

Kinetics and Mechanism of Oxidation of Hydrazine by Vanadium in Solution

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Abstract: The kinetics of oxidation of hydrazine by vanadium(V) has been studied in acid perchlorate medium. The reaction is second order viz. first order with respect to each reactant. However, hydrogen ion dependence is complex. A plausible reaction mechanism has been suggested and the derived rate law (1) conforms to this mechanism.

$$\frac{-d[V(V)]}{dt} = \frac{kK_1[N_2H_5^+][V(V)][H^+]}{1 + K_1[H^+]} \quad (1)$$

Where K_1 is an equilibrium constant for the reaction (2),



Thermodynamic parameters have also been evaluated.

Keywords: Kinetics, Mechanism, Oxidation, Hydrazine, Vanadium.

Introduction:

The role of vanadium compounds as co-factor in halo-peroxidase¹, nitrogenases² and the analog between vanadate and phosphate³ has stimulated increasing interest in understanding better aspects of aqueous vanadium chemistry⁴. The vanadium compound of rate has shown anti-diabetic properties⁵ making vanadium chemistry of current interest for further explorations.

Oxidation of hydrazine with metal complexes yields either N_2 alone or a mixture of molecular nitrogen and ammonia as the end products and as such stoichiometry is dependent on the reaction mechanism. The nature of the reaction may be outer-sphere or inner-sphere depending on the lability of the complex as an oxidizing agent⁶.

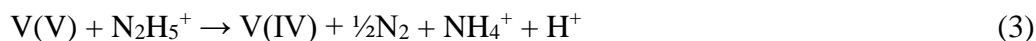
Experimental:

All the reagents employed in this study were of analytical reagent grade and were used as supplied.

Stoichiometry:

Reaction mixture with different concentration of vanadium(V) and hydrazine were kept for about ~ 10 h and excess of the oxidant was estimated iodometrically.

However, 1:1 stoichiometry has been reported when excess of hydrazine was taken.



Hydrazine has been reported⁷⁻¹¹ to be oxidized by one-equivalent oxidizing agents to N_2 and NH_4^+ whereas only N_2 is formed with two equivalent oxidants. Thus the stoichiometry as has been observed in the title reaction adequate indicates vanadium(V) to be One-equivalent oxidant. The hydrazyl radical initially formed undergoes dimerization which on decomposition yields N_2 and NH_4^+ . This has also been reported in oxidation of hydrazine by $Mn(III)$ ¹¹.

Results:

(1) Vanadium(V) Dependence

A plot of Initial rates (k_i , $\text{mol dm}^{-3} \text{sec}^{-1}$) were calculated and a plot of k_i versus $[V(V)]$ yielded a straight line passing through the origin (Fig 1) confirming first order with respect to the oxidant.

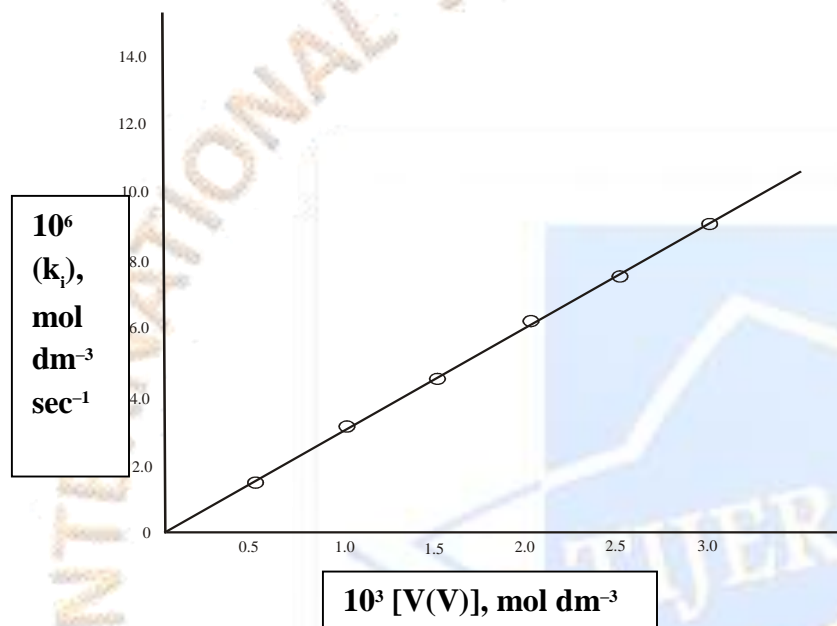


Fig. 1 VARIATION OF VANADIUM PENTAOXIDE

$$[N_2H_5^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3};$$

$$[HClO_4] = 0.5 \text{ mol dm}^{-3} \text{ and } 25^\circ\text{C}$$

(2) Hydrazine Dependence

A plot of Initial rates (k_i , $\text{mol dm}^{-3} \text{sec}^{-1}$) were calculated and a plot of k_i versus $[N_2H_5]$ yielded a straight line passing through the origin (Fig 2) confirming first order with respect to the oxidant. Second order plots for comparable concentrations of the reactants were also made (Fig. 3) to conform further the nature of the reaction to be second order.

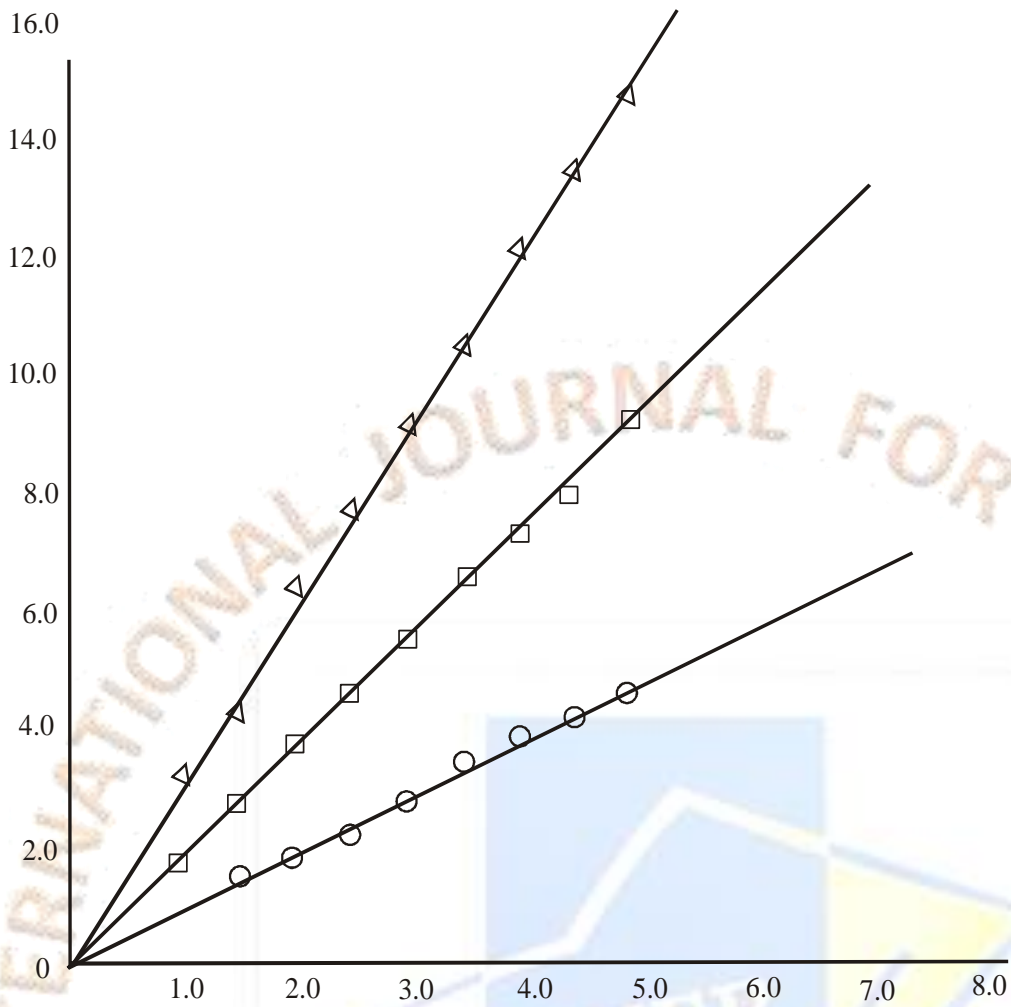


Fig. 2 VARIATION OF HYDRAZINE

[V(V)] = ○, $1.0 \times 10^{-3} \text{ mol dm}^{-3}$; □, $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ Δ, $3.0 \times 10^{-3} \text{ mol dm}^{-3}$
 [HClO₄] = 0.5 mol dm^{-3} and 25°C

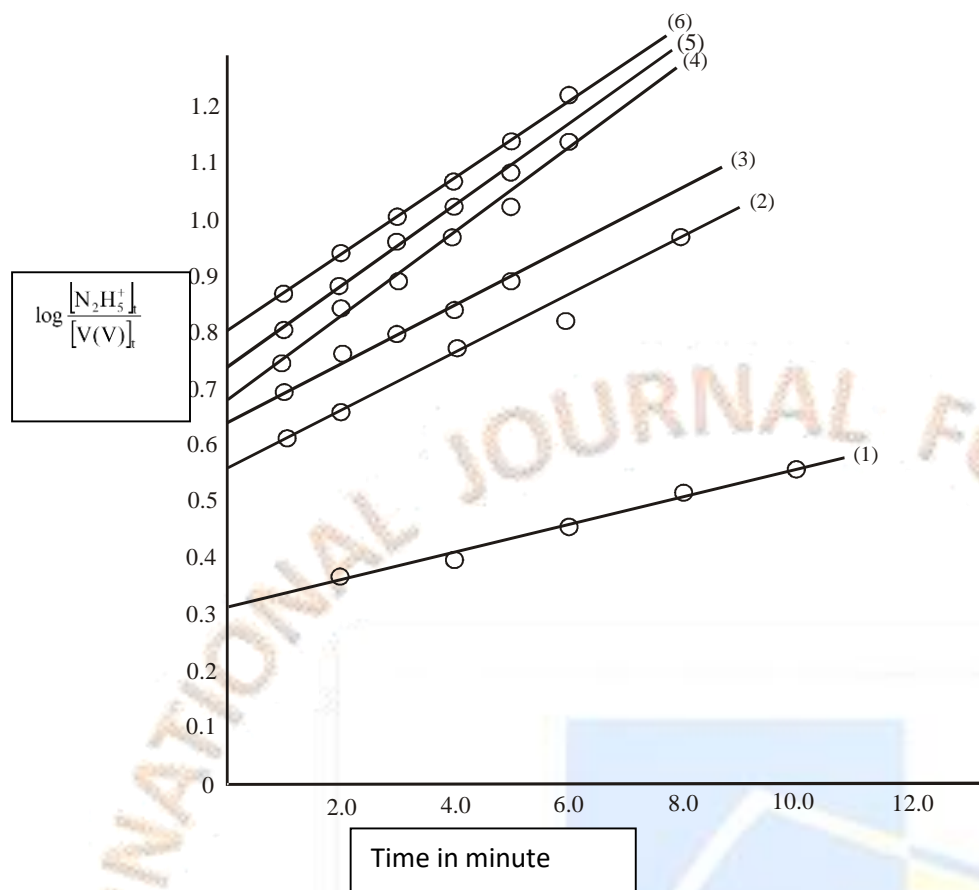


Fig. 3 SECOND ORDER PLOTS*

$$[V(V)] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}; [HClO_4] = 0.5 \text{ mol dm}^{-3}$$

$$[N_2H_5^+] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}; 2.5 \times 10^{-3} \text{ mol dm}^{-3};$$

$$3.0 \times 10^{-3} \text{ mol dm}^{-3}; 3.5 \times 10^{-3} \text{ mol dm}^{-3};$$

$$4.0 \times 10^{-3} \text{ mol dm}^{-3}; 5.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Temperature = 25°C

(3) Hydrogen Ion Dependence

The rate first increases at lower hydrogen ion concentrations and then tends to attain limiting rate at higher hydrogen ion concentrations.

(4) Effect of Temperature

The reaction was also studied at three temperatures viz., 25°, 30° and 35°C, respectively keeping constant concentrations of other reaction ingredients viz. $[V(V)] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[N_2H_5^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 0.5 \text{ mol dm}^{-3}$. A plot of $\log k$ versus $1/T$ was made (Fig 4). The energy of activation was calculated from the slope of the line to be $(48 \pm 1) \text{ kJ mol}^{-1}$. The entropy of activation was calculated in a conventional manner by employing eqn (4) to (-) $(57 \pm 3) \text{ JK}^{-1} \text{ mol}^{-1}$.

$$k_2 = \frac{kT}{h} \cdot e^{-\Delta E^\ddagger / RT} \cdot e^{-\Delta S^\ddagger / R} \quad (4)$$

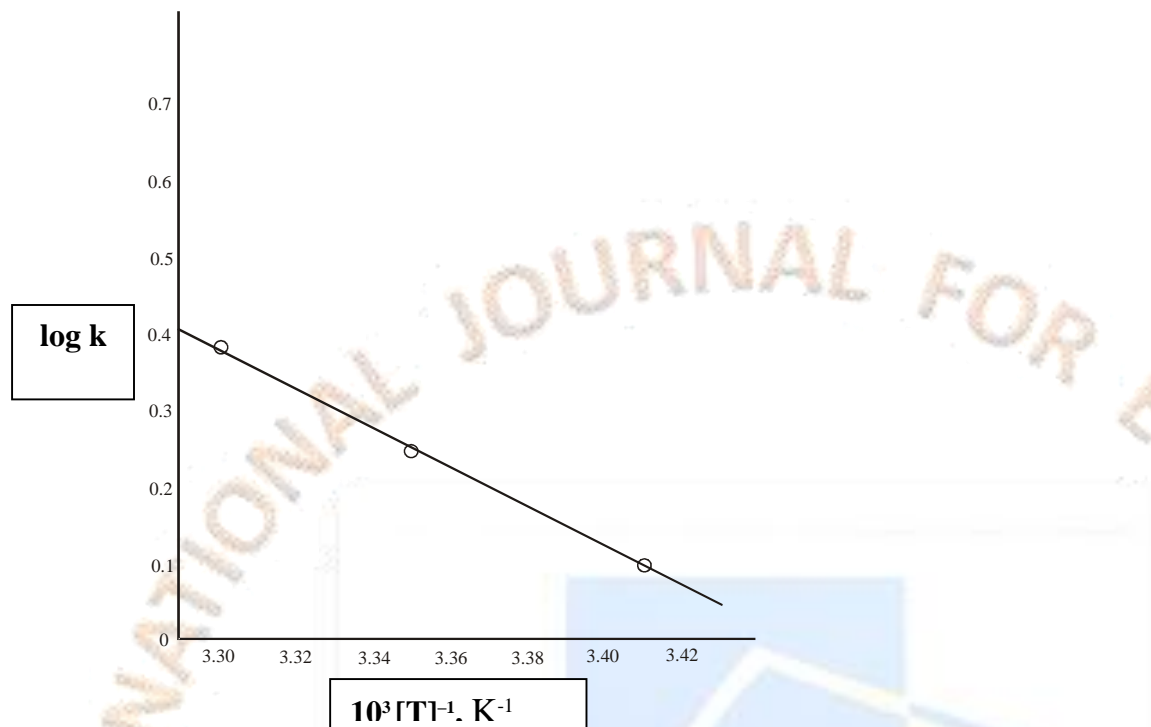
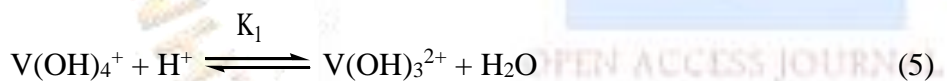


Fig. 4 TEMPERATURE DEPENDENCE

$$[V(V)] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}; [N_2H_5^+] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}; [HClO_4] = 0.5 \text{ mol dm}^{-3}$$

Discussion:

It was later shown¹² that the hydrated form of V(V) such as $V(OH)_4^+$ and not VO_2^+ remains in equilibrium with $V(OH)_3^+$ as in eqn (5) in perchloric acid medium.



Since the reaction is second order viz. first order with respect to V(V) and hydrazine respectively, the order with respect to hydrogen ion is complex. This shows that $V(OH)_3^+$ species is reactive and interacts with hydrazine to form an activated complex to account for the hydrogen ion dependence. Hydrazine in acid medium remains in the protonated state as $N_2H_5^+$. Therefore, the mechanism as envisaged consists of step (5) to (7).



The loss of vanadium (V) leads to the rate law (8),

$$\frac{-d[V(V)]}{dt} = \frac{kK_1K_2[N_2H_5^+][V(V)][H^+]}{1 + K_1[H^+] + K_2[N_2H_5^+]} \quad (8)$$

Thus the inequality of $K_2 [N_2H_5^+] \ll 1$ is valid. If such an inequality is taken into account, the rate law (8) reduces to eqn (9)

$$\frac{-d[V(V)]}{dt} = \frac{kK_1K_2[N_2H_5^+][V(V)][H^+]}{1 + K_1[H^+]} \quad (9)$$

There might be an alternate proposition of the reaction mechanism as follows:



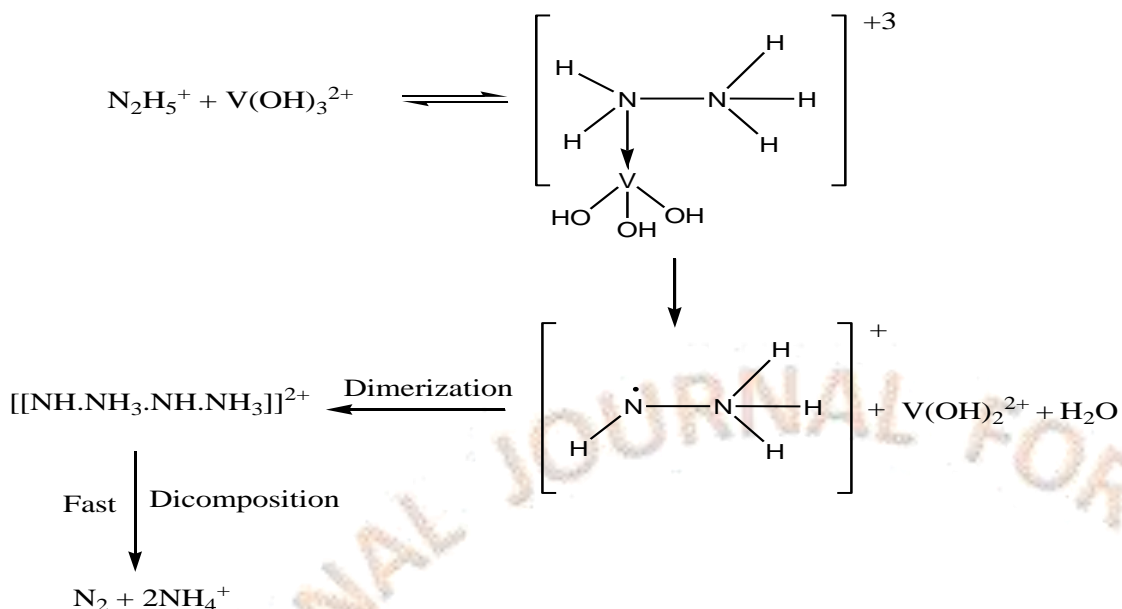
This will lead to the rate law (13) if the complex (K_2') is negligible in the light of first order dependence with respect to the oxidant.

$$\frac{d[V(V)]}{dt} = \frac{k'K_1'K_2'[N_2H_5^+][V(V)][H^+]}{1 + K_1'[H^+]} \quad (13)$$

The hydrated form of V(V) has been considered to be the reactive form and V(V) is in $V(OH)_4^+$ form aq. This rate law (13) is similar as was obtained earlier (eqn. 9)

The thermodynamic parameters show that moderate energy of activation and negative small value of entropy of activation point towards a transition state that leads directly to the formation of hydrazyl radical in one electron oxidation of hydrazine.

So far the mode of electron transfer is concerned, the co-ordination between $V(OH)_3^{2+}$ and a nitrogen donor of hydrazine molecule is a sufficient possibility as mentioned below to facilitate the transfer of electron from hydrazine to the oxidant (Scheme-1).



Scheme-I

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