507. *The Exchange of Oxygen between Alcohols and Water. Part III.*[1] *Acid-catalysed Racemization and Oxygen Exchange of* 1-*Phenylethyl Alcohol in Dilute Aqueous Solutions.*

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For 1-phenylethyl alcohol in dilute aqueous perchloric acid, the ratio of the acid-catalysed rates of oxygen exchange to racemization, after correction for olefin formation, is 0·82 ± 0·04. The ratio is less than unity owing to the shielding by the departing $^{-}OH_2$ group. A simplified model was developed for the quantitative interpretation of this shielding, use of which, with stereochemical data for 1-phenylethyl chloride, showed that OH_2 and Cl^- are equally effective at shielding. The results suggest that the rate of dissociation of the solvated $R^+ \cdots X$ intermediate (which is the first product in the ionization of RX) to a free carbonium ion is slow compared with its rate of substitution with the solvent.

In aqueous perchloric acid, the salt-effect on the specific rate of racemization of 1-phenylethyl alcohol was intermediate between that expected from the H_0 and the C_0 function.

PREVIOUS kinetic studies of the acid-catalysed oxygen exchange between water and alcohols[1, 2] are now extended to the 1-phenylethyl system. Specific rates (k_{exch}) measured in dilute aqueous solution are compared with rates of racemization of optically active alcohol (k_{rac}) and of olefin formation (k_{ol}) under the same conditions. From the measured values of $k_{exch}/(k_{rac} - k_{ol})$, the steric course of the substitution has been deduced. The results supplement studies in the *sec.*-butyl system[3] and provide significant information about the solvation and the reactions of the carbonium-ion intermediates.

EXPERIMENTAL

Materials.—Optically active 1-phenylethyl alcohol, prepared *via* the brucine salt of the phenylethyl hydrogen phthalate by known methods,[4, 5, 6] had b. p. 91—91 5°/(~10 mm.); m. p. [redacted]

−35·2° (c = 1·58); in water, −27·8° (c = 0·96). The (−)-alcohol was of lower optical purity, $[\alpha]_D^{24}$ 28·8°.

(±)-1-Phenylethyl alcohol was obtained pure from the hydrolysis of twice-recrystallized 1-phenylethyl hydrogen phthalate (m. p. 107·5—108·5°) in boiling 5N-sodium hydroxide (10 min.). The alcohol was extracted with pure ether, dried (K_2CO_3), and distilled at 3—4 mm. It had m. p. 19—20°.

Good commercial styrene which had been stored at −20° was distilled at a pressure less than 1 mm. The styrene obtained had a bromine number of 149 ± 5, corresponding to 97 ± 3% purity, and $n_D^{21·7}$ 1·5452.

Isotopically enriched water from the ^{18}O-production plant of the Weizmann Institute was redistilled from alkaline permanganate. Perchloric and hydrochloric acid were of Reagent Grade and were standardized with aqueous sodium hydroxide; potassium hydrogen phthalate obtained from the U.S. National Bureau of Standards served as primary acidimetric standard. Hydrochloric acid was the constant-boiling azeotrope.[7]

Analysis of ^{18}O *in 1-Phenylethyl Alcohol.*—70 ml. samples of 0·08M-alcohol in aqueous perchloric acid were added to sufficient reagent-grade potassium carbonate to give saturated solutions. These were extracted, first with 20 ml., and then three times with 10 ml. of pure ether. The ether extracts were dried (K_2CO_3) and most of the ether was evaporated. The residue of alcohol and a little ether was dried carefully by shaking overnight with 80—100-mesh potassium carbonate, a treatment which removed the last detectable traces of water. The mixture was then centrifuged, and the liquid withdrawn by means of a syringe, and distilled through an efficient micro-column at a pressure of about 1 mm. After complete removal of the ether, successive 150 mg. fractions of distillate were collected, and from each fraction 122 mg. (1 mmole of alcohol) were withdrawn with a calibrated micropipette and analysed [8] for ^{18}O. The only modification of this method [8] used here was to heat the alcohol–CO_2–H_2SO_4 mixtures at 150° for 24 hr., instead of at 170° for 3 hr. This gave better precision and was shown to give isotopic equilibrium between carbon dioxide and the ^{18}O of the alcohol. (Heating for 48 hr. at 150° gave identical results.) The isotopic composition of successive fractions of distillate, determined by this method, proved to be equal to better than ±0·003 atom-% of ^{18}O.

Polarimetry.—Optical rotations were measured by means of a polarimeter (O. C. Rudolph and Sons), using a 2 dm. microtube of 2 ml. volume. The light source was an intense sodium-vapour lamp, with a filter to isolate the sodium D doublet. The mean deviation of single readings varied with the angle between the Nicol prisms of the polarizer in the following way: 1°, ±0·002°; 2°, ±0·003°; 3°, ±0·004°; 4°, ±0·004°; 5°, ±0·005°; 7°, ±0·008; angles in the range 3—4·5° were used in the rate measurements. The precision was considerably worse with a less intense light source which required a larger angle between the Nicol prisms.[9]

For good precision, care was taken to keep the position of the polarimeter tube always the same and to avoid errors due to anisotropy in the cover glasses, due to pressure, by reading the tube from both sides, and by avoiding strong pressure on them. The mean of about 10 readings was taken for each point. The measured rotations were shown to be proportional (±0·002°) to the fraction of active alcohol in the rate-measurements by use of aqueous solutions of active and (±)-alcohol.

Ultraviolet Spectrophotometry.—Concentrations of styrene in the presence of 1-phenylethyl alcohol were measured by means of a Beckman DU spectrophotometer at 2300 and 2450 Å. The molar extinction coefficients were: for styrene, 7900 ± 400 at 2450 Å and 4300 ± 200 at 2300 Å; for 1-phenylethyl alcohol, 82 at 2450 and 20·3 at 2300 Å. The values for the alcohol may be too high because of the difficulty of removing all traces of styrene.

Kinetic Measurements.—Precise measurements of k_{exch} and k_{rac} were possible in spite of the low water solubility of the alcohol (0·12M at 20°) [10] and the even lower water solubility (2—6 × 10^{-4}M) of the styrene [11] produced in the simultaneous elimination reaction. The latter reaction was fortunately very slow, and by using an alcohol preparation which contained initially only a trace of styrene, the reactions could be followed to nearly two half-lives without the appearance of a second phase.

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[7] Foulk and Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1220.

[8] Anbar, Dostrovsky, Klein, and Samuel, *J.*, 1955, 155.

[9] W. Heller, in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., New York, 1949.

[10] Hjort and Kaufmann, *J. pharm. exp. Therap.*, 1920, **15**, 130.

[11] Boundy and Boyer, "Styrene," Reinhold Publishing Corp., New York, 1952.

Samples of kinetic results are shown in Table 1; α is the observed optical rotation, and N the atom fraction of ^{18}O of the alcohol. N_W is the essentially constant atom fraction of ^{18}O of the water in the medium. Both k_{exch} and k_{rac} are listed as *second-order* rate constants, *i.e.*,

$$k_{\text{exch}} = \ln\,[(N_W - N_0)/(N_W - N_t)]/t[H^+] \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$k_{\text{rac}} = \ln\,(\alpha_0/\alpha_t)/t[H^+] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$[H^+]$ is constant in each run. Within experimental error, the data were fitted well by equation (1) or (2) in any given run, and average rate constants were computed by standard least-squares methods. On the basis of the precision of the raw results and of the reproducibility of several duplicate runs, the standard error of the rate constants was estimated as 2% for k_{exch} and 4% for all comparable values of k_{rac}. These figures apply to all results in perchloric acid except those in 0·5N- and 1N-acid, or in hydrochloric and hydrobromic acids. In the exceptional cases, values of α_0 were, for practical reasons, kept rather small, and the accuracy of k_{rac} was only about ±10%.

TABLE 1. *Sample of kinetic results at* 30·4°. Concn. of alcohol, 0·0845M; $HClO_4$, 0·01721N; water enriched in ^{18}O.

Racemization			Exchange		
t (hr.)	α	$10^5 k_{\text{rac}}$ (sec.$^{-1}$ mole^{-1} l.)	t (hr.)	100 N †	$10^5 k_{\text{exch}}$ (sec.$^{-1}$ mole^{-1} l.)
0·0	0·573°	—	0·0	0·204	—
117·8	0·519	1·35	94·5	0·309	1·04
242·5	0·473	1·28	170·0	0·388	1·03
384·3	0·430	1·21	268·3	0·488	1·05
450·6	0·405	1·24	360·9	0·582	1·07
597·3	0·355	1·30	500·6	0·696	1·03
∞	0·000 ± 0·002 *			N_W 1·985 ± 0·03	

* From results at higher temperatures.

† Value after dilution with 6 moles % of normal CO_2.

Two comments are necessary regarding the values of k_{exch}. First, it is possible that some of the exchange occurs *via* the rehydration of the styrene produced in the simultaneous elimination reaction, rather than by a substitution mechanism. In order to check this, the rate constant (k_H) for the acid-catalysed hydration of styrene was measured separately (see below). Using the measured values of k_{01} and k_H, we found that the correction to k_{exch} due to this cause was less than 0·1% in all experiments, so it was neglected. Secondly, one would like to know the magnitude of the kinetic isotope effect involved in k_{exch} before comparing k_{exch} and k_{rac}. Since ^{18}O was *introduced* into the alcohol, and since eqn. (1) contains N_W rather than N_∞, it can be shown [12] that k_{exch} is, in effect, the rate constant for the reaction of $R^{16}OH$ with $H_2{}^{18}O$. For an S_N1 mechanism in which the rate-determining step involves the rupture of the R–O bond, the rate of this reaction must be very nearly equal to that of the reaction of $R^{16}OH$ with $H_2{}^{16}O$. Kinetic isotope effects are therefore negligible in the rate comparisons to be made in this paper.

All runs were made in thermostats of conventional design. Temperatures were constant to 0·05° and were measured with a thermometer calibrated by the National Physical Laboratory. In the measurements at 30·4°, the reaction mixtures were kept in glass-stoppered volumetric flasks well immersed in the thermostat. In all other measurements, sealed ampoules were used. At suitable intervals the reactions were quenched by shaking the ampoules in crushed ice, and the reaction mixtures analysed at once.

Hydration–Dehydration Rate Measurements.—The rate-constants for the acid-catalysed elimination reaction, k_{01}, and for the acid-catalysed hydration of styrene, k_H, were measured in 0·1N- and 0·2N-perchloric acid by following the light absorption of the solutions at 2450 Å and at 2300 Å. In these measurements, the ampoules were filled with the reaction mixture nearly to the top in order to minimize the volume of the vapour phase. Initial rates were measured in solutions of styrene, of alcohol, and of styrene–alcohol mixtures of various compositions. The last yielded an estimate of the equilibrium composition which was consistent with the rate constants obtained from solutions containing only styrene or only alcohol.

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[12] See, for example, Melander, *Arkiv Kemi*, 1954, **7**, 287.

Second-order rate constants (in sec.$^{-1}$ mole^{-1}) are as follows: k_{ol} at 30·4°, $1{\cdot}2 \times 10^{-7}$; at 54·3°, 5×10^{-6}: k_H at 30·4°, 2×10^{-6}; at 54·3°, $1{\cdot}4 \times 10^{-5}$. Owing to the slowness of these reactions, and because of the low solubility of styrene and its many side-reactions,[11] these rate constants are only semi-quantitative. Conservative estimates of the accuracy are ±50% for k_{ol}, and within a factor of two for k_H. Since these rate-constants are needed only to make small corrections to k_{rac} and k_{exch}, their accuracy is adequate.

RESULTS

Racemization.—Experimental values of k_{rac} in aqueous perchloric acid are summarized in Table 2. It is seen that k_{rac} is independent of the alcohol concentration; reaction paths involving alcohol–alcohol interactions may therefore be neglected. On the other hand, there is a prounounced increase in k_{rac} with increasing perchloric acid concentration, which will be shown to be a neutral-salt effect. The rate constants in isotopically enriched water containing 2·2 atoms % of ^{18}O and 1·35 atoms % of D are on the average 3% greater than rate constants obtained under parallel conditions in ordinary water. Although this effect is not statistically significant, it is nevertheless in the right direction for an S_N1 mechanism in which a rapid, reversible proton addition to the alcohol is followed by a slow, unimolecular decomposition of the conjugate acid.[13]

In 0·1M-perchloric acid, rate constants were obtained at several temperatures. Within experimental error, plots of log (k_{rac}/T) against $(1/T)$ were linear, as shown by the agreement of the results in columns 5 and 6 of Table 2. The standard enthalpy and entropy of activation, computed from the data *via* the transition-state theory, were as follows: $\Delta H^{\ddagger}$, 27·68 kcal.; $\Delta S^{\ddagger}$, 10·55 e.u.

TABLE 2. *Second-order rate constants for the acid-catalysed racemization of 1-phenylethyl alcohol in aqueous perchloric acid.*

Temp.	$HClO_4$ (M) [a]	Alcohol (M) [a]	$10^5 k_{rac}$ [b] (sec.$^{-1}$ mole^{-1} l.)	$10^5 k_{rac}$ [c] (calc.)
	(1) Effect of alcohol concentration.			
30·40°	0·1033	0·022	1·48 [d]	—
		0·046	1·45	
		0·066	1·45	
	(2) Effect of acid concentration.			
30·40	0·0172	0·084	1·26 [e]	—
	0·0201	0·079	1·25	
	0·0826	0·078	1·34 [e]	
	0·1033	0·066	1·45	
	0·522	0·06	2·4 [d]	
	1·00	0·023	4·7 [d]	
54·30	0·0170	0·082	41·9 [e]	
	0·0199	0·073	39·7 [d]	
	0·1013	0·039	44·5	
	(3) Effect of temperature.			
30·40	0·1033	0·02—0·07	1·46 [d]	1·49
45·12	0·1027	0·04	13·6 [d]	13·0
54·27	0·1013	0·04	44·5	45·5
64·36	0·1018	0·04	167	167

[a] Corrected for solvent expansion. [b] Eqn. 2. [c] $\log k/T = 12{\cdot}624 - 6051{\cdot}34/T$. [d] Average value, obtained in two or more runs. [e] In isotopically enriched water, containing 2·2 atoms % of ^{18}O and 1·35 atoms % of D.

It was thought just possible that part of the increase in k_{rac} with increasing perchloric acid concentration is due to a bimolecular displacement reaction involving perchlorate ion and ROH_2^+, followed by rapid solvolysis of the perchlorate ester. To test this hypothesis, k_{rac} was measured also in aqueous hydrochloric and hydrobromic acid, with the results shown in Table 3. If there were appreciable S_N2 reaction with anions, displacement by bromide ion would be 4—60 times as fast as displacement by chloride ion,[14] and k_{rac} in hydrobromic acid would be

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[13] Wiberg, *Chem. Rev.*, 1955, **55**, 713.

[14] See, *e.g.*, de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3234.

considerably faster than in hydrochloric acid. Actually, no significant difference in rate is observed. The effect is therefore genuinely a neutral-salt effect.

TABLE 3. *Second-order rate constants* ($10^5 k_{rac}$, *sec.*$^{-1}$ *mole*$^{-1}$ *l.*) *for the acid-catalysed racemization of* 1-*phenylethyl alcohol in aqueous acids at* 30·4°.

Acid concn. (M)	HCl [a]	HBr [a]	$HClO_4$
0·02	1·4	1·5	1·25
0·10	1·8	1·7	1·46
0·47	2·0	2·3	2·3

[a] These rate constants are accurate only to 15% since the alcohol used in the rate determinations was unfortunately of low optical purity.

Oxygen Exchange.—The rate constants for oxygen exchange are listed in Table 4, together with values of k_{rac} measured under identical conditions. The latter have been corrected for the amount of racemization due to olefin formation to give the rate constants, $k'_{rac} = k_{rac} - k_{ol}$, resulting specifically from the substitution reaction. Comparison of k_{exch} with k'_{rac} provides an index of reaction mechanism. Within their standard error of 0·04, the three measured ratios of k_{exch}/k'_{rac} are equal, the mean value being 0·82. If the mechanism were S_N2, this ratio would be 0·5; if it were S_N1 and proceeded through an unshielded carbonium ion, the ratio would be 1·00. The intermediate magnitude of the observed ratio indicates either that there is some shielding of the front side of the carbonium ion by the departing OH_2 molecule, or that substitution proceeds simultaneously by both mechanisms. A quantitative interpretation will be given in the next section.

TABLE 4. *Summary of oxygen-exchange and related results.*

Temp.	$HClO_4$ (M)	$10^5 k_{exch}$ [a]	$10^5 k_{rac}$	$10^5 k'_{rac}$ [b]	k_{exch}/k'_{rac}
30·40°	0·0172	1·05	1·26	1·25	0·84
30·40	0·0826	1·09	1·34	1·33	0·82
54·31	0·0170	33·0	41·9	41·4	0·80

[a] Eqn. 1. [b] $k'_{rac} = k_{rac} - k_{ol}$.

DISCUSSION

Simplified Model for Shielding by the Departing Group.—It seems safe to assume that the solvolysis of 1-phenylethyl compounds in water and other good ionizing solvents proceeds by an S_N1 mechanism, and that the observed deviation of k_{exch}/k'_{rac} is due to shielding by the departing group. In support of this assumption, the solvolysis of optically active 1-phenylethyl chloride leads to virtually the same steric result (83% racemization, 17% inversion of configuration) in water [15] as it does in glacial acetic acid,[16] a solvent of much lower nucleophilic power. To give a rigorous description of the mechanism of shielding is complicated because the mechanism of solvolysis is so complicated. Winstein and his co-workers [17] write equation (3) for the ionization–dissociation process of RX and show that this mechanism, even though involving two

$$\underset{}{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{\text{Intimate}\\ \text{ion-pair}}}{R^+X^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\substack{\text{Solvent-}\\ \text{separated}\\ \text{ion pair}}}{R^+||X^-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R^+ + X^- \qquad . \quad . \quad . \quad (3)$$

discrete ion-pair intermediates, is yet the simplest that will fit their large body of results.[17, 18] Substitution may occur at R^+X^-, at $R^+||X^-$, or at R^+, and it is only after the system has

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[15] Hughes, Ingold, and Scott, *J.*, 1937, 1201.

[16] Steigmann and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2536.

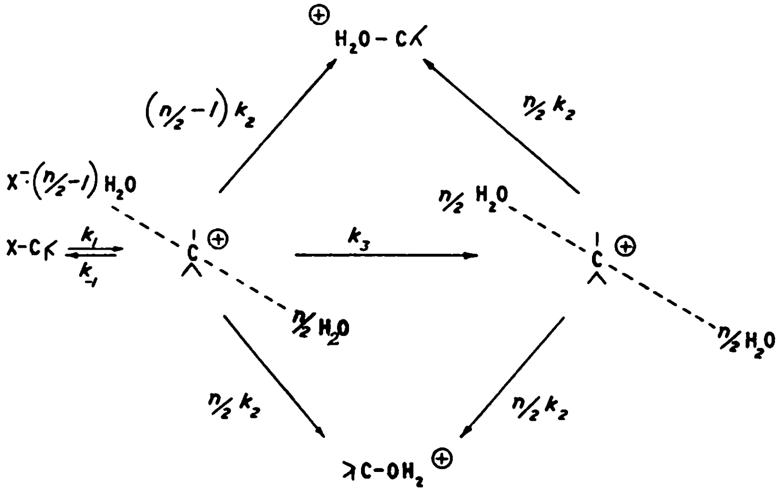
[17] Winstein, Clippinger, Fainberg, Heck, and Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

[18] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763, 2767, 2780; Fainberg, Robinson, and Winstein, *ibid.*, 1956, **78**, 2777; Winstein and Clippinger, *ibid.*, 1956, **78**, 2784.

reached this last stage that the subsequent product is completely racemic. To predict the steric result for any given RX and solvent requires knowledge of as many as five reactivity ratios.

To render the problem manageable, we consider the *special* case where the carbonium ion is quite unstable. R^+X^- then reacts with solvent at a specific rate comparable with, or greater than, k_3. Further, since reaction with solvent proceeds with very low activation energy, the transition state will resemble R^+,[19] and the rate will be rather insensitive to changes in nucleophilic and electrophilic activity [19, 20] such as are caused by the proximity of the departing group X^-. On this basis a simplified kinetic scheme was obtained which is illustrated for hydrolysis in Fig. 1. Shielding by X^- is effective only in the intimate ion pair which reacts with solvent with rate constant $(n - 1)k_2$, where k_2 is the "rate constant" for a single solvent molecule when occupying the same site as X^-. The rate constant for reaction of solvent with $R^+||X^-$ and R^+ is written as nk_2, which assumes not only that k_2 is insensitive to the presence of X^-, but also that in the absence of X^- the arrangement of the water molecules immediately adjacent to R^+ resembles that when X– is a nearest neighbour, the X^- taking the place of one of the water molecules. The structure of X must therefore be such that the area of contact between X^- and the carbonium ion is roughly equal to that between a water molecule and the carbonium ion. Since the carbonium ion is quite reactive, k_{-3} is neglected compared with nk_2. According to this mode, the fractional excess of product with inverted configuration—that is, [inverted product − retained product]/[total product]—is equal to

FIG. 1. *Kinetic scheme showing the shielding of a carbonium ion by the departing group.*



$$f = 1/(n - 1 + k_3/k_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The model will likewise accommodate the rates of acid-catalysed racemization and oxygen exchange of alcohols. With reference to Fig. 1, $X = OH_2$, hence $k_{-1} = k_2$. If olefin formation is discounted, $k'_{rac} = k_1$, and hence

$$k_{exch}/k'_{rac} = (n - 1 + k_3/k_2)/(n + k_3/k_2) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Except for neglect of k_{-3} and small kinetic isotope effects on k_2, eqn. (5) is exact.

Subject to the simplifying assumptions which have been made, equations (4) and (5) serve as a single basis for interpreting (*a*) steric results for different groups X in the same

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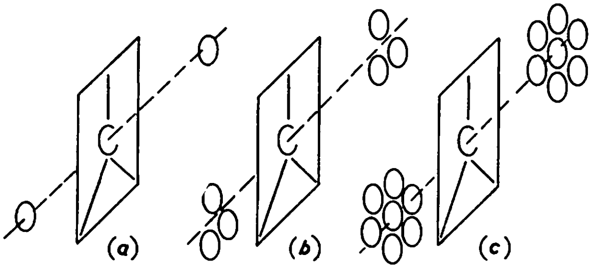
[19] Leffler, *Science*, 1953, **117**, 3039.

[20] Streitwieser, *Chem. Rev.*, 1956, **56**, 627.

solvent, and (*b*) steric results for any one group X in different solvents. Of the parameters involved, k_2 is a function of the solvent, and k_3 is a function of both the solvent and X. A purely formal definition of n has already been given but it is instructive to examine this quantity in greater detail. Referring to Fig. 2, we recognize three somewhat idealized models for the manner in which the carbonium ion may react with molecules in its solvation shell. Fig. 2(*a*) shows reaction as taking place only from the two nearest-neighbour sites just above and just below the central C^+-atom; hence $n = 2$. Fig. 2(*b*) shows another possible model in which the nearest-neighbour sites are arranged symmetrically about the normal to the plane of the carbonium ion passing through C^+. In the example shown, $n = 6$. Fig. 2(*c*) differs from 2(*a*) in that reaction can occur also from next-nearest-neighbour sites, though in general with lower probability. Since X in R^+X^- occupies a nearest-neighbour site, the effective value of n is in the range 2—14. Model 2(*c*) implies that covalent-bond formation to C^+ can occur efficiently even from directions which are not normal to the plane of the carbonium ion. The model is made credible by the fact that in displacement reactions involving a neighbouring group [21] or an S_Ni mechanism the attacking direction is also at a considerable angle from the normal, and even in S_N2 displacement a model with flexible directions of attack is more successful than a rigid one.[22]

FIG. 2. *Some possible models of the solvated carbonium ion.*



Regardless of model, the total range of plausible values for n is seen to be small. For any one carbonium ion the range is likely to be even smaller and, if the solvents in which steric results are obtained are of similar type (*e.g.*, hydroxylic) and molar volume, n may well be quite constant.

Results for the 1-*Phenylethyl System*.—For $Ph\cdot CH(OH_2^+)\cdot CH_3$ in water, $k_{exch}/k'_{rac} = 0{\cdot}82 \pm 0{\cdot}04$, hence from eqn. (5), $n + k_3/k_2 = 6 \pm 1$. For $Ph\cdot CHCl\cdot CH_3$ in water, $f = 0{\cdot}17 \pm 0{\cdot}02$,[15] hence from eqn. (4), $n + k_3/k_2 = 6{\cdot}9 \pm 0{\cdot}8$. Within experimental error, the two values are equal. Steric results for the S_N1 solvolysis of 1-phenylethyl chloride are also available in other one-component solvents.[15, 16] After correction for the S_N2 process, values of f are 0·22 in methanol at 70°, 0·28 in ethanol at 70°, and 0·16 in glacial acetic acid at 50°. The corresponding values of $n + k_3/k_2$ are, respectively, 5·4, 4·6, and 7·3. For 1-phenylethyl toluene-*p*-sulphonate, steric results very similar to those for the chloride have been reported in ethanol and glacial acetic acid,[23] although these results are still to be corrected for the S_N2 process and racemization of the solvolysis products.

The striking feature of the values of $n + k_3/k_2$ is their apparent insensitivity to changes in the nature, particularly charge type, of the departing group, and of the solvent over such wide ranges of solvent properties. The minimum value $n = 2$ being taken, the entire variation of k_3/k_2 is within a factor of 2, and for the two values in water the maximum variation is even smaller. On electrostatic grounds one would have expected the value of

[21] Winstein, Grunwald, and Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.
[22] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.
[23] Kenyon, Phillips, and Taylor, *J.*, 1933, 173.

k_3/k_2 in water to be appreciably greater for OH_2 than for Cl^-, although admittedly this effect may be compensated by solvation effects.

The simplest and, to us, most attractive theory which will account for the results is that k_3/k_2, though not necessarily constant, *is small compared with n*, at least in water, methanol, and ethanol. This means that substitution occurs mainly at the intimate ion-pair stage but, since $n \approx 6$, from more than two sites. The small decrease in n on changing from water to methanol and ethanol can result from the larger size of the alcohol molecules. On this basis, the somewhat larger value obtained in acetic acid indicates that k_3/k_2 is now not negligible.

Steric results for the solvolysis of 1-phenylethyl chloride are available also in acetone–water mixtures.[15] Here the product is more nearly racemic, f being 0·05 in 60% acetone and 0·02 in 80% acetone. However, since this is a two-component solvent, the result may be due to preferential solvation rather than a large value of k_3/k_2. The presence of the departing chloride ion may cause strong preferential solvation of the " front " of the carbonium ion by water, which can form hydrogen bonds to chloride, whereas no such inducement for solvation by water exists at the " back." We may therefore expect to find more acetone molecules at the back than at the front, and this partially counterbalances the shielding by chloride at the front.

Results for sec.-*Butyl and* 1-*Methylheptyl System.*—The solvolysis of optically active 1-methylheptyl bromide in 60% ethanol proceeds with $f \approx 0{\cdot}70$.[24] * If k_3/k_2 is assumed to be small, $n = 2{\cdot}4$ from eqn. (4). Hence, for the acid-catalysed racemization and oxygen exchange of the alcohol, it can be predicted from eqn. (5) that $k_{\text{exch.}}/k_{\text{rac}} = 0{\cdot}58$. The actual value of $k_{\text{exch}}/k_{\text{rac}}$ for 1-methylheptyl alcohol is not available, but Bunton, Konasiewicz, and Llewellyn[3] have reported a value of 0·5 for this ratio for the mechanistically similar *sec.*-butyl alcohol. Although this is a typical result for an S_N2 process, they describe the mechanism as S_N1. Our examination of their data supports this view, and we find that the most probable value is actually 0·52, and even this value may be somewhat too small owing to medium effects: the alcohol concentration in the exchange experiments averaged 1·3M, but was only about 0·8M in the racemization experiments. Although the published data suffice to show that the medium effect due to this discrepancy is not large, an effect of the order of 10—20% is quite possible and, judged by the data for *tert.*-butyl alcohol,[2] its direction would be such as to make k decrease with increasing alcohol concentration.

Although it appears probable that both the 1-phenylethyl and the *sec.*-butyl or 1-methylheptyl compounds solvolyse by mechanism S_N1 in the sense that a metastable intermediate is involved, there are some important differences. From the effect of changing the nucleophilic power of the solvent on the solvolysis rate one can conclude that there is some " push " by solvent in the formation of the intermediate in the secondary alkyl system, but that this is negligible in the 1-phenylethyl system.[25, 26] The present work suggests two additional aspects in which S_N1 reactions may differ: the effective number, n, of sites from which substitution can occur, and the relative magnitudes of the rates of substitution and of dissociation of the intimate ion-pair intermediate. For the more reactive intermediates, products may be formed largely at the intimate ion-pair stage even though specific nucleophilic driving force was not required in the prior ionisation step.

Salt Effect on k_{rac} and the H_0-Function.—In acid-catalysed reactions in which a rapid, reversible, simple proton addition to a substrate is followed by a slow reaction of the conjugate acid, the method of Zucker and Hammett[27] has often been applied to reactions

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* Preferential solvation does not appreciably affect the average steric result when both solvent components are hydroxylic.

[24] Hughes, Ingold, and Masterman, *J.*, 1937, 1196.

[25] Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.

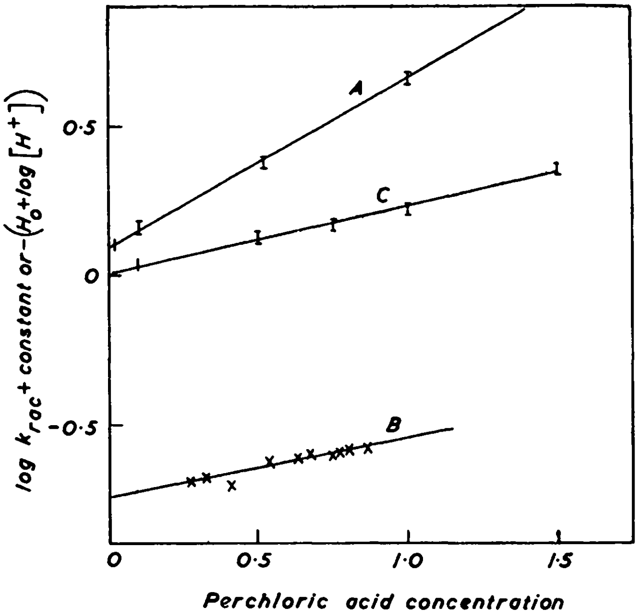
[26] Coburn, Grunwald, and Marshall, *ibid.*, 1953, **75**, 5735.

[27] Zucker and Hammett, *ibid.*, 1939, **61**, 2791.

in aqueous media to determine whether there is participation by a water molecule in the slow reaction step.[3, 27, 28-31] According to this method, if there is no participation, the pseudo-first order rate constant of the substrate is proportional to antilog $(-H_0)$, where H_0 is the acidity function;[32] if there is participation, the rate is proportional to the acid concentration.

The application of this method to our results is shown in Fig. 3. In following the conventional representation of salt effects,[33] $\log k_{rac}$ is plotted against perchloric acid concentration. The slope of the resulting straight line, 0·574, is much greater than the slope, 0·232, of the nearly linear plot of $-(H_0 + \log [H^+])$, where $[H^+]$ is the acid concentration. Evidently the rate is not proportional to antilog $(-H_0)$. A possible explanation of the large slope is that the transition state from $Ph{\cdot}CH(OH_2^+){\cdot}CH_3$ resembles a carbonium ion. The slope of $\log k_{rac}$ against $[H^+]$ would then resemble that of $-(C_0 + \log [H^+])$, where C_0 is the acidity function applicable to equilibria leading to carbonium ions.[34] Recent unpublished results by Professor Deno indicate that the average value of this slope is about 1·0 in the range 0—1M-perchloric acid. The observed magnitude of the salt effect on $\log k_{rac}$ is therefore intermediate between that expected from the two acidity functions, but is not represented accurately by either.

FIG. 3. *Salt effects in aqueous perchloric acid.*



A; 1-Phenylethyl alcohol at 30·4°, slope 0·574 (from Table 2).
B; *sec.*-Butyl alcohol (the data reported at acid concentrations less than 0·25M show considerable scatter and are not shown) (from Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, **604**).
C; $-(H_0 + \log [H^+])$. Values of H_0 from Paul and Long, *Chem. Rev.*, in the press.

Also shown in Fig. 3 are the data for the acid-catalysed racemization of *sec.*-butyl alcohol.[3] The slope, −0·198, is very nearly equal to that for $-(H_0 + \log [H^+])$, indicating

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[28] Long, Dunkle, and McDevit, *J. Phys. Chem.*, 1951, **55**, 829.
[29] Paul, *J. Amer. Chem. Soc.*, 1952, **74**, 141.
[30] Taft, *ibid.*, 1952, **74**, 5372.
[31] Pritchard and Long, *ibid.*, 1956, **78**, 2667.
[32] Hammett and Deyrup, *ibid.*, 1932, **54**, 4239. For a recent review see Paul and Long, *Chem. Rev.*, in the press.
[33] Ciapetta and Kilpatrick, *J. Amer. Chem. Soc.*, 1948, **70**, 639.
[34] Deno, Jaruzelski, and Schriesheim, *ibid.*, 1955, **77**, 3044.

that water does not participate in the rate-determining ionization. This finding conflicts with evidence from solvent effects which indicates that there is participation by solvent in the mechanistically similar solvolysis of *sec.*-butyl bromide.[26] While further work is needed to clear up this discrepancy, the striking difference between the salt-effects for 1-phenylethyl alcohol and *sec.*-butyl alcohol, the recent indications that there may be structural limitations to the correlation of acid–base equilibria by H_0,[35] and previous examples of acid-catalysed reactions whose rates are not correlated neatly by one or the other of the acidity functions [36-38] cause us to feel that the theory of Zucker and Hammett, in the simple form in which it was originally suggested,[27] may not provide a consistently reliable basis for the diagnosis of reaction mechanism.

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[35] N. C. Deno, lecture presented before the Sixth Conference on Reaction Mechanisms, Swarthmore, Penna., September, 1956; Deno and Perizzolo, *J. Amer. Chem. Soc.*, 1957, **79**, 1345.

[36] Bell, Dowding, and Noble, *J.*, 1955, 3106.

[37] Gold and Hilton, *J.*, 1955, 843.

[38] Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240, 3243.