JOURNAL OF CATALYSIS 19, 300–309 (1970)

Oxidation by Co^{3+} Ions in Aqueous Acidic Media

A. MEENAKSHI AND M. SANTAPPA

Department of Physical Chemistry, University of Madras, Madras-25, India

Received January 15, 1970

Kinetics of oxidation of a wide variety of organic compounds by Co^{3+} in aqueous acidic media (H_2SO_4, $HClO_4$, or HNO_3) at constant $[H^+]$ and ionic strength, μ, in the temperature range, 5–25°C have been investigated, the organic compounds chosen being hydroxy-compounds such as benzyl alcohol, allyl alcohol, ethylene glycol, propylene glycol, propane-1,3-diol, pinacol, glycerol, sorbitol, mannitol; ketones such as acetone, ethyl methyl ketone, *n*-propyl methyl ketone, isobutyl methyl ketone, cyclopentanone; acids such as malonic, glutaric, adipic, glycolic, diglycolic, citric, aceturic, crotonic, and itaconic acids; sugars such as glucose, fructose, sucrose; and ethers such as tetrahydrofuran and dioxane. All the reactions invariably obeyed second order kinetics, the order with respect to $[CO^{3+}]$ and [substrate] each being unity. Michaelis-Menten kinetics were observed only in glutaric acid oxidation. Inverse dependence on $[H^+]$ was observed in all the oxidations (except sucrose). Retardation of rate with $[HSO_4^-]$ and effects of μ, added Co^{2+}, and temperature were some other features studied. Relative rates of oxidation in the various acid media followed the sequence, $H_2SO_4 < HNO_3 < HClO_4$. Product analysis by VPC was carried out and the reaction stoichiometry for some oxidations, such as those of benzyl alcohol and pinacol, has been established. The rate laws have been derived and suitable reaction mechanisms were suggested. The second order rate constants (k_2), acid-independent and acid-dependent rates (a and b), the corresponding rate constant ratio, k_b/k_a and the kinetic parameters, ΔE, ΔS , and A have been evaluated and discussed.

INTRODUCTION

The kinetics of oxidation of a number of organic substrates by Co^{3+} in aqueous acidic media (*1–9*) have been a subject of detailed study for the past few decades. We have chosen for kinetic studies a series of organic compounds (hydroxy compounds, ketones, acids, carbohydrates, and ethers*) for oxidation by Co^{3+} mainly in H_2SO_4 medium. Except for preliminary notes by us (*10–12*), the oxidation kinetics of these substrates have not so far been reported. In the light of the experimental results, the rate laws are derived, oxidative paths are proposed and various rate parameters are evaluated and discussed.

EXPERIMENTAL METHODS

Cobaltic salts (sulfate, perchlorate, and nitrate) were prepared by anodic oxidation (*13*) as and when required. All the substrates and reagents employed were of AnalaR grade. Water doubly distilled and deionized over Biodeminrolit mixed bed ion exchange resin (Permutit, U.K.) was used for the preparations of reagents and solu-

---

* The terms in parentheses are the abbreviations used for the substrates: benzyl alcohol (BA), allyl alcohol (A), ethylene glycol (EG), propylene glycol (PG), propane-1,3-diol (PD), pinacol (Pin), glycerol (G), sorbitol (Sor), mannitol (Man), acetone (Ac), ethyl methyl ketone (EMK), *n*-propyl methyl ketone (PMK), isobutyl methyl ketone (BMK), cyclopentanone (CP), malonic acid (Malonic), glutaric acid (Glut), adipic acid (Adipic), Crotonic acid (Crotonic), itaconic (Itaconic), glycolic acid (Glycolic), diglycolic acid (DA), aceturic acid (NAG), citric acid (Citric), glucose (Gl), fructose (Fr), sucrose (Su), tetrahydrofuran (THF) and dioxane (D).

tions for the kinetic measurements. Experiments were conducted in long Pyrex tubes (6 × 1 in.) using a Dewar flask (capacity = 5 liters; diam = 6 in.) as the thermostat. Concentrations of Co^{3+} (initial and during the experiments) were determined by addition of excess Fe^{2+} and estimating unused Fe^{2+} by cerimetry using ferroin as the indicator. Iodimetry was employed (arresting the course of the reaction by adding KI and titrating the liberated iodine against thiosulfate using starch as the indicator) for the oxidations of easily oxidizable compounds like glycols, hydroxyacids, and carbohydrates to avoid these compounds being oxidized by Ce^{4+}, the titrant itself. Under the experimental conditions used ($[Co^{3+}] = 10^{-4}$ to $10^{-3}\,M$; $[\text{substrate}] = 10^{-3}$ to $10^{-1}\,M$, $[H^+] = 1$ to $4\,M$ and $T = 5$ to $25°C$), water oxidation and secondary oxidation of the products were negligible. $[\text{Substrate}] \gg [Co^{3+}]$ was always employed.

RESULTS AND DISCUSSION

Second order kinetics. All the oxidations were found to be of second order, first order each with respect to $[Co^{3+}]$ and [substrate]; plots of $\log a/(a-x)$ or $\log (a-x)$ vs time were linear ($a = [Co^{3+}]_0$ and $(a-x) = [Co^{3+}]_t$) showing that the order with respect to $[Co^{3+}]$ was unity. k', the pseudo-first order rate constant evaluated from the slope of these plots [$k' = \text{slope} \times (2.303/60)$] when plotted against [substrate] was found to be linear passing through the origin (Fig. 1, curve A), showing that the order with respect to [substrate] also was unity. k_2 evaluated (from the slope of the latter plots) at constant $[H^+]$ and μ at various temperatures for various substrates are reported (Tables 1–3). For glutaric acid oxidation, plots of k'^{-1} vs $[\text{Glut}]^{-1}$ were linear with intercept on the ordinate. k_t (rate constant for the disproportionation of the complex) values were evaluated from the intercepts of these plots ($k_t = 1/\text{intercept}$) in $HClO_4$ and H_2SO_4 (Table 3) and K (equilibrium constant for complex formation) values from the slope ($K = \text{intercept/slope}$) and intercept ($K = 12.35 \pm 0.1$ in $HClO_4$ and $K = 1.652 \pm 0.002$ in H_2SO_4). Alternatively, the value of K could be obtained from the slope of a plot of slope (from k'^{-1} vs $[\text{Glut}]^{-1}$ plot) vs $[H^+]$ ($K = 12.27$ in $HClO_4$). K was found to be constant, not varying with temperature.

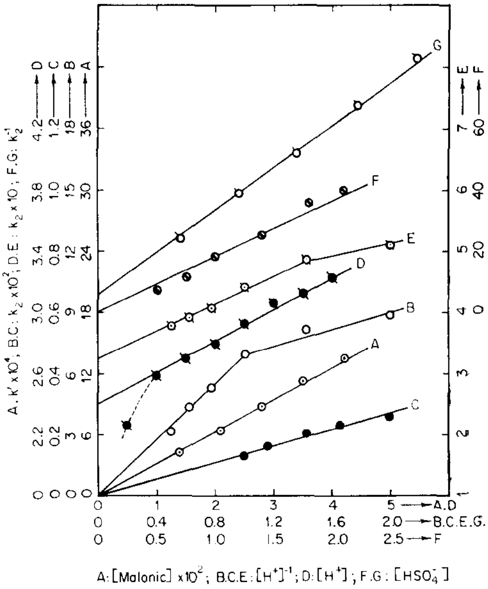


FIG. 1. Curve A: $k' \times 10^4$ vs [Malonic] $\times 10^2$; $[H^+] = 2\,M$; $\mu = 2.1\,M$; 15°C; Medium: H_2SO_4 and substrate: malonic acid. Curve B: $k_2 \times 10^2$ vs $[H^+]^{-1}$; $\mu = 2.1\,M$; 15°C; medium: H_2SO_4 and substrate: malonic acid. Curve C: $k_2 \times 10^2$ vs $[H^+]^{-1}$; $\mu = 1.2\,M$; 20°C; medium: HNO_3 and substrate: acetone. Curve D: $k_2 \times 10$ vs $[H^+]$; $\mu = 4.1\,M$; 10°C; medium: H_2SO_4 and substrate: sucrose. Curve E: $k_2 \times 10$ vs $[H^+]^{-1}$; $\mu = 2.1\,M$; 10°C; medium: H_2SO_4 and substrate: sorbitol. Curve F: k_2^{-1} vs $[HSO_4^-]$; $[H^+] = 0.5\,M$; $\mu = 2.14\,M$; 15°C; medium: H_2SO_4 and substrate: malonic acid. Curve G: k_2^{-1} vs $[HSO_4^-]$; $[H^+] = 0.555\,M$; $\mu = 2.19\,M$; 10°C; medium: H_2SO_4 and substrate: pinacol.

Variation of $[H^+]$. Variation of $[H^+]$ (0.5 to $4\,M$) at constant μ decreased the rate of oxidation except for sucrose and also for fructose at $[H^+] > 2\,M$. The effect of $[H^+]$ was much pronounced for acetone and malonic acid; plots of k_2 vs $[H^+]^{-1}$ were linear passing through the origin (Fig. 1, curves B and C). For the rest, plots of k_2 vs $[H^+]^{-1}$ were linear with intercept on the ordinate (Fig. 1, curve E), deviation from linearity at $[H^+] < 1\,M$ being observed for some alcohols, hydroxyacids, etc. The inverse

TABLE 1

RATE PARAMETERS FOR ALCOHOLS AND CARBOHYDRATES[a]

Medium: H_2SO_4; $[H^+] = 2.0\,M$; $\mu = 2.1\,M$ (Gl, Fr, and Su at 4 MH^+ and 4.1 M μ).

	$k_2 \times 10^2$ (M^{-1} sec^{-1})					
Substrate	5°C	10°C	15°C	ΔE (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u. mole^{-1})	A (M^{-1} sec^{-1})
BA	6.00	14.00	37.50	27.2	33.9	1.49×10^{20}
A	9.23	22.52	48.62	27.0	33.9	1.54×10^{20}
EG	3.41	8.00	18.89	27.9	35.0	2.61×10^{20}
Pin	1.78	4.17	9.17	26.7	29.4	1.59×10^{19}
Pin ($HClO_4$)	3.36	8.38	18.89	26.2	28.9	1.25×10^{19}
PG	11.25	28.40	66.85	27.5	36.2	4.84×10^{20}
PD	7.00	16.25	37.50	26.7	32.2	6.52×10^{19}
G	14.71	40.00	106.7	31.2	50.0	4.88×10^{23}
Sor	17.5	45.45	135.7	31.2	50.4	6.20×10^{23}
Man	14.77	42.85	110.0	31.1	49.5	3.90×10^{23}
Gl	7.06	16.94	40.0	27.5	35.0	2.64×10^{20}
Fr	8.00	22.62	48.44	26.7	32.7	8.42×10^{19}
Su	18.33	34.93	69.44	21.4	14.9	1.08×10^{16}

[a] All the rate parameters (Tables 1 to 6) are subject to ±5% error (estimated by least square method).

dependence of rate on $[H^+]$ may be ascribed to the equilibrium (1)

$$Co(H_2O)_6^{3+} \overset{K_1}{\rightleftharpoons} Co(OH)(H_2O)_5^{2+} + H^+, \qquad (1)$$

and the participation of $Co(OH)^{2+}$ as the oxidant in the reaction. If $Co(OH)^{2+}$ alone were the active oxidant, the plot of k_2 vs $[H^+]^{-1}$ would be passing through the origin. On the other hand if both Co_{aq}^{3+} and $Co(OH)^{2+}$ are the active species, such a plot would leave an intercept on the ordinate, the latter being due to Co_{aq}^{3+} as the active species. Deviation from linearity in the plot of k_2 vs $[H^+]^{-1}$ at $[H^+] < 1\,M$ might be explained on the basis of dimers of Co^{3+} (present at this low acidity) also taking part in the reaction. Direct acidity dependence observed in sucrose oxidation

TABLE 2

RATE PARAMETERS FOR KETONES AND ETHERS

$[H^+] = 1.0\,M$; $\mu = 1.2\,M$ (THF and CP in H_2SO_4 at 2 MH^+ and 2.1 M μ).

		$k_2 \times 10^3$ (M^{-1} sec^{-1})					
Substrate	Medium	15°C	20°C	25°C	ΔE (kcals mole^{-1})	$\Delta S^{\ddagger}$ (e.u. mole^{-1})	A (M^{-1} sec^{-1})
Ac	HNO_3	0.61	1.18	2.24	22.4	4.5	5.82×10^{13}
EMK	H_2SO_4	3.00	6.56	14.73	27.1	24.1	1.09×10^{18}
	HNO_3	6.33	12.77	20.97	20.6	3.1	2.83×10^{13}
	$HClO_4$	7.35	14.89	25.00	22.0	8.0	3.28×10^{14}
PMK	H_2SO_4	3.75	7.93	16.96	25.6	19.2	9.20×10^{16}
	HNO_3	5.95	11.82	20.00	20.8	3.5	3.51×10^{13}
BMK	HNO_3	1.34	2.83	6.05	25.3	16.2	2.08×10^{16}
CP	H_2SO_4	14.19	27.36	56.66	21.2	6.6	1.67×10^{14}
	$HClO_4$	23.33	44.73	91.66	21.5	8.8	4.99×10^{14}
THF	H_2SO_4	3.16	9.00	27.08	33.1	44.7	3.64×10^{22}
D	H_2SO_4	18.71	36.96	73.08	22.9	13.1	4.29×10^{15}
	$HClO_4$	22.43	45.00	104.8	25.7	23.3	7.427×10^{17}

TABLE 3

RATE PARAMETERS FOR ACIDS

$[H^+] = 2\,M$; $\mu = 2.1\,M$; (for Crotonic and Itaconic $[H^+] = 1\,M$; $\mu = 1.2\,M$).

Substrate	Medium	$k_2 \times 10^3$ (M^{-1} sec^{-1}) [for glut, $k_t \times 10^3$ (sec^{-1})]					ΔE (kcal mole^{-1})	$\Delta S^\ddagger$ (e.u. mole^{-1})	A (M^{-1} sec^{-1})
		5°C	10°C	15°C	20°C	25°C			
Malonic	H_2SO_4	—	13.08	31.75	74.35	—	29.8	38.2	1.32×10^{21}
	$HClO_4$	—	—	126.7	300.0	750	31.1	45.2	4.5×10^{22}
Adipic	H_2SO_4	—	—	2.64	7.40	18.9	34.3	48.8	2.76×10^{23}
NAG	H_2SO_4	35.72	84.2	208.4	—	—	27.5	33.7	1.38×10^{20}
Crotonic	H_2SO_4	—	—	1.54	3.67	9.52	30.5	34.5	2.12×10^{20}
Itaconic	$HClO_4$	5.41	15.0	38.8	—	—	29.8	38.3	1.41×10^{21}
Glycolic	H_2SO_4	92.87	210.5	500	—	—	26.9	33.3	1.15×10^{20}
DA	H_2SO_4	80	189.4	421	—	—	27.0	33.6	1.33×10^{20}
Citric	H_2SO_4	47.5	100	219.3	—	—	23.9	21.3	2.76×10^{17}
Glut	H_2SO_4	—	—	1.0	2.00	4.0	21.8	3.6	3.63×10^{13}
	$HClO_4$	—	—	1.11	2.5	6.25	28.2	25.7	2.49×10^{18}

(plot of k_2 vs $[H^+]$ was linear with intercept) (Fig. 1, curve D) might be due to the acid-catalyzed hydrolysis of sucrose and the products of hydrolysis being oxidized along with sucrose by Co^{3+}. Increase in rate with $[H^+]$ for fructose at $[H^+] > 2\,M$ may be due to the enolic form of the ketose being active at high acidities.

Variation of $[HSO_4^-]$. Increase in $[HSO_4^-]$ (0.5 to $2\,M$) at constant $[H^+]$ as well as μ depressed the rate of oxidation in all the oxidations. This retarding effect might be due to the formation of inactive sulfato complexes like $CoSO_4^+$, $Co(SO_4)_2^-$, etc. on the addition of HSO_4^- (*14*). Under the experimental conditions ($[HSO_4^-] = 0.5$ to $2\,M$), $CoSO_4^+$ would be preponderant. The depletion of the active species of Co^{3+} by bisulfate would be represented preferably by equilibrium (2) rather than equilibrium (3).

$$Co(OH)^{2+} + HSO_4^- \overset{K_2}{\rightleftharpoons} CoSO_4^+ + H_2O, \quad (2)$$

$$Co_{aq}^{3+} + HSO_4^- \overset{K_3}{\rightleftharpoons} CoSO_4^+ + H^+. \quad (3)$$

The above suggestion gains support from the fact that the plot of k_2^{-1} vs $[HSO_4^-]$ was linear passing through the origin (Fig. 1, curve F) in the oxidation of malonic acid for which $Co(OH)^{2+}$ alone was found to be the active species. Depletion of $Co(OH)^{2+}$ by HSO_4^- by equilibrium (2) would facilitate equilibrium (1) and hence more of Co^{3+} would be converted into $CoSO_4^+$. Plots of k_2^{-1} vs $[HSO_4^-]$ for the rest of the oxidations were linear with intercept on the ordinate (Fig. 1, curve G).

Effect of ionic strength. Increase in ionic strength (μ) at constant $[H^+]$ decreased the rate in H_2SO_4 and increased the rate slightly in $HClO_4$ and HNO_3 media. As $NaHSO_4$ was used to adjust μ in H_2SO_4, the effect of μ would be due to HSO_4^- or the effect of μ on equilibria (1) and (2). The increase in rate with μ in $HClO_4$ and HNO_3 ($NaClO_4$ and $NaNO_3$ were used, respectively, to adjust μ) might be due to the effect of μ on equilibrium (1) or the formation of weak ion pairs like Co(III) ClO_4^- and Co(III) NO_3^-, respectively.

Effect of added Co^{2+}. Acceleration of rate with added Co^{2+} (0 to $100 \times 10^{-3}\,M$; $[Co^{2+}]/[Co^{3+}] \simeq 50$) at constant $[H^+]$ and μ was observed in most of the oxidations and this could be ascribed to Co^{2+}–Co^{3+} equilibrium. The marked increase in rate observed in the oxidations of the substrates malonic acid and citric acid might be due to the formation of Co^{2+}–substrate complex and the complex being more active than the substrate.

Temperature dependence. The increase in rate with temperature was unusually high. Contrary to $k_{t+10}/k_t \simeq 2$ to 3,

$k_{t+5}/k_t \simeq 2$ to 3 was obtained giving rise to high values of energies of activation. From the plot of log k_2 vs $1/T$, ΔE values were computed for all the oxidations ($\Delta E =$ slope $\times$ 4.576) and presented (Tables 1–3).

Entropies of activation ($\Delta S\ddagger$) and pre-exponential factors (A) were evaluated for all the oxidations at 15°C (Tables 1–3).

Nature of the active species and relative rates of oxidation in the various acid media. Effects of [H^+] and [HSO_4^-] were useful in elucidating the nature of active species of Co^{3+}. $Co(OH)^{2+}$ was assumed to be the active oxidant for malonic acid and acetone, $Co_{aq}{}^{3+}$ for glutaric acid and sucrose, and both $Co_{aq}{}^{3+}$ and $Co(OH)^{2+}$ were found to be the active species for other substrates. Retarding effect of [HSO_4^-] showed that $Co(SO_4)^+$ or other sulfate complexes were not the active species. The relative rates of oxidation in the various acid media were found to follow the sequence, $H_2SO_4 < HNO_3 < HClO_4$ (Table 4). This fact should be explained not only in terms of redox potential but also the presence of sulfato complexes in H_2SO_4 medium.

Oxidative paths and rate laws. (i) Taking into consideration benzyl alcohol as the representative substrate the rate law can be derived based on the following oxidative path.

$$Co_{aq}{}^{3+} + C_6H_5CH_2OH \xrightarrow{k_a} C_6H_5\dot{C}HOH + H^+ + Co^{2+}, \quad (4)$$

$$Co(OH)^{2+} + C_6H_5CH_2OH \xrightarrow{k_b} C_6H_5\dot{C}HOH + H_2O + Co^{2+}, \quad (5)$$

$$Co_{aq}{}^{3+} + C_6H_5\dot{C}HOH \xrightarrow{k_c} C_6H_5CHO + H^+ + Co^{2+}, \quad (6)$$

$$Co(OH)^{2+} + C_6H_5\dot{C}HOH \xrightarrow{k_d} C_6H_5CHO + H_2O + Co^{2+}. \quad (7)$$

Assuming steady state concentration for the radical $C_6H_5\dot{C}HOH$, and assuming that $[Co^{3+}]_T = [Co_{aq}{}^{3+}] + [Co(OH)^{2+}] + [Co(SO_4)^+]$ and equilibria (1) and (2) are operative, it is easy to derive the Eq. (8) for the observed rate constant, k_2:

$$\frac{-d[Co^{3+}]_T}{dt} \Big/ [Co^{3+}]_T[BA] = k_2 = 2\left\{k_a + \frac{k_bK_1}{[H^+]}\right\} \times \left\{\frac{1}{\left(1 + \frac{K_1}{[H^+]} + \frac{K_2K_1[HSO_4^-]}{[H^+]}\right)}\right\}. \quad (8)$$

Since $K_1 \ll [H^+]$ and assuming that K_2K_1 [HSO_4^-] is also negligible, Eq. (8) would be reduced to Eq. (9).

$$k_2 = 2\left\{k_a + \frac{k_bK_1}{[H^+]}\right\} = n\left\{k_a + \frac{k_bK_1}{[H^+]}\right\} = a + \frac{b}{[H^+]}, \quad (9)$$

where n represents the number of cobaltic ions required to produce the final product. This rate law [Eq. (9)] was obeyed by benzyl alcohol. Reactions (6) and (7) may be considered rather important, $C_6H_5\dot{C}HOH$ being a stable radical. A rate law similar to (9) was applicable to most of the oxi-

TABLE 4

Relative Rates in the Various Acid Media

	$k_2 \times 10^3$ (M^{-1} sec^{-1}) at 5°C			$k_2 \times 10^3$ (M^{-1} sec^{-1}) at 15°C		
Substrate	H_2SO_4 medium	$HClO_4$ medium	Substrate	H_2SO_4	HNO_3	$HClO_4$
BA	60.0	162.5	EMK	3.00	6.33	7.35
A	92.32	106.4	PMK	3.75	5.95	8.28
EG	34.07	45.0	BMK	—	1.34	2.15
Pin	17.77	33.61	CP	17.3	—	23.33
Sor	175.0	305.6	Malonic	31.75	—	126.7
Man	147.7	160.0	Adipic	2.64	—	10.52
NAG	35.72	69.33	Crotonic	1.54	—	2.74
Glycolic	92.87	208.4	THF	4.17	—	5.83
DA	80.00	187.5	D	18.71	—	22.43

TABLE 5

VALUES OF a, b, AND k_b/k_a

Medium: H_2SO_4; $\mu = 2.1\,M$.

Substrate	T (°C)	$a \times 10^2$	$b \times 10^2$	k_b/k_a
BA	5	4.1	2.63	131
A	10	15.5	7.03	68
EG	5	2.6	2.03	160
PG	10	17.0	10.72	94
PD	10	7.5	16.07	321
Pin	10	3.1	2.5	121
Pin ($HClO_4$)	15	7.0	20.84	342
G	10	29.5	11.91	60
Sor	10	32.5	11.0	51
Man	10	33.0	11.54	52
CP	20	2.48	0.32	11
Adipic	20	0.6	0.27	37
Glycolic	10	14.4	4.67	48
DA	10	11.3	5.46	94
Citric	10	7.56	1.25	25
NAG	10	6.4	1.67	39
THF	20	1.07	0.16	13
Malonic	15	—	6.82	—
Malonic ($HClO_4$)	20	—	60.94	—

dations except those mentioned under (ii) and (iii) below (values of "a" and "b" appear in Tables 5 and 6).

(ii) For malonic acid and acetone, the rate law $k_2 = b/[H^+]$ can be derived on similar lines considering $Co(OH)^{2+}$ alone as the active oxidant.

(iii) Glutaric acid oxidation, where direct kinetic evidence for complex formation (glutaric acid–Co^{3+}) was observed, obeyed the following rate laws:

$$\frac{1}{k'} = \frac{1}{k_t} + \frac{[H^+]}{k_t K\,[\text{Glut}]} \tag{10}$$

in $HClO_4$ and in $[H_2SO_4] < 1\,M$;

TABLE 6

VALUES OF a, b, AND k_b/k_a

$\mu = 1.2\,M$ (for Su alone, $\mu = 4.1\,M$).

Substrate	Medium	T (°C)	$a \times 10^3$	$b \times 10^3$	k_b/k_a
Ac	HNO_3	20	—	1.33	—
EMK	H_2SO_4	20	4.85	1.19	20
	HNO_3	20	5.8	4.58	65
	$HClO_4$	20	9.6	3.29	28
PMK	HNO_3	20	5.2	5.79	92
BMK	HNO_3	25	3.1	3.42	68
CP	$HClO_4$	20	29.5	12.5	35
Crotonic	H_2SO_4	20	2.2	1.75	65
Itaconic	$HClO_4$	15	19.5	15.0	88
D	H_2SO_4	20	26.8	3.57	11
	$HClO_4$	20	34.0	11.00	27
Su	H_2SO_4	10	240	20	—

$$\frac{1}{k'} = \frac{1}{k_t} + \frac{k_t}{k_t K}\frac{1}{[\text{Glut}]} \tag{11}$$

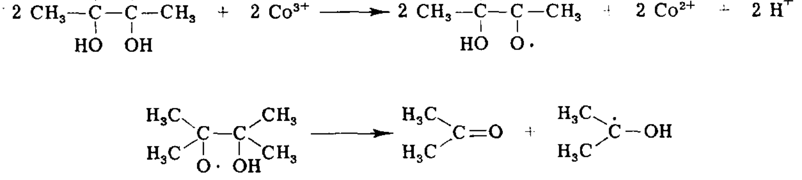
in $[H_2SO_4] > 1\,M$.

In deriving rate laws for reactions in $HClO_4$ and HNO_3 media, it was assumed that $[Co^{3+}]_T = [Co_{aq}{}^{3+}] + [Co(OH)^{2+}]$.

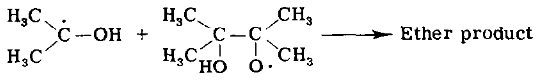
(iv) Oxidative paths for some of the substrates may be represented briefly as given below. C–H fission for allyl alcohol was assumed [cf. oxidation of allyl alcohol by V^{5+} and of substituted alyl alcohols by chromic acid (*15*, *16*)].

$$CH_2 = CH\text{-}CH_2OH + Co^{3+} \rightarrow CH_2 = CH\text{-}\dot{C}HOH + H^+ + Co^{2+}.$$

An interesting feature observed is that polymerization of allyl alcohol ($>10^{-1}\,M$) could be initiated by Co^{3+}. But under the conditions of the experiment (10^{-3} to $10^{-2}\,M$), no polymerization occurred. Pinacol might involve O–H bond fission:



A reaction of the type,

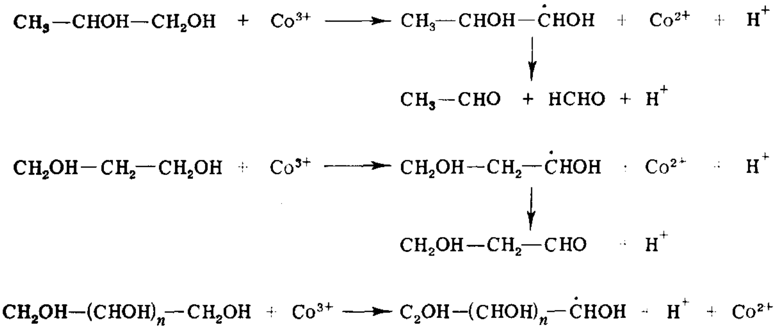


might follow yielding the stoichiometry ($-\Delta[\mathrm{Co}^{3+}]/\Delta[\text{acetone}] = 2$) observed by us contrary to that observed (~ 1) in the oxidations by other metal ions (*17–19*). Increase in stoichiometry in presence of acrylamide ($-\Delta[\mathrm{Co}^{3+}]/\Delta[\text{acetone}] = 3$) could be explained by termination of the polymer radical by Co^{3+}:

$$\mathrm{M}_n^{\cdot} + \mathrm{Co}^{3+} \rightarrow \text{polymer} + \mathrm{Co}^{2+}.$$

For ethylene glycol, an oxidative route involving O–H bond fission might be suggested.

Oxidations of propylene glycol, propane-1,3-diol, glycerol, sorbitol, and mannitol may be depicted by the following routes:

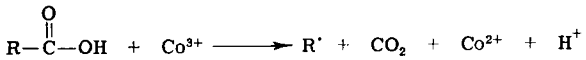


$$\mathrm{CH_3{-}CHOH{-}CH_2OH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{CH_3{-}CHOH{-}\dot{C}HOH} + \mathrm{Co}^{2+} + \mathrm{H}^+ \;\downarrow\; \mathrm{CH_3{-}CHO} + \mathrm{HCHO} + \mathrm{H}^+$$

$$\mathrm{CH_2OH{-}CH_2{-}CH_2OH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{CH_2OH{-}CH_2{-}\dot{C}HOH} + \mathrm{Co}^{2+} + \mathrm{H}^+ \;\downarrow\; \mathrm{CH_2OH{-}CH_2{-}CHO} + \mathrm{H}^+$$

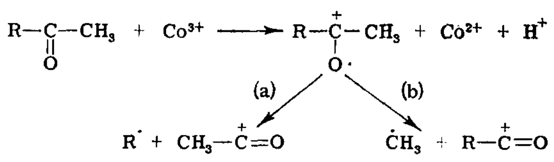
$$\mathrm{CH_2OH{-}(CHOH)_n{-}CH_2OH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{C_2OH{-}(CHOH)_n{-}\dot{C}HOH} + \mathrm{H}^+ + \mathrm{Co}^{2+}$$

ROH and $\mathrm{CH_3OH}$ could undergo further oxidation. For EMK, the products of oxidation identified by VPC are HCHO, HCOOH, $\mathrm{CH_3CHO}$, and $\mathrm{CH_3COOH}$, which indicated that along with the above mechanism involving carbonyl oxygen and cleavage of the radical cation by route (a), a mechanism involving fission of the alkyl group would also be probable. Cyclopentanone oxidation might be depicted by a path similar to cyclohexanone (*23*). For most of the carboxylic acids, the following general oxidative path [cf. Clifford and Waters (*2*)] involving O–H fission of the carboxylic group with the simultaneous evolution of $\mathrm{CO_2}$ would be probable.



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{R}^{\cdot} + \mathrm{CO_2} + \mathrm{Co}^{2+} + \mathrm{H}^+$$

Keto forms were assumed to be active for ketones since rates of oxidation $\gg$ rates of enolization for all the five ketones (*20, 21*). Acetone, ethyl methyl ketone, *n*-propyl methyl ketone, and isobutyl methyl ketone oxidations may be represented by the following oxidative (*22*) route:



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_3} + \mathrm{Co}^{3+} \longrightarrow \mathrm{R{-}\underset{\underset{\displaystyle O^{\cdot}}{|}}{\overset{+}{C}}{-}CH_3} + \mathrm{Co}^{2+} + \mathrm{H}^+$$

$$\text{(a)}\; \mathrm{R}^{\cdot} + \mathrm{CH_3{-}\overset{+}{C}{=}O} \qquad \text{(b)}\; \mathrm{\dot{C}H_3} + \mathrm{R{-}\overset{+}{C}{=}O}$$

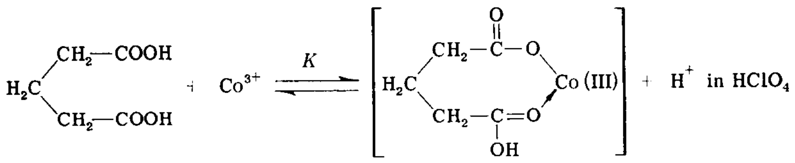
$$\mathrm{R}^{\cdot} + \mathrm{Co}^{3+} + \mathrm{H_2O} \longrightarrow \mathrm{ROH} + \mathrm{H}^+ + \mathrm{Co}^{2+}$$

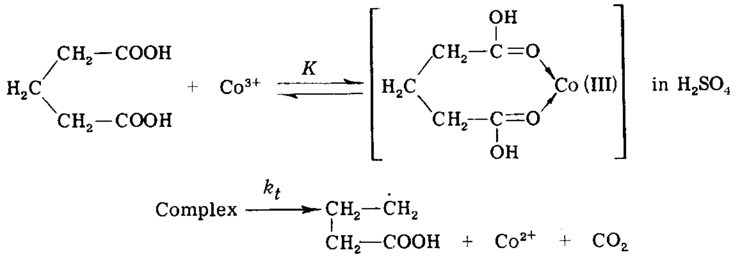
$$\mathrm{CH_3{-}\overset{+}{C}{=}O} + \mathrm{H_2O} \longrightarrow \mathrm{CH_3COOH} + \mathrm{H}^+$$

$$\mathrm{\dot{C}H_3} + \mathrm{Co}^{3+} + \mathrm{H_2O} \longrightarrow \mathrm{CH_3OH} + \mathrm{Co}^{2+} + \mathrm{H}^+$$

$$\mathrm{R{-}\overset{+}{C}{=}O} + \mathrm{H_2O} \longrightarrow \mathrm{R{-}COOH} + \mathrm{H}^+$$

Malonic oxidation alone could be represented more appropriately by C–H cleavage of the reactive methylene group [cf. oxidations by Mn^{3+}, V^{5+}, and Ce^{4+} (*24–26*)]. The complexes formed by glutaric acid in $\mathrm{HClO_4}$ and $\mathrm{H_2SO_4}$ and their disproportionation could be pictured as follows:





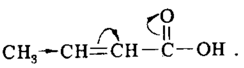
For oxidations of crotonic and itaconic acids, in addition to the general route involving the carboxylic group, cleavage of the double bond (7) is also probable. Reaction mechanisms involving fission of alcoholic C–H would be applied to glucose, fructose and sucrose; for glucose, aldehydic C–H fission also appears probable. Tetrahydrofuran and dioxane oxidations would involve the reaction path given below:

$$>O: + Co^{3+} \longrightarrow >O^{\cdot}_{+} + Co^{2+}$$

$$\text{and/or} \quad >CH_2 + Co^{3+} \longrightarrow >\dot{C}H + Co^{2+} + H^{+}$$

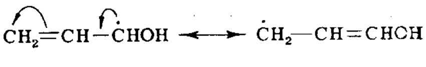
Product analysis and reaction stoichiometry. In addition to VPC, qualitative tests like chromotropic acid test were employed in the identification of HCHO, etc. for some oxidations. Benzaldehyde was found to be the product of oxidation for BA; acetone for Pin; β-hydroxypropionaldehyde for PD; HCHO and HCOOH for allyl alcohol, etc. HCHO was found to be one of the oxidation products for EG, G, Sor, Man, CP, Malonic, Glycolic, DA, THF, and D. HCHO, HCOOH, CH_3CHO, and CH_3COOH were identified in the oxidations of both PG and EMK. Oxidations of PMK and BMK gave CH_3COOH as the main oxidation product. For BA and Pin oxidations, $(-\Delta[Co^{3+}]/\Delta[C_6H_5CHO])$ and $(-\Delta[Co^{3+}]/[acetone])$ were determined, respectively, and found to be equal to 2 in each case. $-\Delta[Co^{3+}]/\Delta[acetone] = 3$ for Pin oxidation in presence of acrylamide was also determined to elucidate the course of the reaction.

The rate parameters. It was observed that polyhydric alcohols in general are rapidly oxidized while substrates like acetone and crotonic acid are less susceptible to oxidation (Tables 1–3). The large values of k_2 for polyhydric alcohols are attributed to the fact that with increased substitution of carbon atoms bearing the hydroxyl groups, the stability of the incipient radical in the activated complex should increase independent of the type of cleavage (*27*). The very slow rate of oxidation of acetone may be due to the increased hyperconjugative stabilization of the compound itself. Similarly the low value of k_2 for crotonic acid may be ascribed to the mesomeric effect stabilizing the compound itself,



$$CH_3\rightarrow CH=CH-\overset{O}{\overset{\|}{C}}-OH\ .$$

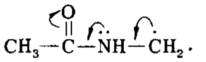
The oxidative sequence, allyl alcohol > benzyl alcohol may be attributed to the increased stability of the radical produced in the former by mesomeric effect.



$$CH_2=CH-\dot{C}HOH \longleftrightarrow \dot{C}H_2-CH=CHCH$$

Oxidation of pinacol < ethylene glycol may be explained on the basis of stringent steric

requirements for the formation of the transition complex for the former. The order of reactivity aceturic acid $\gg$ glycine (quantitative tests with glycine showed that it is oxidized very slowly by Co^{3+}) may be due to the stability of the radical,



$$CH_3-\overset{O}{\overset{\|}{C}}-\dot{N}H-\dot{C}H_2$$

The inertness of glycine may not be due to the presence of protonated nitrogen because aspartic acid (also with protonated nitrogen) is oxidized by Co^{3+} with facility (*9*).

For most of the reactions, $a > b$ or $k_a > k_b K_1$ is observed. Pinacol oxidation in $HClO_4$ and propane-1,3-diol oxidation in H_2SO_4 show the trend, $b > a$. Using the values of K_1 from literature (*28*), K_1 values at the desired temperature can be obtained by graphical extrapolation (assuming that K_1 values are not affected much with μ and the acid media). Values of k_b/k_a can be obtained employing the above K_1 values. It is observed that the values of k_b/k_a range from 11 to 342 (Tables 5, 6) and hence $Co(OH)^{2+}$ being more active than $Co_{aq}{}^{3+}$ is confirmed by these data.

$\Delta E = 20$ to 35 kcal mole^{-1} for all the oxidations observed is in good agreement with the values of ΔE found for reactions involving Co^{3+} (*2*, *3*). Similar values of ΔE for monohydric alcohols and glycols (27 ± 1 kcal mole^{-1}) and polyhydric alcohols (31 kcal mole^{-1}) may be indicative of similar reaction complexes. $\Delta E = 21 \pm 1$ kcal mole^{-1} noted for the oxidations of a number of ketones similar to the values observed for the oxidations of *m*-nitro- and *p*-nitrobenzaldehydes (*29*) by Co^{3+} may be related to the energy required for the removal of an electron from carbonyl oxygen. The higher value of ΔE for adipic acid (34 kcal mole^{-1}) may be due to the fact that the transition complex may be cyclic and hence required special orientation of the substrate. High values of A (10^{13} to 10^{23}) are similar to those observed by Clifford and Waters (*2*) and Wells (*3*). k_2 does not correspond to a simple second order rate constant. Concurrent reactions involving different active species of Co^{3+} involving prior equilibria are taking place and hence the values of A would be high. The large positive values of $\Delta S^{\ddagger}$ observed, characteristic of reactions of Co^{3+}, may be explained based on the suggestion due to Waters (*30*, *31*) that high values of $\Delta S^{\ddagger}$ are due to the concerted fragmentation involved in the breakdown of the reaction complex (*30*) and in particular to the breakdown of the d^6 structure of a Co(III) complex to give d^7 configuration of $Co(II)_{aq}$ (*31*). Since a much less symmetrical and much more loosely coordinated ion is formed, the reaction will be accompanied by a significant gain in entropy. Similar values of $\Delta S^{\ddagger}$ observed for the polyhydric alcohols may be indicative of similar activated complexes and oxidative paths. Glutaric acid oxidation in H_2SO_4 has $\Delta S^{\ddagger}$ less than that in $HClO_4$ in accordance with the structural requirements of the complexes suggested.

ACKNOWLEDGMENT

Acknowledgment is made to C.S.I.R. for the award of Junior Research Fellowship to one of the authors (A.M.).

REFERENCES

1. LITTLER, J. S., AND WATERS, W. A., *in* "Oxidation in Organic Chemistry" (K. B. Wiberg, ed.), p. 216. Academic Press, New York/London, 1965.
2. CLIFFORD, A. A., AND WATERS, W. A., *J. Chem. Soc., London* **1965**, **2796**.
3. WELLS, C. F., *Trans. Faraday Soc.* **63**, 156 (1967).
4. COOPER, T. A., AND WATERS, W. A., *J. Chem. Soc., B* **1967**, 455, 464, 687.
5. SHARAN, P. R., SMITH, P., AND WATERS, W. A., *J. Chem. Soc., B* **1968**, 1322.
6. HILL, J., AND MCAULEY, A., *J. Chem. Soc., A* **1968**, 1169, 2405.
7. SMITH, P., AND WATERS, W. A., *J. Chem. Soc. B* **1969**, 462.
8. JIJEE, K., AND SANTAPPA, M., *Indian J. Chem.* **6**, 262 (1968).
9. JIJEE, K., MEENAKSHI, A., AND SANTAPPA, M., *Z. Phys. Chem. Frankfurt am Main* **59**, 206 (1968).
10. MEENAKSHI, A., AND SANTAPPA, M., *Curr. Sci.* **37**, 43 (1968).
11. MEENAKSHI, A., AND SANTAPPA, M., *Curr. Sci.* **37**, 313 (1968).

12. Meenakshi, A., and Santappa, M., *Curr. Sci.* **38,** 311 (1969).

13. Jijee, K., Santappa, M., and Mahadevan, V., *J. Polym. Sci. Part A1* **4,** 378 (1966).

14. Sutcliffe, L. H., and Weber, J. R., *Trans. Faraday Soc.* **55,** 1892 (1959).

15. Jones, J. R., and Walters, W. A., *J. Chem. Soc., London* **1962,** 2068.

16. Burstein, S. H., and Ringold, H. J., *J. Amer. Chem. Soc.* **89,** 4722 (1967).

17. Drummond, A. Y., and Waters, W. A., *J. Chem. Soc., London* **1953,** 3119.

18. Mino, G., Kaizerman, S., and Rasmussen, E., *J. Amer. Chem. Soc.* **81,** 1494 (1954).

19. Littler, J. S., and Waters, W. A., *J. Chem. Soc., London* **1959,** 1299.

20. Dawson, H. M., and Ark, H., *J. Chem. Soc., London* **1911,** 1742.

21. Bell, R. P., and Smith, P. W., *J. Chem. Soc., B* **1966,** 241.

22. Hoare, D. G., and Waters, W. A., *J. Chem. Soc., London* **1962,** 971.

23. Littler, J. S., and Waters, W. A., *in* "Oxidation in Organic Chemistry" (K. B. Wiberg, ed.), p. 226. Academic Press, New York/London, 1965.

24. Drummond, A. Y., and Waters, W. A., *J. Chem. Soc., London* **1954,** 2456.

25. Littler, J. S., and Waters, W. A., *in* "Oxidation in Organic Chemistry" (K. B. Wiberg, ed.) p. 232. Academic Press, New York/London, 1965.

26. Yadav, R. L., and Bhagwat, W. V., *J. Indian Chem. Soc.* **41,** 389 (1964).

27. Urray, W. H., Stacey, F. W., Huyser, E. S., and Juveland, O. O., *J. Amer. Chem. Soc.* **76,** 450 (1954).

28. Sutcliffe, L. H., and Weber, J. R., *Trans. Faraday Soc.* **52,** 1225 (1956).

29. Cooper, T. A., and Waters, W. A., *J. Chem. Soc., London* **1964,** 1538.

30. Waters, W. A., *Chem. Soc. Spec. Publ.* **19,** 81 (1965).

31. Waters, W. A., *Discuss. Faraday Soc.* **46,** 197 (1968).