994. *Nucleophilic Substitution Reactions of Benzyl Halides. Part II.* Rates and Product Proportions for the Solvolysis of Benzyl Chloride in Ethanol–Water Mixtures.*

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The proportions of the two reaction products for the ethanolysis-hydrolysis of benzyl chloride differ considerably from those required by the Olson–Halford equation.[1] This is explained in terms of the sensitivity of the transition-state structures to changes in the solvent composition.

THIS paper reports overall rates and the proportions of the two reaction products for the solvolysis of benzyl chloride in a number of ethanol–water mixtures. Hughes, Ingold, and their co-workers have shown that Olson and Halford's fugacity rate equation[1] accurately predicts the product proportions in the alcoholysis-hydrolysis of *n*-butyl bromide,[2] which occurs by the more extreme form of the bimolecular mechanism (S_N2), but not in the corresponding reactions of *tert.*-butyl chloride[3] where the unimolecular mechanism (S_N1) is operating. Nucleophilic displacements in benzyl chloride take place in a manner intermediate between the extreme bimolecular and unimolecular mechanisms, at least in partly aqueous solvents, and it was of interest to examine the validity of this equation under such conditions.

* Part I, *J.*, 1957, 4747.

[1] Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644.

[2] Bird, Hughes, and Ingold, *J.*, 1943, 255.

[3] Bateman, Hughes, and Ingold, *J.*, 1938, 881.

For the ethanolysis-hydrolysis of an organic chloride, RCl, Olson and Halford's equation takes the form

$$\mathrm{d[ROH]/d}t = k_{\mathrm{w}}p_{\mathrm{w}}p_{\mathrm{RCl}},\ \mathrm{d[ROEt]/d}t = k_{\mathrm{e}}p_{\mathrm{e}}p_{\mathrm{RCl}}$$

where the k's are the fugacity rate coefficients which are independent of the solvent composition, the p's are the partial vapour pressures and the subscripts w and e refer to water and ethanol, respectively. As the two reactions are of the same kinetic order, this equation predicts that $\mathrm{[ROH]/[ROEt]} = k_{\mathrm{w}}p_{\mathrm{w}}/k_{\mathrm{e}}p_{\mathrm{e}}$ and, hence, that the ratio $\mathrm{[ROH]}p_{\mathrm{e}}/\mathrm{[ROEt]}p_{\mathrm{w}}$ is a constant, independent of the solvent composition.

Solvolysis of benzyl chloride in ethanol–water at 79·94°.

" % " Ethanol *	10^5k †	[ROH]/([ROH] + [ROEt])	$\mathrm{[ROH]}p_{\mathrm{e}}/\mathrm{[ROEt]}p_{\mathrm{w}}$ ‡
100	6·7 §	—	—
90	15·8 §	0·141	0·57
80	38·3	0·348	1·12
70	65·8	0·642	3·02
60	103	0·838	7·50
50	179	0·884	9·67

* " x% " ethanol was prepared by mixing the solvents in the proportions x ml. of ethanol to (100 − x) ml. of water.

† Rate coefficients for overall solvolysis in sec.$^{-1}$.

‡ Vapour pressures extrapolated from data at lower temperatures (International Critical Tables, Vol. III, p. 290).

§ Initial values of decreasing rate coefficients.

The figures in the last column of the Table show clearly that the requirements of the Olson–Halford equation are not met by the present reactions. Unimolecular solvolysis could be responsible for this observation (though for *tert.*-butyl chloride the corresponding increase of $\mathrm{[ROH]}p_{\mathrm{e}}/\mathrm{[ROEt]}p_{\mathrm{w}}$ is much less [3]) but, even in " 50% " ethanol, the solvent most favourable to the operation of this mechanism, not more than a small fraction of the total hydrolysis and ethanolysis can proceed without covalent participation by the solvent (see Part I). Admittedly, the Olson–Halford equation neglects the activity coefficients (f_{w}^* and f_{e}^*) of the transition states.[4] Strictly, $\mathrm{[ROH]}p_{\mathrm{e}}f_{\mathrm{w}}^*/\mathrm{[ROEt]}p_{\mathrm{w}}f_{\mathrm{e}}^*$, and not $\mathrm{[ROH]}p_{\mathrm{e}}/\mathrm{[ROEt]}p_{\mathrm{w}}$, should be constant, but the transition states for bimolecular hydrolysis and ethanolysis are structurally similar so that we would not expect $f_{\mathrm{w}}^*/f_{\mathrm{e}}^*$ to differ much from unity, or to vary appreciably with changing solvent composition.[2] It does not, therefore, seem likely that neglect of these activity coefficients accounts for the large variations now observed.

At this stage it is necessary to comment briefly on the reaction mechanism. The transition state in the reaction of a solvent molecule, S, with RCl can be regarded as the resonance hybrid of the valence-bond structures (I), (II), and (III) :

$$\mathrm{S\ \ R{-}Cl\ (I);\ \ {}^{+}S{-}R\ \ Cl^{-}\ (II);\ \ S\ \ R^{+}\ Cl^{-}\ (III)}$$

In Part I it was concluded that the reaction of benzyl chloride with " 50% " ethanol occurs either *via* two transition states (one for hydrolysis and one for ethanolysis) in which structure (III) is more important than (II), or *via* a whole series of transition states which differ in the contributions of these structures. The effect of solvent changes on the rate suggested that (III) participates to a much smaller extent when no water is present. This is only to be expected since in this structure the electric charges are less dispersed than in (II); it should therefore be more heavily solvated [5] and, hence, be stabilised more than (II) by an increase in the ionising power of the medium. As a result it seems reasonable to consider that (III) becomes progressively more important in the transition state (or

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[4] Crunwald and Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; Gold, *Trans. Faraday Soc.*, 1948, **44**, 506.

[5] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 346.

states) for hydrolysis, or ethanolysis, as the solvent is made more aqueous. It is consistent with this view that the solvolysis of benzyl chloride is accelerated less by the addition of small amounts of water to ethanol than the solvolysis of *n*-butyl bromide [where structure (III) makes only a small contribution], and more by the addition of larger amounts.*

The results in the Table show that the proportion of hydrolysis becomes increasingly greater than predicted by the Olson–Halford equation as the water content of the solvent is raised. As this also leads to an increasing participation of (III) in the structure of the transition states, our results can be explained if it is assumed that the greater the importance of (III), the later the stage in the activation process at which covalent bonding with the solvent begins.† Covalent attachment occurs from within the immediate vicinity of the reacting halide where the better solvating agent, water, is present in a larger proportion than in the bulk of the solvent if some partial ionisation has already taken place. Under these conditions water has a better chance of forming a bond than is indicated by its thermodynamic activity in the solvent, and it is this quantity which appears in the kinetic term for hydrolysis in Olson and Halford's rate equation. Such an effect will become progressively more important as we move towards the more aqueous solvents. This interpretation implies that deviations from the Olson–Halford equation are least in the present reactions when the water content is low. Support for this assumption comes from the results for *n*-butyl bromide which are consistent with the view that this equation is valid when the contribution of (III) to the structure of the transition state is small.

The similar but very much smaller increase of $[\mathrm{ROH}]p_e/[\mathrm{ROEt}]p_w$ in the ethanolysis-hydrolysis of *tert.*-butyl chloride suggests that large variations in this ratio may be characteristic of considerable changes in the transition-state structure with changing solvent composition. If this is the case, a significant participation by both (II) and (III) in solvolytic reactions could be recognised by this method.

EXPERIMENTAL

The experimental techniques were similar to those described in Part I, reaction rates and product proportions being determined from initially *ca.* 0·04M-solutions.

Constant integrated first-order rate coefficients were obtained in all solvents except ethanol and " 90% " ethanol, where these coefficients decreased as the reaction proceeded. This type of behaviour has been noted before and probably results from combination between the liberated acid and the solvent [7]—the reactions were followed by the development of acidity. For these solvents, initial rate coefficients were obtained by graphical extrapolation.

The reaction products after complete solvolysis (*i.e.*, after more than ten " half-lives " had elapsed) were analysed for benzyl alcohol in the following manner, in duplicate or triplicate. Water was added to the solution till it contained equal volumes of ethanol and water. 25 ml. of this mixture were treated with 1 ml. of ammonia (*d* 0·88) to remove excess of acid, and extracted with 10 ml. of light petroleum (b. p. 40—60°). The extract was washed four times with 10 ml. portions of water and cooled to −80°; at this temperature benzyl alcohol was precipitated while benzyl ether remained in solution. The supernatant liquid was decanted off and a stream of air passed at reduced pressure over the residue as it warmed to room temperature, till constant weight was reached; no material was lost as spray provided that the capillary was fine enough. This method gave the amount of benzyl alcohol reproducible to within 1% of the total products, and independent of the presence of up to 0·04 mole of benzyl ether and hydrochloric acid per l. of reaction mixture.

The amount of benzyl ether was found by difference from the initial concentration of the benzyl chloride.

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* This is readily demonstrated by interpolating our rate data to the solvent compositions used in the study of *n*-butyl bromide.[2]

† A similar assumption has recently been made in a different context by Hyne and Robertson.[6]

[6] Hyne and Robertson, *Canad. J. Chem.*, 1956, **34**, 863.

[7] Vernon, *J.*, 1954, 4462.

Most experiments were carried out at 79·94°, but the products for reaction with " 50% " ethanol were also examined at 50·60°; here 82·2% of the total reaction resulted in hydrolysis. Comparison with the data at the higher temperature (see Table) then shows that the activation energy for hydrolysis in this solvent is about 3 kcal. mole^{-1} greater than for ethanolysis, provided that each of these processes takes place *via* a single transition state.

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