CHAPTER - III

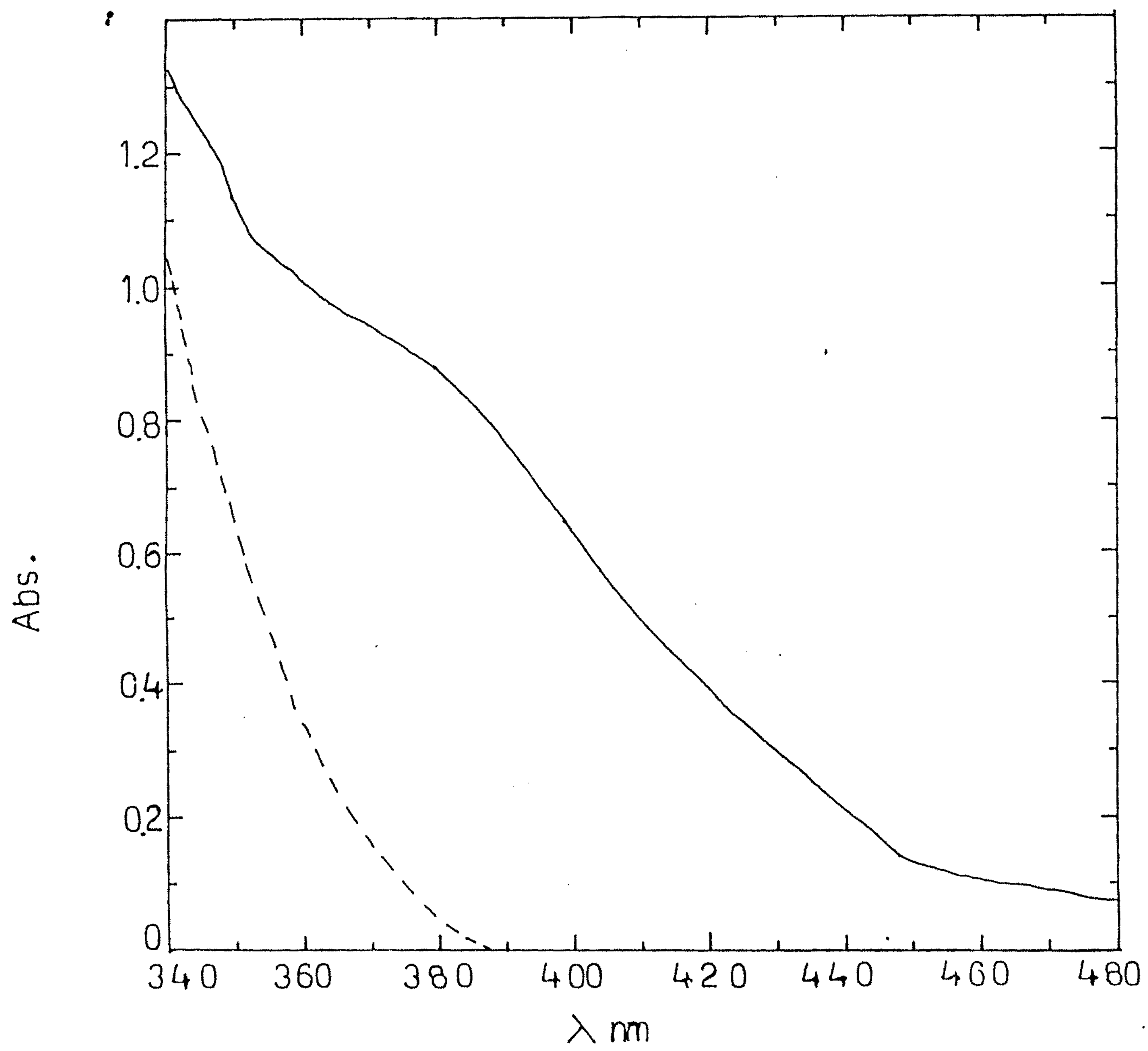
RESULTS AND DISCUSSION: VANADIUM (V) OXIDATION OF THIOSEMICARBAZIDE

The chemistry of thiosemicarbazides and its derivatives has attracted the attention of many investigators due to their biological activity and other applications[115]. They are very good metal chelating agents and find applications in characterization of aldehydes and ketones. They are antitubercular active and also active against influenza, protozoa, small pox and certain kinds of tumor. They are also possible pesticides and fungicides. The study of oxidation of thiosemicarbazides is mainly with positive halogen compounds[116]. In literature there seems to be no attention given to the oxidation of these compounds by transition metal ions. Therefore, the title study was persued to understand the nature of the complex formed between metal ion, vanadium (V), and thiosemicarbazide and its stability in aqueous acidic medium.

The reaction between vanadium (V) and thiosemicarbazide was found to proceed through formation of a complex resulting in a change in the spectrum of vanadium (V) in presence of thiosemicarbazide (Figure 3.1). Therefore the reaction was followed at 390 nm where the absorption is only due to complex. The reaction was occuring rapidly at higher concentrations of the reactants and it was possible to study only the decomposition of the complex. Therefore in order to get information about its formation, the reaction was also studied by lowering the concentrations of reactants by

Figure 3.1. Spectrum of vanadium (V) (.....) and the reaction mixture (——)

$[V^V]$ = [TSC] = 5.0 X 10^{-3} M $[HClO_4]$ = 0.1 M, I = 2.0 M.



ten times the earlier concentrations. The results of both higher and lower concentration range are as follows :

At Higher Concentration Range :

The effect of vanadium (V) was studied between 5.0 X 10^{-4} to 5.0 X 10^{-3} M by keeping the thiosemicarbazide concentration constant at 2.0 X 10^{-3} M. The concentration of perchloric acid was 0.1 M and ionic strength was maintained at 0.2 M at 25°C. The data showing the absorbance change as a function of time is given in Table 3.1. The order in vanadium (V) was found to be 1.1 (Figure 3.2) and the data are given in Table 3.2.

The effect of thiosemicarbazide was studied by keeping the vanadium (V) concentration constant at 3.0 X 10^{-3} M and at a perchloric acid concentration of 0.1 M at an ionic strength 0.2 M maintained with sodium perchlorate. The data showing the absorbance change as a function of time are given in Table 3.3. The order in thiosemicarbazide between 1.0 X 10^{-3} to 5.0 X 10^{-3} M was found to be 0.6 (Figure 3.3). The data are given in Table 3.4.

The concentrations of thiosemicarbazide and vanadium (V) were kept constant at 2.0 X 10^{-3} and 3.0 X 10^{-3} M respectively while studying the effect of perchloric acid on the decomposition of the complex. The data are shown in

Table 3.1. Data showing the absorbance at 390 nm as a function of time runs : Effect of vanadium (V) on the reaction

[TSC] = 2.0 X 10^{-3} M, [$HClO_4$] = 0.1 M,
I = 0.2 M, Temp.= 25°C

Time in Sec.	[V(V)] X 10^{-3}					
	0.5*	1.0	2.0	3.0	4.0	5.0
0	0.089	0.168	0.288	0.308	0.372	0.409
2	0.120	0.174	0.291	0.311	0.372	0.405
4	0.125	0.179	0.294	0.315	0.370	0.400
6	0.122	0.184	0.296	0.317	0.367	0.392
8	0.118	0.188	0.297	0.318	0.363	0.386
10	0.112	0.189	0.297	0.318	0.360	0.379
12	0.107	0.193	0.296	0.317	0.355	0.373
14	0.107	0.194	0.294	0.316	0.351	0.367
16	0.098	0.196	0.293	0.313	0.346	0.361
18	0.094	0.197	0.291	0.312	0.341	0.354
20	0.091	0.197	0.289	0.308	0.337	0.348
30	0.080	0.198	0.276	0.295	0.315	0.322
38	0.080	0.195	0.266	0.283	0.295	0.303
60	--	0.183	0.240	0.255	0.265	0.264
90	--	0.168	0.213	0.226	0.232	0.229
120	--	0.155	0.193	0.205	0.212	0.212

* Time is to be multiplied by 10

Table 3.2 Order in vanadium (V) for decomposition (Higher concentration range)

[TSC] = 2.0 X 10^{-3} M, [$HClO_4$] = 0.1 M,
I = 0.2 M, Temp.= 25°C

[V(V)] X 10^{-3} M	Inl.Rate X 10^{-3} S^{-1}	- log [V(V)]	-log (Inl. Rate)
0.5	0.26	3.30	3.58
1.0	0.40	3.00	3.39
2.0	1.20	2.69	2.92
3.0	1.57	2.52	2.80
4.0	2.20	2.39	2.65
5.0	3.00	2.30	2.52

Figure 3.2. Order in vanadium (V) (conditions as in Table 3.2).

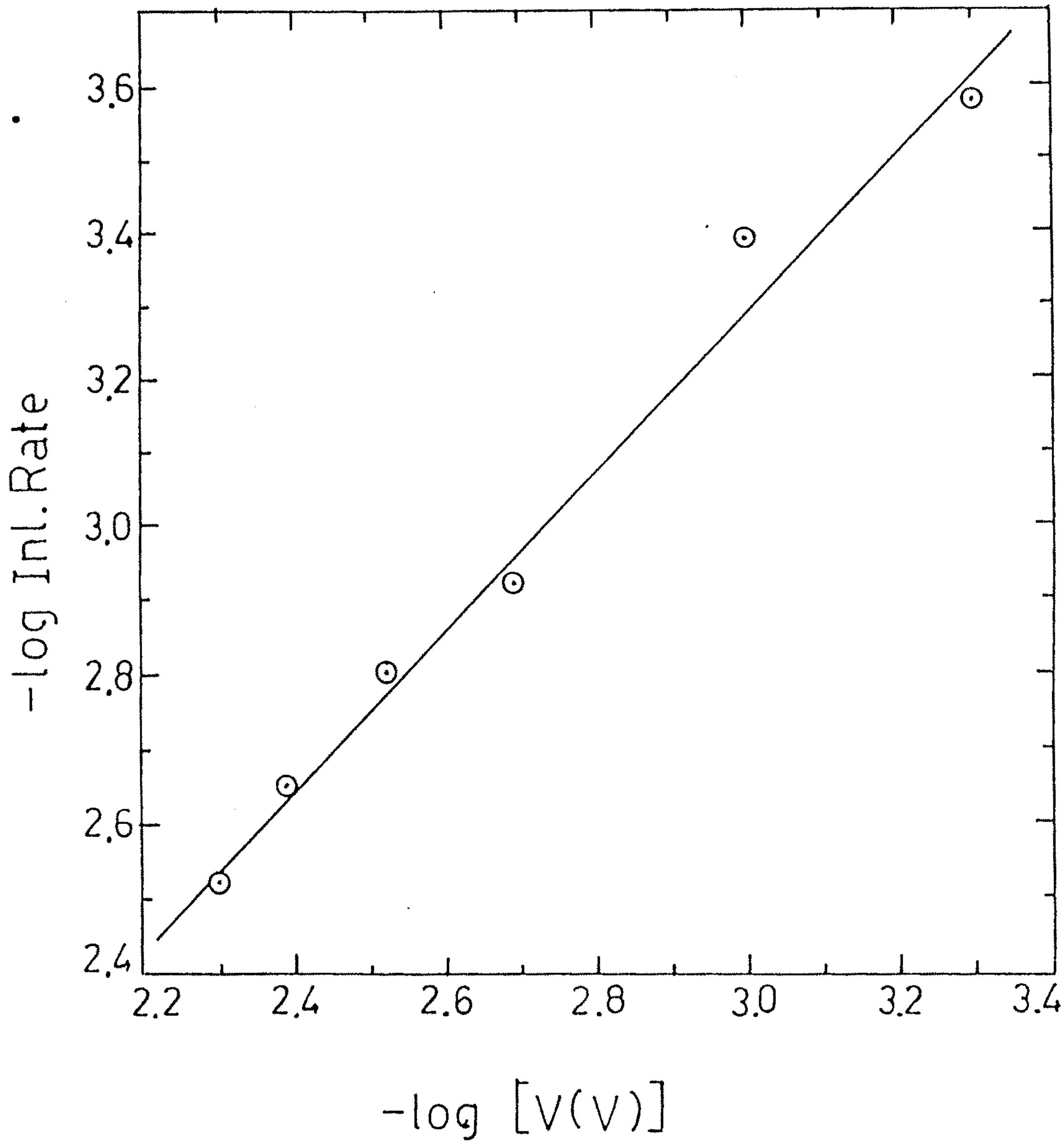


Table 3.3. Data showing absorbance at 390 nm as a function of time : Effect of thiosemicarbazide

$[V(V)] = 3.0 \times 10^{-3}$ M, $[HClO_4] = 0.1$ M,
I = 0.2 M, Temp.= 25°C

Time in Sec.	[TSC] X 10^{-3}					
	1.0	1.6	2.0	3.0	4.0	5.0
0	0.146	0.234	0.310	0.410	0.568	0.754
2	0.147	0.234	0.312	0.435	0.578	0.757
4	0.149	0.234	0.312	0.439	0.586	0.757
6	0.150	0.234	0.312	0.442	0.589	0.753
8	0.150	0.234	0.310	0.442	0.589	0.747
10	0.150	0.233	0.308	0.441	0.587	0.740
20	0.146	0.220	0.293	0.423	0.559	0.691
30	0.140	0.209	0.276	0.400	0.523	0.638
38	0.136	0.199	0.264	0.380	0.494	0.599
60	0.122	0.176	0.235	0.337	0.427	0.511
90	0.108	0.153	0.206	0.290	0.362	0.430
120	0.097	0.137	0.186	0.258	0.323	0.385

Table 3.4 Order in Thiosemicarbazide for decomposition (Higher concentration range)

[V(V) = 3.0×10^{-3} M, $[HClO_4]$ = 0.1 M,
I = 0.2 M, Temp.= 25°C

[TSC] X 10^{-3} M	Inl.Rate X 10^{-3} S^{-1}	- log [TSC]	-log (Inl. Rate)
1.0	0.90	3.00	3.04
1.6	1.20	2.79	2.92
2.0	1.57	2.69	2.80
3.0	1.71	2.52	2.75
4.0	1.90	2.39	2.72
5.0	2.30	2.30	2.63

Figure 3.3. Order in thiosemicarbazide (conditions as in Table 3.4).

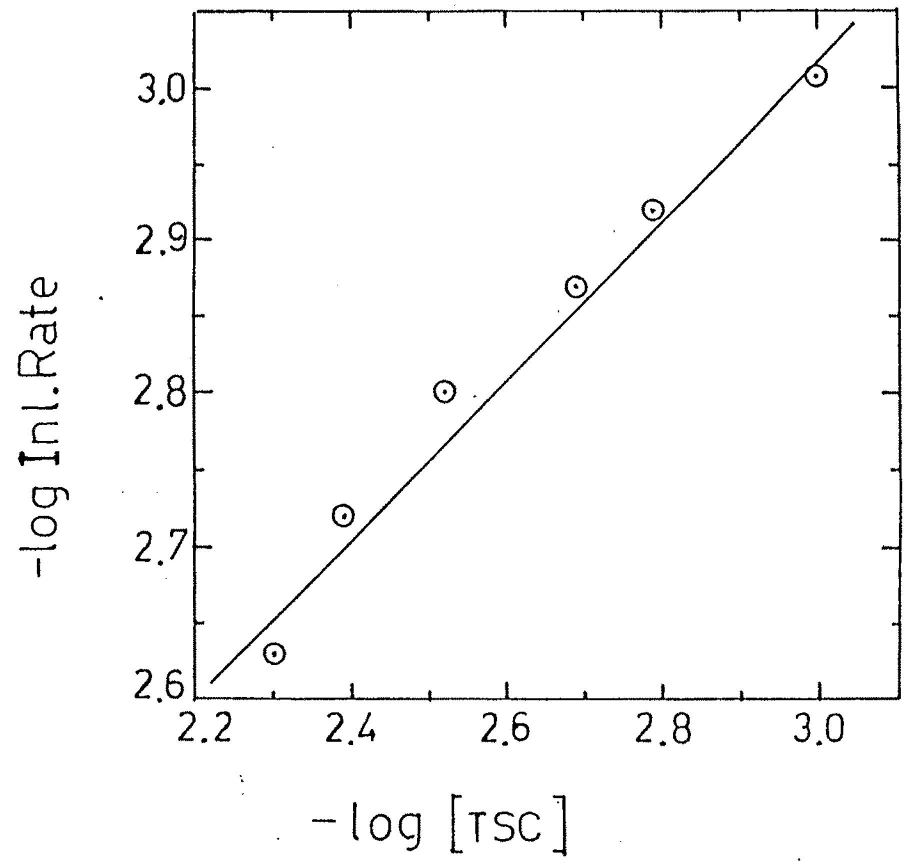


Table 3.5. The increase in perchloric acid concentration decreases the rate steadily as shown in Table 3.6.

At Lower Concentration Range :

In order to study the formation and decomposition of the complex between vanadium (V) and thiosemicarbazide the concentration of perchloric acid was kept constant at 0.1 M at an ionic strength of 0.2 M maintained with sodium perchlorate. The effect of vanadium (V) was studied between 1.0×10^{-4} to 5.0×10^{-4} M at constant concentration of thiosemicarbazide of 2.0×10^{-3} M (Table 3.7) where as the effect of thiosemicarbazide was studied between 2.0×10^{-4} to 2.0×10^{-3} M at constant vanadium concentration of 5.0×10^{-4} M (Table 3.8). The order in vanadium (V) for formation (Table 3.9; Figure 3.4) and decomposition (Table 3.10; Figure 3.5) of the complex were found to be 0.8 and 1.1 respectively. While the order, for formation (Table 3.11; Figure 3.6) and for decomposition (Table 3.12; Figure 3.7) in thiosemicarbazide were 0.9 and 0.6 respectively.

The order of about 0.8 in both the reactants for the formation of the complex indicate that one mole of each are involved in the complex formation. Further the order of more than one in vanadium (V) for the decomposition of the complex may be due to oxidation of the complex by another

Table 3.5. Data showing the absorbance of 390 nm as a function of time : Effect of perchloric acid

$[V(V)] = 3.0 \times 10^{-3}$ M, $[TSC] = 2.0 \times 10^{-3}$ M,
I = 0.2 M, Temp.= 25°C

Time in Sec.	$[HClO_4] \times 10^{-1}$							
	0.375	0.6	0.8	1.0	1.2	1.4	1.6	1.8
0	0.349	0.354	0.327	0.320	0.291	0.276	0.245	0.259
2	0.346	0.353	0.328	0.322	0.295	0.280	0.249	0.263
4	0.340	0.351	0.329	0.323	0.298	0.284	0.254	0.266
6	0.336	0.348	0.328	0.322	0.300	0.286	0.257	0.267
8	0.331	0.344	0.327	0.321	0.300	0.287	0.260	0.267
10	0.325	0.340	0.324	0.320	0.300	0.288	0.261	0.268
20	0.299	0.320	0.308	0.305	0.294	0.284	0.251	0.264
30	0.277	0.300	0.290	0.290	0.283	0.274	0.252	0.255
38	0.260	0.285	0.278	0.278	0.273	0.265	0.245	0.247
60	0.225	0.252	0.249	0.250	0.250	0.242	0.227	0.227
90	0.190	0.219	0.219	0.222	0.225	--	0.208	0.208
120	0.166	0.195	0.197	0.203	0.205	0.203	0.196	0.196

Table 3.6 Effect of perchloric acid on the Inl.Rate for decomposition

[TSC] = 2.0×10^{-3} M [V(V)] = 3.0×10^{-3} M
I = 0.2 M Temp. = 25°C

$[HClO_4] \times 10^{-1}$ M	Inl. Rate $\times 10^{-4}$ s^{-1}
0.375	25.0
0.60	20.9
0.80	17.8
1.0	15.8
1.2	11.1
1.4	10.0
1.6	8.88
1.8	9.0

Table 3.7 Data showing absorbance at 390 nm as a function of time : Effect of vanadium (V)

[TSC] = 2.0×10^{-3} M, $[HClO_4]$ = 0.1 M,
I = 0.2 M, Temp.= 25°C

Time in Sec.	$[V(V)] \times 10^{-4}$				
	1.0	2.0	3.0	4.0	5.0
0	0.029	0.043	0.059	0.073	0.080
5	0.033	0.047	0.065	0.079	0.090
10	0.035	0.051	0.069	0.084	0.098
15	0.038	0.053	0.074	0.089	0.104
20	0.039	0.055	0.075	0.090	0.107
25	0.040	0.056	0.077	0.091	0.111
30	0.042	0.056	0.078	0.091	0.112
35	0.042	0.056	0.078	0.091	0.113
40	0.042	0.056	0.078	0.091	0.114
45	0.043	0.056	0.078	0.090	0.114
50	0.043	0.056	0.077	0.089	0.113
55	0.043	0.056	0.076	0.089	0.112
60	0.043	0.056	0.076	0.088	0.111
90	0.042	0.053	0.071	0.081	0.104
120	0.039	0.050	0.066	0.076	0.096
150	0.038	0.047	0.062	0.071	0.089

Table 3.8 Data showing absorbance at 390 nm as a function of time : Effect of thiosemicarbazide

$[V(V)] = 5.0 \times 10^{-4}$ M, $[HClO_4] = 0.1$ M,
I = 0.2 M, Temp.= 25°C

Time in Sec.	[TSC] X 10^{-3} M				
	0.2	0.5	1.0	1.5	2.0
0	0.032	0.044	0.052	0.063	0.084
5	0.033	0.048	0.057	0.070	0.094
10	0.034	0.050	0.058	0.075	0.101
15	0.034	0.053	0.062	0.078	0.107
20	0.035	0.054	0.063	0.081	0.110
25	0.035	0.055	0.063	0.083	0.112
30	0.036	0.056	0.064	0.083	0.112
35	0.037	0.057	0.064	0.083	0.113
40	0.037	0.057	0.064	0.083	0.113
45	0.037	0.057	0.064	0.083	0.112
50	0.037	0.057	0.063	0.083	0.112
55	0.037	0.057	0.063	0.083	0.112
60	0.036	0.057	0.063	0.082	0.110
90	0.036	0.056	0.060	0.078	0.102
120	0.035	0.054	0.058	0.073	0.094
150	0.034	0.053	0.056	0.068	0.088

Table 3.9 Order in vanadium (V) for formation

[TSC] = 2.0×10^{-3} M, [$HClO_4$] = 0.1 M,
I = 0.2 M, Temp.= 25°C

[V(V)] X 10^{-4} M	Inl.Rate X 10^{-3} s^{-1}	- log [V(V)]	-log (Inl. Rate)
1.0	0.89	4.00	3.05
2.0	1.17	3.69	2.93
3.0	1.67	3.52	2.77
4.0	2.00	3.39	2.69
5.0	3.10	3.30	2.51

Figure 3.4. Order in vanadium (V) for formation of complex (conditions as in Table 3.9).

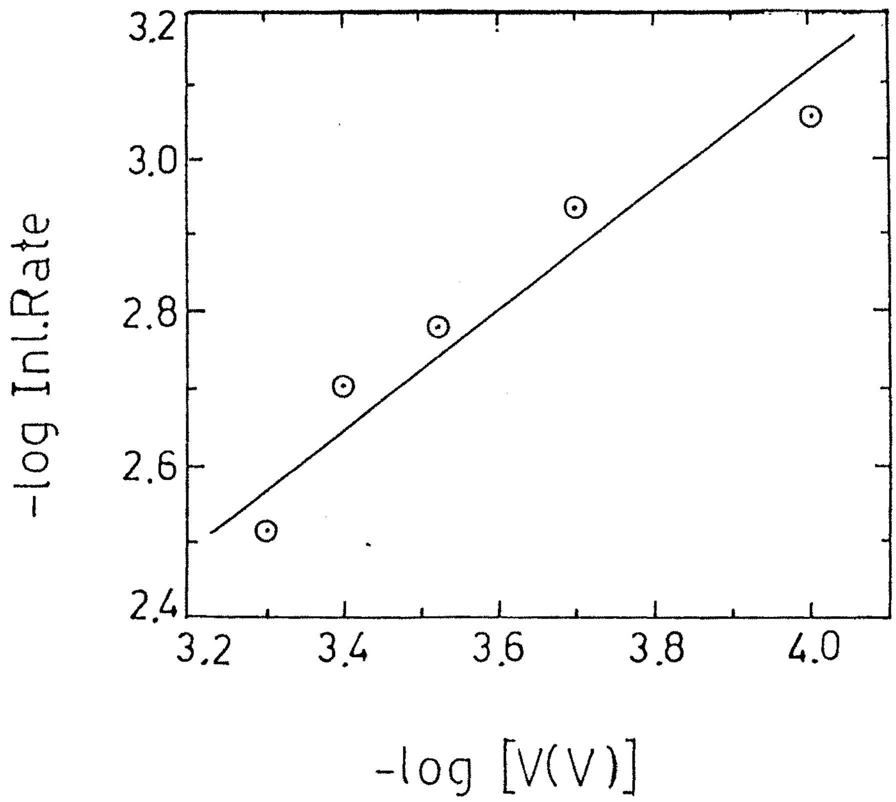


Table 3.10 Order in vanadium (V) for decomposition (Lower concentration range)

$[TSC] = 2.0 \times 10^{-3}$ M $[HClO_4] = 0.1$ M,
I = 0.2 M, Temp.= 25°C

$[V(V)] \times 10^{-4}$ M	Inl.Rate $\times 10^{-4}$ S^{-1}	- log [V(V)]	-log (Inl. Rate)
1.0	1.25	4.00	3.90
2.0	2.00	3.69	3.69
3.0	3.75	3.52	3.42
4.0	4.75	3.39	3.32
5.0	6.56	3.30	3.18

Figure 3.5. Order in vanadium (V) for decomposition (conditions as in Table 3.10).

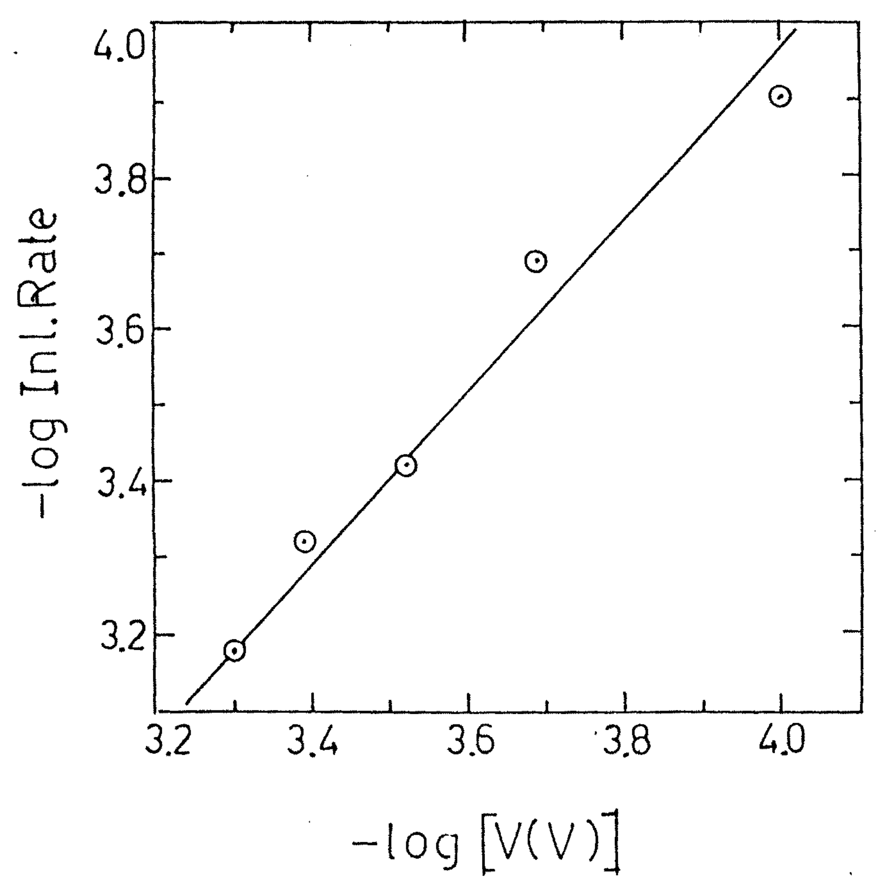
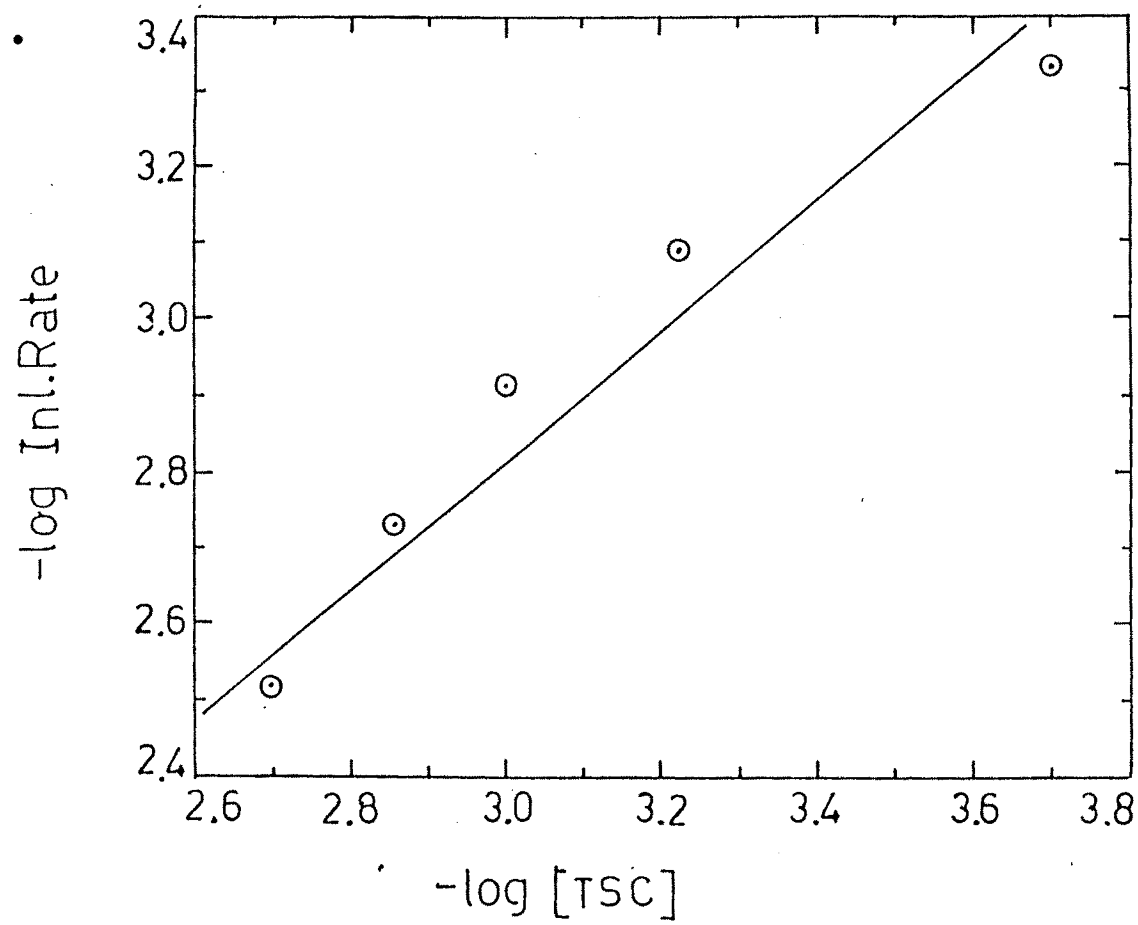


Table 3.11 Order in Thiosemicarbazide for formation

$[V(V)] = 5.0 \times 10^{-4}$ M, $[HClO_4] = 0.1$ M,
I = 0.2 M, Temp.= 25°C

[TSC] X 10^{-3} M	Inl.Rate X 10^{-3} S^{-1}	- log [TSC]	-log (Inl. Rate)
0.2	0.47	3.69	3.32
0.6	0.98	3.22	3.00
1.0	1.23	3.00	2.91
1.4	1.87	2.85	2.73
2.0	3.04	2.69	2.52

Figure 3.6. Order in thiosemicarbazide for formation of complex (conditions as in Table 3.11).

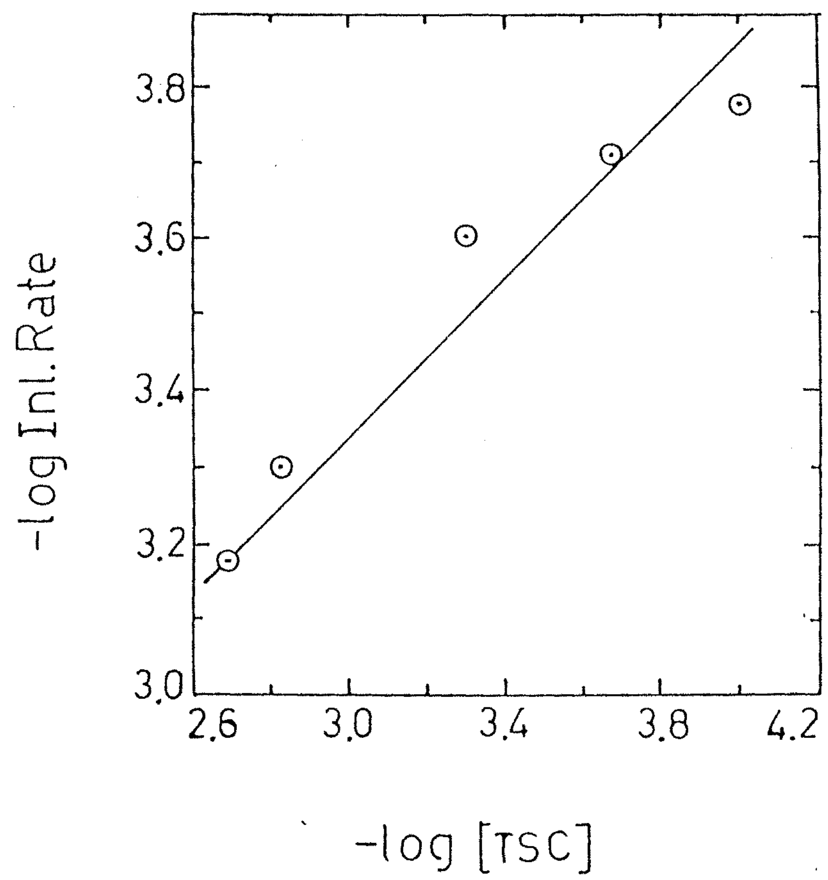


• Table 3.12 Order in thiosemicarbazide for decomposition (Lower concentration range)

$[V(V)] = 5.0 \times 10^{-4}$ M, $[HClO_4] = 0.1$ M,
I = 0.2 M, Temp.= 25°C

[TSC] X 10^{-3} M	Inl.Rate X 10^{-4} s^{-1}	- log [TSC]	-log (Inl. Rate)
0.1	1.66	4.00	3.78
0.2	1.92	3.69	3.71
0.5	2.50	3.30	3.60
1.5	5.00	2.82	3.30
2.0	6.56	2.69	3.18

Figure 3.7. Order in thiosemicarbazide for decomposition (conditions as in Table 3.12).



vanadium (V) ion. Therefore the mechanism of the oxidation of thiosemicarbazide involves formation a complex between the two reactants followed by its oxidation with another vanadium (V) ion which can be represented as follows :

$$V^{V} + TSC \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Complex} \qquad \ldots\ (1)$$

$$\text{Complex} + V^{V} \xrightarrow{k_2} \text{products} + 2V^{IV} \qquad \ldots\ (2)$$

Now the rate of the decomposition or the rate of the reaction leading to the products formation will be given by,

$$\text{Rate} = k_2\ [V^{V}]\ [\text{complex}] \qquad \ldots\ (3)$$

The concentration of the complex can be obtained from equilibrium (1) as,

$$[\text{complex}] = K_1\ [V^{V}]_f\ [TSC] \qquad \ldots\ (4)$$

where, $[V^{V}]_f$ is the uncomplexed $[V^{V}]$

The total concentration of vanadium (V) will be present in free and complexed from. Therefore we have,

$$[V^{V}]_T = [V^{V}]_f + [\text{complex}] \qquad \ldots\ (5)$$

substituting for the [complex] from equation (4) we get,

$$[V^{V}]_T = [V^{V}]_f + K_1\ [V^{V}]_f\ [TSC] \qquad \ldots\ (6)$$

$$[V^V]_f = \frac{[V^V]_T}{1 + K_1 \, [TSC]} \qquad \ldots . \, (7)$$

From equation (7) and (4) we get,

$$[\text{complex}] = \frac{K_1 [V^V]_T}{1 + K_1 \, [TSC]} \qquad \ldots . \, (8)$$

Therefore from equation (3) and (8) the rate of decomposition would be,

$$\text{Rate} = \frac{K_1 k_2 \, [V^V]^2 \, [TSC]}{1 + K_1 \, [TSC]} \qquad \ldots . \, (9)$$

The above rate law satisfactorily explains the order in vanadium (V) more than one and the fractional order in thiosemicarbazide for the oxidation of the complex.

The decrease in rate as the perchloric acid concentration increases may be due to the active species of the oxidant. In acidic medium vanadate ion is found undergo protonation[117] as represented in the equilibria (10) and (11). The results of effect of, perchloric acid indicate that the unprotonated vanadate ion is the probable active species, the concentration of which decreases as the acid concentration increases leading to the decrease in rate.

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \qquad \ldots . \, (10)$$

$$HVO_3 + H^+ \rightleftharpoons VO_2^+ + H_2O \qquad \ldots . \, (11)$$