

Kinetics of oxidation of iodide by vanadium(V)

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Kinetics of oxidation of iodide ion by V^V under uncatalysed and Ru^{III} catalysed conditions in aqueous perchloric acid medium have been studied. The reaction is first order in [V^V] and first order in [I⁻]. With [H⁺], the reaction shows a complex behavior of 1.5 order till [H⁺] is 0.5 M and second order beyond that concentration. In the case of Ru^{III} catalysed oxidation, the reaction exhibits a dual character of first order and zero order in [V^V]. The first order component shows 1.5 order in [I⁻] first order in [Ru^{III}] and 1.5 order in [H⁺]. The zero order component shows first order in [I⁻], first order in [Ru^{III}] and independent of [H⁺]. No catalysis has been observed with Os^{VIII}. Suitable rate laws have been postulated based on the observations.

Kinetics of oxidation of iodide ion by vanadium(v) have been studied by various workers¹. Different rate laws with different mechanisms have been postulated. Secco and co-workers attempted to rationalize all previous reports and suggested that the following equation

$$V \dot{=} \{k_{1,5}[I^-][H^+] + k_{2,5}[I^-][H^+]^2 + k_{4,5}[I^-]^2[H^+]^2\}[H_4VO_4^+]$$

is able to explain all the data of their work and other investigators. But the effects of foreign ions on this reactions have not been studied earlier. So the present communication attempts to throw light on the effect of Ru^{III} in the oxidation of I⁻ by V^V.

Results and Discussion

Catalyzed reactions :

The rate data did not yield constant first order rate constants and the rate constants increased during the course of the reaction. Hence an attempt was made to find out whether the data fitted into zero order rate equation. Zero order rate constant decreased with the increase in percent of reaction. It appeared that this catalyzed reaction might be composed of pseudo-first order and pseudo-zero order rate components. The experimental rates were fitted in the integrated rate equation for the possible resolution of pseudo-first order rate constants and pseudo-zero order rate constants,

$$-\frac{d[V^V]}{dt} = k_1[V^V] + k_0$$

In other words,

$$\frac{V_{t_n}^V - V_{t_{n+1}}^V}{t_{n+1} - t_n} = \frac{V_{t_n}^V + V_{t_{n+1}}^V}{2} k_1 + k_0$$

where V_{t_n}^V and V_{t_{n+1}}^V are the measured concentrations of the disappearing V^V at time t_n and t_{n+1} respectively, k₁ and k₀ are the pseudo-first order and pseudo-zero order rate constants for the reactions. The plot showed that there is definite intercept indicating the presence of pseudo-zero

order and the slope represents pseudo-first order rate constant. The kinetic data thus separated into pseudo-first order and pseudo-zero order rate constants (Table 1).

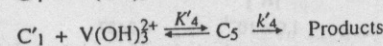
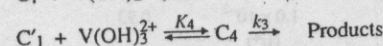
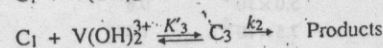
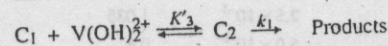
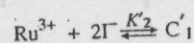
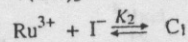
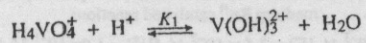
Table I. Oxidation of iodide by vanadium(v) in aqueous perchloric acid medium Ru^{III} catalyzed reactions

[V^V] = 5.0 × 10⁻³ M, [I⁻] = 3.5 × 10⁻² M, [H⁺] = 1.0 × 10⁻¹ M, [NaClO₄] = 0.4 M, Temp. = 30°

Concn. of non-variant (M)	Concn. of variant (M)	k ₁ × 10 ⁴ s ⁻¹	k ₀ × 10 ⁶ mol dm ⁻³ s ⁻¹
[Ru ^{III}] = 1.14 × 10 ⁻⁶	2.5 × 10 ⁻³	1.035	0.5675
	5.0 × 10 ⁻³	0.8	0.572
	7.5 × 10 ⁻³	1.075	0.5995
	1.0 × 10 ⁻²	0.93	0.546
[Ru ^{III}] = 5.7 × 10 ⁻⁷	[H ⁺]		
	1.0 × 10 ⁻¹	0.2427	0.539
	1.5 × 10 ⁻¹	1.2	0.865
	2.0 × 10 ⁻¹	1.4571	0.78
	3.5 × 10 ⁻¹	2.667	0.68
[Ru ^{III}] = 5.7 × 10 ⁻⁷	[Ru ^{III}]		
	0.057 × 10 ⁻⁵	0.2427	0.539
	0.114 × 10 ⁻⁵	0.8	0.572
	0.209 × 10 ⁻⁵	1.1589	1.3435
	0.475 × 10 ⁻⁵	1.7429	1.86
	0.950 × 10 ⁻⁵	3.1429	5.31
[I ⁻]	1.900 × 10 ⁻⁵	13.9375	9.70
	3.5 × 10 ⁻²	0.2427	0.539
	5.0 × 10 ⁻²	0.3375	0.7013
	6.5 × 10 ⁻²	0.8572	0.72
Temp. °C	1.0 × 10 ⁻¹	1.0714	1.17
	30	0.2427	0.539
	40	0.4214	0.952
[Ru ^{III}] = 5.7 × 10 ⁻⁷	50	1.05714	2.388

The following facts emerge from the rate data. (i) The reactions are mixed order in oxidant : first order in $[V^V]$ and zero order in $[V^V]$. (ii) The first order component shows the following kinetic features : it is affected by increase in $[H^+]$ and the reaction has dependence of 1.5 on $[H^+]$. The order with respect to $[Ru^{III}]$ is one and that with respect to $[I^-]$ is 1.5. (iii) The zero order component shows the following kinetic features : it is independent of $[H^+]$, it shows first order dependence on $[Ru^{III}]$ and its dependence on $[I^-]$ is nearly unity. (iv) Vanadium(v) species undergoes a series of reactions under acid conditions giving rise to its hydrolytic species², viz. $[V(OH)_3]^{2+}$, $[V(OH)_2]^{3+}$ and $[VO_2^+]$.

Based on these findings the rate law takes the form,



$$\text{Rate} = k_1 C_2 + k_2 C_3 + k_3 C_4 + k_4 C_5$$

$$= k_1 K_3 C_1 [V(OH)_2^{3+}] + k_2 K_3' C_1 [V(OH)_2^{3+}] +$$

$$k_3 K_4 C_1' [V(OH)_2^{3+}] + k_4 K_4' C_1' [V(OH)_2^{3+}]$$

$$= k_1 K_3 C_1 [V(OH)_2^{3+}] + k_2 K_3' C_1 K_1 [V(OH)_2^{3+}] [H^+] +$$

$$k_3 K_4 C_1' [V(OH)_2^{3+}] + k_4 K_4' C_1' K_1' [V(OH)_2^{3+}] [H^+]$$

$$[V^V] = \frac{[V(OH)_3^{2+}]}{K_1 [H^+]} \{ 1 + K_1 H^+ + K_1 k_1 [H^+]^2 +$$

$$K_1 K_2 K_3 [Ru^{III}] [I^-] [H^+] + K_1 K_2 K_3' [Ru^{III}] [I^-] [H^+]^2 +$$

$$K_1 K_2' K_4 [Ru^{III}] [I^-]^2 [H^+] + K_1 K_1' K_2' K_4' [Ru^{III}] [I^-]^2 [H^+]^2 \}$$

$$\text{Rate} = [V(OH)_2^{3+}] \{ k_1 K_3 C_1 + k_2 K_3' C_1 [H^+] + k_3 K_4 C_1' +$$

$$k_4 K_4' C_1' K_1' [H^+] \}$$

$$= [V(OH)_2^{3+}] \{ k_1 K_2 K_3 [Ru^{III}] [I^-] + k_2 K_1' K_2 K_3' [Ru^{III}] [I^-] [H^+] +$$

$$k_3 K_4 K_2 [Ru^{III}] [I^-]^2 + k_4 K_4' K_1' K_2' [Ru^{III}] [I^-]^2 [H^+] \}$$

$$[V^V] [Ru^{III}] \{ k_1 K_1 K_2 K_3 [H^+] [I^-] + k_2 K_1 K_1' K_2 K_3' [H^+]^2$$

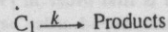
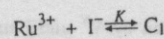
$$+ k_3 K_1 K_2 K_4 [H^+] [I^-]^2 + k_4 K_1 K_1' K_2' K_4' [I^-]^2 [H^+]^2 \}$$

$$+ K_1 K_2 K_3' [Ru^{III}] [I^-] [H^+]^2 + K_1 K_2' K_4 [Ru^{III}] [I^-]^2 [H^+]$$

$$+ K_1 K_1' K_2' K_4' [Ru^{III}] [I^-]^2 [H^+]^2$$

The observed first order in $[V^V]$, 1.5 order in $[I^-]$, first order in $[Ru^{III}]$ and 1.5 order in $[H^+]$ can be rationalized by the above rate law.

The corresponding rate law for zero order component derived as



$$\text{Rate} = K k [Ru^{III}] [I^-]$$

This explains first order on $[Ru^{III}]$, first order on $[I^-]$ and independent of $[H^+]$ and $[V^V]$.

Effect of Os^{VIII} : The reaction is unaffected by the addition of Os^{VIII} . The rate constants in the absence and presence of Os^{VIII} concentration are presented in Table 2. Thus it is seen that these reactions are different from oxidation of I^- with Ce^{IV} where catalysis is observed with both Ru^{III} and Os^{VIII} . Similarly, Mn^{II} has no catalyzing effect in these reactions unlike as in iodide-cerium(iv) reaction. The reaction rate constants are 5.25×10^{-5} , 5.25×10^{-5} and $6.60 \times 10^{-5} \text{ s}^{-1}$ at zero, 0.0002067 M and 0.005 M concentrations of Mn^{II} respectively.

Table 2

$[Os^{VIII}]$, M	$k_1 \times 10^{-5} \text{ s}^{-1}$
0.0	5.25
0.8×10^{-5}	5.29
1.6×10^{-5}	5.12

Arrhenius parameters computed for first order and zero order components in these reactions are presented in Table 3 which are of right order magnitude for bimolecular reactions.

Table 3. Arrhenius parameters for the oxidation of iodide by vanadium(v) Ru^{III} catalyzed reactions in aqueous perchloric acid medium

	ΔE kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger JK ⁻¹ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹	log ₁₀ PZ
1 order component	59.668	57.15	-144.75	101.00	5.537
Zero order component	57.574	55.056	-183.323	110.60	3.9922

Uncatalyzed reactions :

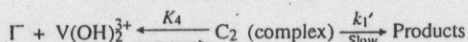
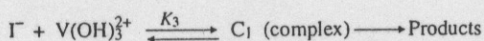
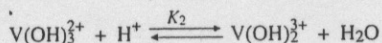
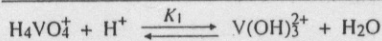
For the purpose of comparison, the uncatalysed reaction of I^- with V^V under similar experimental conditions has been studied and it has been observed that the reactions are first order in $[V^V]$ but the reaction rate decreases with increase of concentration of V^V suggesting the presence of complex retarding influence. The decreasing k attained a limiting value at high-concentration of V^V . The results are presented in Table 4.

Reaction is first order in $[I^-]$ and $[H^+]$ showing an order of 1.5 between 0.05 and 0.5 M $[H^+]$ and beyond 0.5 M the dependence on $[H^+]$ is 2. The sequence of reaction is as follows :

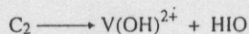
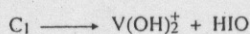
Table 4. Oxidation of iodide by vanadium(v) in aqueous perchloric acid medium uncatalyzed reactions

$[V^V] = 5.0 \times 10^{-3} M$, $[I^-] = 3.5 \times 10^{-2} M$, $[H^+] = 1.0 \times 10^{-1} M$, $[NaClO_4] = 0.4 M$, Temp. = 30

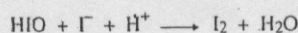
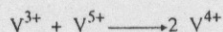
Concn. of non-variant (M)	Concn. of variant (M)	$k_1 \times 10^5$ s^{-1}
	$[V^V]$	
$[H^+] = 1.0 \times 10^{-1}$	2.5×10^{-3}	6.885
	5.0×10^{-3}	5.250
	1.0×10^{-2}	3.738
$[H^+] = 1.5 \times 10^{-1}$	2.5×10^{-3}	11.559
	5.0×10^{-3}	9.848
	7.5×10^{-3}	7.938
	1.0×10^{-2}	7.258
	2.0×10^{-2}	5.695
	$[H^+]$	
	5.0×10^{-2}	2.493
	1.0×10^{-1}	5.250
	1.5×10^{-1}	9.848
	2.0×10^{-1}	14.986
	4.0×10^{-1}	48.66
	6.0×10^{-1}	91.606
	8.0×10^{-1}	287.4
	1.5	1260.0
	$[I^-]$	
$[H^+] = 5 \times 10^{-1}$	0.5×10^{-2}	1.1101
	1.0×10^{-2}	2.0836
	2.5×10^{-2}	6.132
	3.5×10^{-2}	9.848
	6.5×10^{-2}	22.028
	1.0×10^{-1}	32.729



The breakdown of C_1 and C_2 can be visualized as



The products V^{3+} and HIO are immediately converted by fast reactions to V^{4+} and I_2 as



$$V^V = \frac{[V(OH)_3^{2+}]}{K_1[H^+]} \left\{ 1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_3[H^+][I^-] + \frac{K_1K_2K_4[H^+]^2[I^-]}{[I^-]} \right\}$$

Thus, $C_1 = K_3 [I^-][V(OH)_3^{2+}]$

$$= \frac{K_1K_3[V^V][H^+][I^-]}{1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_3[H^+][I^-] + K_1K_2K_4[H^+]^2[I^-]}$$

$$C_2 = K_4[I^-][V(OH)_2^{3+}]$$

$$= \frac{K_1K_2K_4[V^V][I^-][H^+]^2}{1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_3[H^+][I^-] + K_1K_2K_4[H^+]^2[I^-]}$$

$$\text{Rate} = k_1C_1 + k_1'C_2$$

$$= \frac{k_1K_2K_3[V^V][H^+][I^-] + k_1'K_1K_2K_4[V^V][H^+]^2[I^-]}{1 + K_1[H^+] + K_1K_2[H^+]^2 + K_1K_3[H^+][I^-] + K_1K_2K_4[H^+]^2[I^-]}$$

It is necessary to comment upon the interaction of $2 I^-$ with Ru^{III} to form a complex C_1' in the catalyzed reaction under consideration. Prima facie it may suggest a termolecular reaction. What is really envisaged in this process is that the reaction of I^- with Ru^{III} occurs stepwise to form a complex. Similar explanation based on stepwise interaction of I^- with the oxidant has been advanced earlier in the study of kinetics of oxidation of arsenious acid with iodate and chromate ions⁴. It is not possible to discriminate whether the I^- attacks the central vanadium atom or the oxygen centre. By analogy with vanadium oxychloride it is reasonable to postulate that the polarized nucleophile I^- does react at the vanadium(v) centre⁵.

Effect of solvent: The rate constants ($k_1 \times 10^5 s^{-1}$) at 10, 15 and 30% aqueous acetic acid are found to be 12.15, 17.916 and 65.59 respectively. Thus establishing that it is a positive ion and negative ion reaction. The reactive species of vanadium may be either $V(OH)_3^{2+}$ or $V(OH)_2^{3+}$. Similar effect of solvent acetic acid has been noted in the oxidation of I^- by cerium(IV)³.

Effect of DMSO: Addition of DMSO does not result in increase in kinetic rate. This is at variance to what has been observed in DMSO in the reaction of I^- and Ce^{IV} ³.

The rate constants ($k_1 \times 10^5 s^{-1}$) at 30, 40 and 50° are found to be 5.25, 13.587 and 36.905 respectively. Arrhenius parameters presented in Table 5 for uncatalyzed reactions are of the right order of magnitude for bimolecular reaction. It is interesting to point out that the activation energy for uncatalyzed reaction is much higher than that observed for catalyzed reaction. This is quite in order as the catalyzed reactions are much faster due to decrease in activation energy.

Table 5. Arrhenius parameters for the oxidation of iodide by vanadium(v) uncatalyzed reactions in aqueous perchloric acid medium

ΔE kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹	log ₁₀ PZ
77.763	75.245	-79.769	99.414	9.0676

Experimental

Potassium iodide, ammonium metavanadate, perchloric acid, sodium perchlorate and other reagents used were of analytical reagent grade. The reaction kinetics were followed by the following procedure. To the reagent solution (50 ml), the oxidant solution (50 ml) was added (the instant of half delivery being noted as zero time) and shaken well. The progress of the reaction was followed by withdrawing 5 ml aliquots at various time intervals, discharging into a

flask containing ice-cold water. The liberated iodine was analyzed using standard sodium thiosulphate solution. In all the experiments excess of sodium perchlorate was used.

The rate constants were calculated from the slopes of log (a-x) vs time curves using regression analysis from the experimental values in uncatalysed reactions. Linearity was observed in most of the cases up to 80% of vanadium(v) consumption, while in the case of Ru^{III} catalyzed reactions the reaction rates did not fit in the pure first order or zero order rate. The data were fitted into the rate equation,

$$-\frac{d[V^V]}{dt} = k_1(a-x/2) + k_0$$

The plot of dx/dt vs (a-x/2) was drawn; intercept gave the zero order rate constant and the slope gave the first order rate constant. Results were the same even for plots of dx/dt vs (a-x).

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