

## Kinetics and Mechanism of the Reaction between Vanadium(V) and Hydroxylamine within the Hydrogen Ion Concentration Range 0.005 – 0.2 M

GÖSTA BENGTSSON

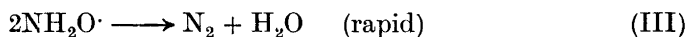
*Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740,  
S-220 07 Lund 7, Sweden*

The studies of the reaction between vanadium(V) and hydroxylamine within the hydrogen ion concentration range 0.2 – 1.0 M reported previously<sup>1,2</sup> have been continued by a corresponding study within the hydrogen ion concentration range 0.005 – 0.2 M. Within this latter hydrogen ion concentration range the two-stage reaction found in more acid solutions apparently becomes a three-stage reaction. It is shown that this change on decreasing  $[H^+]$  is due to a side reaction which becomes appreciable only at  $[H^+] < 0.2$  M. A mechanism valid within the whole hydrogen ion concentration range studied (0.05 – 1.0 M) is proposed.

A previous investigation<sup>1</sup> of the kinetics of the reduction of vanadium(V) by hydroxylamine within the hydrogen ion concentration range 0.2 – 1.0 M showed that this reaction obeys the rate law

$$-dC_{V(V)}/dt = kC_{V(V)}C_{NH_2OH} + k'C_{V(V)}^2C_{NH_2OH} \quad (1)$$

where  $C_{V(V)}$  and  $C_{NH_2OH}$  represent the over-all concentrations of vanadium(V) and hydroxylamine, respectively. At sufficiently low values of  $C_{V(V)}$  ( $\lesssim 5 \times 10^{-4}$  M) the  $k'$  term becomes negligible. The following mechanism was proposed for the reaction path corresponding to the  $k$  term (*cf.* also Ref. 2)



The stability constant  $\beta_1 = [VO_2NH_3OH^{2+}]/[VO_2^+]$  of the rapid pre-equilibrium (I) has been determined<sup>2</sup> and was found to be independent of  $[H^+]$  within the hydrogen ion concentration range studied, thus indicating the existence of a protonated complex.

In less strongly acid solutions ( $[H^+] < 0.2$  M) the kinetics of the reaction (low  $C_{V(V)}$  and a large excess of hydroxylamine) seems to be more complicated. The aim of the present study has been to elucidate the mechanism of this reaction at  $[H^+] = 0.005 - 0.2$  M and, if possible, to correlate the results to those obtained in more acid solutions.

#### SYMBOLS AND NOTATIONS

$C_M$	over-all concentration of the central ion M ( $=VO_2^+$ ). <sup>3</sup>
$C_L$	over-all concentration of the ligand L ( $=NH_3OH^+$ ). <sup>4</sup>
$\epsilon$	molar absorption coefficient (with indices indicating the species).
$A$	absorbance.
$a$	absorption coefficient ( $a = A/l$ ; $l$ = path length).
$\epsilon$	formal molar absorption coefficient ( $\epsilon = a/C_M$ ).
$\lambda$	wave length.
$t$	time.

#### EXPERIMENTAL

The chemicals used were of the same kind and quality as those described in Ref. 1, as were the methods used for the preparation of the stock solutions and the determination of their concentrations. The temperature was  $25.00 \pm 0.05^\circ C$ , the ionic strength 1.0 M. Sodium perchlorate and perchloric acid were used to keep the ionic strength constant.

The kinetic and equilibrium measurements were performed spectrophotometrically at  $\lambda = 225$  nm by a Zeiss PMQ II Spektralphotometer. Absorption curves were recorded with a Hitachi EPS 3-T spectrophotometer. The reactions were initiated by mixing the proper volumes of the reactant solutions either by pipette or by means of an all glass syringe equipped with a device to allow the delivery of a well-defined volume of the solution in question. By the latter method it was possible to achieve complete mixing (in the absorption cell) within about 2 seconds. The experimental (pseudo-first order) rate constants were calculated from plots of  $\ln(A_{\max} - A)$  and  $\ln(a - a_\infty)$  against  $t$  by a least squares program on an electronic computer. The same program was used for the calculation of the intercepts and slopes of the other linear plots in this paper. The error limits represent three standard deviations.

#### MEASUREMENTS AND RESULTS

The measurements were carried out at low over-all concentrations of vanadium(V) ( $C_M = 0.025 - 0.100$  mM) and generally with a large excess of hydroxylamine ( $C_L = 2.50 - 50.0$  mM). At  $[H^+] \geq 0.200$  M the absorbance at 225 nm decreased monotonously with the time after mixing the reactant solutions and the reaction was of the pseudo-first order. At  $[H^+] < 0.200$  M, however, three distinct reaction steps could be observed. There was at first an immediate increase of the absorbance leading to an absorbance value which was the same as in more acid solutions under otherwise identical conditions. The absorbance then increased rather slowly with time, passed through a maximum within a few minutes and finally decreased very slowly until it reached a value after a few hours which was approximately equal to that obtained under the same conditions in more acid solutions. Fig. 1 shows a series of absorbance-time curves for  $C_M = 0.100$  mM;  $C_L = 20.00$  mM at different

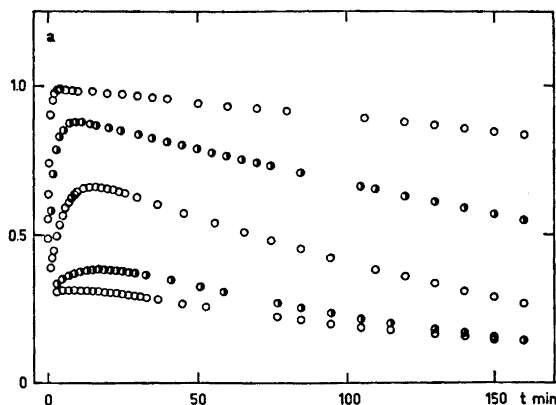
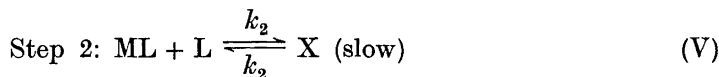
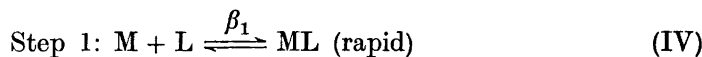


Fig. 1. A few absorbance-time curves determined at different  $[H^+]$ .  $C_M = 0.100$  mM;  $C_L = 20.00$  mM;  $l = 1$  cm;  $[H^+]$  from top to bottom: 0.005 M, 0.010 M, 0.020 M, 0.050 M, and 0.100 M.

values of  $[H^+]$ . The three steps of the reaction are as follows: (1) A rapid complex formation equilibrium with the stability constant  $\beta_1 = 12.5 \pm 0.4 \text{ M}^{-1}$  (cf. Ref. 2). (2) A relatively slow reaction leading to an increase of the absorbance at  $\lambda = 225$  nm. (3) A very slow reaction leading to the formation of vanadium(IV) and probably nitrogen gas (cf. below).

Step 1 has not been the subject of any kinetic study. The equilibrium has been considered in Ref. 2.

Step 2 is under the prevailing conditions of the pseudo-first order as it can be seen from the fact that  $\ln(A_{\max} - A)$  versus  $t$  is linear (Fig. 2) to more than about 60 % of complete reaction (as judged from the height of the maximum). Deviations from the linearity are found at the end of the reaction. These are due to the fact that the succeeding reaction then influences the difference  $(A_{\max} - A)$  to a noticeable extent.  $A_{\max}$  is the absorbance at the maximum of the absorbance-time curve. It is proportional to  $C_M$  at constant values of  $C_L$ ,  $l$ , and  $[H^+]$ . It increases with increasing  $C_L$  and decreases with increasing  $[H^+]$  (cf. Fig. 1), all other factors being kept constant. This indicates that step 2 probably includes an equilibrium reaction in which L is taken up by ML while one or more protons are lost. If it is assumed that steps 1 and 2 constitute the reactions (disregarding the participation of protons)



and the equilibrium constant

$$K_2' = [X]/[ML][L] \quad (2)$$

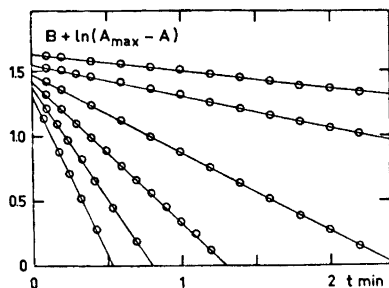


Fig. 2. Step 2.  $\ln(A_{\max} - A)$  versus  $t$  for a series of  $C_L$ -values.  $B$  is an arbitrary constant used to make the lines start at roughly the same value.  $C_M = 0.100$  mM;  $[H^+] = 0.010$  M;  $l = 1$  cm;  $C_L$  and  $B$  from top to bottom: 5 mM, 1.40; 10 mM, 1.05; 20 mM, 0.90; 30 mM, 0.85; 40 mM, 0.85; 50 mM, 0.85.

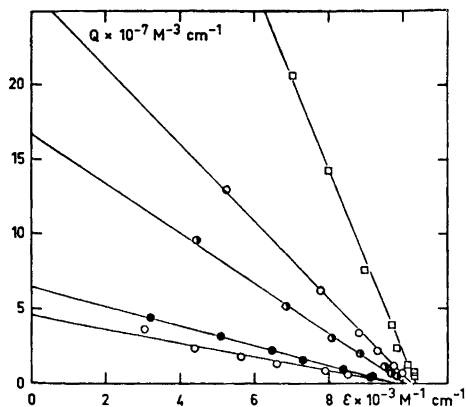


Fig. 3. Step 2. The quantity  $Q$  versus  $\epsilon$ .  $C_M = 0.100$  mM;  $[H^+]$  from top to bottom: 5.00 mM; 7.50 mM; 10.00 mM; 15.00 mM; 20.00 mM.

is defined, the following relation can be derived:

$$\epsilon = \frac{\epsilon_M + \epsilon_{ML}\beta_1[L] + \epsilon_X\beta_1K'_2[L]^2}{1 + \beta_1[L] + \beta_1K'_2[L]^2} \quad (3)$$

Since  $C_M \ll C_L$ , this equation can be transformed to

$$Q = [\epsilon(1 + \beta_1C_L) - \epsilon_M - \epsilon_{ML}\beta_1C_L]/C_L^2 = \epsilon_X\beta_1K'_2 - \epsilon\beta_1K'_2 \quad (4)$$

All the quantities in the left member of eqn. (4) are known ( $\epsilon = a_{\max}/C_M$  is measured as a function of  $C_L$ ;  $\beta_1$ ,  $\epsilon_M$ , and  $\epsilon_{ML}$  are obtained from Ref. 2).  $Q$  versus  $\epsilon$  yields for a constant value of  $[H^+]$  ( $[H^+] = 0.005 - 0.020$  M) a straight line with the intercept  $\epsilon_X\beta_1K'_2$  and the slope  $\beta_1K'_2$  and  $\epsilon_X$  and  $K'_2$  can be calculated. The straight lines obtained are shown in Fig. 3, and the values of  $\epsilon_X$  and  $K'_2$  are found in Table 1.  $K'_2$  is inversely proportional to  $[H^+]^2$ , so the true equilibrium constant is given by:

$$K_2 = K'_2[H^+]^2 = [X][H^+]^2/[ML][L] \quad (5)$$

The results of the kinetic measurements are also in agreement with this interpretation. The pseudo-first order rate constant,  $k_{\text{obs}}$ , increases strongly with increasing  $C_L$  and the order with regard to L is between 1 and 2. From the reactions (IV) and (V) the following expression can be derived

$$k_{\text{obs}}(1 + \beta_1C_L) = k_{-2} + k_{-2}\beta_1C_L + k_2\beta_1C_L^2 \quad (6)$$

since  $C_L \gg C_M$  and step 2 accordingly can be treated as a reversible first order reaction.  $k_{-2}$  can be determined by extrapolating  $k_{\text{obs}}(1 + \beta_1 C_L)$  versus  $C_L$  to  $C_L = 0$ , and then  $k_{-2}\beta_1$  and  $k_2\beta_1$  can be obtained from the linear relation

$$[k_{\text{obs}}(1 + \beta_1 C_L) - k_{-2}]/C_L = k_{-2}\beta_1 + k_2\beta_1 C_L \quad (7)$$

Fig. 4 shows  $[k_{\text{obs}}(1 + \beta_1 C_L) - k_{-2}]/C_L$  versus  $C_L$ . The values of  $k_2$  are shown in Table 1 and are found to be roughly inversely proportional to  $[\text{H}^+]^2$ . The

Table 1. Experimental values of  $K_2'$ ,  $K_2$ ,  $\epsilon_X$ , and  $k_2$ .

$[\text{H}^+]$ mM	$K_2' \times 10^{-3} \text{ M}^{-1}$	$K_2 \text{ M}$	$\epsilon_X \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$	$k_2 \text{ M min}^{-1}$
5	$4.90 \pm 0.32$	$0.120 \pm 0.008$	$10.3 \pm 1.3$	$331 \pm 45$
7.5	$2.06 \pm 0.08$	$0.116 \pm 0.004$	$10.2 \pm 0.7$	$231 \pm 41$
10	$1.34 \pm 0.10$	$0.134 \pm 0.010$	$10.1 \pm 1.3$	$111 \pm 5$
15	$0.535 \pm 0.022$	$0.120 \pm 0.005$	$9.7 \pm 0.7$	$58 \pm 11$
20	$0.385 \pm 0.048$	$0.154 \pm 0.023$	$9.5 \pm 2.6$	$36 \pm 14$

two sets of values of  $k_{-2}$  obtained from graphs corresponding to eqns. (6) and (7) do not agree very well with each other. This can be explained by the fact that  $k_{\text{obs}}$  at low values of  $C_L$  is very unreliable since  $A_{\text{max}}$  is lower than the true equilibrium value as a consequence of the succeeding reaction. This effect is most pronounced at low  $C_L$  (cf. below).

Step 3 is also of pseudo-first order since the lines  $\ln(a - a_\infty)$  versus  $t$  are straight except within a time interval from  $t = 0$  to immediately after the max-

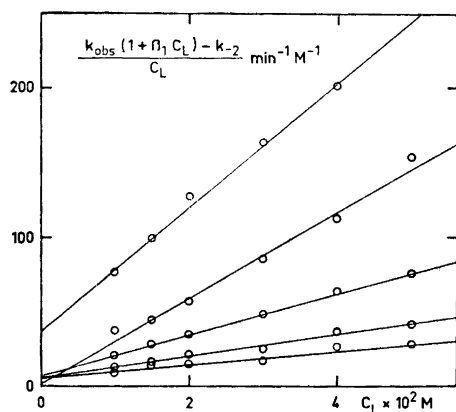


Fig. 4. Step 2.  $[k_{\text{obs}}(1 + \beta_1 C_L) - k_{-2}]/C_L$  versus  $C_L$ .  $C_M = 0.100 \text{ mM}$ ;  $[\text{H}^+]$  from top to bottom: 5.00 mM; 7.50 mM; 10.00 mM; 15.00 mM; 20.00 mM.

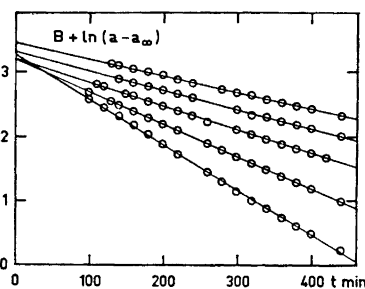
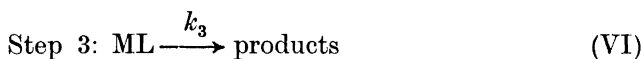


Fig. 5. Step 3.  $\ln(a - a_\infty)$  versus  $t$  for a series of  $C_L$ -values.  $C_M = 0.100 \text{ mM}$ ;  $[\text{H}^+] = 0.010 \text{ M}$ ;  $C_L$  from top to bottom. 50.0 mM; 40.0 mM; 30.0 mM; 20.00 mM; 10.00 mM.

imum (Fig. 5). The experimental rate constant  $k'_{\text{obs}}$  decreases with increasing  $C_L$  ( $[\text{H}^+]$  constant) and increases with increasing  $[\text{H}^+]$  ( $C_L$  constant). The relation between  $k'_{\text{obs}}$  and  $C_L$  can be roughly represented by the equation

$$k'_{\text{obs}} = p + q/C_L \quad (8)$$

where  $p$  and  $q$  are empirical constants. The fact that the rate law contains two terms indicates the existence of two competing reaction paths, one with X as a reactant and one with ML. The empirical relation can be explained by the reactions:



The following relation can be derived from reactions (IV) – (VII), if it is assumed that steps 1 and 2 are much faster than step 3.

$$k'_{\text{obs}} = (k_3\beta_1C_L + k_4\beta_1K_2'C_L^2)/(1 + \beta_1C_L + \beta_1K_2'C_L^2) \quad (9)$$

This equation can be transformed to

$$R = [k'_{\text{obs}}(1 + \beta_1C_L + \beta_1K_2'C_L^2)]/C_L = k_3\beta_1 + k_4\beta_1K_2'C_L \quad (10)$$

Accordingly  $R$  is a linear function of  $C_L$ . Fig. 6 shows this to be the case for  $[\text{H}^+] = 0.005 - 0.015$  M. At higher  $[\text{H}^+]$  step 3 is too rapid for the assumption made above to be true. If  $(1 + \beta_1C_L) \ll \beta_1K_2'C_L^2$ , then eqn. (9) becomes

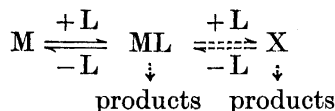
Table 2. Experimental values of  $k_3$  and  $k_4K_2'$ .

$[\text{H}^+]$ mM	$k_3$ min <sup>-1</sup>	$k_4K_2'$ M <sup>-1</sup> min <sup>-1</sup>
5	$0.144 \pm 0.011$	$2.36 \pm 0.35$
10	$0.206 \pm 0.014$	$1.27 \pm 0.41$
15	$0.233 \pm 0.032$	$1.77 \pm 0.99$

analogous to eqn. (8). Table 2 shows that  $k_3$  increases slightly with  $[\text{H}^+]$ , whereas  $k_4K_2'$  rather decreases. The precision hardly permits the establishment of the exact dependence of these quantities on  $[\text{H}^+]$ .

#### DISCUSSION

The mechanism proposed above can be summarized in the following reaction-equilibrium scheme:



The full drawn arrows enote rapid reactions (step 1), the dashed arrows relatively slow reactions (step 2), and the pointed arrows very slow reactions (step 3).

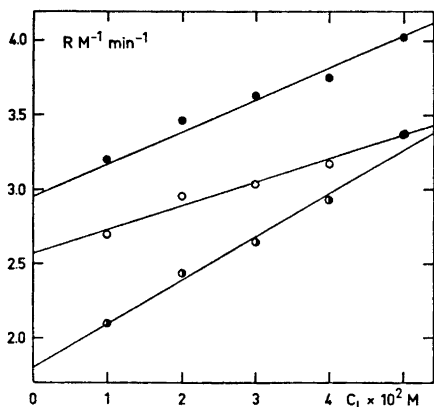


Fig. 6. Step 3. The quantity  $R$  versus  $C_L$ .  $C_M = 0.100 \text{ mM}$ ;  $\bullet$   $[\text{H}^+] = 5.00 \text{ mM}$ ;  $\circ$   $[\text{H}^+] = 10.00 \text{ mM}$ ;  $\circ$   $[\text{H}^+] = 15.00 \text{ mM}$ .

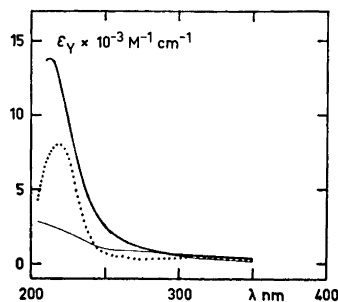


Fig. 7. Absorption curves of the species M (—), ML (---), and X (· · ·).

In strongly acid solutions ( $[\text{H}^+] \geq 0.2 \text{ M}$ ) the equilibrium  $\text{ML} + \text{L} \rightleftharpoons \text{X}$  is so strongly displaced to the left that the  $k_3$  term becomes completely dominating. The formation of X is not noticeable and the over-all reaction is a two-stage reaction. As  $[\text{H}^+]$  is decreased the equilibrium in question is displaced to the right (the rate of the reaction  $\text{ML} + \text{L} \rightarrow \text{X}$  increases) and at sufficiently low  $[\text{H}^+]$  the formation of X becomes noticeable in the beginning of the third step. At the same time the  $k_4$  term becomes appreciable. This indicates that the  $k_3$  term is analogous with the first term of the right member of eqn. (1) and that the corresponding reaction is reaction (II). The product emanating from hydroxylamine in this reaction has been established<sup>1</sup> as  $\text{N}_2$  whereas the product of the reaction corresponding to the  $k_4$  term is still uncertain.

The identity of the intermediate X is not known. The complex ML is formed without any loss of protons so this complex should be  $\text{VO}_2\text{NH}_3\text{OH}^{2+}$ . The addition of a second ligand ( $\text{NH}_3\text{OH}^+$ ) to this complex is very unfavourable since the resultant complex would acquire a high positive charge. By the formation of X two protons are expelled the origin of which has not been possible to establish. Whatever the structure of X may be, it seems to be a reasonable guess that the final product emanating from hydroxylamine in the reaction corresponding to the  $k_4$  term is nitrogen gas. Fig. 7 shows the absorption curves of M, ML, and X within the wave length range 200–350 nm. The curve of ML has been calculated from absorbance values extrapolated to the time  $t = 0$  after mixing the reactant solutions using the known values of  $\epsilon_M$  and  $\beta_1$ . The curve of X has been calculated from the absorbances at maximum of the absorbance-time curve using known values of  $\epsilon_M$ ,  $\epsilon_{\text{ML}}$ ,  $\beta_1$ , and  $K_2'$  at  $[\text{H}^+] = 0.005 \text{ M}$ ;  $C_M = 0.100 \text{ mM}$ ;  $C_L = 0.020 \text{ M}$ .

*Acknowledgement.* The author is indebted to Professor Sture Fronæus for valuable comments on the manuscript, to Mrs. Christina Oskarsson for skilled technical assistance, and to Dr. Peter Sellers for linguistic revision of the manuscript. The studies have been supported by grants from the *Swedish Natural Science Research Council*.

## REFERENCES

1. Bengtsson, G. *Acta Chem. Scand.* **26** (1972) 2494.
2. Bengtsson, G. *Acta Chem. Scand.* *In press*.
3. Rossotti, F. J. C. and Rossotti, H. *Acta Chem. Scand.* **10** (1956) 957.
4. Lumme, P., Lahermo, P. and Tummavuori, J. *Acta Chem. Scand.* **19** (1965) 2175.

Received April 28, 1973.