

Activation in the Solvolytic Substitution Reactions of Unstable Alkoxyethyl Cations

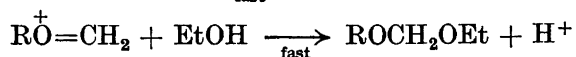
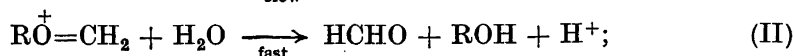
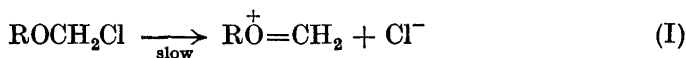
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Measurements have been made of the reaction product composition in the unimolecular solvolysis of methoxymethyl chloride and ethoxymethyl chloride in water-ethanol mixtures at temperatures varying between 0°C and 75°C. In all cases, it was found that the relative amount of formal formed by the solvolysis, as compared with that of formaldehyde, increases with temperature. By the plots of $\log ([\text{formal}] / [\text{formaldehyde}])$ against $1/T$, it was shown that the cation-ethanol reactions have activation energies of about 2 kilocalories per mole higher than the simultaneously occurring cation-water reactions.

The kinetic features of the fast, product-forming stages of unimolecular nucleophilic substitution reactions have been extensively discussed by Ingold, Hughes and co-workers¹⁻³. In one particular case, for the reaction of di-*p*-tolylmethyl chloride in aqueous acetone containing added azide ions³, these authors showed that the relative rate of formation of di-*p*-tolylmethyl azide, in comparison to that of di-*p*-tolylmethyl alcohol, increases with temperature by an amount which indicates that the cation-azide ion reaction has an activation energy of about 4 kilocalories per mole higher than the cation-solvent reaction, and therefore, at least the former process must be activated. On the other hand, there was no experimental evidence as to whether or not the fast cation-solvent reactions of unimolecular substitutions are activated. The theory on unimolecular solvolytic substitutions, developed by Ingold and Hughes, did not include, but did not require, an activation in these reactions.

An illustration of competing unimolecular, purely solvolytic substitution reactions, for which the relative contributions of the simultaneously occurring reactions can be easily measured at different temperatures, is furnished by the solvolysis of alkoxyethyl chlorides in water-ethanol mixtures. According to the earlier study⁴, these reactions take place by the S_N1 mechanism:



The present paper gives the results of a study, in which the solvolysis products of methoxymethyl chloride and ethoxymethyl chloride were determined at various temperatures.

The procedure used to investigate the product-forming reactions (II) was to determine the composition of the solvolysis product, this composition giving a direct measure of the relative rates of reactions (II). This method necessarily involved a performance of measurements in water-ethanol mixtures of such a composition, that the molar percentages of formaldehyde and formal formed by the solvolysis were of a similar order of magnitude, because only in such solvents the relative contributions of reactions (II) could be determined accurately enough. Although in the water-ethanol mixtures employed even the rate-determining reactions (I) were much too rapid to permit of kinetic measurements, still the compositions of the final products could be analysed. The results are collected in Tables 1 and 2. The molar percentage of formaldehyde

Table 1. Molar percentages of formaldehyde formed by the solvolysis of methoxymethyl chloride in water-ethanol mixtures at various temperatures.

43.8 mole % EtOH		60.9 mole % EtOH		78.1 mole % EtOH	
°C	mole % HCHO	°C	mole % HCHO	°C	mole % HCHO
0	60.9	0	47.0	0	29.8
10	58.9	10	44.7	10	28.2
20	54.7	20	42.3	20	23.7
30	51.3	30	38.8	30	22.8
40	50.2	40	37.0	40	22.6
50	47.2	50	34.5	50	22.3
60	45.3	60	31.2	60	20.0
70	43.9	70	30.5	70	18.5

Table 2. Molar percentages of formaldehyde formed by the solvolysis of ethoxymethyl chloride in water-ethanol mixtures at various temperatures.

43.8 mole % EtOH		60.9 mole % EtOH		78.1 mole % EtOH	
°C	mole % HCHO	°C	mole % HCHO	°C	mole % HCHO
0	58.6	0	41.9	0	28.4
		5	39.2		
12	53.5	10	38.8	12	23.6
		15	37.5		
25	50.2	20	35.9	25	21.9
		25	34.8		
38	46.5	30	34.6	38	20.2
		35	32.4		
50	44.6	40	30.7	50	17.5
		45	31.1		
62	41.3	50	27.9	75	14.0
		55	28.5		
75	39.6	60	26.4		
		65	26.1		
		70	25.0		

formed was found to be substantially unaffected by the initial concentration of alkoxymethyl chloride.

The tables show that the composition of the final product of solvolysis is dependent on temperature. In all cases the molar percentages of formaldehyde formed decrease with temperature. This indicates that the relative contribution of the latter reaction (II) increases with temperature, *i. e.* the latter reaction involves a higher energy of activation. Therefore, at least the cation-ethanol reaction must be activated. On the other hand, in view of the fact that both the reactions (II) are apparently of a similar type, there is no reason to assume that the cation-water reaction would not be activated.

Although the actual molecularities of reactions (II) cannot be determined by the available methods, these reactions can be considered as being of the first order, in view of the large excesses of water and ethanol molecules present in the reaction solvents. Supposing the Arrhenius equation to be valid for both the reactions, and denoting their respective Arrhenius parameters by $A_{\text{H}_2\text{O}}$, $E_{\text{H}_2\text{O}}$, A_{EtOH} and E_{EtOH} , and denoting by α the molar ratio of formaldehyde present in the final product, it is seen that

$$\log \alpha = \log (A_{\text{EtOH}} / A_{\text{H}_2\text{O}}) - \Delta E / 2.303 RT \quad (1)$$

in which

$$\Delta E = E_{\text{EtOH}} - E_{\text{H}_2\text{O}} \quad (2)$$

According to eqn. (1), a plot of the values of $\log \alpha$ against $1/T$ should give a straight line. Such plots are made in Figs. 1 and 2. Although there is some scattering of the values, the deviations from eqn. (1) do not exceed the experimental errors in magnitude. The slopes of the lines are seen to be of nearly the same magnitude, *viz.* —400, independently on the halide and solvent mixture used. The average value of the slopes indicates that the activation energy of the cation-ethanol reaction exceeds that of the cation-water reaction by about 1 800 calories per mole.

The theory on unimolecular solvolytic substitution, developed by Ingold and Hughes¹⁻³, suggests that the fast, product-forming reaction stage is an internal collapse of the solvation shell of the intermediate cation. If the theory is applied to the present case, it can be assumed that the inner solvation shell of the alkoxymethyl ion in water-ethanol mixtures consists of a number of water and ethanol molecules. When one of these molecules attains a certain, critical distance from the point of reaction, a destruction of the solvation shell occurs, and the reaction follows. One of the factors involved in the activation energies of reactions (II) may be merely due to the spatial conditions prevailing in the solvation shell. The water or ethanol molecule, which converts the solvated cation to the final product, must be able to overcome a certain amount of steric strain exerted by the neighbouring molecules present in the solvation shell, before the critical separation, which is necessary for the reaction to occur, can be attained. This may be one of the factors which give rise to a higher activation energy for the cation-ethanol reaction, in comparison to that of the cation-water reaction. As the size of ethanol molecules is larger than that of water molecules, the approach of an ethanol molecule to the critical distance of reaction is accompanied by a higher degree of destruction of the solvation shell.

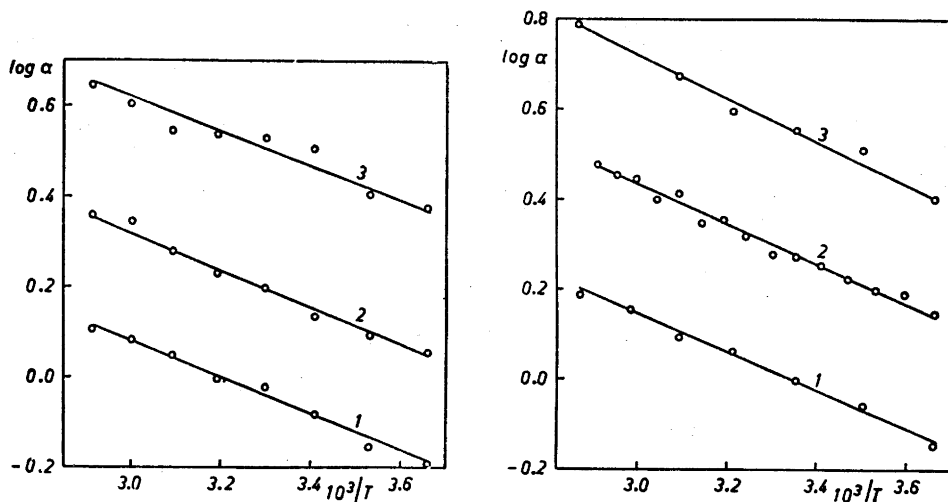


Fig. 1. Plot of $\log \alpha$ against $1/T$ for the solvolysis of methoxymethyl chloride.

Fig. 2. Plot of $\log \alpha$ against $1/T$ for the solvolysis of ethoxymethyl chloride.

1. 43.8 mole % EtOH. 2. 60.9 mole % EtOH. 3. 78.1 mole % EtOH.

Although reactions (II) have a certain amount of activation energy, their enormous rapidity is, however, understood by the activation entropies involved in such processes. The destructions of the solvation shells are accompanied by great decreases in order, *i. e.* the activation entropies must have large positive values, and hence the frequency factors are probably very large.

EXPERIMENTAL

The methods of preparing the materials, and those used for analysing the reaction product compositions were essentially those described earlier⁴. Owing to the great rapidity of the reactions, the product analysis could be performed almost immediately after mixing the reaction components. At relatively high temperatures, *viz.* at 50°C and above this temperature, the method of sealed bulbs was used, in order to eliminate volatility errors. In these experiments, a small, thin-walled glass ampoule containing the alkoxyethyl chloride was sealed together with small pieces of stone into a larger glass bulb which contained the reaction solvent. After the bulb, when immersed in a thermostat, had attained the thermostat temperature, the reaction components were brought together by vigorous shaking by which the small ampoule was broken. As it was verified that the subsequent reactions, the hydrolysis of formal and its reversal, were at relatively high temperatures rapid enough to effect an error in analysis, if the bulbs were kept a prolonged period of time at these temperatures, the bulbs were immersed in an ice-water mixture immediately after mixing the reaction components. After cooling, the bulbs were broken and the reaction product was analysed. By this method reproducible values were obtained even at the highest temperatures used.

Table 3 shows an example of experiments, in which the effect of initial alkoxyethyl chloride concentration on the composition of the final product was investigated. It is seen that the molar percentage of formaldehyde increases with decreasing alkoxyethyl chloride concentration. However, the increase is not material. In order to eliminate the

error due to differences in initial concentrations, all of the determinations, the results of which are included in Tables 1 and 2, were performed using approximately the same initial concentrations of the alkoxymethyl chlorides, viz. about 0.1 M.

Table 3. The solvolysis of ethoxymethyl chloride in 60.9 moles per cent ethanol at 25°C. The influence of the initial concentration on the composition of solvolysis product.

[EtOCH ₂ Cl] initially	0.3050	0.2273	0.1015	0.0627	0.0247
mole % HCHO in the product	32.0	33.9	34.8	35.9	35.2

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