

The Influence of the Solvent on Reaction Velocity

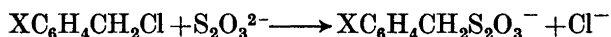
XL. The Reaction between Benzyl Chlorides and Thiosulphate Ion in Acetone-Water, Dioxane-Water, and Dimethyl Sulphoxide-Water Mixtures

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The dependence of the rate constants of the reactions of thio-sulphate ion with benzyl chloride, *p*-methylbenzyl chloride, and *p*-nitrobenzyl chloride in acetone-water, dioxane-water, and dimethyl sulphoxide-water mixtures on solvent composition and temperature has been studied. The rate constants decrease with increasing acetone and dioxane concentration, but increase very rapidly with increasing dimethyl sulphoxide concentration. Salt effects are discussed.

The reactions of hydroxide ion and methoxide ion with benzyl chlorides in mixed solvents have been studied before.^{1,2} The reactions



where X is H, *p*-CH₃, or *p*-NO₂, have now been studied using acetone-water, 1,4-dioxane-water, and dimethyl sulphoxide(DMSO)-water mixtures as media.

EXPERIMENTAL

Benzyl chloride, *p*-methylbenzyl chloride, *p*-nitrobenzyl chloride, acetone, and DMSO were of the same origin and purified by the same method as in previous papers.^{1,3} Dioxane (G.R., E. Merck AG, Darmstadt) was purified by the method of Hess and Frahm.⁴ Potassium iodide, iodine, and sodium thiosulphate were guaranteed reagents from E. Merck AG. The water was distilled immediately before use and was free of carbon dioxide.

The kinetic measurements were carried out in two-compartment reaction flasks. The initial concentrations of both reactants after mixing were 0.02 mole/l as far as possible. The reactions in acetone-water and dioxane-water mixtures were stopped by chilling the reaction vessels rapidly in ice-water and the solutions were titrated immediately with potassium iodide-iodine solution. The reactions in DMSO-water mixtures were stopped by pouring into the reaction flasks a volume of potassium iodide-iodine solution, whose iodine content was equivalent to the initial amount of thiosulphate ion in the reaction flask and the excess iodine was titrated with sodium thiosulphate solution.

The solvolysis reactions of benzyl chlorides in the solvents used are much slower than their reactions with thiosulphate ion. The solvolysis reaction was, however taken into account as described in a previous paper⁵ when the rate constants of the reactions of *p*-methylbenzyl chloride with thiosulphate ion in 60 vol.% water-acetone at 25°, in 50 vol.% water-acetone at 40° and 50°, in 40 vol.% water-acetone at 50°, and in 60 and 50 vol.% water-dioxane at 25° were evaluated. The first-order rate constants of the solvolysis reactions were taken from previous papers.^{3,6} In all the other cases, the second order rate constants are at least 5000 times greater than the first order rate constants of the solvolysis reaction and were calculated from the simple equation for second order reactions. All rate constants were corrected for the thermal expansion of the solvent. The parameters of the Arrhenius equation were calculated by the method of least squares.

RESULTS AND DISCUSSION

The experimental results are given in Tables 1–4. *E* and *A* are the activation energy and the frequency factor, respectively. The calculated activation entropies (ΔS^*) and the free energies of activation (ΔG^*) refer to 25°. The results can be compared with the earlier data of Fuchs and Nisbet in Table 5.⁷ The agreement of the rate constants is good in most cases.

As seen from Fig. 1, where $\log(k/k_w)$ for the reaction of benzyl chloride is plotted against the mole fraction of water, the rate constants in DMSO-water mixtures increase when the water content of the solvent decreases. k_w , the rate constant in pure water was found by extrapolation to be 0.023 l

Table 1. The rates of reactions $\text{XC}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{XC}_6\text{H}_4\text{CH}_2\text{S}_2\text{O}_3^- + \text{Cl}^-$ in acetone-water mixtures.

X	H ₂ O ml/l	wt.% H ₂ O	<i>a</i> ^a mole/l	10 ³ × <i>k</i> (l mole ⁻¹ sec ⁻¹)				<i>E</i> cal/mole	log <i>A</i>	– ΔS^* E.U. (25°)	ΔG^* cal/mole (25°)
				15.00°	25.00°	40.00°	50.00°				
H	700	72.8	0.0075	5.82	13.3	42.9	85.9	14270	8.59	21.22	20010
»	600	63.6	0.0200	3.44	8.20	26.3	53.4	14500	8.53	21.48	20310
»	500	54.0	0.0050	3.17	7.21	22.7	48.2	14360	8.38	22.18	20380
»	500	54.0	0.0100	2.82	6.62	21.0	43.4	14430	8.39	22.13	20440
»	500	54.0	0.0200	2.50	5.54	19.0	38.6	14590	8.45	21.85	20510
»	500	54.0	0.0500	1.91	4.38	15.6	34.0	15310	8.88	19.89	20650
»	400	44.3	0.0200	1.69	4.08	13.0	27.0	14610	8.31	22.50	20730
»	300	34.0	0.0050	1.88	4.32	14.0	29.4	14350	8.15	23.23	20680
<i>p</i> -CH ₃	600	63.6	0.0200		14.1						
»	500	54.0	0.0200	3.80	8.75	28.4		14430	8.52	21.54	20260
»	400	44.3	0.0200	2.50	5.88	19.0		14550	8.44	21.93	20500
»	300	34.0	0.0050	2.62	6.01	19.2		14290	8.26	22.75	20480
<i>p</i> -NO ₂	600	63.6	0.0200		11.8	40.1	85.0	15100	9.14	18.72	20080
»	500	54.0	0.0200	4.62	10.9	36.0	75.1	14740	8.85	20.05	20130
»	400	44.3	0.0200	4.36	10.2	33.3	68.5	14580	8.69	20.74	20170
»	300	34.0	0.0050	6.57	15.0	48.9	98.5	14350	8.70	20.71	19940

^a *a* is the initial total concentration of each of the reactants.

Table 2. The rates of reactions $\text{XC}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{XC}_6\text{H}_4\text{CH}_2\text{S}_2\text{O}_3^- + \text{Cl}^-$ in dioxane-water mixtures.

X	H ₂ O ml/l	wt. % H ₂ O	a mole/l	10 ³ × k (l mole ⁻¹ sec ⁻¹)				E cal/ mole	log A	-ΔS* E.U. (25°)	ΔG* cal/ mole (25°)
				15.00°	25.00°	40.00°	50.00°				
H	600	58.2	0.0188		7.88						
»	500	48.3	0.0200	2.14	5.21	17.2	34.8	14760	8.53	21.49	20570
»	400	38.5	0.0200	1.33	3.13	10.5	22.1	14900	8.42	22.00	20870
»	300	28.9	0.0094	0.821	2.02	6.74	14.4	15120	8.38	22.18	21140
p-CH ₃	600	58.2	0.0188		13.4						
»	500	48.3	0.0200		8.01						
»	400	38.5	0.0200		4.73						
»	300	28.9	0.0094	1.25	3.02	10.1	21.3	14970	8.45	21.86	20900
p-NO ₂	600	58.3	0.0188		14.1						
»	500	48.3	0.0200		12.5						
»	400	38.5	0.0200		9.83						
»	300	28.9	0.0094	3.61	8.26	25.8	52.0	14100	8.25	22.78	20300

Table 3. The rates of reactions $\text{XC}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{XC}_6\text{H}_4\text{CH}_2\text{S}_2\text{O}_3^- + \text{Cl}^-$ in DMSO-water mixtures.

X	H ₂ O ml/l	wt. % H ₂ O	a mole/l	10 ³ × k (l mole ⁻¹ sec ⁻¹)			E cal/ mole	log A	-ΔS* E.U. (25°)	ΔG* cal/ mole (25°)
				0.00°	15.00°	25.00°				
H	600	56.5	0.0130	6.56	24.5	57.9	14070	9.07	19.02	19150
»	500	46.4	0.0200	8.91	34.2	74.9	13800	8.99	19.39	18990
»	500	46.4	0.0100	10.4	39.6	86.6	13750	9.02	19.25	18900
»	400	36.7	0.0200	12.6	46.3	103	13590	8.97	19.48	18810
»	300	27.3	0.0200	27.3	97.1	207	13130	8.94	19.62	18390
»	200	18.2	0.0200	51.4	177	380	12940	9.07	19.02	18020
p-CH ₃	400	36.7	0.0200			157				
»	300	27.3	0.0200			218				
»	200	18.2	0.0200			377				
p-NO ₂	400	36.7	0.0200			245				
»	300	27.3	0.0200			659				
»	200	18.2	0.0200			2100				

mole⁻¹ sec⁻¹. Addition of acetone or dioxane slows down the reaction as it does the reactions of the benzyl chlorides with hydroxide ion.¹

The rates of the reactions with thiosulphate ion are roughly 200 times greater than the rates of the reactions with hydroxide ion in acetone-water

Table 4. The reaction $C_6H_5CH_2Cl + S_2O_3^{2-} \longrightarrow C_6H_5CH_2S_2O_3^- + Cl^-$ in some solvent mixtures at various ionic strengths. Temperature 25°.

Solvent	$Na_2S_2O_3$ mole/l	NaCl mole/l	I^a	\sqrt{I}	$k \times 10^3$ l mole ⁻¹ sec ⁻¹	$\log(k \times 10^3)$	
Acetone-water H ₂ O 600 ml/l	0.0050	0.06	0.015	0.122	10.4	1.015	
	0.0100		0.030	0.173	9.53	0.979	
	0.0200		0.120	0.346	7.23	0.859	
Acetone-water H ₂ O 500 ml/l	0.0075	0.015	0.0225	0.150	6.73	0.828	
	0.0100		0.045	0.212	6.07	0.783	
	0.0100		0.045	0.075	0.274	5.13	0.710
	0.035		0.105	0.324	5.07	0.705	
Acetone-water H ₂ O 300 ml/l	0.00364		0.0109	0.104	4.63	0.666	
	0.00667		0.020	0.141	4.06	0.609	
	0.0100		0.030	0.173	3.84	0.584	
DMSO-water H ₂ O 400 ml/l	0.0050		0.015	0.122	121	2.083	
	0.0100		0.030	0.173	122	2.088	
	0.0400		0.120	0.346	97.5	1.989	

^a I is the initial ionic strength of the reaction mixture.

Table 5. Comparison of kinetic data for reactions $XC_6H_4CH_2Cl + S_2O_3^{2-} \longrightarrow XC_6H_4CH_2S_2O_3^- + Cl^-$ in some mixed solvents obtained in this work with the data of Fuchs and Nisbet.⁷

	Solvent	Acetone-water		Acetone-water		Dioxane-water		DMSO-water
		400		500		400	500	400
	H ₂ O ml/l	H	<i>p</i> -NO ₂	H	<i>p</i> -NO ₂	H	H	H
This work	$10^3 \times k_{30}^a$	4.97	12.7	7.11	13.6	3.94	6.40	12.6 ^b
	E (cal) ^c	14610	14580	14590	14740			
Fuchs and Nisbet	$10^3 \times k_{30}$	4.82	11.9	6.99	13.7	3.48	6.35	14.7 ^b
	E (cal)	15600	15200	14800	15100			

^a Calculated for 30° using the parameters of Arrhenius equation and corrected to the initial $S_2O_3^{2-}$ concentration (0.04 M) using the value -0.83 for the slope of the plot of $\log k$ versus \sqrt{I} . This value was taken from Fig. 2 and relates to the 50 vol. % acetone-water mixture at 25°.

^b Temperature 0.00° and initial $S_2O_3^{2-}$ concentration 0.02 M.

^c Not corrected to the initial $S_2O_3^{2-}$ concentration of 0.04 M.

and DMSO-water mixtures although the hydroxide ion is a much stronger base than thiosulphate ion. The higher rate constants are due to smaller activation energies in the former reactions.

According to Edwards and Pearson,⁸ the reactivity of a nucleophile towards a substrate depends on the basicity and the polarizability of the nucleophile. The effect of polarizability of the nucleophile dominates when the site of electrophilic attack is a tetrahedral carbon atom. The results of this work

Fig. 1. Plots of $\log(k/k_w)$ against x_w , 25° for the reaction of benzyl chloride with thiosulphate ion. Solvent systems: ○ DMSO-water; ● acetone-water; □ dioxane-water.

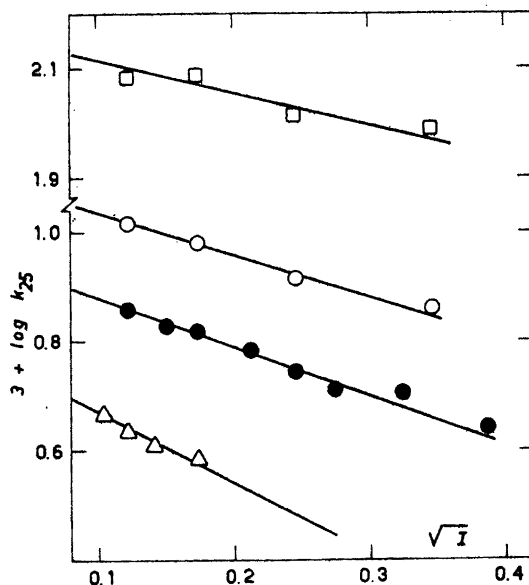
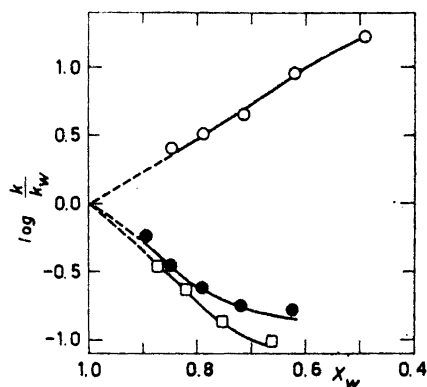


Fig. 2. Plots of $\log k_{25}$ against \sqrt{I} for the reaction of benzyl chloride with thiosulphate ion. Solvent systems: ○ acetone-water, H_2O 600 ml/l; ● acetone-water, H_2O 500 ml/l; △ acetone-water, H_2O 300 ml/l; □ DMSO-water, H_2O 400 ml/l.

are in accordance with this conclusion since the $\text{S}_2\text{O}_3^{2-}$ ion is much more polarizable than the hydroxide ion.

Although the reactions studied involve a neutral molecule and a negative ion, $\log k$ varies linearly with the square root of ionic strength (Table 4, Fig. 2). Fuchs and Nisbet⁹ obtained the same result and ascribed it to ion association. The value 0.26 has been reported for the dissociation constant of the ion pair $\text{Na}^+\text{S}_2\text{O}_3^{2-}$ in water at 25°. At a sodium thiosulphate concentration of 0.02 M, the free thiosulphate ion concentration is 95 % of the total thiosulphate concentration when activity coefficients calculated from the Debye-Hückel limiting law are employed. If we can assume that the ion pairs do not react, or react much slower than free thiosulphate ions with benzyl chlorides, the influence of the ion pair formation on the rate constants in the solvents used is very marked since the value of the dissociation constant of the ion pair must be much smaller in these solvents than in water. The observation that the values of E and $\log A$ for the reaction of benzyl chloride with thiosulphate ion in acetone-water containing 500 ml of water per litre decrease with decreasing initial reactant concentration (Table 1) cannot, however, be explained to be due to the ion association. The dissociation constant will probably decrease slightly with increasing temperature.¹⁰ The smaller the total thiosulphate concentration, the less the decrease with the temperature of the dissociation constant will diminish the concentration of free thiosulphate ion. The rate constants were calculated using the total thiosulphate concentration. The consequence of this should be that E and $\log A$ increase with decreasing initial reactant concentration, which is the opposite of the observed variation.

The ratios of the rate constants of the substituted compounds to those of benzyl chloride were already published by Tommila.¹¹ He also discussed the influence of solvent on substituent effects in terms of an electrostatic theory.

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