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Kinetics of Oxidation of Penta-1-nol and Penta-2-nol with Chromium(VI) Influence of Some Metal Ions and Ligands

M.R. MALI, S.N. KHODASKAR and N.T. PATEL*
Department of Chemistry, Yeshwant Mahavidyalay
Nanded-431 602, India

Kinetics of oxidation of penta-1-nol and penta-2-nol by chromic acid in presence of metal ions like Mn(II), Fe(II) and complexing ligands like EDTA, salicylic acid, phthalic acid and oxalic acid in acetic acid-water mixture in H_2SO_4 medium have been studied. The rate of reaction decreases by addition of metal ions and complexing agents like salicylic and phthalic acid, but it increases by addition of oxalic acid and EDTA.

Key Words: Kinetics, Oxidation, Chromic acid, Penta-1-nol, Penta-2-nol.

INTRODUCTION

Chromic acid is one most versatile oxidizing agent and extensively used in both synthetic and kinetic investigations[1–3]. A review of literature shows that kinetics of oxidation alcohols have been studied by a number of workers[4, 5]. Influence of metal ions added and ligands on oxidation of alcohol by chromic acid was also reported[6].

In the present investigation efforts have been made to explain the influence of metal ions and complexing ligands on the rate of penta-1-nol and penta-2-nol on chromic acid, acetic acid-water mixture in H_2SO_4 medium.

EXPERIMENTAL

The substrates penta-1-nol and penta-2-nol were of extra pure quality (AR grade) and were used after redistillation. All chemicals and the acetic acid used as solvent was of AR grade. Demineralized water was used for preparation of solvent mixture.

The course of reaction was followed by determination of residual chromic acid, spectrophotometrically measuring optical density/iodometrically. The substrate was always taken in sufficient excess over Cr(VI), so that the observed kinetics was pseudo first order.

RESULTS AND DISCUSSION

Effect of varying [oxidant]: The rate of [Cr(VI)] was observed at constant [substrate] and [acid]. Although the rate of disappearance of [Cr(VI)] follows a first order rate law, the rate constants show decreasing trends with increase in initial concentration of Cr(VI) (Table-1). The decreasing trends may be due to hydrolytic equilibrium between $Cr_2O_7^{2-}$ and $HCrO_4^{7-}$.

TABLE-1
EFFECT OF VARYING [OXIDANT]

[Substrate] = 4.385×10^{-2} M; [H_2SO_4] = 0.7894 M;
[HO-Ac] = 50% v/v; Temperature = 35°C

[Cr(VI)] $\times 10^3$ M	Penta-1-nol K $\times 10^2$ min^{-1}	Penta-2-nol K $\times 10^2$ min^{-1}
4.380	4.187	5.977
3.508	5.266	7.572
1.745	6.844	9.577
1.316	8.286	10.010
0.877	9.399	10.200
0.439	10.770	10.790

Effect of variation of [substrate]: The oxidation of penta-1-nol and penta-2-nol by Cr(VI) is first order. The rate of reaction increased with increase in [substrate] (Table-2; Fig. 1).

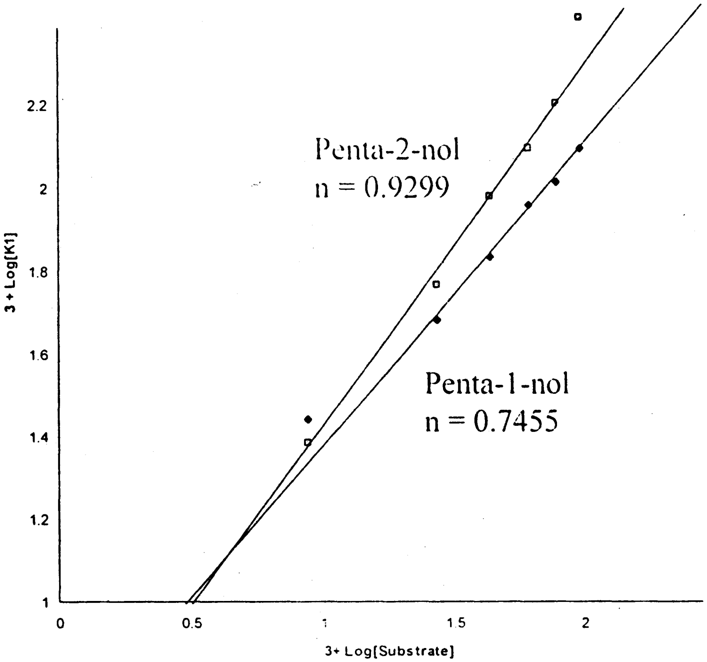


Fig. 1. Effect of varying [substrate] on rate constant ([Cr(VI)] = 1.754×10^{-3} M; [H_2SO_4] = 0.7894 M; [HO-Ac] = 50% v/v; Temperature = 35°C)

TABLE-2
EFFECT OF VARYING [PENTA-1-NOL] AND [PENTA-2-NOL] ON RATE CONSTANT

$[Cr(VI)] = 1.754 \times 10^{-3}$ M; $[H_2SO_4] = 0.7894$ M; [HO-Ac] = 50% v/v; Temperature = 35°C

Substrate $\times 10^2$ M	Penta-1-nol $K \times 10^2\ min^{-1}$	Penta-2-nol $K \times 10^2\ min^{-1}$
0.877	2.771	2.423
2.730	4.819	5.872
4.385	6.844	9.577
6.140	9.123	12.450
7.894	10.350	15.920
9.649	12.480	25.670

Effect of varying [H$^+$]: The rate of reaction was increased by increasing [H$^+$]. The results show a proportional dependence on first power of [H$^+$].

Effect of variation of solvent composition: In the present work, the rate of oxidation of alcohols has been studied in acetic acid-water mixture at varying compositions. The rates of oxidation increase with increase in acetic acid content in solvent mixture. The effect of dielectric constant of media on the rate of reaction has been studied by varying the percentage of acetic acid (20% to 70% v/v). A plot of log K *vs.* 1/D is linear which is in good agreement with the Laidler & Eyring's equation for a dipole-dipole reaction.

Effect of varying temperature: The first order rate constants were determined at temperature ranges 293 K to 323 K. The activation parameters were evaluated. The heat of activation was calculated from plots of log K *vs.* 1/T (Table-3).

TABLE-3
EFFECT OF TEMPERATURES ON REACTION RATE

$[Cr(VI)] = 1.754 \times 10^{-3}$ M; $[Substrate] = 4.385 \times 10^{-2}$; $[H_2SO_4] = 0.7894$ M; [HO-Ac] = 50% v/v

T (K)	$1/T = 10^3$ (K^{-1})	$K \times 10^4$ (sec^{-1})	log K	E_a (kcal/mol)	ΔH* (kcal/mol)	ΔS* (eu)	ΔG* (kcal/mol)	A (sec^{-1})
			Penta-1-nol					+
293	3.41	3.24	–3.49	16.39	15.81	–19.70	21.58	5.47E ± 08
303	3.30	4.62	–3.34	16.39	15.79	–20.91	22.13	3.08E ± 08
308	3.25	11.43	–2.94	16.39	15.78	–20.02	21.95	4.89E ± 08
313	3.19	17.01	–2.77	16.39	15.77	–20.11	22.07	4.74E ± 08
318	3.14	21.37	–2.67	16.39	15.76	–20.51	22.29	3.94E ± 08
323	3.10	30.96	–2.51	16.39	15.75	–20.61	22.41	3.82E ± 08
			Penta-2-nol					
293	3.41	3.90	–3.41	15.10	14.52	–23.73	21.48	7.19E ± 07
303	3.30	9.45	–3.02	15.10	14.50	–23.74	21.70	7.40E ± 07
308	3.25	15.96	–2.80	15.10	14.49	–23.54	21.74	8.32E ± 07
313	3.19	24.16	–2.62	15.10	14.48	–23.53	21.85	8.49E ± 07
318	3.14	31.97	–2.50	15.10	14.47	–23.77	22.03	7.67E ± 07
323	3.10	40.97	–2.39	15.10	14.46	–24.04	22.23	6.79E ± 07

Effect of metal ions: Effect of Mn(II): The added Mn(II) sulphate retards the rate of oxidation of Penta-1-nol and penta-2-nol by chromic acid (Table-4, Fig. 2).

TABLE-4
EFFECT OF VARYING [Mn(II)] ON RATE CONSTANT
(PENTA-1-NOL AND PENTA-2-NOL)

[Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M;
[Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

Mn(II) × 10^{-4} M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	Penta-2-nol ($K_2 \times 10^2$ min^{-1})
2.19	4.0210	6.3360
4.38	3.1990	5.7590
6.57	2.4190	2.6320
8.77	2.0720	2.3070
10.46	1.6790	2.1370
13.15	1.1140	1.8590

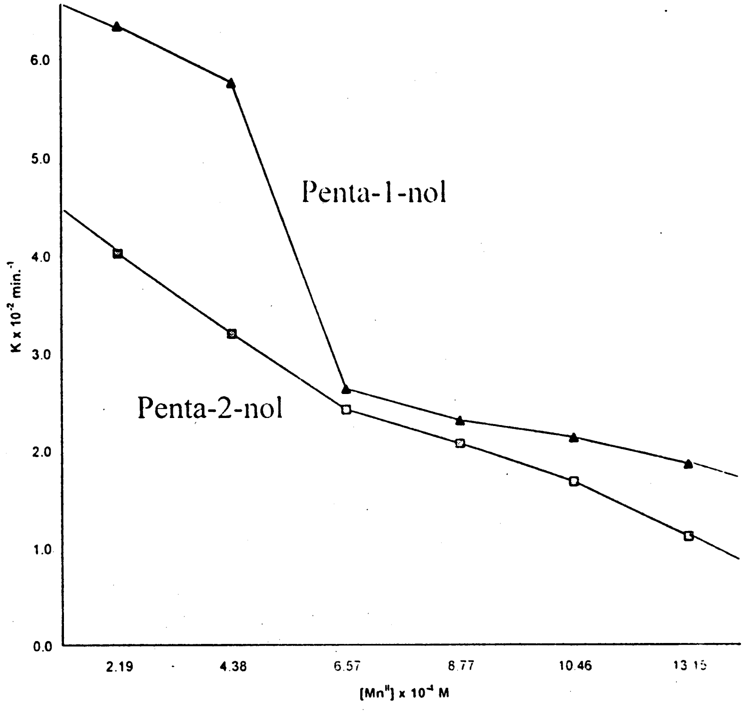


Fig. 2. Effect of Mn(II) ([Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M; Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

Generally Mn(II) retards the rate of organic and inorganic substrates[7-12]. The rate of oxidation of penta-1-nol and penta-2-nol by chromic acid decreases due to dispropottionation of Cr(IV) and Cr(V) to Cr(VI) and Cr(III) catalyzed by Mn(II).

The oxidation of alcohols with Cr(VI) may be represented as:

$$\mathrm{Cr(VI)} + \text{substrate} \xrightarrow{\text{Slow}} \text{Product} + \mathrm{Cr(IV)} \quad (1)$$

$$2\mathrm{Cr(IV)} \longrightarrow \mathrm{Cr(V)} + \mathrm{Cr(III)} \quad (2)$$

$$\mathrm{Cr(IV)} + \mathrm{Mn(II)} \longrightarrow \mathrm{Cr(III)} + \mathrm{Mn(III)} \quad (3)$$

$$\mathrm{Cr(IV)} + \mathrm{C(V)} \longrightarrow \mathrm{Cr(III)} + \mathrm{Cr(VI)} \quad (4)$$

The Mn(III) formed in step (3) being an unstable species, is likely to be used by the substrate and converted to Mn(II). The partial regeneration of Cr(VI) occurs in step (4) from reduced Cr(IV) species, in the absence of any added Mn(II). But added Mn(II) fixes the Cr(IV) species as Cr(III) and thus reduces the concentration of regenerated Cr(VI). Thus, the total concentration of Cr(VI) available in a given time is lowered by the addition of Mn(II). Consequently, the, observed deceleration increases with increasing addition of Mn(II). This view is supported by similar explanations offered to rate retardation effect by adding Mn(II) in oxidation of isopropanol[13].

Effect of [Fe(II)]: It was found that the rate of oxidation of alcohol decreased with increasing concentration of Fe(II) ions (Table-5). The curve plotted for rate constanr K *vs.* concentration of Fe(II) ions represents the effect of Fe(II) ions on the rate constant (Fig. 3). The retardation of rate constant is similar to that of Mn(II), but the extent of this effect is different. The curve plotted between K_{obs} and Fe(II) represents decrease in rate constant with increase in Fe(II). This may be explained with the following reactions:

$$\mathrm{Cr(VI)} + \text{substrate} \longrightarrow \mathrm{Cr(IV)} + \text{Product} \quad (1)$$

$$2\mathrm{Cr(VI)} + \mathrm{Fe(II)} \rightleftharpoons \mathrm{Cr(V)} + \mathrm{Fe(III)} \quad (2)$$

$$\mathrm{Cr(V)} + \mathrm{Fe(II)} \longrightarrow \mathrm{Cr(IV)} + \mathrm{Fe(III)} \quad (3)$$

$$\mathrm{Cr(IV)} + \mathrm{Fe(II)} \longrightarrow \mathrm{Cr(III)} + \mathrm{Fe(III)} \quad (4)$$

TABLE-5

EFFECT OF [Fe(II)]

[Substrate] = 4.385×10^{-2} M; [H_2SO_4] = 0.7894 M;
[Cr(VI)] = 1.754×10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

Fe(II) × 10^{-4} M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	Penta-2-nol ($K_2 \times 10^2$ min^{-1})
2.19	4.7000	5.4300
4.38	4.1600	4.7100
6.57	3.6800	2.8400
8.77	3.3000	2.2200
10.46	2.9800	1.8200
13.15	2.7400	1.4700

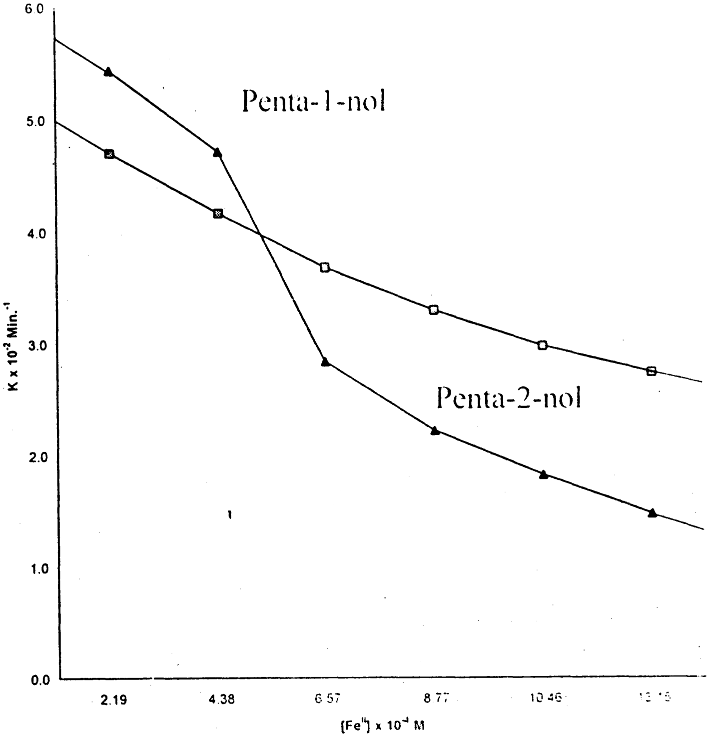


Fig. 3. Effect of Fe(II) ([Substrate] = 4.385×10^{-2} M; [H_2SO_4] = 0.7894 M; Cr(VI)] = 1.754×10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

From the above reactions the Fe(III) ion, produced by Steps (2), (3) and (4), shift the equilibrium of equation (2) towards left, which corresponds to maintaining a higher [Cr(VI)]. The rate gets retarded as more and more of Fe(II) is added[6].

Effect of [ligand]: The effect of added concentration of complexing ligand EDTA on the rate of oxidation of alcohols by chromic acid has been studied. It is observed that the rate of oxidation of alcohols increases with increase in [EDTA] (Table-6). The graphs plotted for the rate constant K *vs.* [EDTA] show the effect of [EDTA] on the rate constants (Fig. 4).

The increase in the rate constant with added [EDTA] salt is explained on the basis of formation of Cr(III)-EDTA complex[14, 15]. The mechanism of oxidation of alcohol with Cr(VI) in presence of EDTA may be represented as:

$$\text{Cr(VI)} + \text{EDTA} \longrightarrow [\text{Cr(VI)}\cdot\text{EDTA}] \tag{1}$$

$$\text{Cr(VI)}\cdot\text{EDTA} + \text{substrate} \overset{\text{slow step}}{\rightleftharpoons} [\text{Cr(IV)}\cdot\text{EDTA}] + \text{products} \tag{2}$$

$$[\text{Cr(IV)}\cdot\text{EDTA}] + \text{substrate} \xrightarrow{\text{several steps}} [\text{Cr(III)}\cdot\text{EDTA}] + \text{products} \tag{3}$$

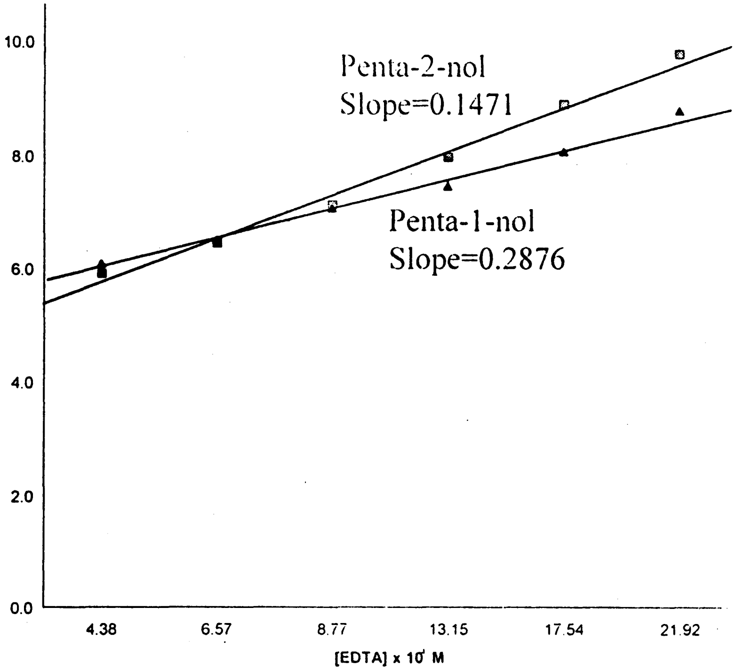


Fig. 4. Effect of [EDTA] ([Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M; Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

TABLE-6
EFFECT OF [EDTA]

[Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M;
[Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

[EDTA] × 10^{-4} M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	Penta-2-nol ($K_2 \times 10^2$ min^{-1})
4.38	5.9100	6.0700
6.57	6.4400	6.5000
8.77	7.1300	7.0500
13.15	7.9600	7.4600
17.54	8.9000	8.0600
21.92	9.7900	8.7800

The acceleration of the rate of oxidation of alcohols by EDTA can be explained by the formation of stable complex with Cr(III) ions, which would give the decrease of Cr(VI).

Effect of [oxalic acid]: When oxalic acid is added in oxidation of alcohol by chromic acid, it was found that the rate of oxidation increases with increase in addition [oxalic acid] (Table-7). The effect of added concentration of oxalic acid is represented in Fig. 5.

TABLE-7
EFFECT OF [Ox-H_2]

[Substrate] = 4.385×10^{-2} M; [H_2SO_4] = 0.7894 M;
[Cr(VI)] = 1.754×10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

[Ox-H_2] × 10^3 M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	Penta-2-nol ($K_2 \times 10^2$ min^{-1})
1.754	8.315	9.919
3.502	9.713	12.17
5.260	11.830	12.94
7.020	15.260	15.51
8.770	18.140	17.29
10.500	21.330	18.67

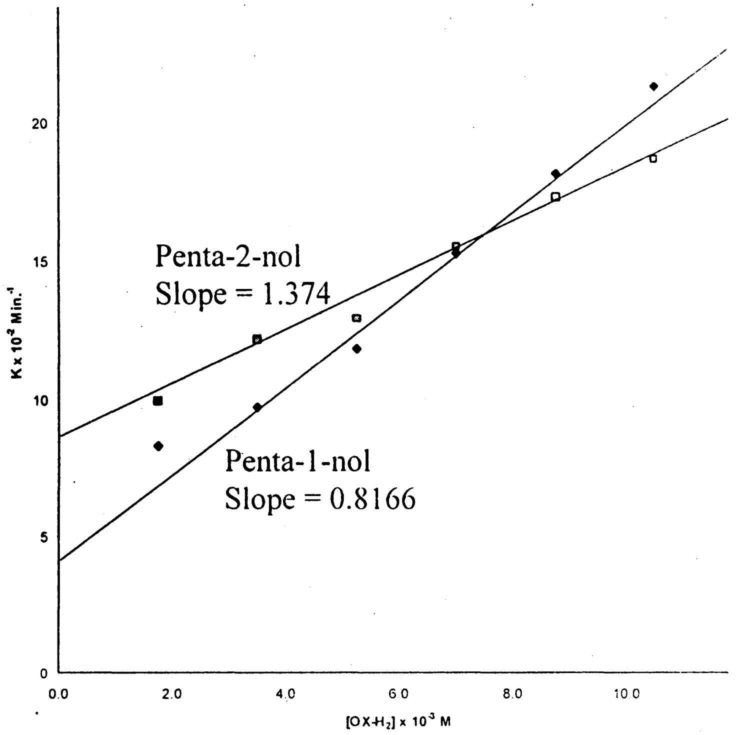
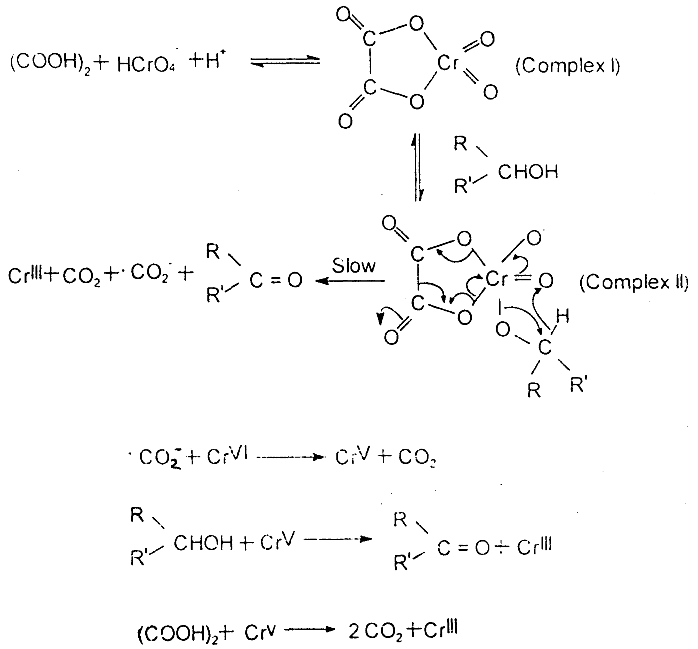


Fig. 5. Effect of [Ox-H_2] ([Substrate] = 4.385×10^{-2} M; [H_2SO_4] = 0.7894 M; Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

The co-oxidation process is responsible for increase in the rate of oxidation of alcohol by Cr(VI) in presence of oxalic acid. For secondary alcohols, the rate constant (K_{obs}) for the oxidation of alcohol and oxalic acid is several times greater than the sum of the rate constants for individual oxidation reactions. Rocek and Hasan[16] put forth a mechanism for the co-oxidation of oxalic acid.

In complex II the cleavage of Cr-O_{alc} bond would be facilitated to a larger extent by electron movement from oxalic acid moiety. This reduces positive charge on α-carbon of alcohol. The increased reactivity is also because of more reactive Cr(VI). It indicates that Cr(VI)-oxalate complex is an oxidizing species. Thus, the formation of more reactive Cr(VI) species has an enhanced reactivity due to co-oxidation, which gives an increased rate of oxidation.



Effect of added [Phthalic acid]: The rate of oxidation of alcohols decreases with increase in concentration of added phthalic acid. It is represented in Table-8 (Fig. 6).

TABLE-8

EFFECT OF $[C_6H_4(COOH)_2]$

[Substrate] = 4.385×10^{-2} M; $[H_2SO_4]$ = 0.7894 M;
[Cr(VI)] = 1.754×10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

$[C_6H_4(COOH)_2]$ $\times 10^3$ M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	Penta-2-nol ($K_2 \times 10^2$ min^{-1})
0.438	5.520	8.957
0.877	5.106	8.052
1.315	4.347	7.548
1.750	3.447	6.874
2.190	2.350	6.182
2.630	1.306	5.788

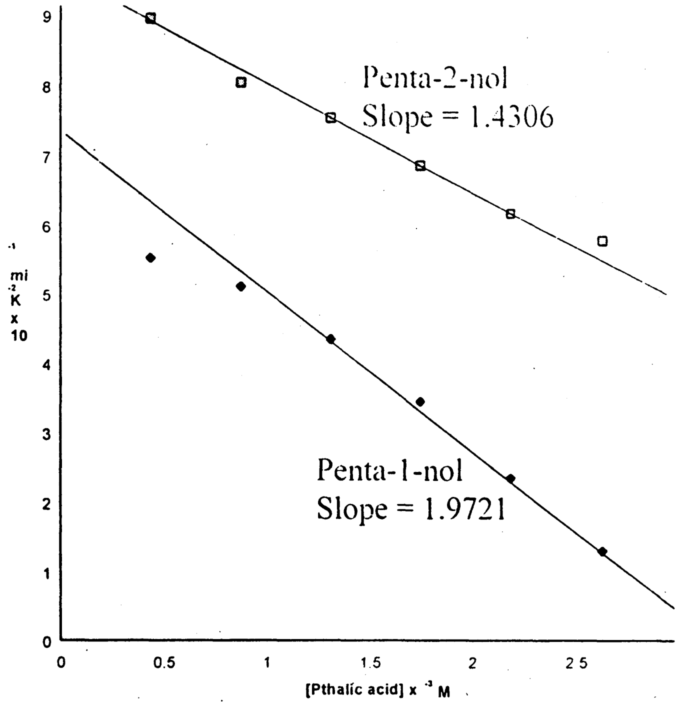


Fig. 6. Effect of $[C_6H_4(COOH)_2]$ ([Substrate] = 4.385×10^{-2} M; $[H_2SO_4]$ = 0.7894 M; Cr(VI)] = 1.754×10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

Phthalic acid is used as complexing agent. It is found that intermediate valence of transition elements can be stabilized by a suitable complexing agent. If the complex has a stability constant greater than that of aquo or aceto complex reaction, the rate can be expected to be changed on adding the complexing agent. If Cr(VI) gets reduced in rate determining to Cr(IV), where it is considered that transition state has favourable geometry for two-electron transfer in each stage, an increase in life-time of Cr(IV) by a ligand which can at the same time favour electron transfer will increase the rate of reaction, while one which inhibits such transfer may retard the rate of reaction[17]. Phthalic acid decreases the rate of oxidation of alcohols represents that it inhibits the transfer of electrons in the above process. The carboxylic acids give a decrease in the rate of oxidation of alcohols. Since acetic acid, is the reaction medium, the acetato complex provides standard comparison with other carboxylic acids. The stability of the complex depends on the size of the ring formed by chelation. The phthalic acid bidentate forms a complex with chromic acid. There is greater ease when the carboxyl group has a *cis*- confirmation. The resistance to electron transfer may be shown by the phthalic acid-chromium complex, which gives a decrease in the rate of reaction. The association of aromatic ring system does not change this aspect of carboxylic acid to decrease the rate of reaction.

Effect of Salicylic Acid: It was found that the rate of oxidation of alcohols by chromic acid decreases with increasing concentration of added salicylic acid (Table-9, Fig. 7).

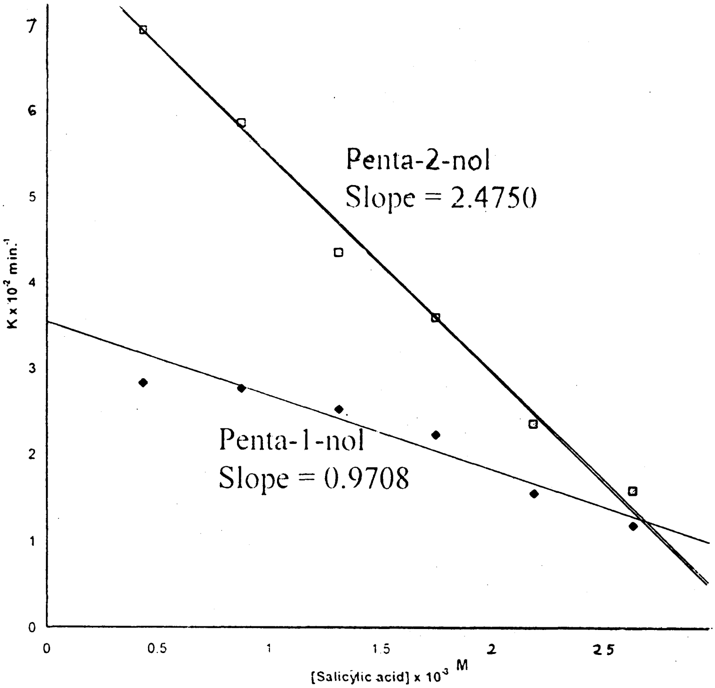


Fig. 7. Effect of [$C_6H_4(OH)(COOH)$] ([Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M; Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v; Temperature = 35°C)

TABLE-9

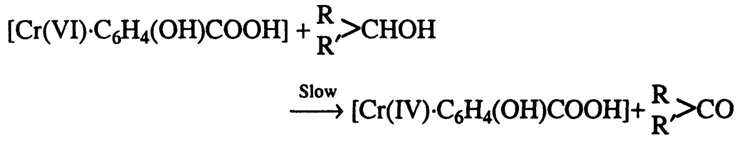
EFFECT OF [$C_6H_4OHCOOH$]

[Substrate] = 4.385 × 10^{-2} M; [H_2SO_4] = 0.7894 M;
[Cr(VI)] = 1.754 × 10^{-3} M; [HO-Ac] = 50% v/v;
Temperature = 35°C

[$C_6H_4OHCOOH$] × 10^3 M	Penta-1-nol ($K_1 \times 10^2$ min^{-1})	2-Penta-2-nol ($K_2 \times 10^2$ min^{-1})
0.438	2.816	6.916
0.877	2.750	5.848
1.315	2.509	4.344
1.750	2.220	3.582
2.190	1.540	2.351
2.630	1.175	1.576

It is found that phthalic acid has retarding effect on the rate of oxidation of alcohols. Similar retarding effect has been observed in the case of salicylic acid. Salicylic acid as a bidentate forms a complex with transition metal, *i.e.*, chromium, which may inhibit for two-electron transfer process in which Cr(VI) gets reduced to Cr(IV), similar to phthalic acid; consequently, the rate of reaction decreases. It has been found that a decrease in the rate of oxidation of alcohol due to addition of salicylic acid is greater than a fall in rate of reaction shown by addition of phthalic acid. It is due to the fact that hydroxyl group in salicylic acid donates more effectively electrons for complex formation with Cr(VI) and leads to the formation of a comparatively more stable complex.

$$\mathrm{Cr(VI)} + \mathrm{C_6H_4(OH)COOH} \rightleftharpoons [\mathrm{Cr(VI)\cdot C_6H_4(OH)COOH}]$$



$$[\mathrm{Cr(VI)\cdot C_6H_4(OH)COOH}] + {}^{\mathrm{R}}_{\mathrm{R'}}\!>\!\mathrm{CHOH} \xrightarrow{\text{Slow}} [\mathrm{Cr(IV)\cdot C_6H_4(OH)COOH}] + {}^{\mathrm{R}}_{\mathrm{R'}}\!>\!\mathrm{CO}$$

In rate determining step the added salicylic acid inhibits to two-electron transfer step; consequently the rate of oxidation of alcohol by chromic acid decreases due to addition of salicylic acid.

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