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## **CHAPTER - IV**

### **RESULTS AND DISCUSSION: VANADIUM (V) OXIDATION OF HYDRAZINE**

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The stoichiometry of vanadium (V) oxidation of hydrazine was reported to be between 3.4 to 4.0.<sup>118</sup> This uncertainty about the stoichiometry makes the prediction of mechanism difficult. It has been also found that sulphate ion accelerates oxidations by vanadium (V),<sup>119</sup> which may be due to the different sulphate complexes of vanadium (V) forming in solution. Therefore, we investigated only the effect of sulphate ion on vanadium (V) oxidation of hydrazine instead of studying the detailed mechanism. The results and their prediction is given bellow.

The effect of reactants were studied by keeping the sulphuric acid constant at  $2.0 \times 10^{-3}$  M and at an ionic strength of 0.01 M at 25°C. The order in vanadium (V) was found to be 0.6 (Figure 4.1) between  $3.0 \times 10^{-3}$  to  $5.0 \times 10^{-3}$  M at a constant hydrazine concentration of  $4.0 \times 10^{-3}$  M. The data giving change in the absorbance as a function of time is shown in Table 4.1 and the initial rates are given in Table 4.2. The effect of hydrazine between  $2.0 \times 10^{-3}$  to  $6.0 \times 10^{-3}$  M at constant vanadium (V) concentration of  $4.0 \times 10^{-3}$  M was studied to determine the order in hydrazine. The data of kinetic runs and values of initial rates are given in Table 4.3 and 4.4 respectively. The order in hydrazine was found to be 0.7 (Figure 4.2).

The effect of sulphuric acid was studied between

Table 4.1 Data showing absorbance at 430 nm as a function of time : Effect of vanadium (V)

[Hydrazine] =  $4.0 \times 10^{-3}$  M, [H<sub>2</sub>SO<sub>4</sub>] =  $2.0 \times 10^{-3}$  M,  
I = 0.01 M, Temp. = 25°C

| Time<br>in<br>Min. | V(V) X 10 <sup>-3</sup> |       |       |       |       |
|--------------------|-------------------------|-------|-------|-------|-------|
|                    | 3.0                     | 3.6   | 4.0   | 4.4   | 5.0   |
| 0                  | 0.750                   | 0.850 | 0.900 | 0.950 | 1.050 |
| 1                  | 0.622                   | 0.740 | 0.807 | 0.875 | 0.952 |
| 2                  | 0.570                   | 0.685 | 0.755 | 0.825 | 0.918 |
| 3                  | 0.518                   | 0.635 | 0.708 | 0.780 | 0.885 |
| 4                  | 0.470                   | 0.590 | 0.667 | 0.747 | 0.853 |
| 5                  | 0.430                   | 0.550 | 0.625 | 0.710 | 0.825 |
| 6                  | 0.390                   | 0.513 | 0.592 | 0.680 | 0.797 |
| 7                  | 0.352                   | 0.478 | 0.555 | 0.650 | 0.775 |
| 8                  | 0.322                   | 0.447 | 0.525 | 0.620 | 0.748 |
| 9                  | 0.292                   | 0.430 | 0.498 | 0.598 | 0.725 |
| 10                 | 0.265                   | 0.388 | 0.470 | 0.575 | 0.708 |
| 15                 | 0.165                   | 0.283 | 0.365 | 0.495 | 0.615 |

Table 4.2 Order in vanadium (V)

[Hydrazine] =  $4.0 \times 10^{-3}$  M,  
I = 0.01 M,

[H<sub>2</sub>SO<sub>4</sub>] =  $2.0 \times 10^{-3}$  M,  
Temp. = 25°C

| [V(V)] X 10 <sup>-3</sup><br>M | Inl. Rate<br>X 10 <sup>-4</sup> S <sup>-1</sup> | - log [V(V)] | -log (Inl. Rate) |
|--------------------------------|---|--------------|------------------|
| 3.0                            | 9.08  | 2.52         | 3.04             |
| 3.6                            | 9.53  | 2.44         | 3.02             |
| 4.0                            | 10.20   | 2.39         | 2.99             |
| 4.4                            | 10.62   | 2.35         | 2.97             |
| 5.0                            | 11.22   | 2.30         | 2.95             |

Figure 4.1. Order in vanadium (V) (conditions as in Table 4.2).

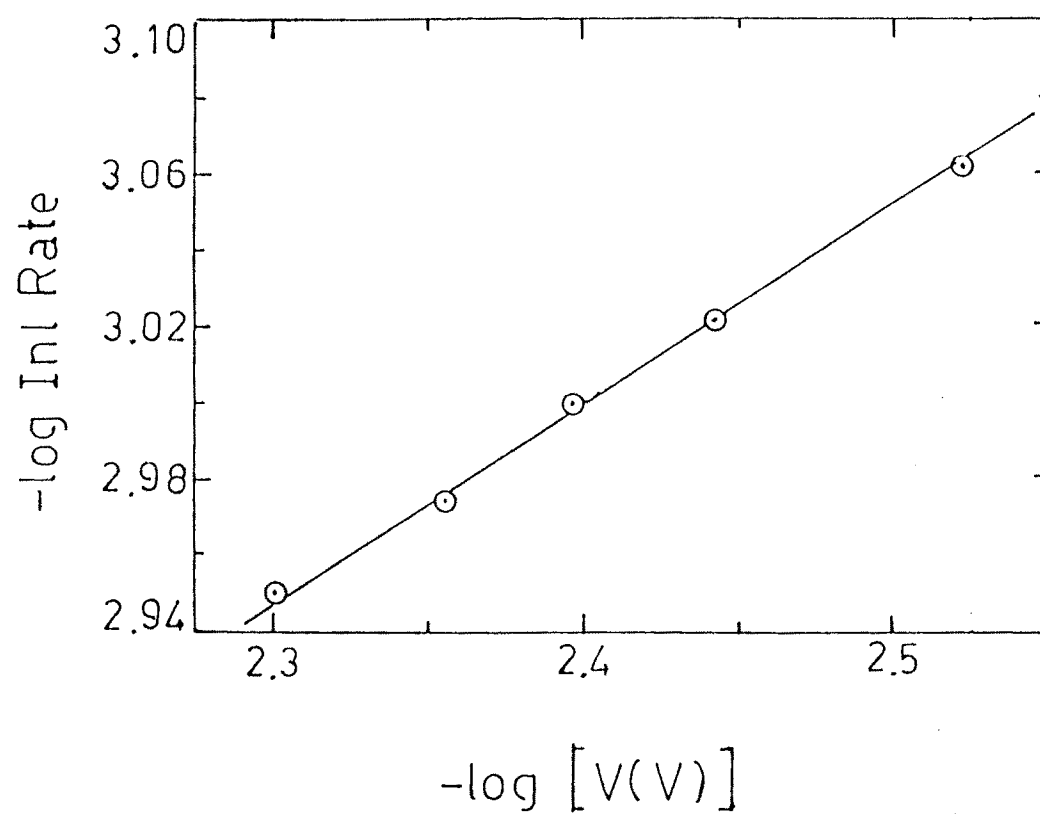


Table 4.3 Data showing absorbance at 430 nm as a function of time : Effect of hydrazine.

$[V(V)] = 4.0 \times 10^{-3} \text{ M}$ ,  
 $I = 0.01 \text{ M}$ ,

$[H_2SO_4] = 2.0 \times 10^{-3} \text{ M}$ ,  
 Temp. =  $25^\circ\text{C}$

| Time<br>in<br>Min. | [Hydrazine] X $10^{-3}$ |       |       |       |       |
|--------------------|-------------------------|-------|-------|-------|-------|
|                    | 2.0                     | 3.0   | 4.0   | 5.0   | 6.0   |
| 0                  | 0.910                   | 0.900 | 0.890 | 0.895 | 0.890 |
| 1                  | 0.865                   | 0.848 | 0.820 | 0.815 | 0.755 |
| 2                  | 0.835                   | 0.795 | 0.765 | 0.750 | 0.690 |
| 3                  | 0.800                   | 0.752 | 0.720 | 0.700 | 0.630 |
| 4                  | 0.778                   | 0.725 | 0.680 | 0.650 | 0.570 |
| 5                  | 0.750                   | 0.695 | 0.640 | 0.600 | 0.520 |
| 6                  | 0.735                   | 0.662 | 0.600 | 0.555 | 0.470 |
| 7                  | 0.722                   | 0.637 | 0.570 | 0.518 | 0.428 |
| 8                  | 0.708                   | 0.610 | 0.540 | 0.475 | 0.385 |
| 9                  | 0.700                   | 0.592 | 0.510 | 0.445 | 0.345 |
| 10                 | 0.682                   | 0.570 | 0.485 | 0.415 | 0.312 |
| 15                 | 0.630                   | 0.490 | 0.370 | 0.290 | 0.185 |

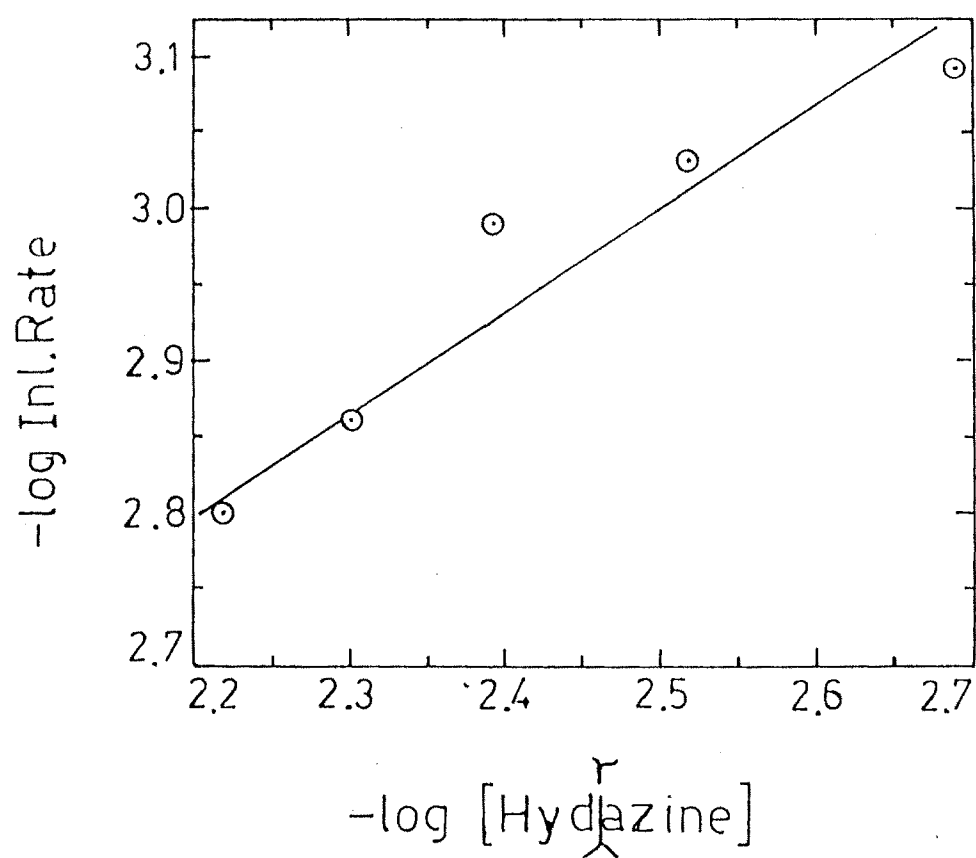
• Table 4.4 Order in Hydrazine

[V(V)] =  $4.0 \times 10^{-3}$  M  
I = 0.01 M,

[H<sub>2</sub>SO<sub>4</sub>] =  $2.0 \times 10^{-3}$  M,  
Temp. = 25°C

| [Hydrazine]<br>$\times 10^{-3}$ | Inl. Rate<br>$\times 10^{-4}$ s <sup>-1</sup> | - log<br>[Hydrazine] | -log (Inl. Rate) |
|---------------------------------|---|----------------------|------------------|
| 2.0                             | 7.98  | 2.69                 | 3.09             |
| 3.0                             | 9.25  | 2.52                 | 3.03             |
| 4.0                             | 10.20   | 2.39                 | 2.99             |
| 5.0                             | 13.80   | 2.30                 | 2.86             |
| 6.0                             | 15.80   | 2.22                 | 2.80             |

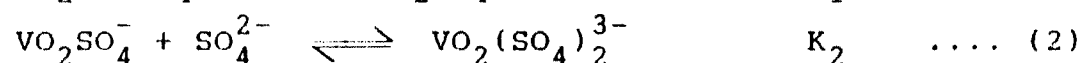
Figure 4.2. Order in Hydrazine (conditions as in Table 4.4).





concentration range of  $2.0 \times 10^{-4}$  to  $2.2 \times 10^{-3}$  M at constant vanadium (V) and hydrazine concentration of  $4.0 \times 10^{-3}$  M each (Table 4.5). The rate increases with increase in sulphuric acid concentration.

The fractional order in vanadium (V) indicate its involvement of a prior equilibria with sulphate ion.<sup>120</sup> The vanadium (V) forms two sulphate complexes as given in the equilibria (1) and (2) :



The rate law for the reaction can be given as,

$$\text{rate} = k [\text{V(V)}] [\text{Hydrazine}] \quad \dots (3)$$

but in acidic medium vanadium (V) exists as  $\text{VO}_2^+$  ion therefore we have,

$$\text{rate} = k [\text{VO}_2^+] [\text{Hydrazine}] \quad \dots (4)$$

Since  $\text{VO}_2^+$  ion is involved in the equilibria 1 and 2 its concentration can be calculated as follows :

$$[\text{VO}_2^+]_T = [\text{VO}_2^+]_f + [\text{VO}_2\text{SO}_4^-] + [\text{VO}_2(\text{SO}_4)_2^{3-}] \quad \dots (5)$$

Where  $[\text{VO}_2^+]_T$  and  $[\text{VO}_2^+]_f$  are total and free  $\text{VO}_2^+$  ion concentration. Substituting for the concentration of  $\text{VO}_2\text{SO}_4^-$  and  $\text{VO}_2(\text{SO}_4)_2^{3-}$  in term of  $\text{VO}_2^+$  ion we get,

Table 4.5. Data showing absorbance at 430 nm as a function of time : Effect of sulphuric acid

[V(V)] = [Hydrazine] =  $4.0 \times 10^{-3}$  M, I = 0.01 M, Temp. = 25°C.

| Time<br>in<br>Min. | [H <sub>2</sub> SO <sub>4</sub> ] X 10 <sup>-4</sup> M |       |       |       |       |       |       |       |       |       |       |
|--------------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|                    | 2.0  | 4.0   | 6.0   | 8.0   | 10.0  | 12.0  | 14.0  | 16.0  | 18.0  | 20.0  | 22.0  |
| 0                  | 0.820  | 0.850 | 0.840 | 0.840 | 0.850 | 0.850 | 0.890 | 0.880 | 0.900 | 0.900 | 0.880 |
| 1                  | 0.780  | 0.820 | 0.785 | 0.775 | 0.800 | 0.810 | 0.820 | 0.830 | 0.845 | 0.840 | 0.835 |
| 2                  | 0.755  | 0.790 | 0.750 | 0.740 | 0.765 | 0.775 | 0.780 | 0.780 | 0.790 | 0.785 | 0.775 |
| 3                  | 0.730  | 0.752 | 0.720 | 0.712 | 0.725 | 0.730 | 0.740 | 0.735 | 0.740 | 0.735 | 0.720 |
| 4                  | 0.705  | 0.725 | 0.690 | 0.682 | 0.695 | 0.695 | 0.710 | 0.695 | 0.700 | 0.695 | 0.673 |
| 5                  | 0.685  | 0.700 | 0.665 | 0.667 | 0.665 | 0.660 | 0.680 | 0.660 | 0.662 | 0.658 | 0.630 |
| 6                  | 0.665  | 0.678 | 0.638 | 0.630 | 0.635 | 0.630 | 0.650 | 0.625 | 0.625 | 0.623 | 0.590 |
| 7                  | 0.655  | 0.655 | 0.610 | 0.600 | 0.602 | 0.600 | 0.620 | 0.595 | 0.595 | 0.590 | 0.550 |
| 8                  | 0.635  | 0.622 | 0.585 | 0.578 | 0.580 | 0.570 | 0.595 | 0.560 | 0.560 | 0.558 | 0.522 |
| 9                  | 0.615  | 0.600 | 0.560 | 0.555 | 0.550 | 0.540 | 0.570 | 0.537 | 0.535 | 0.530 | 0.492 |
| 10                 | 0.595  | 0.580 | 0.540 | 0.532 | 0.525 | 0.520 | 0.545 | 0.512 | 0.508 | 0.505 | 0.462 |
| 15                 | 0.510  | 0.485 | 0.440 | 0.435 | 0.425 | 0.420 | 0.450 | 0.408 | 0.392 | 0.397 | 0.350 |

$$[\text{VO}_2^+]_T = [\text{VO}_2^+]_f + K_1 [\text{VO}_2^+]_f [\text{SO}_4^{2-}] + K_1 K_2 [\text{VO}_2^+]_f [\text{SO}_4^{2-}]^2 \quad \dots (6)$$

$$[\text{VO}_2^+]_T = [\text{VO}_2^+]_f (1 + K_1 [\text{SO}_4^{2-}] + K_1 K_2 [\text{SO}_4^{2-}]^2) \quad \dots (7)$$

The increase in rate is linear with increasing concentration of sulphuric acid (Table 4.6). Therefore probably monosulphate complex is the reactive one. The rate law in terms of monosulphate complex will be,

$$\text{Rate} = k [\text{VO}_2\text{SO}_4^-] [\text{Hydrazine}] \quad \dots (8)$$

The concentration of  $\text{VO}_2\text{SO}_4^-$  is given by,

$$[\text{VO}_2\text{SO}_4^-] = K_1 [\text{VO}_2^+]_f [\text{SO}_4^{2-}] \quad \dots (9)$$

Therefore from (9) and (7) we get,

$$[\text{VO}_2\text{SO}_4^-] = \frac{K_1 [\text{VO}_2^+]_T [\text{SO}_4^{2-}] [\text{Hydrazine}]}{(1 + K_1 [\text{SO}_4^{2-}] + K_1 K_2 [\text{SO}_4^{2-}]^2)} \quad \dots (10)$$

$$\text{Rate} = \frac{k K_1 [\text{VO}_2^+]_T [\text{SO}_4^{2-}] [\text{Hydrazine}]}{(1 + K_1 [\text{SO}_4^{2-}] + K_1 K_2 [\text{SO}_4^{2-}]^2)} \quad \dots (11)$$

The catalysis of the reaction between vanadium (V) and hydrazine is therefore due to the sulphate complexes of vanadium (V) which are more active than  $\text{VO}_2^+$  ion in acidic medium.

Table 4.6. Effect of sulphuric acid on the reaction

[V(V)] = [Hydrazine] =  $4.0 \times 10^{-3}$  M  
I = 0.01 M, Temp. = 25°C

| [H <sub>2</sub> SO <sub>4</sub> ]<br>X 10 <sup>-4</sup> | Inl. Rate<br>X 10 <sup>-4</sup> s <sup>-1</sup> |
|---|---|
| 2.0   | 5.96  |
| 4.0   | 6.44  |
| 6.0   | 7.58  |
| 8.0   | 7.70  |
| 10.0  | 7.91  |
| 12.0  | 8.58  |
| 14.0  | 8.90  |
| 16.0  | 9.53  |
| 18.0  | 10.40   |
| 20.0  | 10.71   |
| 22.0  | 10.90   |