

## Kinetics and Free Energy Relationships of Reactions of Methyl Nitrate With Nucleophiles in Water

S. JOKINEN,<sup>a</sup> E. LUUKKONEN,<sup>b</sup> J. RUOSTESUO,<sup>a</sup> J. VIRTANEN<sup>b</sup>  
and J. KOSKIKALLIO<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of Oulu, Oulu, and <sup>b</sup>Department of Chemistry, University of Helsinki, Helsinki, Finland

Second-order rate constants of reactions of methyl nitrate with 18 different nucleophiles in water were measured at 90°C. A linear free energy relationship (LFER) exists between logarithms of the rate constants of reactions of methyl nitrate with oxygen-containing basic nucleophiles and the  $pK_a$  values of the nucleophiles. The slope has a value of 0.23 which is identical within experimental error with the value of the slopes obtained for similar reactions of methyl perchlorate and methyl benzenesulphonate. A linear free energy relationship exists also between the  $\log k$  values of reactions of methyl nitrate and methyl perchlorate with oxygen-containing basic nucleophiles and between the  $\log k$  values of reactions of the esters with non-basic nucleophiles. In both cases the slope is 1 within experimental error. Activation parameters of the hydrolysis of methyl nitrate are  $\Delta V^* = -7.8 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\Delta H^* = 25.91 \text{ kcal mol}^{-1}$  and  $\Delta S^* = -0.1 \text{ cal degree}^{-1} \text{ mol}^{-1}$  and those of the uncatalysed hydrolysis of methyl nitrate  $\Delta V^* = -6.0 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\Delta H^* = 25.51 \text{ kcal mol}^{-1}$  and  $\Delta S^* = -10.8 \text{ cal degree}^{-1} \text{ mol}^{-1}$ .

### EXPERIMENTAL

*Chemicals.* Methyl nitrate was prepared from nitric acid and methanol.<sup>1</sup> All other chemicals were commercial products of highest purity.

*Rate measurements.* Vapour-free reaction vessels were made by sealing long capillary tubes to 4 ml ampoules. Each reaction mixture was introduced into an ampoule from a syringe. The ampoule was filled to the top of the capillary tube and closed with a plastic bulb. Small gas bubbles that formed at elevated temperatures had a negligible effect on the reaction rate. Rate measurements at high pressures were performed as described earlier.<sup>2</sup>

Some of the nucleophiles *e.g.*  $\text{HS}^-$ ,  $\text{CNO}^-$ , or  $\text{CN}^-$ , were not stable due to hydrolysis, oxidation, or other reactions in the mixture, and no reliable rate constants could be obtained for their reactions with methyl nitrate. In the case of  $\text{HSO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ , the stability of the nucleophile could be improved by adding buffers to the reaction mixtures. When calculating rate constants, corrections due to reactions of the buffer components with methyl nitrate had to be made.

When possible, both the concentration of the nitric acid produced in the simultaneous hydrolysis reaction of methyl nitrate and the concentration of the nucleophiles in the reaction mixture were determined. Acid-base titrations using indicators were performed

when studying the reactions with the nucleophiles  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{SNC}^-$ ,  $\text{AcO}^-$ ,  $\text{CN}^-$ , and  $\text{PhO}^-$  and potentiometric acid-base titrations when studying reactions with the nucleophiles  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $4\text{-NO}_2\text{PhO}^-$ ,  $\text{PhS}^-$ , and  $\text{CO}_3^{2-}$ . Potentiometric titrations with silver nitrate solution were used to determine the concentrations of the nucleophiles  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{SCN}^-$ ,  $\text{CN}^-$ , and  $\text{N}_3^-$  and iodometric titrations to determine the concentrations of the nucleophiles  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$ . The concentrations of methyl acetate formed in the reaction of methyl nitrate with acetate ion were calculated from results of analyses after total hydrolysis of the removed samples. Concentrations of  $\text{NO}_2^-$  ion were calculated from results of analyses after esterification of  $\text{HNO}_2$  with methanol.<sup>3</sup>

*Calculations.* The rate constants of the uncatalysed hydrolysis of methyl nitrate were calculated using the first-order rate equation. When the second-order rate constants of reactions between methyl nitrate and the nucleophiles  $\text{OH}^-$ ,  $\text{N}_3^-$ ,  $\text{AcO}^-$ ,  $\text{PhO}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $4\text{-NO}_2\text{PhO}^-$ , and  $\text{HSO}_3^-$  were calculated, the simultaneous hydrolysis of methyl nitrate was taken into account as described earlier.<sup>4</sup> The reaction of methyl nitrate with acetate ion is accompanied by a consecutive hydrolysis of the methyl acetate formed. The amounts of methyl nitrate that had reacted with acetate ions which were needed for calculating the rate constants were obtained from the amounts of acetate ions and methyl acetate determined separately in two samples taken at same time. No corrections were applied for the simultaneous hydrolysis of methyl nitrate when the relatively fast reactions of methyl nitrate with the nucleophiles  $\text{PhS}^-$ ,  $\text{SO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$  were studied. However, the reaction between methyl nitrate and the carbonate ion used to buffer the reaction mixture had to be taken into account when calculating the rate constants of the reaction between methyl nitrate and the  $\text{S}_2\text{O}_3^{2-}$  ion. Calculations of rate constants of the reaction of methyl nitrate with the  $\text{PO}_4^{3-}$  ion are complicated by the reaction of  $\text{PO}_4^{3-}$  with water to form  $\text{HPO}_4^{2-}$  and  $\text{OH}^-$  which also react with methyl nitrate. The value of the base constant of  $\text{PO}_4^{3-}$  at  $90^\circ\text{C}$  is not known and can be only roughly estimated from values of  $\text{p}K_a$  near room temperature. The value of the rate constant for the reaction of methyl nitrate with  $\text{PO}_4^{3-}$  ion may be less accurate given in Table 1 than the other rate constants in the table.

*Table 1.* Second-order rate constants  $k_2$  of the reactions of methyl nitrate with nucleophiles in water  $90^\circ\text{C}$ ,  $\text{p}K_a$  values<sup>9,14-18</sup> of the conjugate acids of the nucleophiles in water at  $25^\circ\text{C}$  and second-order rate constants<sup>1</sup> of reactions of methyl perchlorate with nucleophiles in water at  $0^\circ\text{C}$ .

No.	Nucleophile	$5 + \log k_2$ $\text{MeNO}_2$	$\text{p}K_a$	$5 + \log k_2$ $\text{MeClO}_4$
1	$\text{PO}_4^{3-}$	2.59	12.38	3.185
2	$\text{OH}^-$	2.170	15.72	2.522
3	$\text{CO}_3^{2-}$	2.155	10.33	2.591
4	$\text{PhO}^-$	2.045	9.99	2.428
5	$\text{HPO}_4^{2-}$	1.316	7.20	1.897
6	$4\text{-NO}_2\text{PhO}^-$	0.846	7.17	1.517
7	$\text{AcO}^-$	0.907	4.76	1.255
8	$\text{H}_2\text{O}$	-1.633	-1.74	-1.048
9	$\text{N}_3^-$	1.602	4.70	2.225
10	$\text{NO}_2^-$	1.373	3.148	2.179
11	$\text{PhS}^-$	4.61	6.5	
12	$\text{SO}_3^{2-}$	3.800	7.20	3.696
13	$\text{S}_2\text{O}_3^{2-}$	3.322	1.60	4.192
14	$\text{HSO}_3^-$	1.022	1.90	
15	$\text{SCN}^-$	1.552		2.591
16	$\text{I}^-$	1.540		2.642
17	$\text{Br}^-$	0.870		1.745
18	$\text{Cl}^-$	(0.512)		0.686

The values of the rate constants of the reactions of methyl nitrate with non-basic and weakly basic nucleophiles were calculated as before.<sup>4</sup> The value of the rate constant obtained for the reaction with the  $\text{SCN}^-$  ion is possibly slightly too high due to simultaneous slow decomposition of the  $\text{SCN}^-$  ion in the reaction mixtures. Reactions of methyl nitrate with halide ions are complicated by the simultaneous hydrolysis of the methyl halides formed in the reactions. From simultaneous analyses of both acid and halide ion concentrations of samples from the reaction mixtures, the amount of methyl nitrate present can be computed. Using a large excess of halide ions relative to methyl nitrate, the first-order rate equation could be employed to calculate the rate constants. When calculating the rate constants, it was assumed that the rate of hydrolysis of methyl nitrate is not altered when halide salts are present in the reaction mixture and a constant ionic strength is maintained with sodium nitrate. The results were checked by determining the methyl halide concentrations in the reaction mixtures by gas chromatography. The rate constants obtained by both methods were in good agreement. The rate constants shown in Table 1 are means of the rate constants computed from at least two series of measurements at different initial nucleophile concentrations.

### DISCUSSION

Various different linear free energy relationships (LFR) have been proposed for reactions of nucleophiles.<sup>5,6</sup> Swain and Scott<sup>5</sup> chose the rate constants of reactions of methyl bromide with nucleophiles as standards and obtained approximately linear correlations between the logarithms of the rate constants of various reactions and the logarithms of rate constants of the standard reactions. In a previous work<sup>7</sup> the reactions of methyl perchlorate with nucleophiles in aqueous solution were studied. The Swain-Scott type LFR was found to be valid only for series of reactions involving nucleophiles of similar type. An LFR was obtained between the logarithms of rate constants of reactions of methyl perchlorate with basic oxygen-containing nucleophiles and the  $\text{p}K_a$  values of the nucleophiles.

For reactions of methyl nitrate with basic nucleophiles containing oxygen as attacking nucleophilic centre, reactions Nos. 1 to 8 in Table 1, the LFR was:

$$\log k_{\text{MeNO}_2} = 1.02 (\pm 0.05) \log k_{\text{MeClO}_4} - 0.60 (\pm 0.09) \quad (1)$$

A similar LFR was also found between the  $\log k$  values of reactions of methyl benzenesulphonate<sup>8</sup> with basic oxygen-containing nucleophiles at 20°C and those of methyl perchlorate with the same nucleophiles at 0°C with basic oxygen-containing nucleophiles in water. The slope of the plot is  $1.08 \pm 0.05$ . The values of the slopes are almost constant but the values of the rate constants of these reactions vary greatly depending on the leaving group. For example the relative rate constants of the reactions with hydroxide ion at 25°C are:



An LFR was also found for the rate constants of reactions of methyl nitrate with basic oxygen-containing nucleophiles:

$$\log k_{\text{MeNO}_2} = 0.23 (\pm 0.02) \text{p}K_a - 5.28 (\pm 0.04) \quad (2)$$

The values of the rate constants and the  $\text{p}K_a$  values used when determining the LFR were not all measured at the same temperature. When values of rate constants<sup>8</sup> of reactions of methyl benzenesulphonate with basic oxygen-containing nucleophiles in water at 20°, 40°, and 60° are plotted

against the  $pK_a$  values of the conjugate acids of the nucleophiles at 25°, values of slopes of 0.25, 0.24, and  $0.24 \pm 0.02$  were obtained at the three temperatures. Moderate changes in temperature alter the values of the slope in eqn. (2) only slightly. When values of  $pK_a$  at 90°C calculated<sup>9,10</sup> for bases  $AcO^-$ ,  $HPO_4^{2-}$  and  $CO_3^{2-}$  were used with the nucleophiles at 90°C, the value of the slope was 0.23. As the effect of a change in temperature on the values of the slopes of equations (1) and (2) is almost negligible, values of the slopes can be compared although the rate constants have been measured at different temperatures.

When eqn. (2) was fitted to the  $\log k$  values of reactions of methyl benzenesulphonate<sup>9</sup> with oxygen-containing basic nucleophiles at 25°C and to those of the reactions of methyl perchlorate with the same nucleophiles measured at 0°C, values of the slopes were 0.25 and  $0.23 \pm 0.01$ , respectively. These can be compared with the value 0.23 of the slope obtained for the reactions of methyl nitrate.

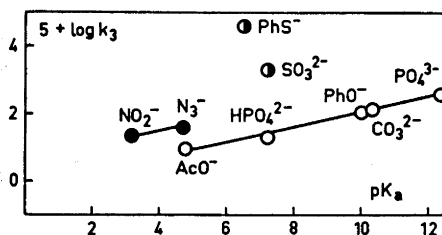


Fig. 1. Logarithm of second-order rate constant of reactions of methyl nitrate with nucleophiles in water at 90°C plotted against  $pK_a$  values of nucleophiles at 25°C.

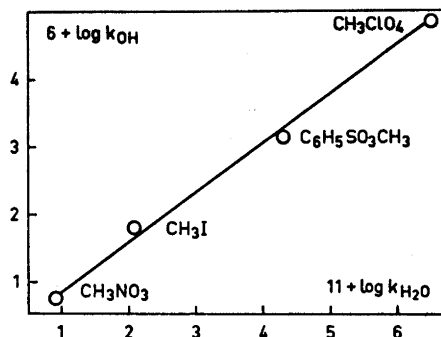


Fig. 2. Logarithm of second-order rate constant of reactions of methyl perchlorate, methyl benzenesulphonate, methyl iodide, and methyl nitrate with hydroxide ion plotted against logarithm of rate constants of respective hydrolysis reactions in water at 25°C.

Values of the rate constants of the reactions of methyl nitrate, methyl benzenesulphonate and methyl perchlorate with hydroxide ion and with water do not fit eqn. (2) although they fit eqn. (1). In order to fit these rate constants to the eqn. (2), obtained for other basic oxygen-containing nucleophiles, the values 10.4, 9.8, and  $9.8 \pm 0.4$  should be used for the  $pK_a$  of the conjugate acid of the hydroxide ion instead of the value 15.72 in the three series of reactions.

The following LFR was derived from the rate constants of the reactions of methyl nitrate, methyl benzenesulphonate, and methyl perchlorate with hydroxide ion and water in aqueous solution at 25°C:

$$\log k_{OH} = 0.71 (\pm 0.02) \log k_{H_2O} + 1.91 (\pm 0.08) \quad (3)$$

Eqn. (3) was found<sup>11</sup> to fit rate constants of hydrolysis of carboxylic esters but the value 0.79 of the slope was somewhat larger.

Rate constants of reactions involving basic nucleophiles containing other atoms than the oxygen atom as the attacking nucleophiles also fit an LFR similar to eqn. (2). For reactions of methyl perchlorate<sup>7</sup> with the nitrogen-containing basic nucleophiles  $\text{CN}^-$ ,  $\text{N}_2^-$  the values of the slope of eqn. (3) is the same as for reactions with oxygen-containing basic nucleophiles but the intercept is larger by 0.93. For reactions of methyl nitrate and methyl perchlorate, the intercepts differ by about 0.82 and 1.00, respectively. Nitrogen-containing nucleophiles are hence about ten times more reactive than oxygen-containing nucleophiles of equal basicity. Nucleophiles containing sulphur are usually even more reactive than nitrogen-containing nucleophiles, but no single LFR was found to apply to reactions of methyl nitrate with sulphur-containing nucleophiles.

The LFR, eqn. (2) fitted to the values of rate constants of reactions of methyl nitrate with non-basic or weakly basic nucleophiles (reactions Nos. 13 and 15 to 18 in Table 1) is:

$$\log k_{\text{MeNO}_2} = 0.98 (\pm 0.05) \log k_{\text{MeClO}_4} - 1.04 (\pm 0.08) \quad (4)$$

Values of the slope of 1.00 and 1.19 of equations similar to eqn. (4) were obtained for the reactions of methyl benzenesulphonate<sup>8</sup> and methyl iodide,<sup>7</sup> respectively, with non-basic nucleophiles. The values 1.02, 1.08, and 1.00 of the slopes of eqn. (1) and (4) for the reactions of basic nucleophiles with methyl nitrate, methyl benzenesulphonate, and methyl perchlorate are slightly larger than the values of slopes 0.98, 1.00, and 1.00 for reactions of non-basic nucleophiles with these esters. A somewhat larger value of the slope (1.19) was obtained for reactions of methyl iodide with non-basic nucleophiles. Separate LFR are often obtained for closely similar reactions as, for example, was found by Taft *et al.*<sup>12,13</sup> when studying equilibria of hydrogen-bonded complexes in organic solvents. In spite of some promising attempts,<sup>8</sup> no satisfactory single LFR has been found for all nucleophilic reactions.

The values of the activation volumes  $\Delta V^\ddagger = -7.8 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$  of the alkaline hydrolysis and  $\Delta V^* = -6.0 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  of the uncatalysed hydrolysis of methyl nitrate in aqueous solution at 90°C are approximately constant

Table 2. Rate constants of the reaction of methyl nitrate with water ( $k_1$ ) and hydroxide ion ( $k_2$ ) in water at pressures from 1 to 2500 atm.

T°C	<i>p</i> atm	$10^5 k_1$ s <sup>-1</sup>	$10^5 k_2$ M <sup>-1</sup> s <sup>-1</sup>
60	1	0.0379	0.0610
90	1	1.28	1.47
	500	1.50	1.65
	1000	1.86	1.75
	1500	1.95	2.02
	2000	2.37	2.26
	2500	2.56	2.70

in the pressure range from 1 to 2500 atm. These values are of the order of magnitude expected for bimolecular reactions. The value of the activation volume of the alkaline hydrolysis reaction was corrected for the compressibility of the reaction mixture by adding  $\kappa RT = 1.5 \text{ cm}^3 \text{ mol}^{-1}$  to the experimental value  $-7.5 \text{ cm}^3 \text{ mol}^{-1}$ .

The values  $\Delta H^\circ = 25.51$  and  $25.91 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -10.8$  and  $-0.1 \text{ cal degree}^{-1} \text{ mol}^{-1}$  were obtained for uncatalysed and alkaline hydrolyses, respectively, of methyl nitrate in aqueous solution at  $75^\circ\text{C}$ . The value of the activation entropy is of the expected order of magnitude but the value for the uncatalysed reaction is somewhat smaller than that usually obtained for bimolecular hydrolysis reactions. The values  $\Delta H^\ddagger = 24.20 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 5.9 \text{ cal degree}^{-1} \text{ mol}^{-1}$  were obtained for the reaction of methyl nitrate with benzenethiolate ion in water at  $25^\circ\text{C}$ .

Sodium nitrate and sodium perchlorate were found not to react with methyl nitrate and both retard the hydrolysis of methyl nitrate. The slope of a plot of  $k_1$  against the salt concentration is  $-0.15$  and  $-0.13$  for sodium nitrate and sodium perchlorate, respectively. An approximately zero salt effect was observed in the hydrolysis of methyl benzenesulphonate<sup>8</sup> and a positive salt effect in the hydrolysis of methyl perchlorate in water.<sup>7</sup> The results cannot be directly compared as the reactions were studied at the temperatures  $90^\circ$  and  $0^\circ\text{C}$ , respectively.

*Acknowledgements.* This work has been supported by the *State Research Council for Natural Sciences*. This support is gratefully acknowledged.

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Received February 12, 1971.