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Electron Transfer Reactions between V(IV) and I(V) Catalyzed by Os(VIII) or Ru(III). A Kinetic Study

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Oxidation of V(IV) by iodate, catalyzed by Os(VIII) or Ru(III) in aq perchloric acid medium, was carried out. The order with respect to oxidant is zero in both the Os(VIII)- and Ru(III)-catalyzed reactions. A unit-order dependence on V(IV) is observed in the case of Os(VIII)-catalyzed reaction and a fractional dependence on V(IV) is noticed in the case of Ru(III)-catalyzed reaction. Both Os(VIII)- and Ru(III)-catalyzed reactions exhibit an inverse unit dependence on acidity. Insensitivity to change in the dielectric constant of medium is observed in both the systems. Effects of salt and ionic strength were studied. A plausible mechanism consistent with the experimental results is postulated, rate laws being derived from the proposed mechanism. The stoichiometry of the reaction has proved to be the same for both the systems.

Oxidation of V(IV) by Cr(VI),[1] Mn(III),[2] or Br(V)[3] has been studied previously. Fuller and Ottaway[4] investigated kinetics of oxidation of V(IV) by IO_3^- with a ratio of oxidant:reductant not less than 25 and found a second-order dependence on IO_3^- and a first-order dependence on V(IV). In the present investigation under a reverse condition of substrate [V(IV)]/oxidant $[IO_3^-]>20$, there was no reaction even after keeping the system overnight at the temperature studied. Thus the facile oxidation of V(IV) with Os(VIII) or Ru(III) and with IO_3^- as a co-oxidant has been systematically investigated. To our knowledge this is the first systematic kinetic report on Os(VIII)- or Ru(III)-catalyzed oxidations of V(IV) by iodate.

Experimental

All the reagents used were of AR grade: BDH(AR) $VOSO_4$ and BDH(AR) KIO_3; 70% BDH(AR) $HClO_4$ and $RuCl_3$ and OsO_4 solutions were diluted before use.

The kinetics of reaction was followed by determining the unreacted iodate iodometrically will standardized sodium thiosulfate and starch iodide indicator end point. No solvent decomposition occurred. $Na_2S_2O_3$ reacts with OsO_4 but not with $RuCl_3$. The error involved in the determination is not more than 6% at the highest concentration of Os(VIII) (15.7×10^{-5} M) ($1\ M=1\ mol\ dm^{-3}$). In the majority of experiments the error is not more than 2%; however, in the computation this error level was taken into account. All rate constants were reproducible within ±3% error.

Stoichiometry. The overall stoichiometry for both the Os(VIII)- and Ru(III)-catalyzed oxidations of V(IV) by IO_3^- was found to be 1:6.

Discussion

Oxidation of V(IV) by I(V) Catalyzed by Os(VIII). Oxidation of V(IV) by iodate catalyzed by Os(VIII) was carried out in aq perchloric acid aq acetic acid–perchloric acid media.

Effect of Varying $[IO_3^-]$ on Reaction Rate. The Os(VIII)-catalyzed IO_3^- oxidation of V(IV) was studied under a pseudo-first-order condition with excess [V(IV)] over $[IO_3^-]$. The disappearance of $[IO_3^-]$ conformed to no first-order pattern as seen from the nonlinearity of plots of $\log[IO_3^-]_t$ *vs.* time. On the other hand, plots of X *vs.* time are fairly linear at least up to double the half-life, indicating a zero-order dependence with respect to the oxidant. Zero-order rate constants are computed from slopes (x/t) of such linear plots. Moreover, k_0 values computed for various initial concentrations of IO_3^- are almost identical, confirming the zero-order dependence with respect to the oxidant (Table 1) in the concentration range studied. Such zero-order dependence on oxidant has been observed in various reactions catalyzed by transition metal ions.

TABLE 1. EFFECT OF VARIATION OF [OXIDANT], [SUBSTRATE], [ACID], AND [CATALYST] AT TEMPERATURE 60 °C

Substrate 10^2[V(IV)]	Oxidant $10^4[IO_3^-]$	Acid $10^2[HClO_4]$	Catalyst 10^5[Os(VIII)]	$\frac{k_0}{10^{-6}\ mol\ l^{-1}\ min^{-1}}$
1.0	2.14	1.0	3.93	2.37
1.0	4.25	1.0	3.93	2.35
1.0	8.35	1.0	3.93	2.43
1.0	12.84	1.0	3.93	2.38
0.25	4.04	1.0	3.93	0.57
0.50	4.14	1.0	3.93	1.15
2.0	4.19	1.0	3.93	5.19
1.0	4.09	0.50	3.93	4.75
1.0	4.12	2.0	3.93	1.24
1.0	3.91	4.0	3.93	0.58
1.0	3.95	1.0	1.96	1.50
1.0	4.41	1.0	7.86	4.99
1.0	4.26	1.0	15.73	8.77

Effect of Varying [V(IV)] on Reaction Rate. Increasing the concentration of V(IV) increases the rate of reaction; rate constants at different concentrations of V(IV) are given in Table 1. The plot of log k_o *vs.* log[V(IV)] is linear with slope unity, indicating a first-order dependence with respect to substrate.

Effect of Varying [Os(VIII)] on Reaction Rate. Increasing the concentration of Os(VIII) increases the reaction rate; rate constants at different concentrations of Os(VIII) are given in Table 1. The plot of log k_o *vs.* log[Os(VIII)] is linear with slope unity, indicating a first-order dependence with respect to Os(VIII).

Effect of Varying [$HClO_4$] on Reaction Rate. The influence of acid on reaction rate was studied with a view to identifying species which participate in the reaction. Increase in the concentration of perchloric acid decreases the rate of oxidation (Table 1). The plot of log k_o *vs.* log[H^+] is linear with a negative slope of unity. Thus the dependence on acid is inverse unity. This inverse dependence on acidity deserves a comment. VO^{2+} on hydrolysis forms $VOOH^+$ *via* the equilibrium

$$VO^{2+} + H_2O \overset{K_h}{\rightleftharpoons} VOOH^+ + H^+.$$

Active species of substrate participating in the reaction is $VOOH^+$, hence the inverse dependence on acidity. It is reported$^{5)}$ that V(IV) in aq acid medium ([H^+]= 0.002—3 M) hydrolyses to $VOOH^+$ with an approximate K_h value of 10^{-6}.

Effect of Varying Concentration of Acetic Acid. These reactions are found to be insensitive to change in dielectric constant of the medium. Increase in the percentage of acetic acid has no effect on the reaction rate. Rate constants at different percent of acetic acid are given in Table 2. Such insensitivity to change in dielectric constant of the medium has been observed also in Ag^+-catalyzed oxidation of α-hydroxy acids by peroxydisulphate.$^{6)}$

Effect of Varying Ionic Strength of the Medium. Change in ionic strength of the medium by varying the concentration of sodium perchlorate has no effect on the reaction rate. Rate constants at different concentrations of sodium perchlorate are given in Table 3. This clearly indicates that the reactions are of ion dipolar type.

Effect of Temperature on Reaction Rate. Reactions were conducted at different temperatures in the range from 50 to 70 °C and respective rate constants are given in Table 4. The plot of log k_o *vs.* $1/T$ is linear. From the slope of the plot of log k_o *vs.* $1/T$ respective Arrhenius parameters were computed and listed in Table 4. These activation parameters are of correct magnitude.

TABLE 2. EFFECT OF VARIATION OF SOLVENT ON REACTION RATE

[V(IV)]=0.01 M, [IO_3^-]=0.5×10^{-3} M, [$HClO_4$]=0.01 M, [Os(VIII)]=3.93×10^{-5} M, temp=60 °C.

% of HOAc	$\frac{k_0}{10^{-6}\ \mathrm{mol\ l^{-1}\ min^{-1}}}$
10	2.24
20	2.05
40	2.05
60	2.68

TABLE 3. EFFECT OF VARIATION OF IONIC STRENGTH

[V(IV)]=0.01 M, [IO_3^-]=0.5×10^{-3} M, [$HClO_4$]=0.01 M, [Os(VIII)]=3.93×10^{-5} M, temp=60 °C.

$\frac{[NaClO_4]}{10^{-2}\ \mathrm{M}}$	$\frac{\mu}{\mathrm{mol\ l^{-1}}}$	$\frac{k_0}{10^{-6}\ \mathrm{mol\ l^{-1}\ min^{-1}}}$
1.0	0.06	2.36
2.5	0.075	2.58
5.0	0.10	2.41
10.0	0.151	2.35

TABLE 4. EFFECT OF VARIATION OF TEMPERATURE AND THERMODYNAMIC PARAMETERS AT 60 °C

[V(IV)]=0.01 M, [IO_3^-]=0.5×10^{-3} M, [$HClO_4$]=0.01 M.

Catalyst	$\frac{T}{°\mathrm{C}}$	$\frac{k_0}{10^{-6}\ \mathrm{mol\ l^{-1}\ min^{-1}}}$
[Os(VIII)]	50	0.97
3.93×10^{-5} M	60	2.43
	70	6.71

$\frac{\Delta E^*}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta H^*}{\mathrm{kJ\ mol^{-1}}}$	$\log_{10} A$	$\frac{\Delta S^*}{\mathrm{J\ K^{-1}\ mol^{-1}}}$
86.2	83.5	6.13	−136

Oxidation of V(IV) by I(V) Catalyzed by Ru(III). As a continuing study, oxidation of V(IV) by Ru(III)-catalyzed iodate was carried out for comparison, salient features observed in the investigation are as follows:

i) The order with respect to oxidant is zero which is similar to the case of Os(VIII)-catalyzed reactions (Table 5).

ii) Increase in the concentration of V(IV) increases the rate of oxidation, rate constants at different concentrations of [V(IV)] being given in Table 5. The plot of log k_o *vs.* log[V(IV)] is linear with a slope less than unity, indicating a fractional dependence on substrate. This differs from the previous observation made in the case of Os(VIII)-catalyzed oxidations.

iii) The dependence on Ru(III) is unity which is analogous to that observed in the case of Os(VIII)-catalyzed reactions (Table 5).

iv) To confirm the dependence on acidity with no attendant ionic strength effect, the dependence on [H^+] at constant ionic strength was determined. The plot of log k_o *vs.* log[H^+] is linear with a slope of −0.5, which shows a fractional dependence on [H^+] (Table 8) and the plot of log k_o *vs.* log[$NaClO_4$] is linear with a slope of −0.5 (Table 7).

v) The apparent dependence on acid is inverse unity, which results from additive effects of ionic strength and acid both being inverse. It may be pointed out that in OsO_4-catalyzed reaction there

TABLE 5. EFFECT OF VARIATION OF [OXIDANT], [SUBSTRATE], [ACID], AND [CATALYST] AT TEMPERATURE 35 °C

Substrate 10^2[V(IV)]	Oxidant $10^4[IO_3^-]$	Acid $10^2[HClO_4]$	Catalyst 10^7[Ru(III)]	$\frac{k_0}{10^{-6}\ \text{mol l}^{-1}\ \text{min}^{-1}}$
1.0	2.03	1.0	7.64	3.65
1.0	4.80	1.0	7.64	3.77
1.0	8.69	1.0	7.64	3.80
1.0	12.78	1.0	7.64	3.77
0.25	5.02	1.0	7.64	1.50
0.50	4.98	1.0	7.64	2.23
2.0	4.46	1.0	7.64	4.49
4.0	5.02	1.0	7.64	5.69
1.0	4.23	0.50	7.64	7.67
1.0	4.68	2.0	7.64	1.98
1.0	4.66	4.0	7.64	1.04
1.0	4.33	1.0	3.82	1.93
1.0	4.05	1.0	14.28	7.47
1.0	4.09	1.0	28.56	14.21

TABLE 6. EFFECT OF VARIATION OF SOLVENT ON REACTION RATE

[V(IV)]=0.01 M, $[IO_3^-]=0.5\times10^{-3}$ M, $[HClO_4]=0.01$ M, [Ru(III)]$=7.64\times10^{-7}$ M, temp=35 °C.

% HOAc	$\frac{k_0}{10^{-6}\ \text{mol l}^{-1}\ \text{min}^{-1}}$
10	3.68
20	3.77
30	3.75
40	3.66
60	3.59
80	3.48

TABLE 7. EFFECT OF VARIATION OF IONIC STRENGTH

[V(IV)]=0.01 M, $[IO_3^-]=0.5\times10^{-3}$ M, $[HClO_4]=0.01$ M, [Ru(III)]$=7.64\times10^{-7}$ M, temp=35 °C

$\frac{[NaClO_4]}{10^{-2}\ \text{M}}$	$\frac{\mu}{\text{mol l}^{-1}}$	$\frac{k_0}{10^{-6}\ \text{mol l}^{-1}\ \text{min}^{-1}}$
1.0	0.069	3.13
5.0	0.10	2.12
8.0	0.131	1.89
10.0	0.151	1.37
20.0	0.251	1.09

is no influence of ionic strength on the reaction as is clear from Table 5.

vi) Solvent influence is similar to what is found in Os(VIII)-catalyzed reaction (Table 6).

vii) Species of Ru(III): It is well known that Ru^{+3} mainly exists as $[Ru(H_2O)_6]^{3+}$ in acid medium.[7)]

viii) The study was carried out at different temperatures in the range 30—40 °C. Rate constants are listed in Table 9. The plot of $\log k_0$ *vs.* $1/T$ is linear. From the slope of the above plot Arrhenius parameters were computed as listed in Table 9. These values are similar to those obtained in the case of Os(VIII)-catalyzed reactions.

TABLE 8. EFFECT OF VARIATION OF ACID AT CONSTANT IONIC STRENGTH

[V(IV)]=0.01 M, $[IO_3^-]=0.5\times10^{-3}$ M, $[NaClO_4]=0.2$ M, [Ru(III)]$=7.64\times10^{-7}$ M, temp=35 °C

$\frac{[HClO_4]}{10^{-2}\ \text{M}}$	$\frac{k_0}{10^{-6}\ \text{mol l}^{-1}\ \text{min}^{-1}}$
0.5	1.57
1.0	1.09
2.0	0.84
4.0	0.49

TABLE 9. EFFECT OF VARIATION OF TEMPERATURE AND THERMODYNAMIC PARAMETERS AT 35 °C

[V(IV)]=0.01 M, $[IO_3^-]=0.5\times10^{-3}$ M, $[HClO_4]=0.01$ M.

Catalyst	$\frac{T}{°\text{C}}$	$\frac{k_0}{10^{-6}\ \text{mol l}^{-1}\ \text{min}^{-1}}$
[Ru(III)] 7.64×10^{-7} M	30	2.37
	35	3.77
	45	9.84

$\frac{\Delta E^*}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^*}{\text{kJ mol}^{-1}}$	$\log_{10} A$	$\frac{\Delta S^*}{\text{J K}^{-1}\ \text{mol}^{-1}}$
73.8	71.1	5.27	−146.8

From the above findings it can be concluded that the catalytic ability of Ru(III) is in general greater than that of Os(VIII) in the present experimental conditions.

Mechanism of Oxidation. *Os(VIII)-catalyzed Oxidation*: The kinetic features observed in the Os(VIII)-catalyzed oxidation of V(IV) by iodate indicate that $VOOH^+$ is the active species. The zero-order dependence on oxidant clearly shows nonparticipation of oxidant in the rate-determining step. The mechanism of oxidation can be envisaged through a hydrolytic equilibrium between VO^{2+} and $VOOH^+$ followed by reaction between $VOOH^+$ and OsO_4 as the rate-determining step to give V(V) and Os(VII).

The Os(VII) formed oxidizes in the subsequent fast step another V(IV) entity to give Os(VI) and V(V). The generated Os(VI) is oxidized in the subsequent fast step by IO_3^- to Os(VIII), thus giving rise to the zero-order dependence with respect to oxidant. The detailed steps are represented in Scheme 1:

$$VO^{2+} + H_2O \overset{K_h}{\rightleftharpoons} VOOH^+ + H^+, \qquad (1)$$

$$VOOH^+ + OsO_4 \xrightarrow[k_1]{\text{slow}} VO_2^+ + OsO_3(OH),$$

$$OsO_3OH + VOOH^+ \xrightarrow{\text{fast}} OsO_3 + VO_2^+ + H_2O,$$

$$3OsO_3 + IO_3^- \xrightarrow{\text{fast}} 3OsO_4 + I^-.$$

Scheme 1.

Rate Law. From Equilibrium 1,

$$K_h = \frac{[VOOH^+][H]^+}{[VO^{2+}]} \text{ or } [VO^{2+}] = \frac{[VOOH^+][H^+]}{K_h},$$

$$[VO^{2+}]_T = VO^{2+} + VOOH^+$$

$$= \frac{[VOOH^+]\{H^+ + K_h\}}{K_h}$$

$$\text{or } [VOOH^+] = \frac{[VO^{2+}]_T K_h}{(H^+ + K_h)},$$

$$\text{Rate} = -\frac{d[IO_3^-]}{dt} = k_1[VOOH^+[[OsO_4]$$

$$= \frac{k_1 L_h [VO^{2+}]_T[OsO_4]}{(H^+ + K_h)}.$$

K_h is of the order of 10^{-6} and can be neglected in comparison to $[H^+]$, hence the rate law is reduced to

$$-\frac{d[IO_3^-]}{dt} = \frac{k_1K_h[VO^{2+}]_T[OsO_4]}{H^+}.$$

Ru(III)-catalyzed Oxidation. The observations noticed in the case of Ru(III)-catalyzed oxidation are analogous to those in the case of Os(VIII)-catalysed reaction, except that the dependence on substrate is fractional. The inverse dependence on acidity indicates that the active species $VOOH^+$ takes part in the reaction. The mechanism of oxidation can be postulated as a formation of an intermediate between $VOOH^+$ and $[Ru(H_2O)_6]^{3+}$ in an equilibrium step. Decomposition of the intermediate takes place in a rate-determining step with one-electron transfer between Ru(III) and V(IV) to give Ru(II) and V(V) in an innersphere mechanism without disturbing the octahedral nature of ruthenium. The Ru(II) formed then reacts with another V(IV) entity in a fast step to give Ru(I) and V(V). The Ru(I) formed is subsequently oxidized by iodate in a fast step to Ru(III), thus giving rise to the zero-order dependence with respect to oxidant. The existence of Ru(II) as an aqua ion $[Ru(H_2O)_6]^{2+}$ has been well documented and the existence of Ru(I) in complexes is well known.[8] Hence the valence states of Ru(II) and Ru(I) as intermediates have been postulated in this mechanism. Various steps involved in the reaction are represented in Scheme 2:

$$VO^{2+} + H_2O \overset{K_h}{\rightleftharpoons} VOOH^+ + H^+, \qquad (1)$$

$$[Ru(H_2O)_6]^{3+} + VOOH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Complex)}}{[Ru(H_2O)_6{}^{3+}\cdots VOOH^+]},$$

$$\underset{\text{(Complex)}}{[Ru(H_2O)_6{}^{3+}\cdots VOOH^+]} \xrightarrow[\text{slow}]{k_2} VO_2^+ + [Ru(H_2O)_6]^{2+} + H^+,$$

$$[Ru(H_2O)_6]^{2+} + VOOH^+ \xrightarrow{\text{fast}} [Ru(H_2O)_6]^+ + VO_2^+ + H^+,$$

$$3[Ru(H_2O)_6]^+ + IO_3^- + 6H^+ \xrightarrow{\text{fast}} 3[Ru(H_2O)_6]^{3+} + 3H_2O + I^-.$$

Scheme 2.

Rate Law. From Equilibrium 1,

$$K_h = \frac{[VOOH^+][H^+]}{[VO^{2+}]} \text{ or } [VO^{2+}] = \frac{[VOOH^+][H^+]}{K_h},$$

$$[VO^{2+}]_T = VO^{2+} + VOOH^+$$

$$= \frac{[VOOH^+]\{H^+ + K_h\}}{K_h}$$

$$\text{or } [VOOH^+] = \frac{[VO^{2+}]_T K_h}{(H^+ + K_h)},$$

$$\text{Complex} = \frac{k_1[Ru(III)][VOOH^+]}{(k_{-1} + k_2)},$$

$$[Ru(III)]_T = [Ru(III)] + [Complex]$$

$$= Ru(III)\left\{1 + \frac{k_1[VOOH^+]}{(k_{-1} + k_2)}\right\},$$

$$[Ru(III)] = \frac{(k_{-1} + k_2)[Ru(III)]_T}{(k_{-1} + k_2) + k_1[VOOH^+]}.$$

$$\text{or } [Ru(III)] = \frac{(k_{-1} + k_2)(H^+ + K_h)[Ru(III)]_T}{(k_{-1} + k_2)(H^+ + K_h) + k_1K_h[VO^{2+}]_T}.$$

$$\text{So, Complex} = \frac{k_1K_h[VO^{2+}]_T[Ru(III)]_T}{(k_{-1} + k_2)(H^+ + K_h) + k_1K_h[VO^{2+}]_T}$$

$$\text{or} \quad = \frac{k_1K_h[VO^{2+}]_T[Ru(III)]_T}{H^+ + K_h + k_1K_h[VO^{2+}]_T}$$

$$\left(\text{where } K_1 = \frac{k_1}{k_{-1} + k_2}\right),$$

$$\text{Rate} = -\frac{d[IO_3^-]}{dt} = k_2[\text{Complex}]$$

$$= \frac{k_2K_1K_h[VO^{2+}]_T[Ru(III)]_T}{H^+ + K_h + K_1K_h[VO^{2+}]_T}.$$

This expression is capable of explaining all the observed facts.

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