

Nucleophilic Reactivity

Part II.* Kinetics of Reactions of Methyl Perchlorate with Nucleophiles in Water

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Second-order rate constants of reactions of methyl perchlorate with a large number of nucleophiles in water were measured at 0°C. New values of nucleophilicity constants of the Swain-Scott equation were calculated from separate linear correlations for basic and non-basic nucleophiles. Rate constants k obtained for reactions of methyl perchlorate with basic nucleophiles and also the nucleophilicity constants n of the Swain-Scott equation fit well the two-parameter equation $\log k = a \text{ p}K_a + b + \text{constant}$. For reactions of methyl perchlorate with basic nucleophiles a is 0.23 and b is equal to 0, 0.93, and 1.79 for nucleophiles containing as the nucleophilic atom oxygen, nitrogen, and sulphur, respectively.

The activation parameters $\Delta S^* = +5.62$ cal/mole deg. and $\Delta H^* = 22.51$ kcal/mole point to a unimolecular $S_N 1$ mechanism for the hydrolysis of methyl perchlorate in water. The values $\Delta S^* = +2.02$ cal/mole deg. and $\Delta H^* = 19.56$ kcal/mole for the alkaline hydrolysis indicate a weak interaction of the nucleophile in the transition state.

Nucleophilic reactivity has been recently discussed by Bunnett² in a review. The Swain-Scott equation³ (1) has been applied to nucleophilic reactions $N + RX \rightarrow NR + X$ with varying degree of success. In this equation

$$\log k - \log k_0 = s n \quad (1)$$

k_0 and k are second-order rate constants of the nucleophilic reactions of the compound RX with water and a nucleophile N , and s is a constant which depends only on the compound RX . The value $s=1$ was arbitrarily chosen for nucleophilic reactions of methyl bromide.³ n is a constant which depends only on the nucleophile N . The accuracy of fitting the Swain-Scott equation to the rate constants is usually of the order of about $\pm 0.2 \log k$ units. Large deviations are, however, observed in some cases as, for example, for reactions

* For Part I, see Ref. 1.

with hydroxide ion.^{2,3} Large changes in nucleophilic reactivity have been observed in reactions in different solvents.^{4,5} Nucleophilicity constants for reactions in water are usually not valid for the same reactions in other solvents, at least not in aprotic solvents.⁴

Some improvement in fit was obtained by Edwards^{6,7} by introducing a four-parameter equation. He assumed that nucleophilicity is related to the basicity and oxidation potential of the nucleophile. A four-parameter equation was recently employed also in molecular orbital calculations of nucleophilic reactivity.⁸ The use of the Edwards equation is often restricted because the necessary constants are not known.

In some cases the logarithms of rate constants have been found^{2,9,10} to be approximately linearly related to pK_a values of nucleophiles. Basicity is, however, not the only factor that determines nucleophilicity since also very weak bases can be powerful nucleophiles. Therefore other effects, including steric effects, are responsible for the large deviations observed in such plots.^{4,5} The purpose of this study was to extend previous kinetic data on nucleophilic reactions of methyl perchlorate to aqueous solutions. Because of the higher solubilities of nucleophiles in water, reactions with several new nucleophiles could be studied.

Table 1. Second-order rate constants k_2 ($l \cdot \text{mole}^{-1} \text{sec}^{-1}$) of reactions of methyl perchlorate and methyl iodide with nucleophiles in water and methanol and pK_a values of basic nucleophiles in water at 25°C.

Nucleophile	pK_a in H_2O at 25°C (Refs. 21 and 22)	$5 + \log k_2$ $MeClO_4$ in H_2O at 0°C	$8 + \log k_2$ $Me I$ in H_2O at 0°C (Refs. 8 and 9)	$5 + \log k_2$ $MeClO_4$ in MeOH at 0°C (Ref. 1)	$8 + \log k_2$ $Me I$ in MeOH at 0°C (Refs. 4 and 10)	$6 + \log k_2$ $Me I$ in MeOH at 25°C (Ref. 11)
$S_2O_3^{2-}$	1.60	4.192	5.186	5.150		5.058
SO_3^{2-}	7.20	3.696				4.648
CN^-	9.25	3.265	3.389	3.884		2.810
PO_4^{3-}	12.32	3.185				
CO_3^{2-}	10.36	2.591				
HO^-	15.74	2.522	2.266			
MeO^-				3.721	2.972	2.413
I^-		2.642	3.396	3.539		3.544
SCN^-		2.591	3.219	3.137	3.477	2.759
PhO^-	9.99	2.428		3.107	2.302	1.864
N_3^-	4.70	2.225		2.903	2.477	1.892
$p\text{-ClPhO}^-$	9.42	2.179				
NO_2^-	3.30	2.052		2.911		1.462
HPO_4^{2-}	7.20	1.897				
$B_2O_7^{2-}$		1.836				
Br^-		1.745	2.326	2.520	2.262	1.902
$p\text{-NO}_2\text{PhO}^-$	7.15	1.517				
AcO^-	4.76	1.255		2.050	0.650	0.432
HCO_3^-	3.76	1.137		1.700		
Cl^-		0.686	1.049	1.864	1.000	0.478
$H_2PO_4^-$	2.16	≥ 0.8				
HSO_3^-	1.90	≥ 0.9				
H_2O	-1.74	-1.041	-3.256			
MeOH				-0.686	-2.745	-0.3886

EXPERIMENTAL

Materials. In addition to the reagents used in the previous work,¹ sodium sulphate, sodium chlorate, dipotassium hydrogen phosphate, and trisodium phosphate (guaranteed reagents, E. Merck AG.), sodium dihydrogen phosphate and phenol (E. Merck AG.) and sodium sulphite (purum, Riedel de Haën AG.) were used as received.

Kinetic experiments. The kinetic measurements were performed and the rate constants calculated as described previously.¹ The extents of two simultaneous reactions, hydrolysis and the reaction with the added nucleophile, were calculated from the amount of perchloric acid produced in the hydrolysis and from the amount of nucleophile consumed whenever possible or alternatively from the amount of methyl perchlorate present in the reaction mixture determined by utilising the fast reaction between thiosulphate ion and methyl perchlorate as described previously.¹ The second-order rate constants of the reactions between methyl perchlorate and the nucleophiles in water at 0°C are given in Table 1.

The rate constants of a concurrent general base-catalysed hydrolysis in the presence of a basic nucleophile reported previously¹ were due to an experimental error. The reactions of methyl perchlorate with the basic nucleophiles were arrested by adding an excess of acid. When the acid was titrated by a base, it reacted to some extent with the methyl perchlorate present in the reaction mixture. This led to erroneous results which were interpreted as indicating a general base-catalysed solvolysis of methyl perchlorate in parallel with the nucleophilic reaction. By repeating these experiments and titrating the samples rapidly at about -20°C, no base-catalysed solvolysis of methyl perchlorate was detected. The rate constants of the nucleophilic reactions in methanol were therefore reinvestigated; the new values are given in Table 1.

RESULTS

Nucleophilicity constants n for nucleophilic reactions in water. The second-order rate constants of reactions of methyl perchlorate with nucleophiles in water at 0°C shown in Table 1 can be used to test the validity of eqn. (1) proposed by Swain and Scott.³ According to eqn. (1), a linear correlation is expected between the logarithms of the rate constants of any two substances with a series of nucleophiles. A plot of values of $\log k$ for reactions of methyl perchlorate and methyl iodide^{11,12} with various nucleophiles in water at 0° (Fig. 1) reveals one linear relationship for non-basic and weakly basic nucleophiles (Cl^- , Br^- , I^- , and SCN^-):

$$\log k_{\text{MeI}} = 1.19 \log k_{\text{MeClO}_4} - 1.83 \pm 0.06 \quad (2)$$

and another linear relationship for basic nucleophiles: (H_2O , HO^- , CN^- , and $\text{S}_2\text{O}_3^{2-}$)

$$\log k_{\text{MeI}} = 1.57 \log k_{\text{MeClO}_4} - 1.74 \pm 0.11 \quad (3)$$

It is therefore not possible to obtain a single set of nucleophilicity constants which would give a good fit of the Swain-Scott eqn. (1) to rates of reactions involving both non-basic and basic nucleophiles. The goodness of the fit of the equation to the experimental rate constants can be improved if separate equations are fitted to the rates of reactions with non-basic or very weakly basic nucleophiles and to the rates of reactions with basic nucleophiles. It is then not possible to include the same value of $\log k_0$ in both equations because the logarithm of the rate constant of the reaction with water does not satisfy the two separate linear equations for non-basic and basic nucleophiles. A more general equation would be

$$\log k = sn + c \quad (4)$$

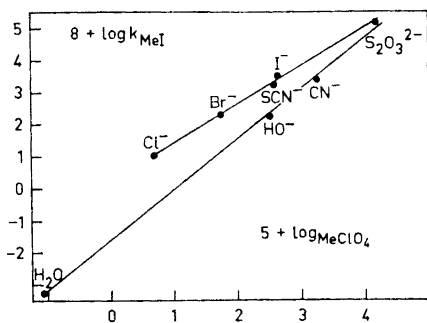


Fig. 1. Plots of logarithms of second-order rate constants of reactions of methyl iodide with nucleophiles against logarithms of rate constants of reactions of methyl perchlorate with the same nucleophiles in water at 0°C. Straight lines are drawn through points referring to reactions with non-basic nucleophiles and through points referring to reactions with basic nucleophiles.

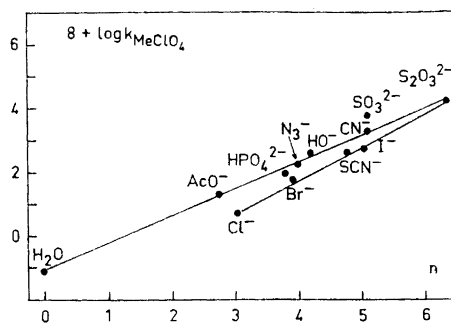


Fig. 2. Plots of logarithms of second-order rate constants of reactions of methyl perchlorate with nucleophiles in water at 0°C against the nucleophilicity constants n . Straight lines are drawn through points referring to reactions with basic nucleophiles and through points referring to reactions with non-basic nucleophiles.

Table 2. Nucleophilicity constants n in water at 0°C calculated from rate constants of reactions of methyl perchlorate and methyl iodide with nucleophiles in water.

Nucleophile	Nucleophilicity constants n					
	Ref. 3	Eqn. (5)	Eqn. (6)	Eqn. (7)	Eqn. (8)	Mean
$S_2O_3^{2-}$	6.36	6.34	6.27	6.40	6.48	6.35
SO_3^{2-}	5.10		5.67			5.67
CN^-	5.10		5.16		5.10	5.13
PO_4^{3-}			5.06			5.06
I^-	5.04	4.87		4.99		4.93
SCN^-	4.77	4.82		4.77		4.80
CO_3^{2-}			4.36			4.36
HO^-	4.20		4.27		4.25	4.23
PhO^-			4.16			4.16
Br^-	3.89	4.02		4.02		4.02
N_3^-	4.00		3.92			3.92
$p\text{-ClPhO}^-$			3.86			3.86
NO_2^-			3.71			3.71
HPO_4^{2-}	3.8		3.52			3.52
$B_2O_7^{4-}$			3.45			3.45
$p\text{-NO}_2\text{PhO}^-$			3.08			3.08
Cl^-	3.04	3.02		2.96		2.99
AcO^-	2.72		2.76			2.76
HCO_3^-	3.8		2.62			2.62
HSO_3^-			2.3			2.3
$H_2PO_4^-$			2.2			2.2
F^-	2.0		< 2.1		1.88	1.88
SO_4^{2-}	2.5	< 2.1				< 2.1
NO_3^-	1.03	< 2.1				< 2.1
HSO_4^-		< 2.1				< 2.1
ClO_3^-	< 0.0	< 2.1				< 2.1
ClO_4^-	< 0.0	< 2.1				< 2.1
H_2O	0.00		0.00		0.03	0.01

The rate constants of methyl perchlorate and methyl iodide^{11,12} with nucleophiles in water at 0°C form a uniform set of data which can be used to calculate accurate values of nucleophilicity constants for a large number of nucleophiles. A plot of values of $\log k$ for reactions of methyl perchlorate against the Swain-Scott nucleophilicity constants³ results in two different, but approximately linear plots (Fig. 2), one for non-basic nucleophiles (Cl^- , Br^- , I^- , and SCN^-):

$$\log k_{\text{MeClO}_4} = 1.06 n - 7.52 \pm 0.08 \quad (5)$$

and another for basic nucleophiles (H_2O , AcO^- , N_3^- , HO^- , CN^- , and $\text{S}_2\text{O}_3^{2-}$):

$$\log k_{\text{MeClO}_4} = 0.835 n - 6.05 \pm 0.05 \quad (6)$$

These equations were used to obtain the new values of nucleophilicity constants n shown in Table 2.

Second-order rate constants of the reactions of methyl iodide with nucleophiles^{11,12} in water at 0°C (Table 1) also yield two linear plots, one for non-basic nucleophiles (Cl^- , Br^- , I^- , and SCN^-):

$$\log k_{\text{MeI}} = 1.20 n - 10.50 \pm 0.05 \quad (7)$$

and another for basic nucleophiles (CN^- , HO^- , $\text{S}_2\text{O}_3^{2-}$, and H_2O):

$$\log k_{\text{MeI}} = 1.31 n - 11.30 \pm 0.08 \quad (8)$$

The rate constants for the reactions with thiosulphate ion seem to satisfy equally well the linear relationships obtained for both non-basic and basic nucleophiles in reactions with both methyl iodide and methyl perchlorate. Eqns. (7) and (8) were used to calculate the values of nucleophilicity constants n shown in Table 2.

The mean values of the nucleophilicity constants calculated from rate constants of reactions of nucleophiles with methyl perchlorate and methyl iodide in water at 0°C shown in Table 2 do not deviate much from the previous values,³ the mean difference being $\pm 0.06 \log k$ units for both non-basic and basic nucleophiles with the exception of the nucleophilicity constants of SO_4^{2-} , SO_3^{2-} , HCO_3^- and HPO_4^{2-} ions. The previously³ reported values 2.5, 5.1, 3.8, and 3.8 of the nucleophilicity constant for these ions are possibly erroneous as they differ considerably from the respective calculated values < 2.1 , 5.76, 2.62, and 3.52. Several new values of nucleophilicity constants not reported previously are given in Table 2. Because of the pronounced basicity of fluoride ion, its nucleophilicity constant was calculated using eqn. (8) instead of the eqn. (7) used for calculating nucleophilicity constants of the other halide ions.

The linear increase of the first-order rate constant of reaction of methyl perchlorate with increasing concentration of a weakly nucleophilic electrolyte may be due to a positive salt effect. In the hydrolysis of *tert*-butyl chloride in water,¹³ the salt effect was found to be different for electrolytes of different charge type. The value of about $2 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec}^{-1}$ of the slope a (Table 3) obtained for several 1:1 electrolytes is most likely due solely to a salt effect. The larger values of a obtained for the 1:1 electrolytes NaH_2PO_4 , NaHSO_3 ,

Table 3. Values of the constant a of the equation $k = k_0 + ac$, expressing the linear dependence, of the first-order rate constant of decomposition of methyl perchlorate on electrolyte concentration in water in the presence of different electrolytes in the concentration range from about 0.1 to 0.8 M. In addition to the salt effect, the values of a may include a contribution from a possible nucleophilic reaction. Only in the case of sodium chloride was it possible to determine separate rate constants for both the nucleophilic reaction and the hydrolysis of methyl perchlorate; in this case a reflects only the salt effect.

Electrolyte	$10^5 a$ l mole ⁻¹ sec ⁻¹
NaClO ₄	2.8
NaClO ₃	2.2
NaNO ₃	2.4
NaCl	2.1
NaF	1.9
Na ₂ SO ₄	7.2
NaHSO ₄	5.6
NaHSO ₃	5.7
NaH ₂ PO ₄	6.4

and NaHSO₄ are due to salt effects and possibly partly to a nucleophilic reaction with methyl perchlorate. The larger value of a obtained for the 2:1 electrolyte Na₂SO₄ may reflect a larger salt effect due to the different charge type or may include some nucleophilic contribution also. Only upper limits $\log k < -0.3$ and $n < 2.1$ can therefore be calculated for the weak nucleophiles F⁻, NO₃⁻, SO₄²⁻, HSO₄⁻, ClO₃⁻, and ClO₄⁻ (Tables 1 and 2).

Nucleophilicity constants n for reactions in methanol. Parker *et al.*⁴ showed that no linear correlation exists between logarithms of rate constants of reactions in two different solvents if one is a protic and the other an aprotic solvent. An approximate linear relationship can be expected for rate constants of reactions in two solvents of the same type, both either protic or aprotic solvents. The rate constants reported previously for reactions of methyl perchlorate¹ and methyl iodide^{5,7} with nucleophiles in methanol can be used to study the solvent dependence of nucleophilicity constants. A curved plot is obtained when the logarithms of the rate constants of reactions of methyl perchlorate with nucleophiles in water are plotted against the logarithms of the rate constants of respective reactions in methanol whereas the rate constants of reactions of methyl iodide with nucleophiles in these solvents give an approximately linear plot. A different set of nucleophilicity constants are thus needed for reactions in methanol.

As rate constants of nucleophilic reactions of methyl bromide in methanol are not available, rate constants obtained for methyl iodide were used instead to calculate nucleophilicity constants. The rate constants of reactions of methyl iodide with nucleophiles in water and methanol at 0°C are approximately equal. Therefore values of rate constants of the reactions in methanol were chosen as reference values and were substituted in eqns. (7) or (8) to obtain nucleophilicity constants n for reactions in methanol (Table 3).

Approximately linear relationships were found between the logarithms of rate constants of the reactions of methyl perchlorate and methyl iodide with weakly basic nucleophiles (Cl^- , Br^- , SCN^-) in methanol at 0°C .

$$\log k_{\text{MeI}} = 1.94 \log k_{\text{MeClO}_4} - 0.91 \pm 0.01 \quad (9)$$

and with basic nucleophiles (MeOH , AcO^- , N_3^- , PhO^- and MeO^-) in the same solvent at the same temperature:

$$\log k_{\text{MeI}} = 1.29 \log k_{\text{MeClO}_4} - 3.39 \pm 0.16 \quad (10)$$

The values of the logarithms of rate constants of the reactions of methyl perchlorate with nucleophiles can also be used to derive nucleophilicity constants. When these are substituted in eqn. (9) or (10), values of " $\log k_{\text{MeI}}$ " are obtained which, when substituted in eqn. (7) or (8), respectively, yield the values of nucleophilicity constants shown in Table 3.

A set of rate constants⁷ obtained for reactions of methyl iodide with nucleophiles in methanol at 20° are related to the rate constants obtained for the same reactions at 0° as expressed by the equation

$$\log k_{\text{MeI},0} = 1.22 \log k_{\text{MeI},25} - 0.57 \pm 0.10 \quad (11)$$

Values of $\log k_{\text{MeI},0}$ obtained using eqn. (11) can also be employed to calculate nucleophilicity constants (Table 4).

Table 4. Nucleophilicity constants in methanol calculated from rate constants of reactions of methyl perchlorate and methyl iodide with nucleophiles in methanol and differences between nucleophilicity constants in water and methanol ($\Delta n = n_{\text{H}_2\text{O}} - n_{\text{MeOH}}$).

Nucleophile	Nucleophilicity constant n						Mean	Δn
	Eqn. (7)	Eqn. (8)	Eqns. (9) and (7)	Eqns. (10) and (8)	Eqns. (11) and (7)	Eqns. (11) and (8)		
SO_3^{2-}				6.18		7.32	6.73	-0.28
$\text{S}_2\text{O}_3^{2-}$						6.92	6.92	-1.28
I^-			5.63			5.78	5.70	-0.77
CN^-	4.98		4.97		4.98		4.98	-0.17
SCN^-				4.95		5.22	5.08	-0.28
MeO^-		4.80		4.77		4.84	4.80	-0.57
PhO^-	3.97		3.98		4.11		4.02	0.00
N_3^-		4.41		3.94		4.37	4.24	
Br^-		4.28		4.16		4.35	4.26	-0.10
NO_2^-				3.93		3.96	3.94	-0.23
AcO^-	2.92		2.92		2.97	2.66	2.87	+0.12
Cl^-		3.02		3.12		3.10	3.05	-0.29
HCO_3^-				2.78			2.78	-0.16
F^-				2.15			2.15	-0.27
NO_3^-			<0.4				<0.4	
MeOH		0.42		0.43		0.41	0.42	-0.40

The mean values of nucleophilicity constants calculated from rates of reactions in methanol are not much different from the respective values obtained for reactions in water. The differences $n_{\text{water}} - n_{\text{methanol}}$ are small for

non-basic nucleophiles with the exception of iodide ion (-0.77). A positive value indicates a greater reactivity in water and a negative value a greater reactivity in methanol. The mean difference between the nucleophilicity constants of basic nucleophiles in these two solvents is -0.27 ± 0.04 when the differences -1.28 for the thiosulphate ion, -0.40 for water and methanol, and -0.57 for hydroxide and methoxide ions are omitted. The large negative differences obtained for the nucleophiles HO^- and MeO^- , and H_2O and MeOH indicate a greater nucleophilicity of MeO^- and MeOH compared to HO^- and H_2O .

No electrophilic catalysis of the hydrolysis of methyl perchlorate by silver ion was observed in water at 0°C . The first-order rate constant of hydrolysis in water containing 0.05 mole/l silver nitrate, $k_1 = 5.0 \times 10^{-5}$ l mole $^{-1}$ sec $^{-1}$, is close to the rate constant in the absence of silver nitrate, $k_1 = 5.04 \times 10^{-5}$ l/mole·sec, at 0°C .

DISCUSSION

Activation parameters. The first-order rate constants 5.04×10^{-5} , 46.6×10^{-5} , 179×10^{-5} sec $^{-1}$ were obtained for the hydrolysis of methyl perchlorate in water at 0° , 15° , and 25°C , respectively. The activation parameters $\Delta H^* = 22\,530$ cal·mole $^{-1}$ and $\Delta S^* = +5.62$ cal·mole $^{-1}$ deg $^{-1}$, were calculated from the first-order rate constants. The positive value of the activation entropy indicates an $\text{S}_{\text{N}}1$ mechanism for the hydrolysis of methyl perchlorate in water. However, a negative value $\Delta S^* = -20.84$ cal·mole $^{-1}$ deg $^{-1}$ was obtained for the reaction in methanol. This value is typical of bimolecular solvolysis reactions such as the methanolysis of methyl iodide and methyl benzenesulphonate (Table 5).

Table 5. Activation parameters of some nucleophilic reactions in methanol and water. The activation entropies were calculated from first-order rate constants of the uncatalysed solvolysis reactions and from second-order rate constants of the base-catalysed solvolytic reactions.

Reaction	t°	Solvent	ΔS^* cal·mole $^{-1}$ deg $^{-1}$	ΔH^* kcal·mole $^{-1}$	Ref.
$\text{MeClO}_4 + \text{H}_2\text{O}$	12	H_2O	+ 5.62	22.51	This work
$\text{MeClO}_4 + \text{MeOH}$	12	MeOH	- 20.84	15.76	14
$\text{MeI} + \text{H}_2\text{O}$	50	H_2O	- 3.94	25.36	12
$\text{MeI} + \text{MeOH}$	80	MeOH	- 18.2	22.9	4
$\text{PhSO}_3\text{Me} + \text{H}_2\text{O}$	50	H_2O	- 11.58	20.01	12
$\text{PhSO}_3\text{Et} + \text{H}_2\text{O}$	56	H_2O	- 9.78	22.03	16
$\text{PhSO}_3\text{Et} + \text{EtOH}$	56	EtOH	- 19.38	21.08	17
$\text{MeClO}_4 + \text{HO}^-$	12	H_2O	+ 2.02	19.56	This work
$\text{MeClO}_4 + \text{MeO}^-$	12	MeOH	- 8.05	15.51	1
$\text{MeI} + \text{HO}^-$	32	H_2O	+ 0.50	24.00	11,15
$\text{MeI} + \text{MeO}^-$	32	MeOH	- 3.90	21.75	15

The methanolysis of methyl perchlorate was found to change from a bimolecular into a unimolecular reaction in acetone-methanol mixtures of low methanol content.¹⁴ It is therefore not unexpected that a mechanism may change from

S_N2 in methanol to S_N1 in water as the polarity of the solvent increases. An increase of solvent polarity often causes a greater increase in the rate of a unimolecular solvolysis than in the rate of a bimolecular solvolysis. The activation enthalpy, 22.53 kcal/mole for the S_N1 hydrolysis of methyl perchlorate in water is about 7 kcal/mole larger than the activation enthalpy for the methanolysis occurring by the S_N2 mechanism. Similar large differences are usually observed when reactions occurring by two different mechanisms, unimolecular and bimolecular, are compared. The solvolyses of methyl iodide and ethyl benzenesulphonate occur by the same bimolecular mechanism in water, methanol, and ethanol. The differences between the activation enthalpies for these reactions in water and alcohol are only about 2.5 and 1.0 kcal/mole, respectively (Table 5).

If the hydrolysis of methyl perchlorate in water is a unimolecular reaction, no second-order rate constant can be obtained for the reaction that can be substituted in the Swain-Scott equation.³ However, the logarithm of the first-order rate constant of the hydrolysis of methyl perchlorate in water divided by the water concentration unexpectedly satisfied the linear eqn. (6) obtained for reactions of methyl perchlorate with basic nucleophiles.

The second-order rate constants 3.33×10^{-3} , 20.8×10^{-3} and 72.2×10^{-3} l mole⁻¹sec⁻¹ were obtained for the reaction between methyl perchlorate and hydroxide ion in water at 0°C, 10°C, and 25°C, respectively. The values of the activation parameters are $\Delta H^* = 19.580$ cal/mole and $\Delta S^* = +2.02$ cal/deg·mole. The positive values of the activation entropy obtained for the alkaline hydrolysis of methyl perchlorate and methyl iodide¹⁵ in water are seldom obtained for bimolecular reactions of this charge type (Table 5). A positive activation entropy instead of the "normal" negative value indicates a weak interaction between hydroxide ion and methyl perchlorate in the transition state. This view is in agreement with the tendency of reactions of methyl perchlorate to occur by a unimolecular mechanism. The activation entropies are negative for the reactions of both methyl perchlorate and methyl iodide with methoxide ions in methanol (Table 5). The decrease in activation entropy is accompanied by an increase in activation energy for both reactions when the solvent changes from water to methanol.

Reaction constants s. Eqn. (4) was fitted to the rate constants of the nucleophilic reactions of methyl perchlorate and methyl iodide using the new nucleophilicity constants. The values of the new parameters of eqn. (4) are shown in Table 6. Although the equation is expected to be only approximately

Table 6. Values of the constants of eqn. (4) for reactions of methyl perchlorate and methyl iodide with nucleophiles in water and methanol at 0°. New values of nucleophilicity constants were used.

Reactant	Solvent	Non-basic nucleophiles			Basic nucleophiles		
		<i>s</i>	<i>c</i>	Mean deviation	<i>s</i>	<i>c</i>	Mean deviation
MeClO ₄	H ₂ O	1.02	- 7.30	0.06	0.82	- 5.99	0.05
MeI	H ₂ O	1.23	- 10.65	0.02	1.31	- 11.17	0.10
MeClO ₄	MeOH	0.65	- 4.95	0.04	1.01	- 5.46	0.08
MeI	MeOH	1.22	- 10.59	0.01	1.36	- 10.36	0.10

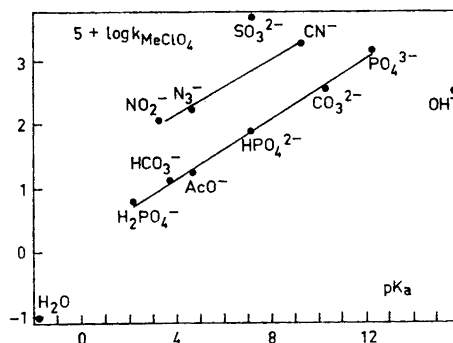
valid, the fit is fairly satisfactory as the mean deviation is only about 0.1 log k unit when eqn. (4) was fitted separately to the rates of reaction of methyl perchlorate and methyl iodide with non-basic and basic nucleophiles. The difference between the s values for the two groups of reactions indicates a difference in the sensitivities of the reactions to changes in nucleophilicity. Methyl perchlorate is somewhat less sensitive than methyl iodide to changes in nucleophilicity of non-basic nucleophiles in water at 0°C. Perchlorate ion is possibly a better leaving group than iodide ion and the nucleophilic reactions of methyl perchlorate possess more S_N1 character and involve a weaker interaction of the nucleophile in the transition state than the reactions of methyl iodide. The tendency of reactions of methyl perchlorate to occur by the S_N1 mechanism has been already demonstrated. The s value may serve as an additional criterion of the extent of participation of a nucleophile in the transition state.

The change in solvent from water to methanol has a pronounced effect on the rates of reactions of methyl perchlorate with nucleophiles. The s values of the reactions of methyl iodide with nucleophiles in the two solvents are almost identical because the rates of these reactions were used as reference values when calculating the nucleophilicity constants. The sensitivity of methyl perchlorate to changes in nucleophilicity of non-basic nucleophiles is much smaller in methanol than in water. The rates of the reactions of methyl perchlorate with nucleophiles are almost ten times higher in methanol than in water, although the rates of methyl iodide with the same nucleophiles in these two solvents are nearly equal. Similarly as the hydrolysis reactions of alkyl halides,¹⁸ nucleophilic reactions occurring by a mechanism involving weak nucleophilic interaction in the transition state can be expected to be more susceptible to electrophilic assistance by protic solvents. The electrophilic assistance of methanol is possibly stronger than that of water. The higher rates in methanol may also be due to other effects such as a greater electrostatic interaction in the transition state between the negatively charged nucleophile and the positively charged carbon atom of the methyl perchlorate dipole in this solvent of lower dielectric constant.

Nucleophilic reactivity and basicity. The nucleophilic reactions of methyl perchlorate reflect the different reactivities of basic and non-basic nucleophiles. That basicity is an important property affecting the reactivity of nucleophiles has been demonstrated also by Edwards.⁶ The rate constants did not satisfy Edwards' equation with any reasonable accuracy. When the logarithms of the rate constants of reactions with basic nucleophiles have been plotted against the pK_a values of the nucleophiles, only very approximately linear correlations have been found.^{9,10} Steric effects, which are negligible in acid-base equilibria, are important in nucleophilic reactions. Because of steric and other effects, simple correlations between basicity and nucleophilicity are difficult to detect.^{2,45,7,8} In Fig. 3 logarithms of the rate constants of reactions of basic nucleophiles with methyl perchlorate are plotted against the pK_a values of the nucleophiles. A good linear correlation is obtained separately for oxygen nucleophiles, excluding hydroxide ion and water, and separately for nitrogen nucleophiles

$$\log k = 0.23 pK_a + Ab - 0.74 \pm 0.06 \quad (12)$$

Fig. 3. Plots of logarithms of the second-order rate constants of reactions of methyl perchlorate with nucleophiles in water at 0°C against the pK_a values of the nucleophiles in water at 25°C. Straight lines are drawn through points referring to reactions with oxygen-containing nucleophiles excluding hydroxide ion and water and points referring to reactions with nitrogen-containing nucleophiles.



The slopes are almost identical, 0.23, and of the order of magnitude usually found for nucleophilic reactions at alkyl carbon atoms.¹⁹ When the leaving group is less basic than the attacking group as is the case in nucleophilic reactions of methyl perchlorate with basic nucleophiles, the observed low sensitivity of the reaction rate to the changes in basicity of the nucleophile indicates a small change in the charge of the nucleophile when the transition state is formed. This result is in accordance with the view that there is only a weak interaction between the nucleophile and methyl perchlorate in the transition state.

For nucleophiles containing oxygen, nitrogen and sulphur as nucleophilic atoms the values of Δb are 0, 0.93, and 1.79, respectively. Weak nucleophilic reactivity was observed for OH^- ($\Delta b = -2.10$) and H_2O ($\Delta b = -1.64$) and an exceptionally high reactivity for $\text{S}_2\text{O}_3^{2-}$ ($\Delta b = +2.83$). The reactions of all these nucleophiles are expected to be subject to negligible steric effects, a condition which has to be met in order to obtain satisfactory linear free energy.

Approximately linear plots are obtained when rate constants of methyl perchlorate with nucleophiles in methanol are plotted against pK_a values of the nucleophiles in water. The somewhat smaller values of the slope obtained for reactions in methanol as compared with water result mainly from using the pK_a values in water. If pK_a values in methanol are used, the slope of the $\log k$ versus pK_a plot is 0.23 which is equal to the value obtained for the reactions of methyl perchlorate with AcO^- and PhO^- in water. Rates of reactions¹⁷ of methyl perchlorate with amines are also approximately linearly related to the basicities of the latter but the correlation is not so good as for the reactions shown in Fig. 3, possibly because of greater steric and perhaps also other effects. These reactions will be discussed²⁰ in Part III.

Linear relationships between $\log k$ and pK_a for basic nucleophiles must result in linear relationships between nucleophilicity constants n and pK_a values.

$$n = 0.283 pK_a + \Delta b + 1.49 \pm 0.08 \quad (13)$$

where b is 0, 1.14, and 2.14 for, respectively, oxygen, nitrogen, and sulphur nucleophiles. These equations may serve as an approximate method of estimating nucleophilicity constants for basic nucleophiles when kinetic data are not available for their evaluation. The equation for sulphur nucleophiles is based on only one nucleophilicity constant n (for SO_3^{2-}) and more data are needed to establish a possible general linear relationship.

According to these examples, the following linear free energy equation for nucleophilic reactivity can be proposed:

$$\log k = a \cdot pK_a + b + \Delta b \quad (14)$$

where $b=0$ for basic anionic nucleophiles containing oxygen as the nucleophilic atom. The constant a measures the sensitivity of the reaction to the basicity of the nucleophile and Δb the sensitivity of the reaction to a change from oxygen to some other nucleophilic atom such as nitrogen or sulphur. As the nucleophilicity constants are based on the nucleophilic reactions of methyl bromide, the values of the constants of eqn. (13) show that reactions of methyl bromide are more sensitive than reactions of methyl perchlorate to changes in the basicity of the nucleophile ($a=0.283$ and 0.23) and also to changes in the nucleophilic atom ($\Delta b=1.14$ and 0.93 for nitrogen nucleophiles and $\Delta b=2.14$ and 1.79 for sulphur nucleophiles). A linear relationship exists also between the values of a and Δb of these two sets of reactions. The values of a possibly depend on differences in the polarizability of the nucleophilic oxygen and nitrogen atoms when compared at the same basicity. The lower sensitivity of nucleophilic reactions of methyl perchlorate to changes in the properties of nucleophiles is in accordance with the fact that perchlorate ion is an especially good leaving group resulting in a looser structure of the transition state.

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