Kinetics and Mechanism of the Oxidation of Hydroxylamine by Aquavanadium(v) Ions in Aqueous Perchlorate Media

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This oxidation has been investigated in the acidity range 1—5 mol dm^{-3} $HClO_4$ at a constant ionic strength of 5 mol dm^{-3} over the temperature range 25—60 °C. The consumption ratio $|\Delta[V^V]|:|\Delta[NH_2OH]|$ is found to lie between 1 : 1 and 2 : 1 using an excess of V^V. With an excess of NH_2OH, the reaction is first order in $[V^V]$ and the order in $[NH_2OH]$ is between zero and one. The variation of the pseudo-first-order rate constant with $[NH_2OH]$ and $[H^+]$ shows that two pathways operate, one *via* the complex $VO_2{}^+\cdot NH_3OH^+{}_{aq.}$ and the other *via* $V(OH)_2{}^{3+}\cdot NH_3OH^+$. Values for the overall enthalpy and entropy of activation are determined for each pathway.

Of the ions which oxidise hydroxylamine, Ag^{II} [1] and Mn^{III} [2] produce nitrate ions, whereas Ce^{IV},[3-5] Ag^I,[6] Cu^{II},[7] $[Fe(CN)_6]^{3-}$,[8,9] V^V,[10] Cr^{VI},[11] and Fe^{III} [12] produce either nitrogen or dinitrogen oxide, or mixtures of both: with Co^{III}, the products appear [13] to depend on the media used, but the principal one is probably nitrite in aqueous perchloric acid. The kinetics of the oxidation by V^V in acidic aqueous perchlorate media have been investigated [10,14] over a range of $[HClO_4]$ from 0.005 to 1.00 mol dm^{-3} at one temperature only. Over the range $[HClO_4] = 0.2$—1.0 mol dm^{-3}, the rate equation (1) was found [10] to operate, with k and k' independent of the acidity; an intermediate complex has been detected spectrophotometrically.[15] At acidities with $[HClO_4] < 0.2$ mol dm^{-3}, the reaction becomes [13] complex with the rate equation including a term involving the square of $[NH_2OH]$ and the rate decreasing with increasing acidity; further complexation of V^V by NH_2OH occurs during this reaction. We have investigated the oxidation of NH_2OH by V^V in aqueous perchlorate media at higher acidities in the range 1—5 mol dm^{-3} $HClO_4$ and over a range of temperatures.

$$-d[V^V]/dt = k[NH_2OH][V^V] + k'[NH_2OH][V^V]^2 \quad (1)$$

EXPERIMENTAL

Materials.—AnalaR hydroxylamine hydrochloride was used. Acrylonitrile was washed with three successive 25 cm^3 quantities of 1 mol dm^{-3} Na[OH] to remove the phenolic stabilizer and subsequently washed four times with distilled water: after drying over anhydrous $Na_2[SO_4]$, the acrylonitrile was distilled under nitrogen at reduced pressure. The other materials used were all as described previously.[16]

Procedure.—The decay of $[V^V{}_{aq.}]$ was measured spectrophotometrically as described earlier.[16] Concentrations of $V^V{}_{aq.}$ were determined by sampling into solutions containing Fe^{II}, also as described earlier.[16]

RESULTS AND DISCUSSION

Stoicheiometry.—Values of the consumption ratio $|\Delta[V^V]|:|\Delta[NH_2OH]|$ determined using an excess of V^V with a constant initial $[NH_2OH] = 1.00 \times 10^{-3}$ mol dm^{-3} were found for a range of initial $[V^V]$, $[HClO_4]$, and temperatures. The absorption of light due to the V^{IV} formed was allowed for as described previously.[16] The results in Table 1 show that the consumption ratio varies between 1.10 : 1 and 1.60 : 1 without any systematic variation with $[V^V]$, $[HClO_4]$, and temperature. The average value is 1.29 ± 0.04 : 1. Such a fractional consumption ratio is quite common for the oxidizing ions which produce N_2 and N_2O from hydroxylamine.

TABLE 1

Stoicheiometry for initial $[NH_2OH] = 1.00 \times 10^{-3}$ mol dm^{-3}

θ_c/°C	$[HClO_4]$/ mol dm^{-3}	Initial $[V^V]$/ 10^3 mol dm^{-3}	$\dfrac{|\Delta[V^V]|}{|\Delta[NH_2OH]|}$
35.0	3.00	5.00	1.53
40.0	1.00	10.0	1.27
40.0	1.00	5.00	1.17
40.0	1.00	3.00	1.17
40.0	3.00	3.00	1.10
40.0	3.00	10.0	1.13
40.0	5.00	10.0	1.31
40.0	5.00	5.00	1.43
40.0	5.00	3.00	1.41
45.5	1.00	3.00	1.31
45.5	3.00	5.00	1.24
45.5	5.00	3.00	1.45
50.0	1.00	3.00	1.27
50.0	1.00	10.0	1.64
50.0	3.00	3.00	1.17
50.0	3.00	10.0	1.15
50.0	5.00	3.00	1.43
50.0	5.00	10.0	1.59
60.0	1.00	3.00	1.31
60.0	1.00	10.0	1.37
60.0	3.00	3.00	1.22
60.0	3.00	10.0	0.95
60.0	5.00	3.00	1.46
60.0	5.00	10.0	1.35

Bengtsson [10] found a value of 1.12 : 1 for the consumption ratio for V^V with the principal product being gaseous nitrogen, the deviation from the expected consumption ratio of 1.0 : 1 being due to the formation of some N_2O. It is interesting to note that, for the oxidation by Ce^{IV} in aqueous sulphate media,[4] the equivalent consumption ratio varied between 2.08 : 1 at a high initial ratio $[Ce^{IV}]:[NH_2OH]$ to 1.23 : 1 at a low initial ratio $[Ce^{IV}]:[NH_2OH]$.

Preliminary Rate Measurements.—In all the kinetic measurements the ionic strength was maintained at 5.00 mol dm^{-3} by the addition of sodium perchlorate. With $[NH_2OH] \gg [V^V{}_{aq.}]$, linear plots were always obtained for plots of log (optical density) against time, showing that the reaction is always first order in [$V^V{}_{aq.}$] under the conditions used here. As the hydroxylamine was always added as the hydrochloride, the effect of adding chloride ions on the rate of oxidation of hydroxylamine by $V^V{}_{aq.}$ was investigated. Table 2 shows that the rate only begins to vary with [Cl^-] when the latter exceeds 0.1 mol dm^{-3}, so a value for [NH_2OH] between 0.01 and 0.10 mol dm^{-3} was used in nearly all the subsequent rate measurements with the initial [$V^V{}_{aq.}$] *ca.* 1.0 × 10^{-3} mol dm^{-3}.

TABLE 2

The effect of added [Cl^-] on the pseudo-first-order rate constant, k_0, for the oxidation of 1.0 × 10^{-2} mol dm^{-3} NH_2OH by 1.0 × 10^{-3} mol dm^{-3} V^V at 25 °C

[$HClO_4$]/mol dm^{-3}	[Cl^-]/mol dm^{-3}	$10^5\ k_0$/s^{-1}
5.00		23.00
5.00	0.10	24.00
5.00	1.00	96
2.00		8.0
2.00	0.10	8.1

For [$HClO_4$] = 3.00 mol dm^{-3} with initial [$V^V{}_{aq.}$] = 1.00 × 10^{-3} mol dm^{-3} and initial [NH_2OH] = 0.10 mol dm^{-3}, the pseudo-first-order rate constant determined under nitrogen at 40.0 °C was found to be 6.8 × 10^{-4} s^{-1} which compares well with the value of 6.7 × 10^{-4} s^{-1} found for the same concentrations of acid and reactants at the same temperature in the presence of air. All subsequent rate constants were determined in air.

TABLE 3

Values for the pseudo-first-order rate constant, $10^4\ k_0$ (s^{-1}), with varying [NH_2OH], [$HClO_4$], and temperature at an ionic strength of 5.00 mol dm^{-3}

		[NH_2OH]/mol dm^{-3}							
θ_c/°C	[$HClO_4$]/ mol dm^{-3}	0.010	0.0125	0.020	0.040	0.060	0.080	0.10	0.20
25.0	5.00	2.15		2.91	3.67		4.28	4.40	5.6
25.0	4.00	1.80		2.20	3.10		3.50	3.90	
25.0	2.00	1.30		1.67	1.98	2.52	2.85	3.38	
25.0	1.00	0.94		1.49	1.95	2.11	2.48	2.99	
35.0	5.00	6.4		9.0	13.0	15.0	16.0	17.0	
35.0	4.00	5.2		7.8	11.0	12.8		14.8	
35.0	3.00	4.06		6.6	9.4	11.8	13.4	13.8	
35.0	2.00	3.24		5.4	8.7	10.3	11.6	11.9	
35.0	1.00	3.14		5.3	8.5	10.3	11.9	12.9	
40.0	5.00	8.4		13.3	17.4	19.9	20.3	23.2	
40.0	4.00	6.8		11.1	16.6	18.6	20.7	22.3	
40.0	3.00	4.13	6.2	8.1	13.7		16.4	18.5	
40.0	2.00	3.96		7.9	11.1	14.4	15.0	16.2	
40.0	1.00	3.46		5.5	8.2		12.8	14.8	
45.5	5.00	17.3		27.4	37.8	43.2	49.3	56	
45.5	4.00	15.3		24.9	38.6	43.2	51	55	
45.5	3.00	11.0		18.6	29.1	35.2	38.8	43.5	
45.5	2.00	9.4		15.7	25.2	31.4	35.8	37.6	
45.5	1.00	8.3		14.7	23.0	27.2	30.2	33.7	
59.9	5.00	53		94	130	147			
59.9	4.00	36.7		62	79	87		130	
59.9	3.00	36.5		63	92	134	121		
59.9	2.00	24.4		34.8	66	94	112	141	
59.9	1.00	26.2		37.4	54	68	70	78	

Variation of Rate with [NH_2OH] *and* [$H^+{}_{aq.}$].—The variation of rate with concentration of hydroxylamine was investigated for a range of acidities at several temperatures. Except for 5 mol dm^{-3} $HClO_4$ at 25 °C, the value of [NH_2OH] never exceeded 0.1 mol dm^{-3} and was varied within the range 0.01—0.10 mol dm^{-3} at acidities 1—5 mol dm^{-3} $HClO_4$ with ionic strength maintained at 5.00 mol dm^{-3}. Initial [$V^V{}_{aq.}$] was *ca.* 1.0 × 10^{-3} mol dm^{-3}. The values obtained for the pseudo-first-order rate constants, k_0, are given in Table 3 for 25.0, 35.0, 40.0, 45.5, and 59.9 °C. Plots of k_0 against [NH_2OH] are curves, but plots of $k_0{}^{-1}$ against [NH_2OH]$^{-1}$ are always linear with positive intercepts on the ordinate: these latter plots for 35.0 °C are shown in Figure 1. Table 3 and Figure 1 also show that the reaction is retarded by increasing acidity.

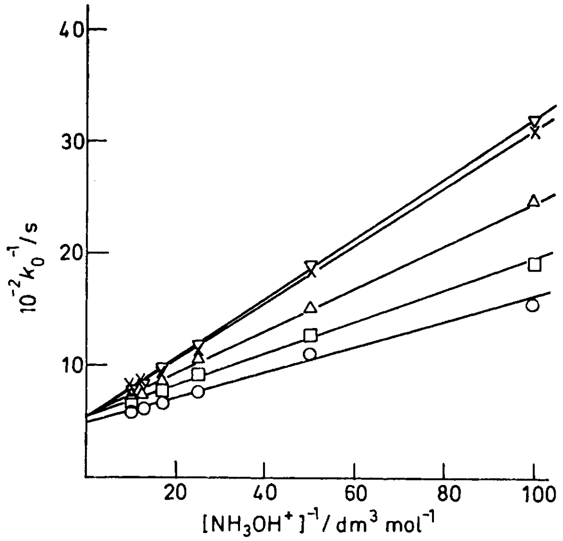

FIGURE 1 Plots of the reciprocal of the pseudo-first-order rate constant, $k_0{}^{-1}$, against [NH_3OH^+]$^{-1}$ at a constant ionic strength of 5.00 mol dm^{-3} and 35.0 °C with values of [$HClO_4$] of: 1.00 (▽); 2.00 (×); 3.00 (△); 4.00 (□); and 5.00 mol dm^{-3} (○)

Mechanism of the Oxidation.—The linear plots of

k_0^{-1} against $[NH_2OH]^{-1}$ show that complexes are formed between $V^V{}_{aq.}$ and NH_2OH at these high acidities, as well as at $[H^+] < 1$ mol dm^{-3} as shown spectrophotometrically.[15] The evidence in the literature for the protonation of $VO_2{}^+{}_{aq.}$ has been summarised elsewhere.[17] With $pK_a = 5.97$ at 25 °C,[18] all the NH_2OH will exist as NH_3OH^+ under the conditions used in this work. The following pre-equilibria [equations (2)—(6)] may therefore be involved. These will be followed by the rate-

$$VO_2{}^+{}_{aq.} + H^+{}_{aq.} \overset{K_1}{\rightleftharpoons} VO(OH)^{2+}{}_{aq.} \qquad (2)$$

$$VO_2{}^+{}_{aq.} + NH_3OH^+{}_{aq.} \overset{\beta_1}{\rightleftharpoons} VO_2{}^+{\cdot}NH_3OH^+{}_{aq.} \qquad (3)$$

$$VO(OH)^{2+}{}_{aq.} + NH_3OH^+{}_{aq.} \overset{\beta_1'}{\rightleftharpoons} VO(OH)^{2+}{\cdot}NH_3OH^+{}_{aq.} \qquad (4)$$

$$VO_2{}^+{\cdot}NH_3OH^+{}_{aq.} + H^+{}_{aq.} \overset{K_2}{\rightleftharpoons} VO(OH)^{2+}{\cdot}NH_3OH^+{}_{aq.} \qquad (5)$$

$$VO(OH)^{2+}{\cdot}NH_3OH^+ + H^+{}_{aq.} \overset{K_3}{\rightleftharpoons} V(OH)_2{}^{3+}{\cdot}NH_3OH^+{}_{aq.} \qquad (6)$$

determining steps (7)—(9). In the oxidation of NH_2OH by Ce^{IV}, e.s.r. measurements[19] have shown that the intermediate free radical is $\cdot ONH_2$. Reactions (7)—(9)

$$VO_2{}^+{\cdot}NH_3OH^+{}_{aq.} \xrightarrow{k_1} VO^{2+}{}_{aq.} + \cdot ONH_2 + H_2O \qquad (7)$$

$$VO(OH)^{2+}{\cdot}NH_3OH^+{}_{aq.} \xrightarrow{k_1'} VO^{2+}{}_{aq.} + \cdot ONH_2 + H^+{}_{aq.} \qquad (8)$$

$$V(OH)_2{}^{3+}{\cdot}NH_3OH^+{}_{aq.} \xrightarrow{k_1''} VO^{2+}{}_{aq.} + \cdot ONH_2 + H_2O + 2H^+{}_{aq.} \qquad (9)$$

will then be mainly followed by the very rapid step (10).[10] The rate of (10) relative to the rates of reaction

$$2\ \cdot ONH_2 \longrightarrow N_2 + 2H_2O \qquad (10)$$

(7)—(9) is such that the system $V^V + NH_2OH$ under nitrogen does not initiate the polymerization of acrylonitrile.

From the above, the rate of disappearance of the total added $[V^V{}_{aq.}]_T$ is given by (11), where $h = [H^+{}_{aq.}]$,

$$\frac{-d[V^V{}_{aq.}]_T}{dt} = \frac{n\beta_1(k_1 + k_1'K_2h + k_1''K_2K_3h^2)[V^V{}_{aq.}]_T[NH_3OH^+]}{1 + K_1h + \beta_1[NH_3OH^+](1 + K_2h + K_2K_3h^2)} \qquad (11)$$

subscript T indicates the total added $[V^V{}_{aq.}]$, $[NH_3OH^+]$ is the total added concentration of hydroxylamine, and n = the consumption ratio $|\Delta[V^V{}_{aq.}]| : |\Delta[NH_2OH]|$. The pseudo-first-order rate constant k_0 is given by (12).

$$\frac{1}{k_0} = \frac{1 + K_1h}{n\beta_1(k_1 + k_1'K_2h + k_1''K_2K_3h^2)[NH_3OH^+]} + \frac{1 + K_2h + K_2K_3h^2}{k_1 + k_1'K_2h + k_1''K_2K_3h^2} \qquad (12)$$

From (12) it is seen that the slopes of the linear plots of k_0^{-1} against $[NH_2OH]^{-1}$ should be given by (13), as $K_1h \leqslant 1$.[16,17] These slopes have been determined by the least-squares procedure and plotted against various functions of h. Only the data at 25 °C gave any semblance of a linear plot for $(\text{slope})^{-1}$ against h, the plots for

$$(\text{slope})^{-1} = n\beta_1(k_1 + k_1'K_2h + k_1''K_2K_3h^2) \qquad (13)$$

all other temperatures being quite distinct curves. However, the plots of $(\text{slope})^{-1}$ against h^2 (Figure 2) are linear with positive intercepts on the ordinate for all temperatures, including 25 °C. Although this does not exclude any influence of the term in $k_1'K_2h$ in equation (13), reaction (8) can only play at most a very minor role in the oxidation compared with (7) and (9). Assuming that the oxidation is restricted to the latter two reactions, the intercepts of the linear plots of $(\text{slope})^{-1}$ against h^2 are equal to $n\beta_1k_1$ and the slopes equal to $n\beta_1K'k_1''$, where $K' = K_2K_3$. The values for these determined by the least-squares procedure are given in Table 4.

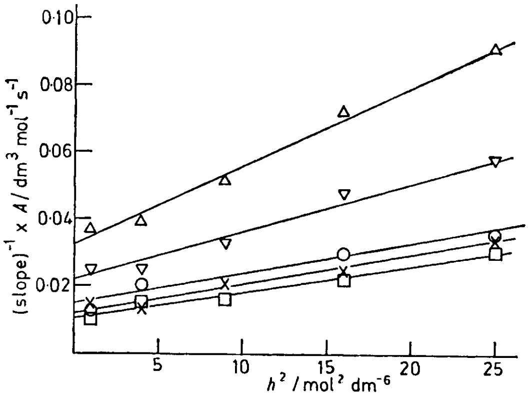

FIGURE 2 Reciprocals of the slopes of the plots of k_0^{-1} *versus* $[NH_3OH^+]^{-1}$ plotted against h^2 for a constant ionic strength of 5.00 mol dm^{-3} and at temperatures: 25.0, $A = 1.00$ (○); 35.0, $A = 1.00$ (△); 40.0, $A = 0.25$ (□); 45.5, $A = 0.25$ (▽); and 59.9 °C, $A = 0.05$ (×)

TABLE 4

Values of $n\beta_1k_1$ (10^2 dm^3 mol^{-1} s^{-1}) and $n\beta_1K'k_1''$ (10^4 dm^9 mol^{-3} s^{-1}) at an ionic strength of 5.00 mol dm^{-3} and various temperatures

θ_c/°C	$n\beta_1k_1$	$n\beta_1K'k_1''$
25.0	1.48	8.8
35.0	3.23	23.7
40.0	4.05	31.8
45.5	9.0	58
59.9	25.0	170

Bengtsson[10] ascribed his observation of a consumption ratio $|\Delta[V^V{}_{aq.}]| : |\Delta[NH_2OH]|$ slightly greater than 1 : 1 to the production of N_2O *via* reactions (14) and (15). He claimed that reaction (14) accounted for his observation of a term in $[V^V]^2$ in the rate equation under his condi-

$$V^V + V^VNH_2OH \xrightarrow{\text{slow}} 2\ V^{IV} + HNO \qquad (14)$$

$$2\ HNO \xrightarrow{\text{fast}} N_2O + H_2O \qquad (15)$$

tions.[10] However, he found that this term disappeared at low $[V^V]$; and no term in $[V^V]^2$ is found in this present study when initial $[V^V]$ are *ca.* 1.0×10^{-3} mol dm^{-3}. Therefore, although our consumption ratio is determined with $[V^V] \gg [NH_2OH]$, where (14) and (15) will probably operate these reactions will be excluded under the conditions of our kinetic experiments where NH_2OH is in a large excess. Thus, it is reasonable to conclude for the kinetic observations that $n = 1.00$ and that the values in Table 4 are for $\beta_1 k_1$, and $\beta_1 K' k_1''$. This corresponds too with the observations of Waters and Wilson[4] on the oxidation of NH_2OH by Ce^{IV}. They found that the consumption ratio $|\Delta[Ce^{IV}]| : |\Delta[NH_2OH]|$ decreased towards 1 : 1 as the initial ratio of reactant concentrations $[Ce^{IV}] : [NH_2OH]$ decreased. They found no term in $[Ce^{IV}]$ in their rate equation with an order greater than unity and they ascribed their consumption ratio $>1.0 : 1$ to the participation of reaction (15) and (16). However, they assumed that for the conditions of

$$\cdot ONH_2 + Ce^{IV}_{aq.} \longrightarrow Ce^{III}_{aq.} + HNO + H^+_{aq.} \quad (16)$$

their kinetic experiments with an initial ratio $[Ce^{IV}] : [NH_2OH] < 0.06 : 1$ that (16) was excluded.

Plots of log $\beta_1 k_1$ and log $\beta_1 K' k_1''$ against the reciprocal of absolute temperature are linear. By the application of the least-squares procedure to these plots, for $\beta_1 k_1$ the enthalpy of activation $\Delta H^\ddagger = 66 \pm 5$ kJ mol^{-1} and the entropy of activation $\Delta S^\ddagger = -61 \pm 15$ J K^{-1} mol^{-1}, and for $\beta_1 K' k_1''$ $\Delta H^\ddagger = 68 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -77 \pm 10$ J K^{-1} mol^{-1}.

As reaction (8) is excluded from the mechanism, the terms in $k_1' K_2 h$ and $K_2 h$ can be excluded from equation

$$\frac{(k_1 + k_1'' K' h^2)\beta_1[NH_3OH^+]}{k_0} = 1 + K_1 h + \beta_1[NH_3OH^+](1 + K'h^2) \quad (17)$$

(12). This modified equation (12) can then be rearranged to give equation (17), assuming that $n = 1.00$ and putting $K' = K_2 K_3$. Using the value of $(\text{slope})^{-1}$ derived from the plots of k_0^{-1} against $[NH_3OH^+]^{-1}$ for $(k_1 + k_1'' K' h^2)\beta_1$ at any particular value of h, the left-hand side of equation (17) can be plotted against $[NH_3OH^+]$ for a range of acidities at each temperature. Linear plots are always obtained passing through the value of unity on the ordinate: these plots for 35 °C are shown in Figure 3. The common intercept of unity for all these plots over all the acidities and temperatures confirms the assumption made above and the observation[16,17] made from the oxidation of other ligands by $V^V_{aq.}$ that $K_1 h \ll 1$. A least-squares analysis of these plots confirms that they have such a common intercept of unity and Figure 4 shows that plots of their slopes against h^2 give reasonably straight lines for 35 and 45.5 °C: the errors at this stage are too large to distinguish the type of variation obtained at 25, 40, and 59.9 °C. From equation (17), the intercepts of these plots should be equal to β_1 and the slopes equal to $\beta_1 K'$. Bearing in mind the errors at this stage, only approximate values can be deduced from Figure 4: β_1 is *ca.* 18 dm^3 mol^{-1} at 35 and 45.5 °C and $\beta_1 K'$ is *ca.* 1.1 dm^9 mol^{-3} at 35 °C and *ca.* 0.6 dm^9 mol^{-3} at 45.5 °C, making K' *ca.* 6×10^{-2} dm^6 mol^{-2} at 35 °C and K' *ca.* 3×10^{-2} dm^6 mol^{-2} at 45.5 °C. It is interesting to note that in his spectrophotometric examination of the complex formed in the acidity range 0.2—0.9 mol dm^{-3} $HClO_4$ at 25 °C, Bengtsson found the formation equilibrium constant to be independent of acidity: from comparison with our kinetic experiments in the acidity range 1—5 mol dm^{-3} $HClO_4$, one concludes that either the extinction coefficient for $VO_2^+ \cdot NH_3OH^+_{aq.}$ is closely similar to that for $V(OH)_2^{3+} \cdot NH_3OH^+_{aq.}$ or that the influence of the latter only becomes significant at $[H^+] > 1$ mol dm^{-3}. Bengtsson's acid-independent formation equilibrium constant lying in the range 13—19 dm^3 mol^{-1} at 25 °C is in good agreement with our β_1 of *ca.* 18 dm^3 mol^{-1} at 35 °C.

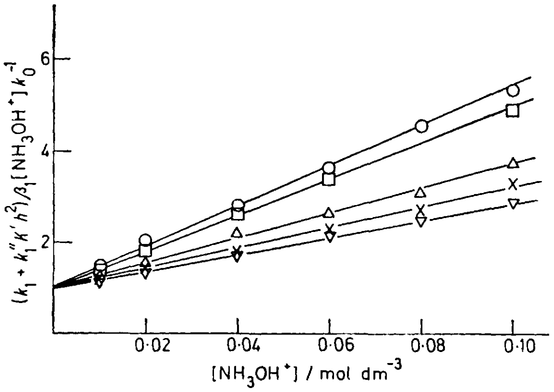

FIGURE 3 Plots of $(k_1 + k_1''K'h^2)\beta_1[NH_3OH^+]k_0^{-1}$ against $[NH_3OH^+]$ for a constant ionic strength of 5.00 mol dm^{-3} and at 35.0 °C with values of $[HClO_4]$ of 1.00 (▽); 2.00 (×); 3.00 (△); 4.00 (□); and 5.00 mol dm^{-3} (○)

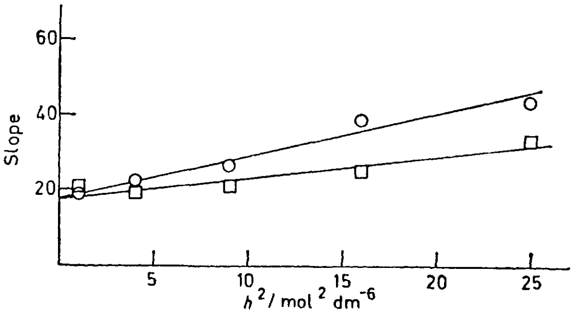

FIGURE 4 Slopes of the plots of Figure 3 against h^2 for 35.0 °C (○); and similarly for 45.5 °C (□)

As Bengtsson's investigation was restricted to 25 °C it is not possible to compare our values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ obtained in 1—5 mol dm^{-3} $HClO_4$ with values at lower acidities. The overall values for $\Delta H^\ddagger$ for the two pathways are virtually the same, any differences arising in $\Delta S^\ddagger$. Both values for the overall $\Delta S^\ddagger$ are negative, reflecting the increased restriction in the transition state imposed by the formation of the complex with its high charge.

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