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Kinetics of Oxidation of Isopropyl Alcohol, Sorbitol, Diglycollic Acid & Tetrahydrofuran by V^{5+}

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The kinetics of oxidation of isopropyl alcohol, sorbitol, diglycollic acid and tetrahydrofuran have been investigated in aqueous sulphuric acid ($\leq 2M$). The total order of the reaction is found to be 2 for all the redox systems. The rate of oxidation increases with $[H^+]$, $[HSO_4^-]$ and μ . The nature of the probable active species has been discussed and a plausible reaction scheme suggested. The various rate parameters have also been evaluated.

OXIDATION of organic as well as inorganic substrates by V^{5+} has been extensively studied¹⁻⁵. But no detailed kinetic study has so far been made for the oxidation of isopropyl alcohol (IPA), sorbitol (Sorb), diglycollic acid (DGA), and tetrahydrofuran (THF) by V^{5+} . It was, therefore, of interest to study the kinetics of V^{5+} oxidation of these organic substrates. Orders with respect to $[V^{5+}]$ and $[Substrate]$ were determined. The effects of $[H^+]$, $[HSO_4^-]$ and ionic strength (μ) on the redox systems at 40°, 50° and 60°C were studied. From the experimental results, a feasible scheme was derived and the rate parameters computed.

Materials and Methods

NH_4VO_3 (Riedel), DGA (Fluka AG), and sorbitol (Sarabhai Merck India) were used. The other chemicals used were of Analar grade. The preparation of the oxidant- V^{5+} solution, the experimental method and the determination of the rate of V^{5+} disappearance ($-R_0$) were described earlier⁶.

Results and Discussion

Rate of V^{5+} disappearance ($-R_0$)—The kinetics of the four redox systems, V^{5+} -substrate (DGA, IPA, Sorb and THF) studied showed similar behaviour:

(i) In each system second order kinetics, first order each with respect to $[V^{5+}]$ and $[Substrate]$ was observed. The plots of $-R_0$ versus $[V^{5+}]$, $-R_0$

versus $[Substrate]$, $\log(a/a-x)$ versus time and k , (pseudo first order rate constant) versus $[Substrate]$ (Fig. 1, plots A-C) gave straight lines with zero intercepts indicating the order with respect to $[V^{5+}]$ and $[Substrate]$ being unity each. The values of second order rate constant, k , for the four redox systems were evaluated and are given in Table 1.

(ii) At constant $[HSO_4^-]$, the rate increased with increase in $[H^+]$, the plots of k versus $[H^+]$ (Fig. 1, curve E) gave straight lines with intercept on the ordinate showing that the course of oxidation took both acid dependent and acid independent paths and hence both protonated $[V(OH)_2^{3+}]$ and non-protonated (VO_2^+) species of V^{5+} may be active oxidants. Plot of $\log k$ versus $-H_0$ was linear but with slope values 0.433 to 0.2 (Fig. 1, curve H), suggesting that H_2O was taking part in the formation of transition complex⁷. Hence the following equilibrium⁴ may be operative:



(iii) Increase in the rate with increase of $[HSO_4^-]$ at constant $[H^+]$ was observed. Plots of k versus $[HSO_4^-]$ (Fig. 1, curve F) gave intercepts on the ordinate indicating that bisulphate complex $[V(OH)_2HSO_4]^+$ of V^{5+} might possibly be active along with VO_2^+ and protonated species.

The increase in the rate with $[HSO_4^-]$ as well as $[H^+]$ may be ascribed to species $V(OH)_2^{3+}$ and

TABLE 1 — RATE PARAMETERS FOR V^{5+} -REDOX SYSTEMS

{Substrate: IPA, $[H_2SO_4] = 1.5M$ and $\mu = 2.0M$; substrate: sorbitol, $[H_2SO_4] = 1.0M$ and $\mu = 1.0M$; and substrates: THF and DGA, $[H_2SO_4] = 2.0M$ and $\mu = 2.1M$ }

Substrate	$k \times 10^5$, litre mole ⁻¹ sec ⁻¹			Constants (at 50°C)			For k		
	40°C	50°C	60°C	$a \times 10^5$	$b \times 10^5$	$c \times 10^5$	ΔE kcal/mole	ΔS^\ddagger e.u. (at 323.2°K)	A litre mole ⁻¹ sec ⁻¹
IPA	0.79	1.96	4.99	0.70	0.06	0.41	18.49	-23.04	6.2×10^{11}
THF	1.11	3.72	—	1.13	0.05	0.61	24.31	-3.74	9.34×10^{11}
DGA	13.63	37.50	—	18.00	—	4.17	19.83	-1.46	9.64×10^8
Sorb	9.41	23.3	55.0	9.90	—	11.22	18.30	-18.72	5.47×10^8

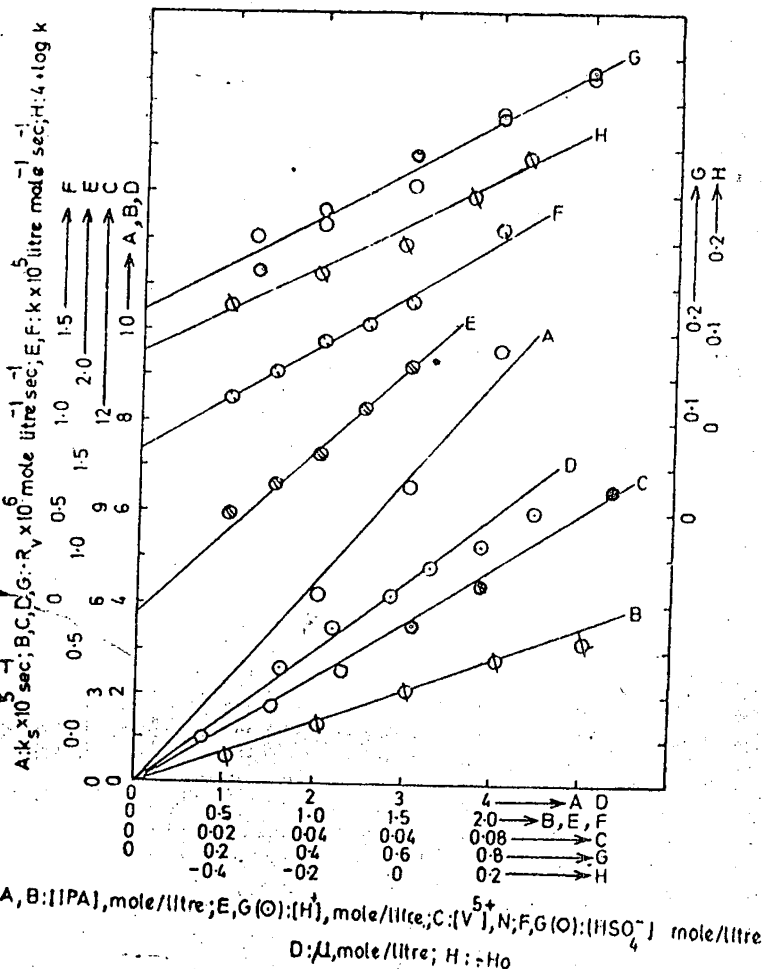
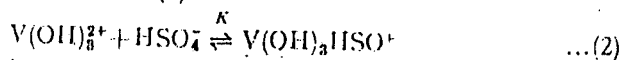


Fig. 1 — Rate plots for $V^{6+} + IPA$ system in aqueous H_2SO_4 medium (plots A to F) and $V^{6+} + Sorb$ system in aqueous H_2SO_4 medium (plots G and H) (Plot A: k_1 versus [IPA]; $[H^+] = 1.5M$, $\mu = 2.0M$ and temp. = $50^\circ C$. Plot B: $-R_v$ versus [IPA]; $[H^+] = 1.5M$, $\mu = 2.03M$, $[V^{6+}] = 0.0295N$ and temp. = $60^\circ C$. Plot C: $-R_v$ versus $[V^{6+}]$; $[H^+] = 1.5M$, $\mu = 2.0M$, [IPA] = $2.0M$ and temp. = $60^\circ C$. Plot D: $-R_v$ versus μ ; $[H^+] = 1.5M$, [IPA] = $2.0M$, $[V^{6+}] = 0.0757N$ and temp. = $50^\circ C$. Plot E: k versus $[H^+]$; $\mu = 2.045M$ and temp. = $50^\circ C$. Plot F: k versus $[HSO_4^-]$; $[H^+] = 1.5M$, $\mu = 2.045M$ and temp. = $50^\circ C$. Plot G (O): $-R_v$ versus $[HSO_4^-]$; $[H^+] = 1.0M$, $\mu = 1.022M$, [Sorb] = $0.1M$, $[V^{6+}] = 0.02253N$ and temp. = $50^\circ C$. Plots G (O) and H: $-R_v$ versus $[H^+]$ and $\log k$ versus $-H_0$ respectively; $\mu = 1.022M$, [Sorb] = $0.1M$, $[V^{6+}] = 0.02253N$ and temp. = $50^\circ C$)

$V(OH)_3HSO_4^+$ being active. The acid independent path observed in all these systems also suggested that VO_2^+ was also active. In the case of Sorb and DGA, increase of $-R_v$ with respect to both $[H^+]$ and $[HSO_4^-]$ was found to be of the same order. Therefore, the plots of k versus $[H^+]$ and that of k versus $[HSO_4^-]$ gave identical slope and intercept values. This suggested that all the $V(OH)_3^{2+}$ formed in equilibrium (1) was utilized in the formation of the bisulphato complex in accordance with the equilibrium (2).



But with the systems $V^{6+} + IPA$ and $V^{6+} + THF$ the increment in the $-R_v$ values with $[H^+]$ was less than that with $[HSO_4^-]$. The intercept value obtained from the plot of k versus $[H^+]$ and intercept of plot k versus $[HSO_4^-]$ suggested that the latter included both acid dependent and acid independent rate parameters. Therefore, possibly only a portion of $V(OH)_3^{2+}$ may be utilized in the formation of bisulphato complex.

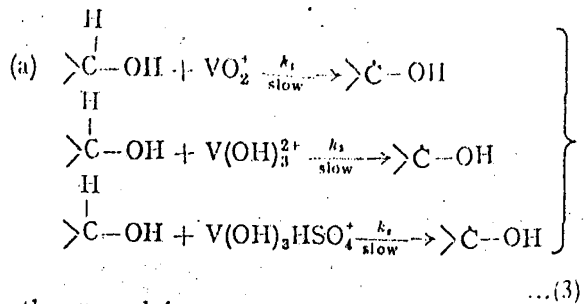
(iv) The increase in ionic strength (μ) increased the rate of V^{6+} disappearance (Fig. 1, curve-D) showing that ionic species were involved in the rate determining step.

Product analysis — The end product in the oxidation of IPA by V^{6+} was identified as acetone through its 2,4-DNP; m.p. 122° . In the case of

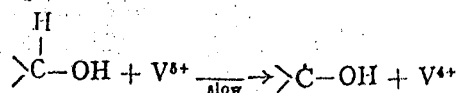
oxidation of Sorb and DGA by V^{6+} , evidence for the presence of HCHO was obtained (chromotropic acid test — purple colour).

Rate laws and rate expressions: (a) $IPA + V^{6+}$ and (b) $THF + V^{6+}$ systems — From the foregoing results the following mechanism is suggested and the rate expressions derived.

Taking into consideration equilibrium (1) and (2) and assuming $[VO_2^{+}]_{total} = [VO_2^+] + [V(OH)_3^{2+}] + [V(OH)_3HSO_4^+]$, the rate determining steps, assuming fission of C—H bond in each case, are:



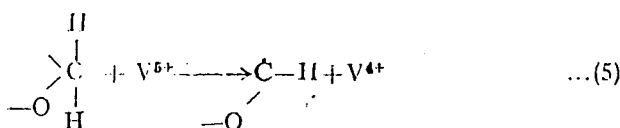
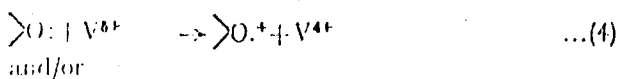
or the general form



where $V^{6+} = VO_2^+$, $V(OH)_3^{2+}$ and/or $[V(OH)_3HSO_4^+]$; $k = k_1, k_2$ and/or k_3 .

Addition of alcohols to acidic solutions of V⁵⁺ generally deepened the colour from yellow-orange to red¹, suggesting the formation of V⁵⁺-substrate complex. However, the extent of complex formation was not sufficient to be kinetically detectable. There will not be any difference in the main kinetic features even if complex formation step is included in the mechanism now proposed. Littler and Waters⁴ have suggested the complex formation in the kinetic study of V⁵⁺+ cyclohexanol though kinetic evidence for complex formation was not observed. And hence, outersphere mechanisms for the oxidations of the substrates by V⁵⁺ were suggested.

(b) The oxidative paths may involve direct attack on the etheral oxygen atom or on the C-H bond of the -CH₂- group or on both⁶:



On the basis of the reactive species in Eq. (3)

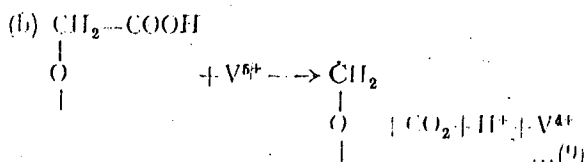
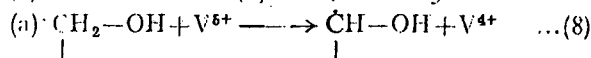
$$-R_v = k[S][\text{VO}_2^+] = k_1[\text{VO}_2^+][S] + K_1k_2[\text{VO}_2^+][S][\text{H}^+] + K_1K_2k_3[\text{VO}_2^+][\text{H}^+][\text{HSO}_4^-][S] \quad \dots(6)$$

$$k = k_1 + K_1k_2[\text{H}^+] + K_1K_2k_3[\text{H}^+][\text{HSO}_4^-] \quad \dots(7)$$

or $k = a + b[\text{H}^+] + c[\text{H}^+][\text{HSO}_4^-]$

where [S] = [IPA] or [THF]; $a = k_1$; $b = K_1k_2$ and $c = K_1K_2k_3$.

(a) V⁵⁺+Sorb and (b) V⁵⁺+DGA systems



and

$$-R_v = k_1[\text{VO}_2^+][S] + K_1K_2k_3[\text{VO}_2^+][S][\text{H}^+][\text{HSO}_4^-] \quad \dots(10)$$

$$\frac{-R_v}{[\text{VO}_2^+][S]} = k = k_1 + K_1K_2k_3[\text{H}^+][\text{HSO}_4^-] \quad \dots(11)$$

or $k = a + c[\text{H}^+][\text{HSO}_4^-]$

where [S] = [Sorb] or [DGA]; $a = k_1$ and $c = K_1K_2k_3$.

Evaluation of rate parameters— k values were evaluated by the following three methods:

(i) From the plot of $\log a/a-x$ versus time, k was evaluated ($k = \text{slope} \times 2.303/60$) which when plotted against [Substrate] gave straight line. From the slope of the latter plots, k was evaluated.

(ii) Plots of $-R_v$ versus [Substrate] and (iii) plots of $-R_v$ versus [V⁵⁺] were linear passing through origin. k was evaluated from the slopes of these plots. The average k values are given in Table 1.

Apart from k , the constants a , b and c were also computed. The plots of k versus [H⁺] at constant [HSO₄⁻] and k versus [HSO₄⁻] at constant [H⁺] gave slope = $b+c[\text{HSO}_4^-]$; intercept = a ; and slope = $c[\text{H}^+]$ and intercept = $a+b[\text{H}^+]$ respectively. Therefore, from the values of the slopes and intercepts of these plots a , b and c were evaluated for V⁵⁺+IPA and V⁵⁺+THF systems (Table 1).

In the case of V⁵⁺+Sorb and V⁵⁺+DGA systems where both the acid dependent rate and HSO₄⁻ dependent rate and the acid independent and HSO₄⁻ independent rates were identical; the plots of $-R_v$ versus [H⁺] (and [HSO₄⁻]) gave a straight line with intercept = $a[S][\text{VO}_2^+]$ and slope = $c[S][\text{VO}_2^+][\text{HSO}_4^-]$ (and $c[\text{H}^+][\text{VO}_2^+][S]$) (Fig. 1, plot G) and hence the constants a and c were computed (Table 1).

The oxidative sequence H₂SO₄ > HClO₄ observed by Littler and Waters⁴ for cyclohexanol oxidation by V⁵⁺ was encountered in the system V⁵⁺+IPA (ref. 5) ([HClO₄] = 3.0M, $\mu = 3.1M$; $k = 2.3 \times 10^{-6}$ litre mole⁻¹ sec⁻¹). Under identical conditions in H₂SO₄ medium $k = 5.43 \times 10^{-6}$ litre mole⁻¹ sec⁻¹. It, therefore, provided further evidence for the suggestion that the sulphato or the bisulphato complexes of V⁵⁺ were better oxidants than V(OH)₂³⁺ for the oxidation of alcohols.

The thermodynamic parameters ΔE and ΔS^\ddagger were calculated (Table 1) and they show an agreement with the values reported by Waters *et al.*³ ($\Delta E = 14$ to 23 kcal; $\Delta S^\ddagger = -20.0$ to -13.0 e.u.) for the systems V⁵⁺+mandelic acid, V⁵⁺+cyclohexanol, V⁵⁺+lactic acid, V⁵⁺+cyclohexanone and V⁵⁺+formic acid.

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STABILITY CONSTANTS IN AQUEOUS SOLUTION OF COMPLEXES OF URANYL ION WITH MIXED DIBASIC ACIDS

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Abstract—Systems of uranyl ion–succinic–adipic; uranyl ion–succinic–thiomalic and uranyl ion–succinic–itaconic acids were studied by pH titration method at $\mu = 0.1$ (NaClO_4) and $T = 31^\circ\text{C}$. The formation of 1:1:1 complexes was inferred from the titration curves and their stability constants are reported.

INTRODUCTION

ALTHOUGH stability constants of a number of complexes involving U^{6+} are available in literature[1], no investigation on complexes involving mixed ligand systems appears to have been made. Recently Carey and Martell[2] in their study of U^{4+} mixed ligand systems reported the relative magnitude of the equilibrium constants for combination of secondary ligands with U^{4+} -primary ligand chelates. In addition, it was stated that U^{4+} mixed ligand chelates were more stable than Th^{4+} by 1–3 log K units. Our earlier studies[3] revealed that uranyl ion formed 1:1 complexes, with a number of carboxylic acids (mono as well as di) leaving two or more co-ordinating sites free for other reactions such as hydrolysis, polymerization or olation. Addition of a bidentate ligand to these systems (1:1 complexes) could possibly fill either two more co-ordination sites or the entire co-ordination sphere of the UO_2^{2+} ion, forming thereby probably a stable mixed ligand complex (1:1:1 or 1:1:2) resistant to hydrolysis over a longer range of pH. As a part of our studies on UO_2^{2+} -mixed ligand systems by pH titration method, systems of uranyl ion–succinic–adipic; uranyl ion–succinic–thiomalic and uranyl ion–succinic–itaconic acids were studied at $\mu = 0.1$ (NaClO_4) and $T = 31^\circ\text{C}$ with a view to determine the compositions and stability constants of the complexes in the pH region 1.5–3.5 in which the hydrolysis of uranyl ion may be completely neglected[4].

EXPERIMENTAL

Materials. Preparation of uranyl perchlorate as well as other reagents and their estimations have been given earlier[3]. Succinic (Ridel, Pure), adipic (Fluka; Purum), thiomalic (Evans Chemetics, Inc.

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