attached to a flask containing backing electrolyte which was then degassed. When degassing was complete the flask and side arm were isolated from the pumping line and the side arm was gently warmed, resulting in the solution of the organic halide.

Rate Determinations.—The rates were determined as previously described [13] in Kohlrausch conductance cells with shiny platinum electrodes. The dimensions of the cells were adjusted to give resistances of 1—30 kΩ at 1 kc. over the concentration and temperature ranges

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[1] Vernon, *J.*, 1954, 243, 4462, and references therein.
[2] Fierens and Berkowitch, *Tetrahedron*, 1957, **1**, 129, and references therein.
[3] Berliner and Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849.
[4] Dewar and Sampson, *J.*, 1956, 2924; 1957, 2789.
[5] Olivier, *Rec. Trav. chim.*, 1934, **53**, 891.
[6] Wilputte-Steinert and Fierens, *Bull. Soc. chim. belges*, 1956, **65**, 736.
[7] Robertson and Laughton, *Canad. J. Chem.*, in the press.
[8] Fierens and Kruys, *Bull. Soc. chim. belges*, 1956, **65**, 736; 1955, **64**, 542.
[9] Evans and Hamman, *Trans. Faraday Soc.*, 1951, **47**, 25.
[10] Bensly and Kohnstam, *J.*, 1957, 4747; 1956, 287.
[11] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341, 3345, 3350, 3353, 3355, 3357.
[12] Barnard, Heppolette, Robertson, and Scott, unpublished results.
[13] Robertson, *Canad. J. Chem.*, 1955, **33**, 1536.

investigated. Temperatures were controlled to ±0·005° and were measured with a platinum resistance thermometer in conjunction with a Leeds–Northrup 8069 Mueller bridge. The platinum resistance thermometer was calibrated by the National Research Council Heat Laboratories. The rate data so determined are recorded in Tables 1—4 together with the root-mean-square deviation from n separate first-order plots. The temperature dependence of the rates could be expressed within the experimental error by the equation

$$\log k = A/T + B \log T + C \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

TABLE 1. *Rates of hydrolysis of benzyl chloride.*

Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n	Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n
65·013°	92·71 ± 0·13	92·22	−0·0023	3	40·008°	7·659 ± 0·012	7·656	−0·00024	4
60·002	58·63 ± 0·17	58·23	−0·0030	8	35·002	4·366 ± 0·005	4·367	+0·00013	3
55·006	36·04 ± 0·07	36·15	+0·0012	6	30·011	2·437 ± 0·013	2·437	−0·0007	3
54·998	35·99 ± 0·11	36·10	+0·0013	4	20·029	0·7028 ± 0·0019	0·7031	+0·00019	4
49·988	21·96 ± 0·07	21·95	−0·0002	9	14·968	0·3562 ± 0·002	0·3592	+0·0036	3
45·001	13·12 ± 0·04	13·12	−0·00045	4					

$\Delta^{\ddagger} = \log k$ (calc.) − $\log k$ (obs.).

TABLE 2. *Rates of hydrolysis of allyl chloride.*

Temp.	10^5k (obs. (sec.$^{-1}$)	10^5k (calc. (sec.$^{-1}$)	$\Delta^{\ddagger}$	n	Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n
84·990°	68·41 ± 0·23	68·30	−0·00071	3	65·006°	11·48 ± 0·02	11·49	+0·00062	8
82·467	55·45 ± 0·30	55·37	−0·00062	4	60·036	7·050 ± 0·012	7·045	−0·00029	4
80·023	44·96 ± 0·06	45·03	+0·00069	3	54·996	4·194 ± 0·008	4·230	+0·0037	4
77·497	36·03 ± 0·065	36·19	+0·0018	4	50·024	2·473 ± 0·005	2·470	−0·00028	4
74·990	29·08 ± 0·11	29·02	−0·00098	4	40·002	0·7908 ± 0·0021	0·7893	−0·00083	4
69·919	18·32 ± 0·02	18·30	−0·00050	4	34·997	0·4294 ± 0·0017	0·4300	+0·00063	3

TABLE 3. *Rates of hydrolysis of allyl bromide.*

Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n	Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n
65·007°	142·3 ± 0·2	141·8	−0·0015	6	39·955°	10·77 ± 0·01	10·74	−0·0011	4
59·999	88·96 ± 0·43	88·51	−0·0022	4	35·063	6·057 ± 0·009	6·054	−0·0002	4
54·983	54·21 ± 0·07	54·06	−0·0012	4	30·052	3·268 ± 0·009	3·269	+0·0001	4
51·006	36·13 ± 0·09	35·97	−0·0019	4	25·005	1·698 ± 0·005	1·712	+0·0035	4
50·886	35·63 ± 0·05	35·52	−0·0013	3	20·036	0·8710 ± 0·001	0·8768	+0·0029	3
50·002	32·39 ± 0·07	32·40	+0·0015	4	14·997	0·4294 ± 0·001	0·4312	+0·0018	3
44·987	18·88 ± 0·06	18·90	+0·0005	4					

TABLE 4. *Rates of hydrolysis of allyl iodide.*

Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n	Temp.	10^5k (obs.) (sec.$^{-1}$)	10^5k (calc.) (sec.$^{-1}$)	$\Delta^{\ddagger}$	n
75·013°	129·7* ± 0·7	124·5	—	3	55·037°	16·61 ± 0·05	16·62	+0·0002	6
72·449	100·0* ± 0·2	97·82	—	6	49·995	9·541 ± 0·012	9·525	−0·0007	4
70·011	78·02 ± 0·24	77·47	−0·0031	4	45·025	5·381 ± 0·011	5·366	−0·0012	6
67·595	60·61 ± 0·12	61·18	+0·0040	6	40·023	2·924 ± 0·012	2·937	+0·0019	8
64·994	46·84 ± 0·13	47·26	+0·0038	6	29·986	0·8668 ± 0·0065	0·8108	+0·0021	4
63·483	36·80 ± 0·07	36·62	−0·0021	8	24·967	0·4103 ± 0·0012	0·4086	−0·0018	6
59·992	28·56 ± 0·065	28·29	−0·0041	8					

* Not used in computing A, B, and C by least-squares method for reasons given on p. 1598.

TABLE 5. *Constants and derived parameters from the three-parameter equation* (1) *for benzyl chloride and allyl chloride, bromide, and iodide.*

	Benzyl chloride	Allyl chloride	Allyl bromide	Allyl iodide
A	−7306·022	−8345·295	−8794·772	−8304·459
B	−19·30920	−24·18912	−28·72687	−22·55956
C	67·40443	81·91612	95·81302	78·28866
$\Delta C_p^{\ddagger}$	−40·4	−50·1	−59·1	−46·7
$\Delta H_0^{\ddagger}$	33·430	38·185	40·242	37·999
$\Delta S_0^{\ddagger}$	220·85	277·47	332·12	264·32

$\Delta C_p^{\ddagger}$ in cal. mole^{-1} deg.$^{-1}$; $\Delta H_0^{\ddagger}$ in kcal. mole^{-1}; $\Delta S_0^{\ddagger}$ in cal. mole^{-1} deg.$^{-1}$.

The values of A, B, and C for each individual compound were determined by the method of least squares. By adopting the usual convention,[14]

$$A = -\Delta H_0^{\ddagger}/2{\cdot}3026\boldsymbol{R} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$B = \Delta C_p^{\ddagger}/\boldsymbol{R} + 1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$C = (\Delta S_0^{\ddagger} - \Delta C_p^{\ddagger})/2{\cdot}3026\boldsymbol{R} + \log \boldsymbol{k}/\boldsymbol{h} \quad . \; . \; . \; . \; . \quad (4)$$

where
$$\Delta H_T^{\ddagger} = \Delta H_0^{\ddagger} + \Delta C_p^{\ddagger} T \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

and
$$\Delta S_T^{\ddagger} = \Delta S_0^{\ddagger} + 2{\cdot}3026\Delta C_p^{\ddagger} \log T \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

we converted empirical quantities A, B, and C into the pseudo-thermodynamic parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta C_p^{\ddagger}$. Values of A, B, and C appropriate to each compound are recorded in Table 5 together with the derived values of $\Delta H_0^{\ddagger}$, $\Delta S_0^{\ddagger}$, and $\Delta C_p^{\ddagger}$. Values of $\Delta H_T^{\ddagger}$ and $\Delta S_T^{\ddagger}$ at 0°, 25°, 50°, and 100° are recorded in Table 6.

FIG. 1. *Allyl chloride* ▽, *allyl bromide* □, *allyl iodide* ●, *benzyl chloride* ○.

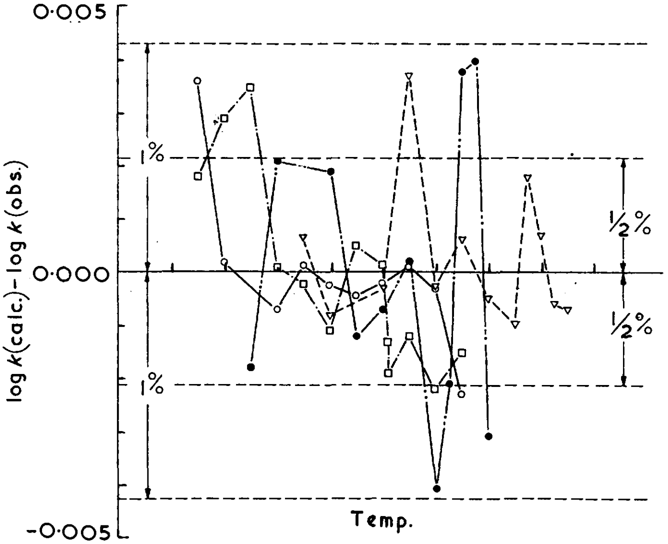

TABLE 6. *Enthalpies and entropies of activation for benzyl chloride and allyl chloride, bromide, and iodide at various temperatures.*

	Benzyl chloride		Allyl chloride		Allyl bromide		Allyl iodide	
Temp.	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
0·00°	22·41	−5·56	24·51	−3·34	24·11	0·73	25·25	2·51
25·00	21·40	−9·09	23·26	−7·73	22·63	−4·46	24·08	−1·58
50·00	20·39	−12·34	22·01	−11·76	21·15	−9·20	22·91	−5·34
75·00	19·38	−15·35	20·76	−15·49	19·68	−13·61	21·74	−8·82
100·00	18·37	−18·15	19·51	−18·96	18·20	−17·71	20·58	−12·05

$\Delta S^{\ddagger}$ is in cal. mole^{-1} deg.$^{-1}$. $\Delta H^{\ddagger}$ is in kcal. mole^{-1}.

Errors and Previous Results.—In Fig. 1 the function log k (calc.) − log k (obs.) is plotted against temperature. The deviations are quite random and are usually $<\frac{1}{2}\%$ except for allyl iodide where they are somewhat greater. Allyl iodide was the most difficult to investigate for reasons which are not completely understood. At the end of some of the determinations the reaction solutions were coloured, and the colour was proved to be due to free iodine. Such coloration was especially prevalent in the high-temperature region and was perhaps due to the incursion of some free-radical process.

Robertson, *J. Chem. Phys.*, 1956, **25**, 375.

TABLE 7. *Previously reported results for the hydrolysis of benzyl chloride.*

Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc.) * (sec.$^{-1}$)	Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc.) * (sec.$^{-1}$)
30°	5	$2\cdot42 \times 10^{-5}$	$2\cdot43 \times 10^{-5}$	40·00°	6	$7\cdot76 \times 10^{-5}$	$7\cdot66 \times 10^{-5}$
25	2	$1\cdot38 \times 10^{-5}$	$1\cdot32 \times 10^{-5}$	47·10	6	$1\cdot61 \times 10^{-4}$	$1\cdot63 \times 10^{-4}$
20·02	6	$7\cdot65 \times 10^{-6}$	$7\cdot31 \times 10^{-6}$	60·000	7	$5\cdot828 \times 10^{-4}$	$5\cdot823 \times 10^{-4}$
30·00	6	$2\cdot51 \times 10^{-5}$	$2\cdot43 \times 10^{-5}$				

* Calculated from the above three-parameter equation: so also in Tables 8 and 9.

TABLE 8. *Previously reported results for the hydrolysis of allyl chloride.*

Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc.) * (sec.$^{-1}$)	Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc.) * (sec.$^{-1}$)
19·10°	8	$5\cdot36 \times 10^{-7}$	$5\cdot22 \times 10^{-7}$	50·00°	8	$2\cdot62 \times 10^{-5}$	$2\cdot46 \times 10^{-5}$
25·00	8	$1\cdot11 \times 10^{-6}$	$1\cdot18 \times 10^{-6}$			$2\cdot74 \times 10^{-5}$	
40·00	8	$8\cdot34 \times 10^{-6}$	$7\cdot89 \times 10^{-6}$	74·989	7	$2\cdot948 \times 10^{-4}$	$2\cdot90 \times 10^{-4}$

TABLE 9. *Previously reported results for the hydrolysis of allyl bromide.*

Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc.) (sec.$^{-1}$)	Temp.	Ref.	k (obs.) (sec.$^{-1}$)	k (calc. (sec.$^{-1}$)
15·00°	8	$4\cdot21 \times 10^{-6}$	$4\cdot32 \times 10^{-6}$	51·00°	8	$3\cdot47 \times 10^{-4}$	$3\cdot60 \times 10^{-4}$
25·00	8	$1\cdot62 \times 10^{-5}$	$1\cdot71 \times 10^{-5}$	60·00	7	$8\cdot94 \times 10^{-4}$	$8\cdot85 \times 10^{-4}$
40·00	8	$1\cdot06 \times 10^{-4}$	$1\cdot08 \times 10^{-4}$				

In Tables 7—9 previous results for the rates of hydrolysis of benzyl chloride, allyl chloride, and allyl bromide in water are recorded [k (obs.)], together with rates calculated [k (calc.)] from the appropriate three-parameter equation. These results are in satisfactory agreement with our own.

DISCUSSION

The method of proceeding from the parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta C_p^{\ddagger}$ to conclusions regarding the properties of the transition state is not clear. Winstein [15] has noted that these parameters do not provide a sufficient basis for the systematization of the effect of structure on reactivity, without allied initial-state data. A similar viewpoint has been adopted by Moelwyn-Hughes [16] and a detailed discussion made by Robertson, Heppolette, and Scott.[17] Evans and Hamman [9] noted a parallelism between the entropy of ionization for amines and the entropy of activation for structurally related solvolytic substrates, *e.g.*, trimethylamine and t-butyl chloride, etc. These relationships were considered to demonstrate the similarity in solvation between ammonium and carbonium ions. Kohnstam [10] has suggested that the ratio $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ can be used as diagnostic of mechanism but the basis of this test has not been clearly stated. By using the method adopted in this communication for converting A, B, and C of equation (1) into $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta C_p^{\ddagger}$, Kohnstam's ratio becomes

$$\Delta C_p^{\ddagger}/\Delta S^{\ddagger} = \Delta C_p^{\ddagger}/(\Delta S_0^{\ddagger} + \Delta C_p^{\ddagger} \ln T) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For all the substrates [12] where the parameters $\Delta S_0^{\ddagger}$ and $\Delta C_p^{\ddagger}$ have been determined, the former has always been positive and the latter negative. In consequence, the denominator of equation (7) will become zero when $T = \exp(-\Delta S_0^{\ddagger}/\Delta C_p^{\ddagger})$ and the ratio infinite. Below this temperature $\Delta S^{\ddagger}$ is positive and above it negative, so as well as displaying a discontinuity the ratio will also change sign. Two of the compounds reported in this paper behave in this way between 0° and 100°, as do several others for which data are available.[7] It is difficult to envisage the physical significance of a ratio which behaves in this manner. The fact that the entropy of activation changes sign within the range of experimental investigation also makes the sign and magnitude of this quantity difficult to interpret. In consequence, the most satisfactory way of using the available entropy

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[15] Winstein and Fainburg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[16] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **220**, 386.

[17] Robertson, Heppolette, and Scott, *Canad. J. Chem.*, 1959, **37**, 803.

data appears to be to discuss changes in $\Delta S^{\ddagger}$ with variations in the structure of the substrate.*

Heat Capacities of Activation.—The heat capacities of activation for the four organic halides now reported are all negative, in conformity with previous studies in water, alcohol, and mixed solvents.[10,13,17] These heat-capacity changes are of the same sign and magnitude as those derived from studies of the ionization of weak acids.[18] The latter is an unambiguous ionogenic reaction and in consequence the heat capacity is in the present study suggestive of an ionization. These heat capacities of activation do not show the same kind of relation as are found between the free energy, enthalpy, and entropy of activation for the methyl and allyl series (see below). This parameter, however, is obtained from the second differential of the rate with respect to temperature and so is the least accurate of the derived parameters. Alternatively, the heat capacities of activation may reflect finer differences in the activation process to which the free energy and enthalpy are insensitive.

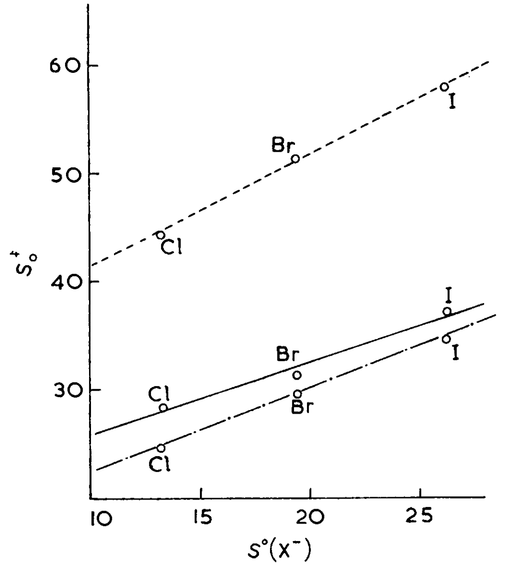

FIG. 2.
. . . . s-Pr; —— Me; —·—·— Allyl.
Temp. 298·16°.

Entropy of Activation.—It was noted on p. 1599 that the pseudo-thermodynamic parameters which characterize the activation process do not provide a sufficient basis for the discussions of differences in transition states of solution reactions. Robertson, Heppolette, and Scott [17] have suggested that the equation

$$S^{0}_{\ddagger} = S_{g}^{0} + \delta_{g}S + \Delta S^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

can be used to characterize the transition state. Unfortunately, in the present instance only $\Delta S^{\ddagger}$ of the terms on the right-hand side of equation (8) is known and hence some means

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* This is part of a wider problem presented by the data which are reported. The quantities $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$ probably have no significance but are artifacts arising from the convention used for converting *A*, *B*, and *C* of our empirical equation (1) into pseudo-thermodynamic parameters. A similar situation arises with the parameters obtained from studies of the dissociation constants of weak acids over a wide temperature range (cf. Everett and Wynne-Jones [18]). However, the quantities $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at any temperature between 0° and 100° are considered to have significance. The temperature dependence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is a consequence of heat-capacity terms (see below and Table 6) and requires the choice of some arbitrary temperature for their comparison. For water this is logically 50°, although this will not always coincide with the temperature of optimum accuracy of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for individual substrates, which is the middle point of experimental range over which the temperature dependence of the rate is determined.

[18] Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

of estimating S_g^0 and $\delta_s S$ are necessary. The initial-state data for the methyl halides where S_g^0 and $\delta_s S$ are known, can be used for the allyl halides.[12] $S_\ddagger^0$ for the methyl and the s-propyl halides is linearly related to the standard-state entropy S^0 (X⁻) of the corresponding halide ion: see ref. (17) and Fig. 2.

$$S_\ddagger^0 = mS^0\,(\mathrm{X}^-) + c \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

A similar relation holds for the allyl chloride, bromide, and iodide, the value of m being intermediate between that found for the methyl and the s-propyl halides. Superficially, the value of m could be considered to indicate the charge development in the transition state,[17] but such a direct interpretation of the variation of m with the nature of the organic group needs further consideration.

The standard-state entropy of a monatomic ion can be divided into three parts, and several equations have been suggested for this purpose. For reasons which have been stated elsewhere,[17] the equation due to Laidler [19] will be adopted:

FIG. 3.

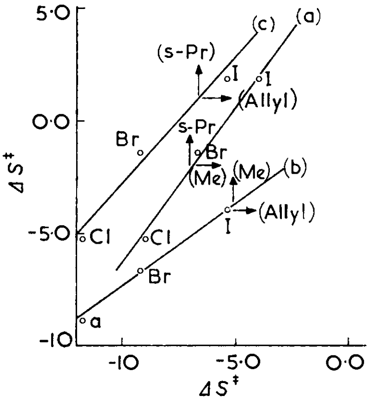
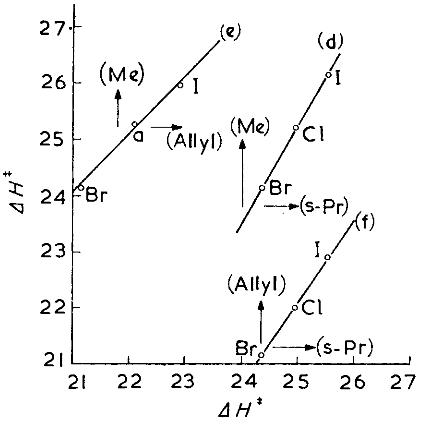


FIG. 4.



$$S^0\,(\mathrm{X}^-) = \tfrac{3}{2}\boldsymbol{R}\ln M - Aq^2\boldsymbol{e}^2/r_\mathrm{u} + \text{const.} \quad . \; . \; . \; . \; . \quad (10)$$

where q is the charge and $\boldsymbol{e}$ is the electronic charge, A a constant, and r_u the univalent radius of the ion.

The first two terms in equation (10) represent respectively the translational and electrostatic entropy (Born charging) of the ions. If in equation (9) m is equal to unity, this suggests that the ions are completely formed in the transition state, since they must have their full complement of solvating water molecules and also their full ionic translational entropy. However, values of $m < 1$ do not immediately imply that the charge development is less than unity, *i.e.*, the charge development could be unity but the translational entropy might be less than that appropriate to free ions. Whilst the evidence presented here gives little detailed information of what is occurring around the group R (which is part of the molecule where mechanistic questions are important) it does suggest that the positive charge on the organic part must approach unity in the transition state, irrespective of how it is distributed. The entropies of activation as might be expected from equation (9) also give relationships of the form (see Figs. 3 and 4 and Table 11):

$$\Delta S^\ddagger\,(\mathrm{A}) = m\Delta S^\ddagger\,(\mathrm{B}) + \text{const.} \quad . \; . \; . \; . \; . \; . \; . \quad \mathbf{(11)}$$

and similarly for the enthalpy of activation:

$$\Delta H^\ddagger\,(\mathrm{A}) = m'\Delta H^\ddagger\,(\mathrm{B}) + \text{const.}' \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

[19] Laidler, *Canad. J. Chem.*, 1956, **34**, 1107.

where *e.g.*, A = Me and B = Allyl, etc. It is tentatively suggested that these relationships indicate a common mechanistic pattern.

Resonance Contributions to the Transition State: The Free Energy and Enthalpy of Activation.—The benzyl and allyl halides all react faster than the corresponding methyl and ethyl * compounds in water. The increase in rate in both cases is due solely to a decrease in the enthalpy of activation since the corresponding entropy trends are $\Delta S^{\ddagger}(\text{Me}) \sim \Delta S^{\ddagger}(\text{Et}) > \Delta S^{\ddagger}(\text{Allyl}) > \Delta S^{\ddagger}(\text{Benzyl})$ (Tables 10 and 6). The reasons for this negative trend in entropy with increasing unsaturation are not clear but may originate from the effect of the double bonds on the solvation of the initial state.[7] Allyl chloride, bromide, and iodide react in the same peculiar [7] rate sequence as the corresponding methyl

FIG. 5.

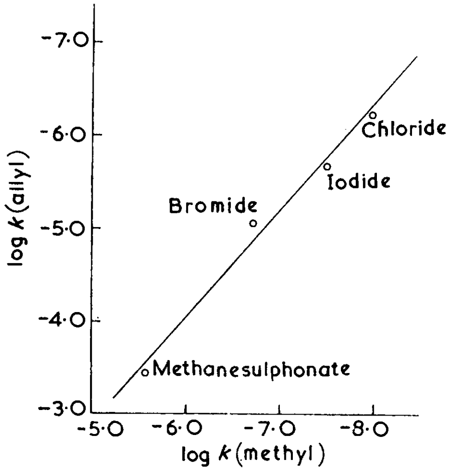


TABLE 10. *Enthalpies and entropies of activation for the methyl and ethyl halides at* 50·00°.

	Chloride		Bromide		Iodide	
	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Methyl	25·26	−8·89	24·14	−6·65	25·95	−3·94
Ethyl	24·96	−5·24	24·26	−7·10	25·61	−3·61

For sources of these data and methods of calculation see refs. 12 and 17.

TABLE 11. *Thermodynamic and related data for equations* (11) *and* (12).

$T = 50{\cdot}00°$

Entropy equation (see Fig. 3) — *Observed and values calculated from the curves*

							s-Pr	s-Pr		
						s-Pr	calc.	calc.	Allyl	
A	B	*m*	const.	Curve		obs.	from *a*	from *c*	calc. from *b*	
s-Pr	Me	1·38	7·41	*a*	Cl	−5·25	−4·98	−4·98	−11·76	−11·85
Allyl	Me	1·26	−0·543	*b*	Br	−1·43	−1·79	−2·09	−9·20	−8·93
s-Pr	Allyl	1·13	8·27	*c*	I	1·86	1·96	2·25	−5·34	−5·51

Enthalpy equation (see Fig. 4) — *Observed and values calculated from the curves*

							s-Pr	s-Pr		
						s-Pr	calc.	calc.	Allyl	
A	B	*m′*	const.′	Curve		obs.	from *d*	from *f*	calc. from *e*	
s-Pr	Me	0·632	9·07	*d*	Cl	24·96	25·04	24·93	22·01	22·16
Allyl	Me	0·935	−1·91	*e*	Br	24·36	24·32	24·37	21·15	21·10
s-Pr	Allyl	0·695	10·44	*f*	I	25·52	25·47	25·53	22·91	22·81

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* The ethyl halides are probably best considered as the primitive member of the above series but since they have not been investigated kinetically over as wide a range of temperature as the methyl halides the latter will be used for some of the comparisons.

halides: Br > I > Cl. The approximate linear free-energy relationships between the allyl and methyl derivatives again suggest a common mechanism (see Table 12 and Fig. 5).

The enhancement of reactivity of allyl and benzyl solvolytic substrates over that shown by structurally related saturated compounds is usually attributed to an increase in resonance energy in proceeding from the reactants to the transition state.[1,20] Resonance energy is a potential energy and is correctly discussed in terms of ΔE_0 of the absolute rate equation:

TABLE 12. *Rate data for the methyl and allyl series:* $T = 20{\cdot}02°$.

	k (allyl) (sec.$^{-1}$)	k (methyl) (sec.$^{-1}$)
Chloride ...	$5{\cdot}94 \times 10^{-7}$	$1{\cdot}07 \times 10^{-8}$ 12
Bromide ...	$8{\cdot}74 \times 10^{-6}$	$1{\cdot}76 \times 10^{-7}$ 12
Iodide	$2{\cdot}02 \times 10^{-6}$	$3{\cdot}32 \times 10^{-8}$ (12)
Methanesulphonate	$3{\cdot}61 \times 10^{-4}$ (12)	$2{\cdot}70 \times 10^{-6}$ (12)

$$k = (\boldsymbol{k}T/\boldsymbol{h})Z^{\ddagger}Z \exp\,(-\Delta E_0/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where ΔE^0 is the difference in the zero-point levels of the reactants and the transition state. Unfortunately, the enthalpy of activation measured at room temperatures is indirectly related to ΔE^0:

$$\Delta H^{\ddagger} = \Delta E^0 + \int_0^T C_p{}^{\ddagger}\,.\,\mathrm{d}T - \int_0^T C_p\,.\,\mathrm{d}T = \Delta E^0 + \int_0^T \Delta C_p{}^{\ddagger}\,.\,\mathrm{d}T$$

At temperatures for which the data are reported, $\Delta C_p{}^{\ddagger}$ is large and negative but even with this added information conclusions are not possible about ΔE^0 since in principle $\Delta C_p{}^{\ddagger}$ is also a function of temperature. Evans and Polanyi [21] suggested that $\Delta G^{\ddagger}$ behaves more like ΔE^0 than does $\Delta H^{\ddagger}$ and in consequence potential-energy quantities are usually discussed in terms of the free-energy parameter.[1,4] Our $\Delta H^{\ddagger}$ values at a given temperature do follow the expected trends in ΔE^0, with increased unsaturation in the side chain. Hence, the decrease in the energy of activation in the allyl and benzyl compounds can be tentatively attributed to increased resonance, from the reactants to the transition state.

It does not appear possible to give a consistent interpretation of electronic effects for a given reaction if the transition states are changing in character. The methyl, ethyl, allyl, and benzyl halides are generally considered to react at different positions along the S_N1-S_N2 spectrum,[21,23] and indeed the values of m in equation (9), where they have been determined, indicate that something of this nature is occurring. In the gas phase, the methyl, ethyl, allyl, and benzyl carbonium ions show very considerable differences in stability as shown in the variation of the enthalpy of the reaction [23] $RX \longrightarrow R^+ + X^-$, and these differences, although still apparent in the solvolytic reaction, are considerably reduced. The entropy relationship, equation (9), is compatible with complete charge transfer in the transition state but the enthalpies of activation (Tables 10 and 6) imply that if the positive charge is stabilized internally then some factor is responsible for the reduction in the differences which are apparent in the gaseous ionization. This is obviously the solvation of the positive charge (cf. Mason [23]).

Our discussion suggests that the transition states for the solvolytic reaction in water can be either (I) or (II), where (I) involves only non-specific interaction with the positive charge (S_N1) and (II) involves definite covalent interaction (S_N2) as well as non-specific solvation. There is some evidence to suggest that in water (II) is the more probable. Winstein and Marshall [24] have pointed out that, in the methyl, ethyl, s-propyl, and t-butyl

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[20] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1953, Ch. 6, and references therein.

[21] Polanyi and Evans, *Trans. Faraday Soc.*, 1936, **32**, 1333.

[22] Streitwieser, *Chem. Rev.*, 1956, **56**, 571.

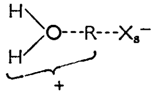
[23] Mason, *J.*, 1958, 808.

[24] Winstein and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 1120.

halides, the addition of each methyl group should be equivalent to a factor of six units in log *k* if the reaction is limiting in character. In water the s-Pr : Me ratios are small,[12] from which, on the basis of the above premise, it is concluded that for primary and secondary centres these reactions are not limiting in character. Also the benzyl : allyl ratios at 25° for the reactions (*a*) bimolecular I–Cl exchange in acetone, (*b*) hydrolysis, and (*c*) formolysis are respectively: 2·2,[25,26] 11·0, and 45.[9] Thus even if limiting kinetics (S_N1) is assumed in formic acid, which is very dubious for primary centres,[22,27] we must conclude that the reaction is not limiting (S_N1) in character in water, and takes place by what is essentially a bimolecular displacement reaction in which the transition state is very polar.

$R_s^{+}\cdots X_s^{-}$

(I)



(II)

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[*Received, February* 22*nd*, 1960.]

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[25] Fierens, *Bull. Soc. chim. belges*, 1959, **68**, 177.
[26] Fierens, *Helv. Chim. Acta*, 1955, **37**, 2009.
[27] Streitwieser, *J. Amer. Chem. Soc.*, 1955, **77**, 1117.