A Kinetic Study of the Reduction of Vanadium(V) by Hydroxylamine in Strongly Acid Perchlorate Solutions

GÖSTA BENGTSSON

Division of Inorganic Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

The kinetics of the reaction between vanadium(V) and hydroxylamine has been studied within the hydrogen ion concentration range 0.2 – 1.0 M. The main product emanating from hydroxylamine is probably nitrogen gas, but some dinitrogen oxide also seems to be formed. Vanadium(V) is reduced to vanadium(IV).
The rate law is

$$- \frac{d[V(V)]}{dt} = k[NH_2OH][V(V)] + k'[NH_2OH][V(V)]^2$$

The experimental rate constants, k and k', have been determined from initial rates and from integrated approximate rate laws. A mechanism has been proposed which interprets the experimental results within the hydrogen ion concentration range studied.

In a previous paper,[1] a kinetic study of the reaction between hydrazine and vanadium(V) was described. The present paper is devoted to a corresponding study of the reduction of vanadium(V) by hydroxylamine in strongly acid ($[H^+] = 0.2 - 1.0$ M) perchlorate solutions. This reaction does not seem to have been subject to any previous studies, neither in respect to the reaction products nor to the kinetics. Within the hydrogen ion concentration range in question, vanadium(V) is present as VO_2^+ and hydroxylamine as NH_3OH^+. Strong oxidizing agents oxidize hydroxylamine to nitrous acid whereas weak oxidants oxidize it to nitrogen gas. VO_2^+ is a moderately strong oxidizing agent $(VO^{2+} + H_2O \rightleftharpoons VO_2^+ + 2H^+ + e^-;\ E^\circ = 1.00$ V).[3] It therefore seems reasonable to believe that the products of the reaction in question are nitrogen gas or dinitrogen oxide, or both of them, whereas the formation of nitrous acid seems less likely.

SYMPOLS AND NOTATIONS

[V(V)]   over-all concentration of vanadium(V) (within the hydrogen ion concentration range used $= [VO_2^+]$).

$[V(V)]_0$ over-all concentration of vanadium(V) at the time $t = 0$ after mixing.

[NH$_2$OH] over-all concentration of hydroxylamine ($=$ [NH$_3$OH$^+$]).
[NH$_2$OH]$_0$ over-all concentration of hydroxylamine at the time $t = 0$ after mixing.
ε molar absorption coefficient.
A absorbance ($A = \varepsilon\, c\, l$; $c =$ concentration; $l =$ path length).
A_0 absorbance at the time $t = 0$ after mixing.
A_∞ absorbance at complete reaction ($t = \infty$).
a linear absorption coefficient ($a = A/l$).
λ wave length.
V total volume of gas in the gas buret.
T temperature.
P pressure in the closed system ($=$ the atmospheric pressure).
n number of mol N$_2$ evolved.

EXPERIMENTAL

Vanadium(V) perchlorate solutions were prepared by dissolving vanadium pentoxide containing more than 99.9 % V$_2$O$_5$ in perchloric acid. Alternatively, V$_2$O$_5$ was dissolved in sodium hydroxide solution which was then acidified by the addition of perchloric acid. By the latter procedure, the difficulties due to the very slow dissolution of V$_2$O$_5$ at low acidities were avoided. The concentration of vanadium(V) was calculated from the weight of V$_2$O$_5$.

Hydroxylamine solutions were prepared from hydroxylamine hydrochloride of analytical grade (Riedel de Haën). The concentrations of the hydroxylamine solutions were checked titrimetrically by the addition of an excess of potassium bromate solution, followed after 15 min by the addition of potassium iodide. The iodine formed was titrated by sodium thiosulphate solution with starch as an indicator.[4] It was found that if the hydrogen ion concentration of the titrand exceeded about 2 M, the reproducibility was poor and too high values were obtained. The results obtained at [H$^+$] $= 1 - 1.5$ M by this procedure agreed within $0.3 - 0.5$ % with the values calculated from the weight of hydroxylamine hydrochloride. The solutions were used within one or two days and tests showed that they were perfectly stable during this time. No decrease of the concentrations could be detected even after ten days.

All the chemicals used were of analytical grade. The water was doubly distilled. The ionic strength was kept constant at 1.0 M. The temperature was $25.00 \pm 0.05°$C.

The spectrophotometric measurements were carried out using a Zeiss PMQ II Spektralphotometer. The reaction was initiated by mixing equal volumes of thermostated vanadium(V) solution and hydroxylamine solution. Measurements which were performed with solutions degassed before mixing showed that the reaction rate was not influenced by the presence of dissolved air in the solution.

A few measurements of the rate of gas evolution were performed in the following manner.[5] The vanadium(V) and hydroxylamine solutions to be mixed were thermostated and at the same time saturated by nitrogen by bubbling nitrogen gas through them for $20 - 25$ min. The appropriate volumes of reactant solutions were mixed in 100 ml Erlenmeyer flasks equipped with ground-glass joints. The flask was immediately connected to a thermostated gas buret by means of a narrow PVC tube. The gas buret was fitted with a levelling tube so that the pressure in the closed system could be kept equal to the atmospheric pressure. Stirring was achieved in the Erlenmeyer flask using a glass-covered magnet. When the evolution of gas became stable ($5 - 15$ min after mixing) its rate was followed with the gas buret.

MEASUREMENTS AND RESULTS

Preliminary measurements were carried out to establish the nature of some of the reaction products, to determine the stoichiometry and to determine suitable wave lengths for the subsequent measurements. All these preliminary

measurements were carried out in solutions which contained 1.000 M perchloric acid.

The absorption curve within the wave length range $320-900$ nm was recorded for a solution with $[V(V)]_0 = 10$ mM and $[NH_2OH]_0 = 20$ mM when the reaction was complete. The curve agreed within very narrow limits with that obtained for a solution of $VOSO_4$ under identical conditions.

The stoichiometry was determined by measuring the absorbances after the reaction had ceased for two parallel series of solution with $[V(V)]_0 = 10$ mM and $[NH_2OH]_0 = 0-8$ mM, *i.e.* with V(V) in excess. The mean values of the results of the two series are shown in Table 1. In the calculation of the

Table 1. Determination of the stoichiometry of the reaction. $[V(V)]_0 = 10$ mM; $\lambda = 340$ nm; $l = 1$ cm; $\varepsilon_{V(V)} = 201.4$ M^{-1} cm^{-1}; 1.000 M $HClO_4$.

$[NH_2OH]_0$ mM	a_∞	mol V(V)/mol NH_2OH
0	2.017	—
0.5	1.905	1.11
2	1.567	1.13
4	1.132	1.11
6	0.659	1.13
8	0.226	1.12

number of mol V(V) consumed per mol NH_2OH, the molar absorption coefficient $\varepsilon_{V(V)} = 201.4$ M^{-1} cm^{-1} was used (*cf.* Ref. 1). It is seen that 1.12 mol V(V) are consumed per mol NH_2OH under these conditions, and that the stoichiometry is independent of the proportions between the reactants. Furthermore, it seems to be independent of $[H^+]$ within the hydrogen ion concentration range studied $(0.2-1.0$ M).

The rate law was determined by measuring the initial rates (in 1.00 M $HClO_4$) at a constant $[V(V)]_0$ and different $[NH_2OH]_0$, and at a constant $[NH_2OH]_0$ and different $[V(V)]_0$. These measurements were carried out at the wave length 340 nm. The results are shown in Tables 2 and 3. The values

Table 2. Initial rates at a constant $[V(V)]_0$.
$[V(V)]_0 = 5.00$ mM; $\lambda = 340$ nm; $\varepsilon_0 = 207.0$ M^{-1} cm^{-1}.

$[NH_2OH]_0$ mM	$-\left(\dfrac{\Delta[V(V)]}{\Delta t}\right)_0 \times 10^5$ M min^{-1}
2	0.68
4	1.33
6	2.03
8	2.59
10	3.24

Table 3. Initial rates at a constant $[NH_2OH]_0$.
$[NH_2OH]_0 = 10.0$ mM; $\lambda = 340$ nm; $\varepsilon_0 = 207.0$ M^{-1} cm^{-1}.

$[V(V)]_0$ mM	$-\left(\dfrac{\varDelta[V(V)]}{\varDelta t}\right)_0 \times 10_5$ M min^{-1}
1	0.403
2	0.939
3	1.56
4	2.28
5	3.34
6	4.16
7	5.25
8	6.47
9	7.88
10	8.99

in these tables represent the means of $2-5$ measurements. The reaction rate is proportional to $[NH_2OH]$, but the dependence of $[V(V)]$ is more complicated. $-(\varDelta[V(V)]/\varDelta t)_0/[V(V)]_0$ *versus* $[V(V)]_0$ is a straight line, so the rate law is

$$- \frac{d[V(V)]}{dt} = k[NH_2OH][V(V)] + k'[NH_2OH][V(V)]^2 \qquad (1)$$

Approximate values of k and k' were obtained from the intercept and slope of the straight line mentioned above. These were calculated by means of a least squares program on a Hewlett-Packard desk top computer. $k = 0.36 \pm 0.06$ min^{-1} M^{-1}; $k' = 56 \pm 8$ min^{-1} M^{-2}. The error limits throughout this paper represent three standard deviations. The rate was found to be independent of $[H^+]$ for $[H^+] \approx 0.2$ M but at lower values of $[H^+]$ it increased with decreasing $[H^+]$. Measurements in the presence of added vanadium(IV) showed that the reaction rate is independent of the concentration of VO^{2+}.

Eqn. (1) can be rewritten as

$$- \frac{d[V(V)]}{dt} = k[NH_2OH][V(V)]\left(1 + \frac{k'}{k}[V(V)]\right) \qquad (2)$$

By keeping $[V(V)]$ sufficiently small, the second term of the parenthesis can be made negligible ($k'/k \approx 156$ M^{-1}). Then if $[NH_2OH]_0 \gg [V(V)]_0$, the reaction becomes formally of the first order:

$$- \frac{d[V(V)]}{dt} = k_a[V(V)] \qquad (3)$$

where

$$k_a = k[NH_2OH] \qquad (4)$$

For 156 $[V(V)]$ to be much less than 1, $[V(V)]$ should not exceed about 1×10^{-4} M. At this low concentration the absorbances at wave lengths above about 300 nm are very low, even at the longest possible path length accessible. Therefore, a wave length range with considerably greater molar absorption

coefficients was sought in the ultra-violet region of the spectrum. Absorption curves were determined for the following solutions (in 1.000 M $HClO_4$) within the wave length range $200-350$ nm: (1) 0.100 mM $V(V) + 20.0$ mM NH_2OH at complete reaction; (2) 0.100 mM $V(V)$; (3) 0.100 mM $V(V) + 20.0$ mM NH_2OH immediately after mixing (values extrapolated to the time $t = 0$). These curves are shown in Fig. 1. The latter two curves almost coincide for $\lambda > 250$ nm,
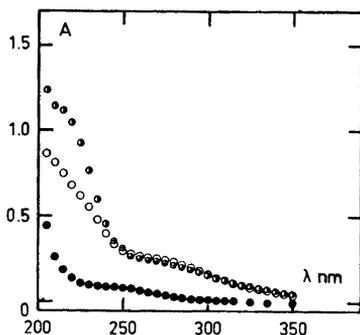

Fig. 1. Absorption curves. ●, 0.1 mM $V(V) + 20$ mM NH_2OH at complete reaction; ○, 0.1 mM $V(V)$; ◑, 0.1 mM $V(V) + 20$ mM NH_2OH immediately after mixing. $l = 3$ cm.

but for $\lambda < 250$ nm the solution containing hydroxylamine has a considerably higher absorbance. There is also a large difference between the initial (solution 3) and final (solution 1) absorbances within the whole wave length range studied. The high absorbances of solutions 2 and 3 show that measurements can be performed within the wave length range $200-250$ nm even at very low vanadium(V) concentrations.

A series of kinetic measurements were carried out at the wave length 225 nm with $[V(V)]_0 = 0.025-0.100$ mM and $[NH_2OH]_0 = 5-20$ mM. The values of k_a were calculated from the integrated rate law

$$k_a t = \ln \frac{A_0 - A_\infty}{A - A_\infty} \tag{5}$$

$\ln (A - A_\infty)$ versus t fitted a straight line very closely (cf. Fig. 2) and the k_a-values were calculated by the least squares program. The results are shown in Table 4. The values obtained for a constant $[V(V)]_0$ while $[NH_2OH]_0$ is changing show that k_a is proportional to $[NH_2OH]_0$. The validity of Beer's law was confirmed by plotting A_0 (extrapolated values) versus $[V(V)]_0$ (Fig. 3). The experimental values fitted a straight line($[NH_2OH]_0$ $= 20.0$ mM) with the intercept 0.019, which was in excellent agreement with the value obtained for 20.0 mM hydroxylamine solution (0.020). k was calculated from the values of k_a obtained in 1.000 M $HClO_4$, and the mean value $k = 0.315 \pm 0.012$ min^{-1} M^{-1} was obtained.

The corresponding measurements at lower hydrogen ion concentrations showed that k is independent of $[H^+]$ for $[H^+] \geq 0.2$ M. At still lower hydrogen ion concentrations the route of the reaction seems to be more complicated (cf. below).
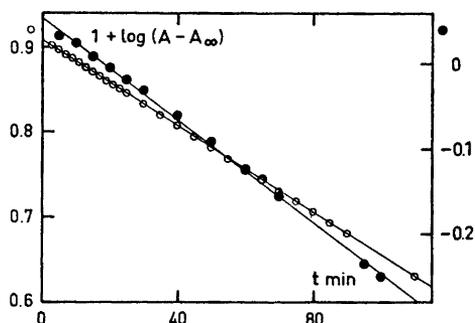
Fig. 2. ln $(A - A\infty)$ versus t. O, $[V(V)]_0 =$ 0.1 mM, $[NH_2OH]_0 = 20$ mM, $\lambda = 225$ nm, $l = 3$ cm; ●, $[V(V)]_0 = 10$ mM, $[NH_2OH]_0 =$ 0.5 mM, $\lambda = 340$ nm, $l = 1$ cm.
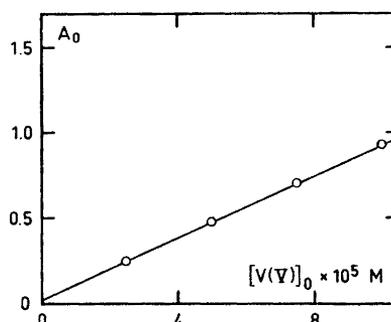
Fig. 3. A_0 versus $[V(V)]_0$. $[NH_2OH]_0 = 20$ mM; $\lambda = 225$ nm; $l = 3$ cm.

Table 4. Experimental values of the pseudo-first order rate constant k_a. $\lambda = 225$ nm; $l = 3$ cm.

$[NH_2OH]_0$ mM	$[V(V)]_0$ mM	$[H^+]$ M	$k_a \times 10^3$ min^{-1}
20.0	0.025	1.000	6.60
	0.050		6.14
	0.075		6.18
	0.100		6.13
15.0	0.100		4.77
10.0	0.100		3.11
5.0	0.100		1.77
20.0	0.100	0.500	6.00
20.0	0.100	0.200	5.90

With a large excess of vanadium(V) the rate law can be approximated to

$$- \frac{d[V(V)]}{dt} = k_x [NH_2OH] \qquad (6)$$

where

$$k_x = k[V(V)] + k'[V(V)]^2 \qquad (7)$$

According to the determination of the stoichiometry at $[V(V)]_0 = 10$ mM and $[NH_2OH]_0 = 0.5$ mM

$$\frac{d[V(V)]}{d[NH_2OH]} = 1.11 \qquad (8)$$

and thus

$$- \frac{d[NH_2OH]}{dt} = - \frac{1}{1.11} \frac{d[V(V)]}{dt} \tag{9}$$

$$- \frac{d[NH_2OH]}{dt} = k_b [NH_2OH] \tag{10}$$

where

$$k_b = k_x/1.11 \tag{11}$$

On integrating eqn. (10) one obtains

$$k_b \, t = \ln \frac{A_0 - A_\infty}{A - A_\infty} \tag{12}$$

since the change of $[NH_2OH]$ is measured *via* the change of the absorbance of vanadium(V). A series of kinetic measurements were performed at 340 nm with $[V(V)]_0 = 10.0$ mM and $[NH_2OH]_0 = 0.500$ mM (1.000 M $HClO_4$). ln $(A - A_\infty)$ *versus* t fitted a straight line (*cf.* Fig. 2) and k_b was calculated from the slope of this line. The mean value from nine measurements was $k_b = (7.76 \pm 1.64] \times 10^{-3}$ min^{-1}. Since $k = 0.315 \pm 0.012$ min^{-1} M^{-1}, $k' = 55 \pm 20$ min^{-1} M^{-2} is obtained.

DISCUSSION

The stoichiometry of the reaction indicates that the main product emanating from hydroxylamine is nitrogen gas but that some nitrogen compound of higher oxidation number, probably dinitrogen oxide, is also formed. Tests for nitrate and nitrite with ferrous sulphate and sulphuric acid were negative. The sole product emanating from vanadium(V) is vanadium(IV).

The fact that the absorption curve recorded immediately after mixing solutions of vanadium(V) and hydroxylamine deviates from the absorption curve of pure vanadium(V) indicates that the first step is the rapid formation of a complex between vanadium(V) and hydroxylamine. The occurrence of two terms in the rate law shows that there are two competing reaction paths. The one corresponding to the second-order term is probably an intra-molecular electron transfer within a mononuclear complex formed in the first rapid step. The third-order term might represent a reaction path with the formation of a binuclear transition complex. Alternatively, there might be a rapid and reversible formation of a binuclear intermediate. These reaction steps can be represented by the formulae

$$V(V) + NH_2OH \overset{K_1}{\rightleftharpoons} VNH_2OH \qquad \text{(rapid)} \tag{I}$$

$$VNH_2OH \overset{k_2}{\longrightarrow} V(IV) + NH_2O\!\!\!\!/ + H^+ \tag{II}$$

$$V(V) + VNH_2OH \overset{k_3}{\longrightarrow} 2 \, V(IV) + HNO \tag{III}$$

These formulae merely indicate the features of the reaction steps and do not show the structure of the complex, which is still unknown. The fact that the

rate law does not include $[H^+]$ indicates that the complex between vanadium(V) and hydroxylamine is formed without any loss or uptake of protons

The subsequent reaction steps are rapid and might be the following:[3,6,7]

$$2 \, NH_2O \longrightarrow N_2 + 2 \, H_2O \tag{IV}$$

$$2 \, HNO \longrightarrow N_2O + H_2O \tag{V}$$

$$HNO + NH_2OH^+ \longrightarrow N_2 + 2 \, H_2O \tag{VI}$$

The proposed mechanism yields the following rate law:

$$-\frac{d[V(V)]}{dt} = k_2 K_1 [NH_2OH][V(V)] + 2 \, k_3 K_1 [NH_2OH][V(V)]^2 \tag{13}$$

which is analogous to the experimental rate law with $k = k_2 K_1$ and $k' = 2k_3 K_1$. k_3 might include an equilibrium constant for the formation of a binuclear complex from "free" vanadium(V) and the mono-nuclear complex.

The objection might be raised that reactions I – V would be sufficient to account for the experimental results. This is not true, however, as can be seen from the following reasoning. If reactions I – V are the only ones occurring, it can be shown that the stoichiometry should be

$$\frac{d[V(V)]}{d[NH_2OH]} = \frac{k + k'[V(V)]}{k + k'[V(V)]/2} \tag{14}$$

Using the experimental values $k = 0.315 \pm 0.012 \, min^{-1} \, M^{-1}$ and $k' = 56 \pm 8 \, min^{-1}$ M^{-2} for $[V(V)]_0 = 10$ mM (and in so large excess that the change of $[V(V)]$ during the whole reaction can be neglected) $\Delta[V(V)]/\Delta[NH_2OH] = 1.47 \pm 0.05$ is calculated. This is much higher than the experimental value $\Delta[V(V)]/\Delta[NH_2OH] = 1.11 \pm 0.02$. It therefore seems reasonable to assume that hydroxylamine is also consumed in some side reaction such as VI (cf. Ref. 8).

The existence of reaction VI is also indicated by the rate of nitrogen gas evolution. By using the procedure for determining this quantity described in the experimental part of this paper, it can be assumed that the dinitrogen oxide formed remains dissolved in the reacting solution since the solubility of N_2O in aqueous solution is very high. Thus, only nitrogen gas is evolved from the solution. If only reactions I – V occur, the rate of formation of N_2

$$\frac{d[N_2]}{dt} = \frac{k}{2}[V(V)][NH_2OH \tag{15}$$

will be where k has the same meaning as in eqn. (1). If, however, reaction VI is also occurring, the rate will be greater than the value calculated from eqn. (15).

A few measurements of the "initial" rate of gas evolution were performed with $[V(V)]_0 = 20$ mM and $[NH_2OH]_0 = 10$ mM. Measurements at lower $[V(V)]$ were very unreliable due to the long time after mixing before the rate of gas

evolution became stable. The following relation exists between the rate of change of the gas volume and the rate of change of the number of mol N_2:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{RT}{P}\frac{\mathrm{d}n}{\mathrm{d}t} \qquad (16)$$

Knowing the volume of the solution (100 ml), the temperature (25.0°C), and the pressure (1 atm), the quantity $(\mathrm{d}[N_2]/\mathrm{d}t)_0 = (6.2 \pm 0.4) \times 10^{-5}$ M min^{-1} was claulcted from $(\mathrm{d}V/\mathrm{d}t)_0 = 0.152 \pm 0.011$ ml min^{-1}. This value is much higher than that calculated according to eqn. (15) $(\mathrm{d}[N_2]/\mathrm{d}t)_0 = (3.2 \pm 0.1) \pm 10^{-5}$ M min^{-1}. Thus, both the stoichiometry and the rate of nitrogen gas evolution indicate the existence of reaction VI.

Both the experimental rate constants k and k' have been determined by two different methods, one based on the initial rates and the other on integrated approximate rate laws. The values of k obtained by the two methods agree within the experimental error limits. These are much wider for the value obtained from the initial rates and therefore the value obtained from the integrated approximate rate law shown in eqn. (5) is considered to be the most reliable one. The agreement between the values of k' obtained by the two methods is also very good. The error limits are, however, greatest for the value obtained from the integrated approximate rate law. This is due to the fact that for k_b to remain approximately constant during the whole reaction, $[NH_2OH]_0$ must be much less than $[V(V)]_0$ and thus the differences $A - A_\infty$ become very small (< 0.1 for $A_0 \approx 2$). Thus $k' = 56 \pm 8$ min^{-1} M^{-2} has been accepted as the most reliable value.

The mechanism outlined above represents a proper interpretation of the experimental results only within the approximate hydrogen ion concentration range $[H^+] = 0.2 - 1.0$ M. Only preliminary measurements have been performed at $[H^+] < 0.2$ M but they indicate that the mechanism at lower hydrogen ion concentrations is far more complicated. A detailed study of the mechanism at lower hydrogen ion concentrations is planned.

REFERENCES

1. Bengtsson, G. *Acta Chem. Scand.* **25** (1971) 2989.
2. Rossotti, F. J. C. and Rossotti, H. *Acta Chem. Scand.* **10** (1956) 957.
3. Latimer, W. M. *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs.
4. Vogel, A. I. *A Text-book of Quantitative Inorganic Analysis*, Longmans, London 1961.
5. Fronæus, S. and Östman, C. O. *Acta Chem. Scand.* **22** (1968) 2827.
6. Waters, W. A. and Wilson, I. R. *J. Chem. Soc.* **A 1966** 534.
7. Jindal, V. K., Agrawal, M. C. and Mushran, S. P. *J. Chem. Soc.* **A 1970** 2060.
8. Bray, W. C., Simpson, M. E. and MacKenzie, A. A. *J. Am. Chem. Soc.* **41** (1919) 1363.