

## The Influence of the Solvent on Reaction Velocity

### XXIX. Solvolysis of Benzyl Chlorides in Dimethyl Sulphoxide-Water Mixtures

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The first-order rate constants of the solvolysis of benzyl chlorides decrease with decreasing water content in a much lesser degree in dimethyl sulphoxide-water mixtures than in aqueous acetone, dioxan, or ethanol. The substituent effects decrease with the water concentration and with rising temperature. The activation parameters and the influence of the dielectric constant of the solvent are considered. The mechanism of the reaction is discussed.

In recent years a number of papers have been published on the solvolysis of benzyl chlorides in mixed solvents. A previous communication of this series dealt with the reactions in various acetone-water and dioxan-water mixtures.<sup>1</sup> Hyne *et al.* studied the solvolysis in ethanol-water mixtures.<sup>2,3</sup> Böhme and Henning,<sup>4</sup> and Sadek *et al.*<sup>5</sup> investigated the solvolysis of benzyl chloride in dioxan-water, and Tommila and Virtanen<sup>6</sup> the reaction in dimethyl sulphoxide-water mixtures, but at one temperature only. In this paper are reported results of kinetic measurements of the solvolysis of benzyl chloride and *p*-methyl-, *p*-chloro-, *m*-chloro-, and *p*-nitrobenzyl chlorides in various dimethyl sulphoxide-water mixtures. The investigation was undertaken in view of the growing interest in dimethyl sulphoxide (DMSO) as a solvent in chemical kinetics. The substituents were chosen so that their effects would be in both directions and as pronounced as possible in order that the changes in them caused by variation of the solvent could be detected with the highest relative accuracy.

#### EXPERIMENTAL

Benzyl chloride (Baker's Analyzed grade), *p*-methylbenzyl chloride prepared by chlorination of *p*-xylene (Fluka AG, pro analysi), and *p*-chlorobenzyl and *m*-chlorobenzyl chlorides obtained by chlorination of the corresponding chlorotoluenes (Fluka AG, reinst) were carefully distilled at reduced pressure before use. The boiling points of the fractions used were: benzyl chloride 67.5°/15 mm, *p*-methylbenzyl chloride 93°/21 mm, *p*-chloro-

benzyl chloride 100°/16 mm, *m*-chlorobenzyl chloride 97.5°/14 mm. *p*-Nitrobenzyl chloride (Fluka AG, purissimum) was recrystallized from ethanol and it melted at 72.5°. Dimethyl sulphoxide (Nitroglycerin AB, Gyttorp, Sweden) was distilled at reduced pressure and crystallized from the melt until its melting point was 18.50–18.55°. Freshly redistilled carbon dioxide-free water was used in the preparation of the solvent mixtures.

The method used in the kinetic experiments was the same sealed ampoule technique as was employed in previous investigations of the solvolysis of benzyl chlorides.<sup>1</sup> The acid formed was titrated with a 0.02 N sodium hydroxide using cresol red as indicator. The end point of the titration was always very sharp. However, in the experiments using mixtures of high water content, in which the organic chlorides are very sparingly soluble and in which the reactions are fast, another technique was used. Measured volumes of the solvent were kept in glass-stoppered flasks in the thermostat until they had acquired its temperature, after which a drop of the organic chloride was added and brought into solution by vigorous shaking. After suitable time intervals reaction vessels were taken from the thermostat and quickly cooled by putting them into a mixture of ice and water, and the acid formed was titrated as described above. In order to determine the infinity value, the hydrolysis was then continued at 75° about 4–5 h and the titration was carried out on the following day. The number of separate determinations in each run was about eight. Many runs were made in duplicate or triplicate. Five- or ten-milliliter microburets were used in all titrations. Owing to the poor solubility of *p*-nitrobenzyl chloride and the chlorobenzyl chlorides in solvents of high water content, the experiments with these substances were not extended to mixtures containing more water than 500–700 ml/l.

The first-order rate equation was employed in the calculation of the rate constants. The Arrhenius parameters were computed from the mean rate constant values at various temperatures by the method of least squares and from these the activation entropies and enthalpies were obtained by the usual formulas.

It has been previously found that the rates of the reactions in dioxan-water<sup>7</sup> and acetone-water<sup>1</sup> mixtures increase somewhat as the initial concentration is decreased. This is the case also for the rates in DMSO-water mixtures as seen from the following results for benzyl chloride in aqueous DMSO containing 400 ml of water per litre at 50°:

<i>a</i> , mole/litre	0.10	0.05	0.02	0.01
10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>	2.23	2.28	2.66	2.89

Therefore, as far as possible, the same initial concentration, 0.02 M, was always used. In highly aqueous solutions, however, smaller initial concentrations had to be used, but even then the initial concentration was in general the same for all the compounds. Owing to the different initial concentrations, the rate constant values in Table I differ slightly from those of Tommila and Virtanen.<sup>6</sup> That the reaction, despite its dependence on the initial concentration, simulates so closely a true first-order one is due to the retarding effect of the reaction products, benzyl alcohol and hydrochloric acid.<sup>7</sup>

## RESULTS AND DISCUSSION

Tables 1–5 contain the experimental data for the compounds studied, *k* and *A* being expressed in sec<sup>-1</sup>. Also the initial concentrations *a* of the organic halides are given. The compositions of the solvent mixtures are given in Table 6.

*The reaction rates.* It has been found in a great number of cases that DMSO accelerates reactions in which a negative ion is one participant. In contrast, it was found in the previous work<sup>6</sup> that the first-order rate constant of the solvolysis of benzyl chloride in DMSO-water mixtures decreases with decreasing water concentration, but in a much lesser degree than in aqueous acetone or dioxan. The data of Tables 1–5 show that the dependence on the solvent composition is markedly different for different compounds and follows the order *p*-Me > H > *p*-Cl > *m*-Cl > *p*-NO<sub>2</sub>. The plots of log *k* against the logarithm of the molar water concentration of the solvent are of special interest.

Table 1. The solvolysis of benzyl chloride in DMSO-water-mixtures.

Water ml/l	<i>a</i> mole/l	$10^6k, \text{sec}^{-1}$				<i>E</i> cal	log <i>A</i>	$\Delta S^*$ (40°)	$\Delta G^*$ cal
		25.00°	40.00°	50.00°	60.00°				
1000	0.005	13.5 <sup>a</sup>	70.3	186		20 430	10.000	-14.4	24 320
900	0.005	10.2	53.2	143	367	20 190	9.816	-15.7	24 480
800	0.01	8.75	43.8	116	305	19 970	9.584	-16.8	24 600
700	0.01	6.90	33.8	89.4	224	19 600	9.211	-18.5	24 762
600	0.01	4.93	24.8	64.7	166	19 780	9.199	-18.6	24 960
500	0.02	3.33	16.6	43.5	111	19 760	9.011	-19.4	25 210
400	0.02	2.16	10.4	26.6	71.9	19 650	8.737	-20.6	25 490
300	0.02	1.21	5.98	15.8	37.6	19 420	8.328	-22.5	25 850
200	0.02	0.594	2.85	7.37	18.1	19 260	7.896	-24.5	26 300
100	0.02	0.186	0.859	2.23	5.51	19 090	7.266	-27.4	27 040

<sup>a</sup> 30°:  $23.8 \times 10^{-6}$ .Table 2. The solvolysis of *p*-methylbenzyl chloride in DMSO-water mixtures.

Water ml/l	<i>a</i> mole/l	$10^6k, \text{sec}^{-1}$				<i>E</i> cal	log <i>A</i>	$\Delta S^*$ (40°)	$\Delta G^*$ cal
		25.00°	40.00°	50.00°	60.00°				
1000		291	1390	3850	10400	20 130	11.217	-9.3	22 420
900	0.005	182	925	2400	6100	19 500	10.586	-12.2	22 700
800	0.005	96.2	456	1160	2860	19 100	9.989	-14.9	23 150
700	0.01	63.0	281	745	1760	18 820	9.605	-16.7	23 420
600	0.01	39.4	157	432	970	18 200	8.933	-19.7	23 760
500	0.02	18.2	78.6	204	472	18 400	8.749	-20.6	24 220
400	0.02	8.58	39.0	99.6	231	18 600	8.572	-21.4	24 680
300	0.02	4.25	18.9	48.7	118	18 750	8.370	-22.3	25 120
200	0.02	1.68	7.18	19.1	45.1	18 850	8.032	-23.9	25 700
100	0.02	0.393	1.77	4.43	10.9	18 700	7.311	-27.2	26 580

Table 3. The solvolysis of *p*-nitrobenzyl chloride in DMSO-water mixtures.

Water ml/l	<i>a</i> mole/l	$10^6k, \text{sec}^{-1}$				<i>E</i> cal	log <i>A</i>	$\Delta S^*$ (40°)	$\Delta G^*$ cal
		25.00°	40.00°	50.00°	60.00°				
600	0.006	0.302	1.74	4.84	13.3	21 290	9.095	-19.0	26 620
500	0.01	0.271	1.50	4.30	11.8	21 240	9.004	-19.4	26 690
400	0.02	0.260	1.39	3.90	10.9	21 000	8.812	-20.3	26 730
300	0.02	0.237	1.24	3.32	9.21	20 670	8.521	-21.6	26 820
200	0.02	0.211	1.06	2.86	7.45	20 070	8.039	-23.8	26 910
100	0.02	0.148	0.671	1.66	4.08	18 700	6.880	-29.1	27 190

Table 4. The solvolysis of *m*-chlorobenzyl chloride in DMSO-water mixtures.

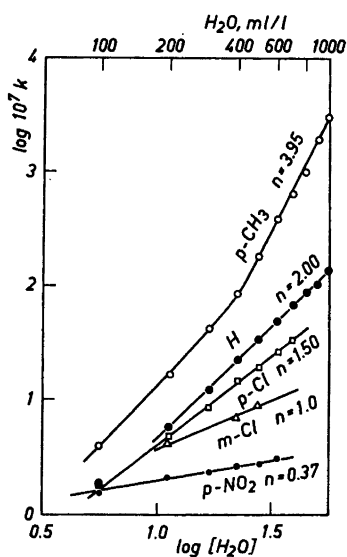
Water ml/l	$\alpha$ mole/l	$10^6 k \text{ sec}^{-1}$				$E$ cal	$\log A$	$\Delta S^*$ (40°)	$\Delta G^*$ cal
		25.00°	40.00°	50.00°	60.00°				
500	0.02	0.913	4.45	12.5	33.2	20 250	8.803	-20.3	25 990
400	0.02	0.702	3.67	9.70	23.5	19 800	8.375	-22.3	26 160
200	0.02	0.414	1.78	4.91	12.1	19 100	7.615	-25.8	26 560

Table 5. The solvolysis of *p*-chlorobenzyl chloride in DMSO-water mixtures at 25°.

Water, ml/l	700	600	500	400	300	200	100
$\alpha$ , mole/l	0.01	0.01	0.025	0.05	0.05	0.05	0.05
$10^6 k$ , sec <sup>-1</sup>	3.40	2.63	1.95	1.31	0.877	0.493	0.180

Table 6. The solvent mixtures.

Water, ml/l	1000	900	800	700	600	500	400	300	200	100
DMSO, wt. %	0	11.1	22.4	33.0	43.5	53.6	63.3	72.7	81.9	90.9
$x_{\text{DMSO}}$	0	0.028	0.062	0.102	0.151	0.210	0.285	0.380	0.510	0.698

Fig. 1. Plot of  $\log k$  against  $\log [\text{H}_2\text{O}]$ .  
Temperature 25°.

If, namely,  $n$  water molecules participate in the solvolysis reaction, the rate law is <sup>8</sup>

$$dx/dt = k'[\text{H}_2\text{O}]^n (a-x)$$

and hence

$$\log k = \log k' + n \log [\text{H}_2\text{O}] \quad (1)$$

Thus the plot of  $\log k$  against  $\log [\text{H}_2\text{O}]$  should yield a straight line of slope  $n$ , if  $k'$  remains constant. Fig. 1 shows such plots for 25°. In agreement with the previous results,<sup>6</sup> the plot for benzyl chloride is a straight line of slope 2.0 over the range from pure water to mixtures which contain about 180 ml or 10 moles of water per litre. For *p*-methylbenzyl chloride the slope is about 4.0 in the region from pure water to a water content of about 400 ml/l or 23 moles per litre, and then it diminishes towards a value of two. For *p*-chlorobenzyl chloride  $n$  is about 1.5 throughout the solvent range studied, *i.e.* from a water content of 700 ml to 100 ml/l. The value of  $n$  for *m*-chlorobenzyl chloride is about 1.0 and that for *p*-nitrobenzyl chloride only 0.4. Similar results were obtained at the other temperatures. These values of  $n$  differ greatly from those found for the reactions in acetone-water and dioxan-water mixtures<sup>1</sup> and also in aqueous ethanol.<sup>2,3</sup> In the first two solvent systems  $n$  is 6 for benzyl chloride and *p*-methylbenzyl chloride when water is the major solvent component. For *p*-chlorobenzyl chloride  $n$  is 5, and for *p*-nitrobenzyl chloride about 4. In solvents containing less water than about 400 ml/l,  $n$  is smaller, about 3 for benzyl and methylbenzyl chlorides and 2 for the nitro compound. Thus only for *p*-methylbenzyl chloride is the slope of the same magnitude as the slope for the compound in the other mixed solvents, but even then  $n$  is smaller than in the latter.

*The activation parameters.* In all cases investigated, the activation energies in the same solvent follow the order  $p\text{-NO}_2 > m\text{-Cl} > \text{H} > p\text{-CH}_3$ , *i.e.* the activation energy is the higher the slower the reaction. In aqueous acetone<sup>1,9</sup> and in aqueous ethanol<sup>2,3</sup> not only electron-attracting ( $\text{NO}_2$ , Cl) but also electron-repelling ( $\text{CH}_3$ ) substituents increase the energy of activation. The results of Fierens *et al.*<sup>10</sup> in various solvents show variations in both directions.

The enthalpies and entropies of activation for the solvolysis of benzyl chlorides,<sup>1-3</sup> alkyl halides,<sup>8,11</sup> and alkyl benzenesulphonates<sup>12</sup> tend to exhibit strong extrema in aqueous organic solvents, whereas  $\Delta G^*$  (because of compensating phenomena) varies uniformly with the composition of the solvent. The behaviour of the activation parameters of the reactions in DMSO-water mixtures is simpler than, for instance, those of the reactions in aqueous acetone: in all cases investigated,  $\Delta G^*$  varies monotonously with solvent composition, and  $\Delta H^*$  shows a minimum only for the unsubstituted compound and for *p*-methylbenzyl chloride, and even for these the minima are shallow (Figs. 2 and 3). The curves for *m*-chloro- and *p*-nitrobenzyl chlorides probably show no minima. For the sake of comparison, also the curves for benzyl chloride in aqueous acetone are drawn in Fig. 2. The deep minima are conspicuous, and we see also that when the water concentration is less than about 600 ml/l, the activation enthalpy is higher than for aqueous DMSO. The mole fractions in aqueous acetone and aqueous DMSO are almost identical at equal water concentrations, and thus the curves relate also to equal mole fractions.

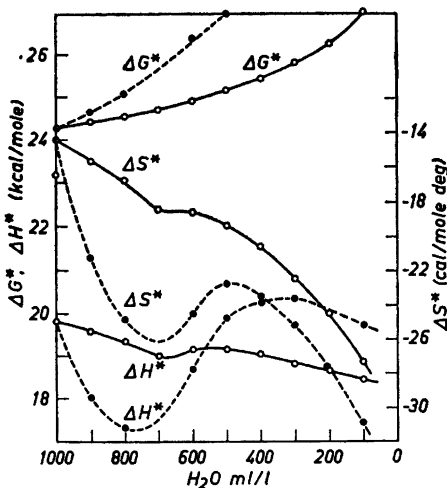


Fig. 2. Benzyl chloride. Variation of  $\Delta H^*$ ,  $\Delta S^*$ , and  $\Delta G^*$  with solvent composition. — DMSO-water, - - - acetone-water.

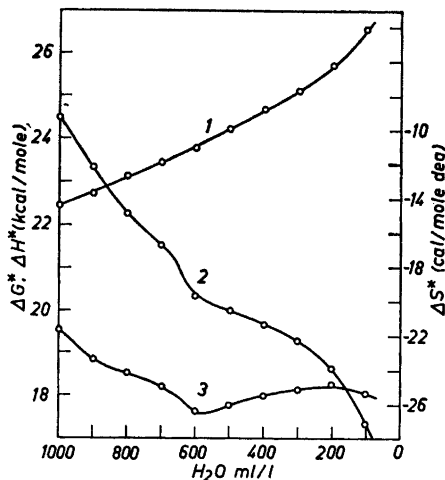


Fig. 3. *p*-Methylbenzyl chloride. Variation of  $\Delta H^*$  (3),  $\Delta S^*$  (2), and  $\Delta G^*$  (1) with solvent composition.

The effect of the change in the activation entropy with varying solvent composition outweighs the opposite effect of the change in activation enthalpy, with the result that the reaction rate decreases continuously as the water content of the solvent mixture is decreased. The rise in the activation enthalpy for the *p*-methyl compound and benzyl chloride after the minimum alters the rate in the same direction as the change in the activation entropy, but is small and its retarding effect weak compared to that caused by the change in the activation entropy.

Extrema in the enthalpies and entropies of activation have been found also for bimolecular processes, *e.g.* for the hydrolysis of esters.<sup>13</sup> The effect of solvent on reaction velocity can to a remarkable extent be treated in terms of changes in  $\Delta G^*$ , but if we wish to understand the fundamentals of solvent effects, changes in  $\Delta H^*$  and  $\Delta S^*$  must also be carefully examined.

Different explanations have been given for the occurrence of the extrema. Tommila<sup>13,8</sup> has suggested that the minima and maxima observed in the enthalpy and entropy curves arise from changes in the solvation of the transition state and the ground state, the water molecules having a specific attraction for the hydrophilic part and the organic molecules for the alkyl or other groups of the reactants or of the transition state. A change in the composition of the solvent can thus bring about a change in the difference between the solvation of the transition state and the initial state, and this has an effect on the activation parameters. The question has been discussed in detail by Hyne,<sup>2,3,14</sup> Arnett and his collaborators<sup>15</sup> have found that the partial molal heats of solution for salts and nonelectrolytes show endothermic maxima where  $\Delta H^*$  for solvolysis usually is a minimum, and from this they conclude

that changes in the solvation of the initial state are more important than changes in the solvation of the transition state. They have also tried to estimate the changes in the solvation of the transition state. In a recent paper,<sup>16</sup> Whalley *et al.* suppose that the existence of a minimum in the acid hydrolysis of methyl acetate can be ascribed mainly to the change in thermal expansivity when organic liquid is added to water. However, one must not forget that extrema occur in bimolecular processes also, although the thermal expansion of the solvent is taken into account in the values of the rate constants. It is remarkable that the isodielectric activation energies and frequency factors for the solvolysis of organic halides do not show any extrema.<sup>1,8</sup> Not without interest in this connection is the observation of Koivisto<sup>17</sup> that the heat of reaction for the neutralization of sodium hydroxide with phenol or acetic acid in mixed solvents varies similarly as the enthalpy of activation of, *e.g.*, ester hydrolysis.

The relationships between the enthalpies and entropies of activation have often been discussed.<sup>13,18-20</sup> Fig. 4 shows that the relationship is linear for the solvolysis of *p*-nitrobenzyl chloride in aqueous DMSO over the whole range investigated, from a water content of 600 ml/l to 100 ml/l. For the unsubstituted compound the plot has two linear parts corresponding to water contents from 1000 to 700 ml/l and below 550 ml/l. For *p*-methylbenzyl chloride the plot is linear only in the region from pure water to a water content of 600 ml/l. The breaks in the lines coincide with those in Figs. 2 and 3. For the solvolysis in aqueous acetone, the plots are N-shaped.<sup>1</sup>

*The reaction rate and the dielectric constant of the solvent.* According to the prevailing theories, solvolysis reactions should be favoured in polar solvents,<sup>21</sup> and there should exist an approximate linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant of the

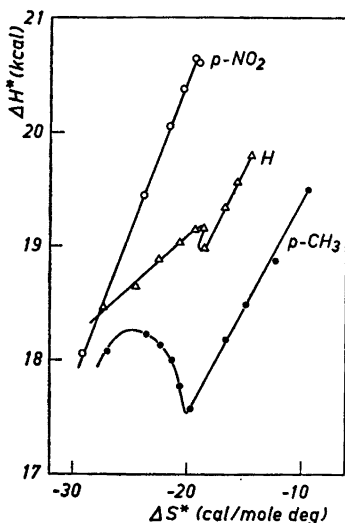


Fig. 4. Plot of  $\Delta H^*$  against  $\Delta S^*$ .

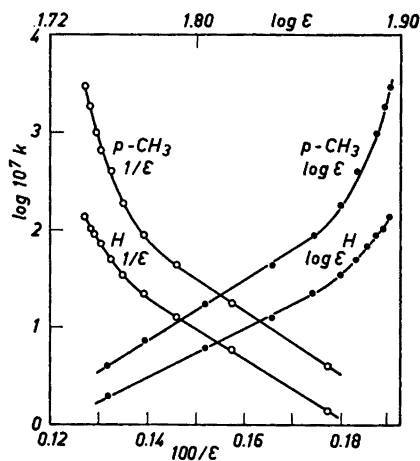


Fig. 5. Plot of  $\log k$  against  $1/\epsilon$  and against  $\log \epsilon$ . Benzyl chloride, 25°.

medium.<sup>22</sup> For the solvolysis of benzyl chlorides in acetone-water or dioxan-water mixtures, the plots are linear only in the range where the water concentration is less than 400 ml/l.<sup>1</sup> Better linear relationships over whole ranges of mixtures are often obtained if  $\log k$  is plotted against the dielectric constant  $\epsilon$  itself,<sup>1,8</sup> or against its logarithm.<sup>4,23,24</sup> No theoretical explanation for the former proportionality has been given, but the connexion between  $\log k$  and  $\log \epsilon$  becomes apparent if  $\log \epsilon$  is a linear function of the logarithm of the water concentration, as, in fact, it is approximately for acetone-water and dioxan-water mixtures.<sup>25</sup> In such cases we have at a constant temperature

$$\log \epsilon = n' \log [\text{H}_2\text{O}] + \text{const.}$$

Insertion of the expression for  $\log [\text{H}_2\text{O}]$  derived from this equation in eqn. (1) gives

$$\log k = n \frac{\log \epsilon}{n'} - n \frac{\text{const.}}{n'} + \log k'$$

or

$$\log k = m \log \epsilon + \text{const.} \quad (2)$$

where  $m = n/n'$  is a constant.

Addition of DMSO to water causes only small changes in the dielectric constant until the water concentration is about 400 ml/l.<sup>6</sup> As the rate constant decreases regularly with water concentration, the relationships between  $\log k$

Table 7. The relative rates  $k/k_w$ .<sup>a</sup>

Water ml/l	Benzyl chloride				<i>p</i> -Methylbenzyl chloride			
	25°	40°	50°	60°	25°	40°	50°	60°
1000	1	1	1	1	1	1	1	1
900	0.780	0.766	0.753	0.748	0.685	0.649	0.630	0.612
800	0.661	0.638	0.626	0.610	0.341	0.313	0.297	0.283
700	0.523	0.491	0.471	0.452	0.225	0.202	0.190	0.179
600	0.376	0.358	0.345	0.337	0.137	0.117	0.106	0.969
600	0.252	0.240	0.231	0.225	0.0640	0.0554	0.0509	0.0469
400	0.161	0.151	0.146	0.141	0.0303	0.0267	0.0248	0.0230
300	0.0928	0.0857	0.0816	0.0779	0.0148	0.0132	0.0123	0.0115
200	0.04500	0.0410	0.0387	0.0367	0.00572	0.00516	0.00484	0.00456
100	0.0140	0.0126	0.0118	0.0111	0.00140	0.00125	0.00116	0.00109
	<i>p</i> -Nitrobenzyl chloride				<i>m</i> -Chlorobenzyl chloride			
	$k/k_{600}$				$k/k_{600}$			
600	1	1	1	1	1	1	1	1
500	0.885	0.880	0.876	0.872	1	1	1	1
400	0.849	0.831	0.819	0.812	0.798	0.781	0.761	0.737
300	0.760	0.721	0.699	0.681				
200	0.689	0.627	0.587	0.556	0.452	0.418	0.391	0.370
100	0.485	0.392	0.343	0.306				

<sup>a</sup> The  $k$  values were calculated by the Arrhenius equation.



Table 8. The values of  $k_X/k_H$ , DMSO-water.<sup>a</sup>

Water, ml/l	X = <i>p</i> -CH <sub>3</sub>				X = <i>p</i> -NO <sub>2</sub>			
	25°	40°	50°	60°	25°	40°	50°	60°
1000	21.4	21.00	20.67	20.4				
900	18.8	17.8	17.3	16.7				
800	11.0	10.3	9.81	9.47				
700	9.25	8.66	8.34	8.07				
600	7.80	6.87	6.37	5.88	0.0615	0.0693	0.0750	0.0801
500	5.43	4.85	4.56	4.25	0.0811	0.0909	0.0982	0.105
400	4.02	3.71	3.51	3.33	0.121	0.137	0.145	0.155
300	3.41	3.24	3.12	3.02	0.189	0.209	0.222	0.236
200	2.73	2.64	2.59	2.54	0.354	0.379	0.393	0.409
100	2.15	2.07	2.04	2.00	0.800	0.771	0.745	0.740
	X = <i>m</i> -Cl							
500	0.270	0.277	0.289	0.295				
400	0.333	0.343	0.349	0.346				
200	0.686	0.677	0.676	0.668				

<sup>a</sup> The  $k$  values were calculated by the Arrhenius equation.

and the dielectric constant differ greatly from those observed for the other solvent systems. The plot of  $\log k$  against  $1/\epsilon$  is approximately linear only for mixtures containing less water than 400 ml/l, as was found already in the previous work.<sup>6</sup> In this range also the plots of  $\log k$  vs.  $\log [H_2O]$  and  $\log k$  vs.  $\log \epsilon$  are approximately linear (Fig. 5).

*The solvent effect and temperature.* In Table 7 the relative rates,  $k/k_w$ , at different temperatures are given. The rate constants were calculated by the Arrhenius equation;  $k_w$  is the rate constant in water. The data show that the relative rate decreases with rising temperature, but that this dependence on temperature is not large.

*The dependence of the substituent effect on solvent and temperature.* As seen from the ratios of the rate constants of the substituted compounds,  $k_X$ , to those of the unsubstituted benzyl chloride,  $k_H$ , in Table 8, the substituent effect is greatly dependent on the solvent and temperature. If the substituent is electron-repelling (CH<sub>3</sub>),  $k_X/k_H$  decreases with decreasing water concentration and with increasing temperature. If the substituent is electron-attracting (Cl, NO<sub>2</sub>), the reverse is true. (However, at very small water concentrations,  $k_X/k_H$  seems to decrease with increasing temperature also in this case). A general statement, is thus that the effect of a substituent on the reaction rate decreases with decreasing water concentration and with increasing temperature. The substituent effects become weaker as the water concentration is decreased also in acetone-water mixtures, but the effect of temperature seems to be weaker than in aqueous DMSO.<sup>1</sup> These relationships have already been preliminarily discussed elsewhere,<sup>26</sup> and a more detailed treatment will be given in a subsequent paper.

*The  $\rho\sigma$  relationship.* It is a general experience that the plots of  $\log k$  vs. the Hammett substituent constants,  $\sigma$ , for the reactions of substituted benzyl

Table 9. The values of  $\rho$  under various conditions.

Temperature °C	Water, ml/litre, in the DMSO-water solvent mixture					
	600	500	400	300	200	100
25°	-1.56	-1.40	-1.18	-0.93	-0.58	-0.13
40°	-1.48	-1.34	-1.12	-0.88	-0.54	-0.15
50°	-1.45	-1.29	-1.07	-0.84	-0.52	-0.16
60°	-1.41	-1.25	-1.05	-0.81	-0.50	-0.17

halides show a definite curvature, being markedly concave up, which indicates a shift of the mechanism towards the  $S_N1$  limit on going from electron-attracting substituents to electron-repelling substituents.<sup>19</sup> For the solvolysis in aqueous acetone the fit to a straight line is relatively good if the points for *p*-alkylbenzyl compounds are omitted.<sup>1</sup> For DMSO-water mixtures the fit is only barely satisfactory, but the use of the  $\sigma^+$  constants of Brown and Okamoto<sup>27</sup> rather than the  $\sigma$  parameters of Hammett reduces the scatter of the points. The  $\rho$  values of Table 9 refer to  $\sigma$ . They were obtained from straight lines drawn through the points for the unsubstituted compound and *p*-nitrobenzyl chloride. The points for the chlorobenzyl chlorides are scattered equally on both sides of these lines, and thus the values can be regarded as approximations as good as can be achieved on the basis of our experimental data. The values of  $\rho$  referring to  $\sigma^+$  values are about 1 % smaller than the values given in Table 9. The values of Table 9 do not differ much from those found for the reactions in aqueous acetone. Conspicuous is the great dependence of  $\rho$  on the composition of the solvent.

*The mechanism of the reaction.* As found in the previous work,<sup>1</sup> the solvolyses of benzyl chloride and the three methylbenzyl chlorides, like the solvolyses of tert.-butyl halides<sup>8</sup> and isopropyl benzenesulphonate,<sup>12</sup> which are generally regarded as  $S_N1$  reactions, are of the sixth order with respect to water in acetone-water and dioxan-water mixtures containing more water than 400 ml/l per litre. However, when the acceleration of the reactions of benzyl chlorides by hydroxide ion, the activation energies and frequency factors and other circumstances were taken into account, it was concluded<sup>1</sup> that the mechanism is not  $S_N1$ , but that the solvolysis of these four compounds in this range of solvents takes place by a mechanism which is essentially  $S_N2$  but not far from the  $S_N1$  limit (the  $S_N2(1)$  mechanism of Laidler<sup>22c</sup>). The solvolysis of *p*-nitrobenzyl chloride occurs by a mechanism which is far from the  $S_N1$  limit, and that of the chlorobenzyl chlorides is between these two extrema.

The low values of the water molecularity  $n$  in eqn. (1) for the reactions in DMSO-water mixtures is rather surprising. The value  $n = 0.4$  found for *p*-nitrobenzyl chloride can under no circumstances be a true one, because at least one water molecule is involved in the reaction. Also, for a definite reaction in water,  $n$  must always be the same; the possibility that, e.g.,  $n$  for the solvolysis of benzyl chloride in water equals 6 when derived from the plot for acetone-water or dioxan-water mixtures, but equals 2 when taken from the

plot for DMSO-water mixtures is quite unreal. Further, the dielectric constants of DMSO-water mixtures are greater than those of aqueous acetone or aqueous dioxan of the same water content, and the mechanism should shift towards the  $S_N1$  limit as the ionising power of the solvent increases. Thus,  $n$  should be six for the solvolysis of benzyl chloride and its *p*-methyl derivative in aqueous DMSO, as this value seems to be characteristic of  $S_N1$  and  $S_N2(1)$  reactions. These difficulties can be overcome if we assume that the number of water molecules,  $n$ , is the same for the reactions in DMSO-water mixtures as in the other aqueous solvents. This assumption, which was made already by Murto<sup>28</sup> implies that DMSO actually promotes the reaction, as is the case in the alkaline hydrolysis of esters<sup>29</sup> and benzyl chlorides.<sup>30</sup> If the values of the experimental first-order rate constants given in Tables 1–5 are divided by  $[H_2O]^n$ , where  $n$  has the values found for the solvolysis in acetone-water (and also in dioxan-water) mixtures in the range from pure water to a water content of about 400 ml/l, *i.e.*  $n = 6$  for benzyl chloride and *p*-methylbenzyl chloride, 5 for *p*-chlorobenzyl chloride, 4.5 for *m*-chlorobenzyl chloride, and 3.7 for *p*-nitrobenzyl chloride, and we write  $k/[H_2O]^n = k'$ , the following values are obtained for  $10^{14}k'$  at 25°:

water, ml/l	1000	900	800	700	600	500	400	300	200	100
<i>p</i> -Me	1.00	1.17	1.25	1.84	2.90	4.00	7.20	20.0	90.0	1340
H	0.0463	0.0656	0.114	0.201	0.363	0.735	1.81	5.70	31.8	630
<i>p</i> -Cl	(1.02)			3.86	6.42	11.9	24.4	68.5	293	3380
<i>m</i> -Cl	(2.30)					29.2	60.0		814	
<i>p</i> -NO <sub>2</sub>	(12.5)				70.2	124	260	716	2850	26000

In acetone-water and dioxan-water mixtures  $k'$  is constant over the whole range between the water concentrations 1000 and 400 ml/l, and has for each compound the value given above for its reaction in water. In DMSO-water mixtures,  $k'$  increases with increasing DMSO concentration, the increase being especially pronounced at high DMSO concentrations. Still greater values at high DMSO concentrations are obtained if values of  $n$  relating to high acetone concentrations are used.

The values of  $k'$  decrease in the order  $p\text{-NO}_2 > m\text{-Cl} > p\text{-Cl} > \text{H}$ , which is the order that should result from a bimolecular attack of a nucleophile. On the other hand,  $k'$  decreases in the order  $p\text{-Me} > \text{H}$ . It is not unusual that a reaction of benzyl halides shows a rate minimum for the unsubstituted compound, for this is common for their reactions with anions.<sup>31</sup> It seems reasonable to assume that the increase of  $k'$  in the presence of DMSO is due to the fact that, besides "normal" water molecules, water molecules hydrogen-bonded to DMSO act as nucleophiles. It is well known that DMSO is a powerful hydrogen bond acceptor, and thus the nucleophilicity of the hydroxyl group of a water molecule is surely greatly enhanced when the water molecule is bound by one of its hydrogen atoms to the oxygen of the DMSO molecule (as in  $\text{HO}-\text{H}\cdots\text{OSMe}_2$ ). At low DMSO contents the number of adducts is very close to the number of DMSO molecules, because practically every DMSO molecule is bound to water. Thus, if the reaction rate is proportional to the concentration of the adducts,  $k'$  should obey the equation

$$k' = k_0' + k''[\text{DMSO}]$$

where  $k_0'$  is the rate constant in pure water. According to this equation the plot of  $k'$  against [DMSO] should be linear, which, however, is not the case.

Since the reaction rate is not simply proportional to the concentration of the adducts, there must be also other factors associated with DMSO that exert an effect. In a way similar to that used in the deduction of eqn. (1), it is found that if  $n$  DMSO molecules are involved in the transition state, the following equation should be obeyed:

$$\log (k' - k_0') = n \log [\text{DMSO}] + \text{const.}$$

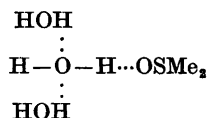
Not even a log-log plot is linear, which indicates at least that no constant number of DMSO molecules is involved in the transition state.

Kingsbury<sup>32</sup> has found that the plot of  $\log (k_{\text{obs.}} - k_0)$  vs. [DMSO] is linear for certain bimolecular negative ion displacement reactions in methanol-DMSO mixtures. This indicates that the following mathematical relationship is obeyed:

$$\log (k_{\text{obs.}} - k_0) = r[\text{DMSO}] + \text{const.} \quad (3)$$

He found that  $r$ , which he supposed to be a measure of the sensitivity of the system to catalysis by DMSO, is approximately constant, *ca.* 0.275, for the systems he investigated. Similar results with  $r$  values of the same order of magnitude are obtained for the reactions between benzyl chlorides and methoxide ion in methanol-DMSO mixtures.<sup>33</sup> The corresponding plots of  $\log (k' - k_0')$  vs. [DMSO] are shown in Fig. 6. Their linearity is good up to a water concentration of about 400 ml/l and the values of  $r$  obtained from the figure is 0.278 for benzyl chloride and 0.230 for *p*-methylbenzyl chloride, *i.e.* practically the same values as were mentioned above for the systems studied by Kingsbury.

The steep rise of  $k'$  at high DMSO concentrations (see, *e.g.*, Fig. 6) may be explained in the following manner. One or two other water molecules may be joined by hydrogen bridges to the oxygen atom of a water molecule bound to DMSO,



and these must be dislodged in the nucleophilic attack. With increasing DMSO concentration, this 'solvation' of the adduct will be reduced and its nucleophilic activity will be greater. This phenomenon occurs only at high DMSO concentrations.

It seems thus probable that several factors associated with DMSO have an effect on the reaction rate. In the above considerations, an examination of different plots has played an important part. In addition, it may be mentioned that very good straight lines over the whole range of mixtures investigated are obtained for all the benzyl chlorides, except *p*-methylbenzyl chloride, if

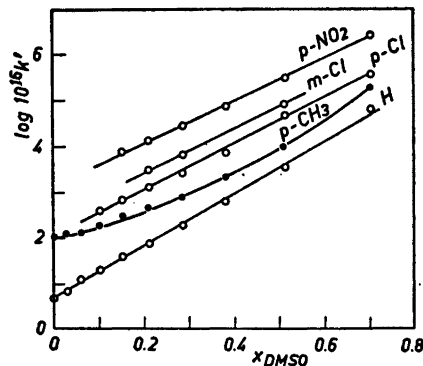
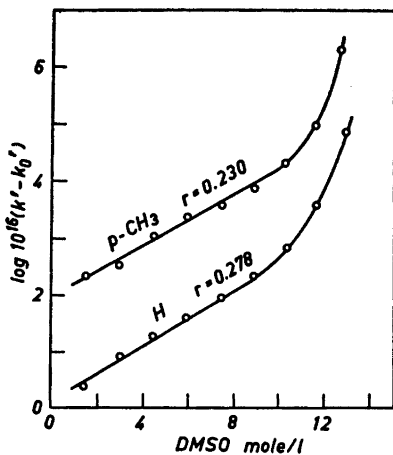


Fig. 6. Plot of  $\log(k' - k'_0)$  against  $[\text{DMSO}]$ ,  $25^\circ$ . Fig. 7. Plot of  $\log k'$  against the mole fraction of DMSO,  $25^\circ$ .

the values of  $\log k'$  are plotted against the mole fraction  $x$  of DMSO, as seen in Fig. 7. The equations of the general form

$$\log k' = b + mx \quad (4)$$

are:

$$\begin{array}{ll} \text{H:} & \log k' = -15.33 + 5.7 x \\ p\text{-Cl:} & \log k' = -13.95 + 5.0 x \\ m\text{-Cl:} & \log k' = -13.60 + 4.8 x \\ p\text{-NO}_2: & \log k' = -12.90 + 4.5 x \end{array}$$

The interpretation of these relationships is not easy. However, it is possible that they are only consequences of the simultaneous effects of the above-mentioned factors.

It may be pointed out that the division of  $k$  by  $[\text{H}_2\text{O}]^n$  leads to no appreciable change in the activation energies, but the frequency factors will be reduced by the factor  $[\text{H}_2\text{O}]^n$ .

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#### REFERENCES

1. Tommila, E., Paakkala, E., Virtanen, U. K., Erva, A. and Varila, S. *Ann. Acad. Sci. Fennicae A II* 1959 No. 91.
2. Hyne, J. B., Wills, R. and Wonkka, R. E. *J. Am. Chem. Soc.* **84** (1962) 2914.
3. Hyne, J. B. and Wills, R. *J. Am. Chem. Soc.* **85** (1963) 3650.
4. Böhme, H. and Henning, H.-J. *Z. Naturforsch.* **1** (1946) 580.
5. Sadek, H., Halim, F. M. A. and Khalil, F. Y. *Suomen Kemistilehti B* **36** (1963) 141.
6. Tommila, E. and Virtanen, O. *Suomen Kemistilehti B* **34** (1961) 139.
7. Beste, G. W. and Hammett, L. P. *J. Am. Chem. Soc.* **62** (1940) 2481.

8. Tommila, E., Tiilikainen, M. and Voipio, A. *Ann. Acad. Sci. Fennicae A II* **1955** No. 65.
9. Bennett, G. M. and Jones, B. *J. Chem. Soc.* **1935** 1815.
10. Adam-Bries, M., Bivort, P. and Fierens, P. *J. C. Bull. Soc. Chim. Belges* **65** (1956) 501; Wilputte-Steinert, L. and Fierens, P. *J. C. Ibid.* **65** (1956) 719; Bivort, P. and Fierens, P. *J. C. Ibid.* **65** (1956) 975.
11. Winstein, S. and Fainberg, A. H. *J. Am. Chem. Soc.* **79** (1957) 5937.
12. Tommila, E. *Acta Chem. Scand.* **9** (1955) 975.
13. Tommila, E., Koivisto, A., Lyyra, J. P., Antell, K. and Heimo, S. *Ann. Acad. Sci. Fennicae A II* **1952** No. 47.
14. Hyne, J. B. *J. Am. Chem. Soc.* **82** (1960) 5129.
15. Arnett, E. M., Bentrude, W. G., Burke, J. J. and Duggleby, P. McC. *J. Am. Chem. Soc.* **87** (1965) 1541.
16. Baliga, B. T., Witney, R. J., Poulton, D. and Whalley, E. *Trans. Faraday Soc.* **61** (1965) 517.
17. Koivisto, A. *Acta Chem. Scand.* **9** (1955) 166.
18. Blackadder, D. A. and Hinshelwood, C. N. *J. Chem. Soc.* **1958** 2728, and the papers cited there.
19. Leffler, J. E. and Grunwald, E. *Rates and Equilibria of Organic Reactions*, Wiley, New York and London 1963.
20. Exner, O. *Collection Czech. Chem. Commun.* **29** (1964) 1094; Malawski, M. *J. Roczniki Chem.* **38** (1964) 1129; Petersen, R. C. *J. Org. Chem.* **29** (1964) 3133.
21. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, G. Bell and Sons, London 1955, p. 345.
22. (a) Laidler, K. J. and Eyring, H. *Ann. N.Y. Acad. Sci.* **39** (1940) 303;  
(b) Laidler, K. J. and Landskroener, P. A. *Trans. Faraday Soc.* **52** (1956) 200;  
(c) Laidler, K. J. *Suomen Kemistilehti A* **33** (1960) 44.
23. Böhme, H. and Schürhoff, W. *Chem. Ber.* **84** (1951) 28.
24. Fainberg, A. H. and Winstein, S. *J. Am. Chem. Soc.* **78** (1956) 2770.
25. Åkerlöf, G. *J. Am. Chem. Soc.* **54** (1932) 4125; Åkerlöf, G. and Short, O. A. *Ibid.* **58** (1936) 1241.
26. Tommila, E. *11. Pohjoismainen Kemistikokous — 11. Nordiska Kemistmötet*, Turku 1962, 347; *Organic Reaction Mechanisms*. An International Symposium held at Cork, The Chemical Society 1965, p. 150.
27. Brown, H. C. and Okamoto, Y. *J. Am. Chem. Soc.* **80** (1958) 4979.
28. Murto, J. and Hiio, A.-M. *Suomen Kemistilehti B* **37** (1964) 177.
29. Tommila, E. and Murto, M.-L. *Acta Chem. Scand.* **17** (1963) 1947;  
Tommila, E. and Palenius, I. *Ibid.* **17** (1963) 1981; Tommila, E. *Suomen Kemistilehti B* **37** (1964) 117; Roberts, D. D. *J. Org. Chem.* **29** (1964) 2039.
30. Tommila, E. and Pitkänen, I. P. *Acta Chem. Scand.* **20** (1966) 937.
31. Fuchs, R. *J. Am. Chem. Soc.* **79** (1957) 6531.
32. Kingsbury, C. A. *J. Org. Chem.* **29** (1964) 3262.
33. Tommila, E. and Savolainen, M. *Acta Chem. Scand.* **20** (1966) 946.

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