# KINETICS AND MECHANISM OF OXIDATION OF NITROUS ACID BY VANADIUM(V)

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Abstract—The kinetics of the oxidation of nitrous acid by vanadium(V) has been studied spectrophotometrically at 320nm in 1 M perchloric acid medium The mechanism proposed leads to the rate equation.

Rate =  $-\frac{d[V(V)]}{dt} = \frac{2k_1k_3K[VO_2^+]^2[HNO_2][H^+]}{k_2[NO_3] + k_3[VO_2^+]}$ 

The rate has been found to increase with increase in ionic strength. The activation parameters have been determined to be  $E_a = 16.25 \text{ kcal/mole}$ ,  $\Delta H^* = 15.64 \text{ kcal/mole}$ ,  $\Delta S^* = -13.05 \text{ cal/deg}$ . mole and  $\Delta G^* = 19.60 \text{ kcal/mole}$ . Bisulphate ion has been found to accelerate the reaction markedly.

## INTRODUCTION

The kinetics and mechanism of oxidation of nitrous acid has been studied with many oxidants like chromium(VI)[1], iodine[2], bromine[3,4], chlorine[5,6], hydrogen peroxide[11], oxygen[7-10], hypochlorite[12-14], chlorite[14], hypobromite[15], peroxide [16], permanganate [17-19], manganese(III) [20] and 1,2diaminocyclohexanetetraacetatomanganate(III)[21]. Α few workers [22, 23] have also reported the kinetics and mechanism of electrochemical oxidation of nitrous acid. The mechanism of oxidation is complex, varying considerably from one oxidant to another. In this communication, we present the kinetics of oxidation of nitrous acid by vanadium(V) in aqueous perchloric acid medium.

### **EXPERIMENTAL**

Reagents. An approximately 0.2 M stock solution of sodium vanadate was prepared and standardized according to the method of Gopalo Rao *et al.* [24].

An approx. 0.1 M solution of vanadium(IV) was prepared by the electrolytic reduction of vanadium(V) in 0.1 M perchloric acid using a diaphragm cell. A platinum gauze was used as the cathode and a bright platinum rod as the anode. The electrolysis was carried out till the solution gave a negative test for vanadium(V) (nearly 4 hr) using a Toshniwal Electrolytic Analyser type CM 16 at a constant voltage of 8 V. The vanadium(IV) content was determined with standard cerium (IV) sulphate using Rhodamine 6G as indicator [25]. The free hydrogen ion concentration in this solution was estimated by passing it through Amberlite IR-120 in H<sup>+</sup> form (applying correction for the H<sup>+</sup> ions displaced by vanadium(IV).

A 0.1 M nitrite solution was prepared once in a week by dissolving sodium nitrite (B.D.H., AnalR) in boiled out distilled water and its strength verified [26].

"Pro Analysis" grade perchloric acid 70% supplied by E. Merck (India) and sodium perchlorate prepared by neutralisation of this acid with sodium carbonate (B.D.H., AnalaR) were used.

Apparatus. Shimadzu UV-vis Double Beam Spectrophotometer (140–02) with 1 cm silica cells was used for absorbance measurements.

Lab Constant Temperature Liquid Circulatory Bath S-36(SEW-India) was used as the thermostat.

### RESULTS

Stoichiometry. Aliquots of known concentrations of sodium nitrite were mixed with known excess of vanadium(V), keeping the overall concentration of perchloric acid at 1 M. The solutions were kept overnight at room temperature and the unreacted vanadium(V) was estimated spectrophotometrically. The stoichiometry of the reaction was found to correspond to the equation.

$$2\text{VO}_2^+ + \text{HNO}_2 + 2\text{H}^+ \rightarrow \text{HNO}_3 + 2\text{VO}^{2+} + \text{H}_2\text{O}.$$

Kinetic procedure. A study of the absorption spectra of vanadium(V), vanadium(IV), nitrite and nitrate ions in 1 M perchloric acid medium showed that the reaction can be monitored at 320 nm where vanadium(V) has considerable absorbance and all other ions have negligible absorbances. All kinetic runs were carried out at a constant temperature of  $30 \pm 0.1$ °C, unless otherwise mentioned. Kinetic runs were carried out under pseudo first order conditions isolating vanadium(V). The reaction was initiated by transfering calculated amount of thermostated nitrite solution into a thermostated Jena glass reaction bottle, containing the required amounts of vanadium(V), perchloric acid and sodium perchlorate. Log(absorbance) vs time plots revealed that the reaction follows pseudo first order behaviour upto 65% completion of the reaction. The pseudo first order rate constants were represented by k'.

Effect of products. Even a 20-field molar excess of vanadium(IV) did not have any influence on the rate of the reaction. However, the other product, nitrate was found to retard the reaction considerably. In the presence of nitrate neither the log(absorbance) vs time plot nor the 1/absorbance vs time plot was a straight line; hence the initial rate method was adopted to study its effects on the rate. The initial rates were found to decrease with an increase in the [nitrate], the plot of 1/initial rate vs [nitrate] being a straight line with an intercept on the rate axis as shown in Fig. 1. However, in the absence of added nitrate, since, the reaction was found to follow pseudo first order behaviour upto 65%



Fig. 1. Effect of  $[NO_3^-]$  on the reaction rate  $[V(V)] = 1.0 \times 10^{-3}$ M;  $[H^+] = 1.0$  M;  $\mu = 1.0$ ;  $[HNO_2] = 1.0 \times 10^{-2}$  M; temp = 30°C.

completion of the reaction, all other studies were carried out in the absence of nitrate.

Effects of ionic strength  $(\mu)$ . The influence of ionic strength on the rate of the reaction was studied by varying the concentration of sodium perchlorate from 1.0 to 3.0 M, keeping the concentration of all other ions constant. The pseudo first order rate constants were found to increase with increase in ionic strength as may be seen from Table 1.

Order with respect to vanadium(V). Kinetic runs were carried out varying the concentration of vanadium(V) from 0.50 to  $1.20 \times 10^{-3}$  M and keeping the concentration of all other ions constant. The pseudo first order rate constants obtained at various [vanadium(V)] were found constant (Table 2) indicating the order with respect to vanadium(V) to be unity.

Order with respect to nitrous acid. The order with respect to nitrous acid was determined carrying out kinetic runs at nitrite concentrations varying from 0.6 to  $1.0 \times 10^{-2}$  M and keeping the concentrations of all other ions constant. When the pseudo first order rate constants thus obtained (Table 3) were plotted against nitrite concentration, a straight line passing through origin was obtained showing the order with respect to nitrous acid to be one.

Effect of hydrogen ion. The effect of  $[H^+]$  on the rate of the reaction was studied from 0.50 to 2.00 M at a constant ionic strength of 2.0 M keeping the concentration of all other ions constant. The pseudo first order rate constants were found to increase with an increase in  $[H^+]$ , as may be seen from Table 4.

Activation parameters. To determine these parameters the pseudo first order rate constants were measured at four different temperatures (25, 30, 35, and 40°C) and the rate constants thus obtained were shown in Table 5. From the plot of log (pseudo first order rate constant) vs 1/absolute temperature the reaction was found to obey Arrhenius' temperature dependence. The values of  $E_a$ ,  $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$  and  $\Delta G^{\neq}$  calculated from this plot were found to be 16-25 kcal/mole, 15.64 kcal/mole, -13.05 cal/deg. mole and 19.60 kcal/mole respectively.

#### DISCUSSION

Vanadium(V) species in aqueous acid solution. A perusal of the literature [27-36], shows that the preponderant species of vanadium(V) in aqueous acidic solution is  $VO_2^+$ . Further, vanadium(V) oxidations are accelerated by hydrogen ions and this acceleration was invariably

Table 1. Effect of ionic strength on k'

$[V(V)] = 1.0 \times 10^{-3}$	M; [HNC 1.0 M Temp	$[2_2] = 1.0$ $(2_2) = 30^{\circ}(2_1)$	) × 10 <sup>-2</sup>	² M;	[H <sup>+</sup> ] =
Ionic Strength $\mu$	1.0	1.5	2.0	2.5	3.0
$k' \times 10^4 \text{ sec}^{-1}$	4.60	6.52	8.33	11.35	15.04

Table 2.	Effect	of	[vanadium	(V)	on	k
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$[\mathrm{HNO2}] = 1.0 \times 10$	0 <sup>-2</sup> M; [H	[ <sup>+</sup> ] = 1.	0 M; μ	. = 1.0;	Temp	= 30°C	
$[V(V)] \times 10^3 M$	0.5	0.6	0.7	0.8	1.0	1.2	
k' × 10 <sup>4</sup> sec <sup>-1</sup>	4.51	4.61	4.61	4.79	4.61	4.51	

Table 3. Effect of  $[HNO_2]$  on k'

$[V(V)] = 0.5 \times 10$	<sup>-3</sup> M; [H	<sup>+</sup> ] = 1.(	)M;μ	≈ 1.0; <sup>°</sup>	Temp =	= 30°C	
$\frac{\text{HNO}_2] \times 10^2 \text{ M}}{\text{k}' \times 10^4 \text{ sec}^{-1}}$	0.60	0.70	0.80	0.85	0.90 4.07	1.00	

Table 4. Effect of  $[H^+]$  on k'

$[V(V)] = 0.5 \times 10^{-3} M$	; [HNC	0 <sub>2</sub> ] = 1.0 30℃	0 × 10 <sup></sup>	<sup>2</sup> Μ; μ	. = 2.0;	Temp. =
$[\mathbf{H}^+]\mathbf{M}$	0.5	0.8	1.0	1.2	1.5	2.0
k' × 10 <sup>4</sup> sec <sup>-1</sup>	4.80	6.72	8.35	9.79	12.67	16.12

Table 5. Effect of temperature on k'

$[V(V)] = 1.0 \times 10^{-1}$	<sup>3</sup> Μ; [NO 1.0 Μ; μ	$\left[\frac{1}{2}\right] = 1.0 \times 1.0 \times 1.0$	< 10 <sup>-2</sup> M;	[H <sup>+</sup> ] =
Temp. Å $k' \times 10^4 \text{ sec}^{-1}$	293	298	303	308
	1.92	2.76	4.61	7.68

correlated with the transformation of the predominant species  $VO_2^+$  into more electrophilic forms like  $V(OH)_3^{2+}$  or  $VO_3^{3+}$ .

Nitrous acid species. According to Turney and Wright [35], in aqueous solution nitrous acid may be best regarded as the hydroxylated form of the nitrosonium ion (NO<sup>+</sup>) implying that OH<sup>-</sup> can be replaced by other bases, to give NOX. Spectroscopic evidence exists for the species NO<sup>+</sup> [36-38] and HONO [33, 34] in aqueous perchloric acid solution. The formation of NO<sup>+</sup> is favoured by high acidity and it has been detected in concentrated acids. The existence of the nitrous acidium ion  $(H_2NO_2^+)$  in acidic media has been suggested by Baylies and Watts [37]. However, Seal [39], from the consideration of isoelectronic molecules, claimed that its stability would be low. While discussing the nature of nitrous acid species, Jones [40] stated that highly acidic solutions favour the formation of NO<sup>+</sup>, or its hydrated equivalent  $H_2NO_2^+$  while in dilute acid the unionized species HONO is present.

In view of this data and in view of the fact that the dissociation constant of nitrous acid [41] is  $1.1 \times 10^{-3}$  all the nitrite used in the present investigation may be presumed to be present almost exclusively as HONO.

Taking into consideration the nature of the vanadium(V) and nitrous acid species in acid solutions the following mechanism has been proposed to explain the observed results.

Mechanism.

$$VO_{2}^{+} + H_{3}O^{+} \rightleftharpoons V(OH)_{3}^{2+}$$
$$V(OH_{3}^{2+} + HONO \rightleftharpoons_{k_{2}}^{k_{1}} NO_{3}^{-} + V(III) + 2H_{2}O$$
$$VO_{2}^{+} + V(III) \xrightarrow{k_{3}} 2VO^{2+}.$$

Applying steady state approximation to [vanadium(III)] and assuming K to be small.

Rate = 
$$\frac{-d[V(V)]}{dt} = \frac{2k_1k_3K[VO_2^+]^2[HNO_2][H^+]}{k_2[NO_3^-] + k_3[VO_2^+]}$$
.

This rate equation neatly explains the observed first order with respect to nitrous acid and hydrogen ion. It also explains the first order dependence on vanadium(V) in the absence of added nitrate. However, in the presence of added nitrate, the order with respect to vanadium(V) should lie in between 1 and 2. In order to verify this, the order with respect to vanadium(V) has been determined in presence of a 20-fold excess of nitrate (compared to [vanadium(V)]) adopting the initial rate method; the order thus determined turned out to be 1.45, in agreements with what is expected from the rate equation.

Further, the rate equation, predicts that the plot of 1/rate vs  $[NO_3^-]$  should be a straight line with a positive intercept on the rate axis. It may be seen from Fig. 1 that the curve obtained is exactly similar to the one expected, thus fully substantiating the proposed mechanism. From the slope and intercept of this plot the values of  $k_1 K$  and  $k_2/k_3$  have been calculated to be  $8.51 \text{ mol}^{-2}$  lit<sup>2</sup> sec<sup>-1</sup> and  $3.72 \times 10^{-2}$  respectively.

It has also been noticed that bisulphate ion markedly accelerates the reaction, the rate increasing linearly with  $[HSO_4]$ . This acceleration by bisulphate may be attributed to the formation of 1:1 complex of bisulphate ion with vanadium(V), which, according to Waters and Littler [30], is a better oxidizing species than vanadium(V) unassociated with bisulphate ion.

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