

## Kinetics & Mechanism of Oxidation of Nitrilotriacetic Acid with Aquo Cobaltic Ions

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The oxidation of nitrilotriacetic acid with cobaltic(III) ions in the aqueous perchloric acid has been studied over a wide range of acidities at two different ionic strengths. The kinetic data reveal that the rate of decomposition of aquo cobaltic ion in perchlorate media by nitrilotriacetic acid varies inversely with acidity in the acid concentration range 1-5M at  $\mu = 5M$  whereas it varies directly with acidity in the acid concentration 5-7M at  $\mu = 7M$ . The shift in mechanism has been found to occur at an acid concentration between 4M and 5M. The mechanisms of the oxidation at these two different stages are discussed and the activation parameters reported.

MUCH interest has been evinced in recent years on the kinetic and mechanistic features of the oxidation of organic compounds by aquo cobaltic ion. Most of the observed rates have been accounted for by a general relation,  $k_0 = a + b/[H^+]$ . Sheik and Waters<sup>1</sup> have proposed an outersphere mechanism for the oxidation of some amino acids and amines by aquo cobaltic ion without an experimental evidence for an intermediate complex. Rao<sup>2</sup> investigated the oxidation of some amino polycarboxylic acids with Ce(IV) ion and proposed an outersphere mechanism for the oxidation. Recently Russian workers<sup>3</sup> have proposed an innersphere mechanism for the same oxidation process. Hanna *et al.*<sup>4</sup> studied the oxidative decarboxylation of these acids by Ce(IV) and discussed the mechanism in terms of 'favourable and fixed geometry of nitrogen ligands'. In our recent studies on oxidation of glycine with cobaltic ion in perchloric acid medium we have proposed an innersphere mechanism<sup>5</sup>. A survey of literature shows that no detailed kinetic study has been carried out on the oxidation of amino polycarboxylic acids. The present paper deals with the kinetic aspects of the oxidation of nitrilotriacetic acid (NTA) at different acidities and ionic strengths.

### Materials and Methods

The experimental procedure has been described elsewhere<sup>6</sup>. Nitrilotriacetic acid (AR) was converted quantitatively into its trisodium salt and the pH adjusted to 7 by adding a few drops of standard perchloric acid (GR).

*Kinetic measurements* — Kinetic runs were carried out after diluting the stock solution and observing the decay in optical density of the reaction mixture in 1 cm cells at 270 nm. As it was practically impossible to study kinetics with  $[NTA] > 6 \times 10^{-3}M$ , the reactions beyond this being too fast, kinetic runs were confined below this concentration. The samples were thermostated at the desired temperature before

the kinetic runs and the reactions were followed in the thermostated cell compartment of either a Unicam 700 or SP 500 spectrophotometer, the former equipped with an external recorder and connected to an electronic timer. For the latter, an accurate stop watch was used for recording the time and reactions being fast, optical density was recorded at every 10th second for the fastest ones and at every 15th second for the slower ones.

Ionic strength of the medium was always adjusted by the addition of sodium perchlorate. Doubly distilled water was used throughout.

*Product analysis* — The oxidation products were identified to be iminodiacetic acid, glycine, formaldehyde and carbon dioxide. Formaldehyde was detected by chromotropic acid and positive Schiff reaction, while glycine and iminodiacetic acid were detected by paper electrophoresis supplemented by a paper chromatography.

The separations were effected in 1M acetic acid solution and the colour development was done in 0.6% ninhydrin solution in *n*-butanol. The current density was kept constant at 12 mA at a voltage range of 350-200 V. After each run the strips were dried in the oven at 75° for 5 min and then rapidly dipped in ninhydrin solution. These were drained and again dried in the oven at this temperature for 10 min. Test runs were compared with specimens of expected products applied concurrently in the electrophoretic cell on different paper strips.

Effervescence of carbon dioxide was remarkable when highly concentrated nitrilotriacetic acid was reacted with excess cobaltic ion solution.

All graphs were drawn to obtain the best fit by applying the method of linear regression.

The energies of activation were calculated from the Arrhenius plots of rate constants and the entropies were determined using the relation

$$\Delta S^\ddagger = R \ln \frac{Ah}{ekT}$$

## Results and Discussion

*Stoichiometry*—It has been found that stoichiometry varies with acidity in acidity ranges 1-5M and 5-7M (Table 1). However, the values reach a limiting stage after about 1 hr. When the [acid] exceeds 4M, the rates of oxidation increase and the stoichiometry also increases. The effect of acidity on the progress of the reaction as shown kinetically is thus further substantiated by the increasing stoichiometries as the acidity arises from 5.0M onwards. At lower acidities again, the reverse case conforms to the kinetic observations. Taking into consideration the competing reaction of water oxidation by Co(III) aq. at such high temperatures, appropriate values for water oxidation under identical conditions were subtracted to obtain the actual consumption of cobaltic ion in these reactions. The concentration of cobaltic ion was kept at ten-fold higher than that of the substrate in all stoichiometric samples. Determinations were performed spectrophotometrically<sup>6</sup>.

*Rate measurement in the presence of excess NTA*—The rate of disappearance of cobaltic ion in the presence of excess nitrilotriacetic acid is always first order and the data in Table 2 show that the rate is inversely proportional to acidity. There is, however, a competing trend in the rates at 4M and 5M perchloric acid. The rate increases smoothly after 5M perchloric acid. The data in Table 3 show that rate is directly proportional to acidity above 5M. Inspection of rate at two ionic strength regions shows that it is enhanced by increasing ionic strength. It has been seen that the rate of oxidation is independent of added [Co(II)] and that the rate decreases with increasing [Co(III)]. Further, in the presence of added acrylonitrile a polymer was rapidly precipitated indicating that intermediate free radicals are involved in this oxidation reaction.

*Determination of pseudo-first order rate constants*—The plots of logarithm of optical density against time were found to be linear after necessary corrections for water oxidation by cobaltic ion in the experimental temperatures. The pseudo-first order rate constants,  $k_0$ , were determined at [NTA] in the range 0.001M to 0.006M over a wide range of perchloric acid concentration keeping the ionic strength at two different values. The logarithms of optical densities against time give good linear plots up to more than 60% of Co(III) consumption, which show that pseudo-first order reaction condition still holds in the experimental range of NTA concentrations. Plots of  $k_0$  against [NTA] are not linear, as the rate constants at higher [NTA] do not follow the same sequence as at lower [NTA]. Moreover these plots make different intercepts at different acid concentrations. These observations led to the belief that intermediate complexes are formed.

*Mechanism of oxidation*—The marked changes in the rate between acidities 1 and 5M and 5 to 7M show that the equilibria involved in these two acidity ranges might be different and so separate treatments are put forward.

(i) *Mechanism of oxidation of NTA between acidities 1M and 5M*—Though equilibria (i-iv) may exist

TABLE 1 — STOICHIOMETRIES OF OXIDATION

{Initial [Co<sup>III</sup>] = 0.0129M; time 5 hr; [substrate] = 0.001M; temp. 22°}

Values at $\mu = 5M$		Values at $\mu = 7M$	
[HClO <sub>4</sub> ] M	$\Delta[\text{Co}^{\text{III}}]/[\text{NTA}]$	[HClO <sub>4</sub> ] M	$\Delta[\text{Co}^{\text{III}}]/[\text{NTA}]$
5	1.95	6.0	3.52
4	2.08	6.5	3.55
3	2.30	7.0	4.04
2	2.21	—	—
1	2.90	—	—

TABLE 2 — VALUES FOR OBSERVED RATE CONSTANTS IN THE ACIDITY RANGE 1M-5M

{ $\mu = 5M$ ; [Co<sup>III</sup>] =  $1 \times 10^{-3}M$ }

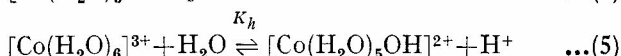
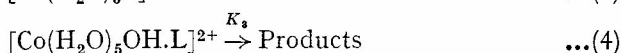
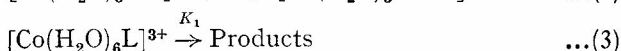
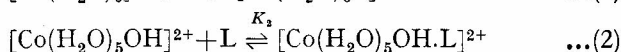
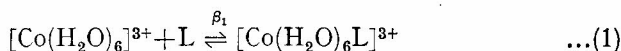
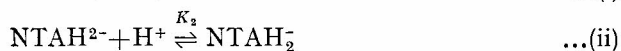
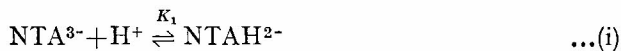
Temp. °C	[NTA] M	$k_0 \times 10^4$ (sec <sup>-1</sup> ) at [HClO <sub>4</sub> ] (M)				
		5	4	3	2	1
20	0.001	26.07	30.13	34.55	28.80	38.38
	0.002	46.65	38.38	46.05	46.05	76.77
	0.003	57.57	67.60	57.52	73.30	106.33
	0.004	61.40	76.77	80.80	88.28	117.82
	0.005	74.37	84.05	90.05	100.95	106.33
	0.006	86.37	95.95	88.28	106.28	116.97
23	0.001	27.17	20.73	24.68	28.15	70.55
	0.002	34.40	38.38	32.11	54.01	109.25
	0.003	60.32	50.96	50.06	68.21	175.50
	0.004	76.76	57.56	54.83	76.76	202.33
	0.005	116.66	81.25	68.51	95.05	196.66
	0.006	99.13	85.21	100.75	96.76	202.33
25	0.001	23.03	38.38	40.78	43.86	69.09
	0.002	46.06	53.73	60.32	69.09	93.82
	0.003	65.80	79.96	80.25	102.35	129.91
	0.004	86.36	105.55	112.59	124.01	153.53
	0.005	109.67	115.15	132.59	138.18	153.53
	0.006	139.14	138.38	153.53	153.53	170.59
27	0.001	45.36	42.89	46.06	52.10	—
	0.002	71.28	63.97	63.06	62.81	—
	0.003	103.63	80.25	92.12	108.75	—
	0.004	120.63	119.93	124.74	106.29	—
	0.005	174.00	121.54	133.06	125.62	—
	0.006	175.46	122.82	127.94	119.41	—

TABLE 3 — OBSERVED RATE CONSTANTS IN ACIDITY RANGE 5M-7M

{ $\mu = 7M$ ; [Co<sup>III</sup>] =  $1 \times 10^{-3}M$ }

Temp. °C	[NTA] M	$k_0 \times 10^4$ (sec <sup>-1</sup> ) at [HClO <sub>4</sub> ] M				
		5.0	5.5	6.0	6.5	7.0
20	0.001	46.07	46.07	49.89	65.80	98.70
	0.002	57.38	65.81	56.56	108.38	143.94
	0.003	69.10	72.93	105.55	120.63	177.15
	0.004	79.95	92.12	109.66	161.21	216.75
	0.005	108.38	138.18	126.66	175.46	230.30
	0.006	123.70	163.53	134.34	230.30	331.06
25	0.001	89.56	92.12	101.40	115.20	—
	0.002	116.20	130.00	150.23	164.42	—
	0.003	134.54	145.40	195.74	209.31	—
	0.004	157.52	169.60	219.92	242.40	—
	0.005	197.43	218.90	230.34	268.68	—
	0.006	214.90	216.80	248.00	281.50	—
27	0.001	86.36	115.20	103.60	115.22	—
	0.002	136.11	153.61	206.06	198.94	—
	0.003	150.50	172.70	230.30	230.30	—
	0.004	193.91	197.40	294.31	281.50	—
	0.005	198.90	230.31	318.98	362.00	—
	0.006	230.32	307.00	318.98	364.64	—

for NTA in the experimental conditions of acidity, the concentration of  $\text{NTA}^{3-}$  could be assumed equal to  $\text{NTAH}_3$  or  $\text{NTAH}_4^+$  and hence the individual acid association constants will not be significant, as in the case of Anderegg's data for anion formation at low ionic strength<sup>7</sup>. NTA may thus be represented as a neutral species L, in this acidity range. The reaction, under such conditions, can be visualized to take place by the steps (1-5), steps (3) and (4) rapidly following (1) and (2).



The rate is then given by Eq. (6)

$$-\frac{d\text{Co(III)}_T}{dt} = n\text{Co(III)}_{\text{aq}}L[k_1\beta_1 + k_3K_2\beta_1(\text{H}^+)^{-1}K_h] \quad (6)$$

where  $[\text{H}^+]^{-1}$  stands for reciprocals of perchloric acid concentrations.

Cobaltic ion could act either as a dimer ( $n = 1$  in Eq. 6) or as a monomer ( $n = 2$  in Eq. 6). It is generally accepted that Co(III) is mostly monomeric at acidity  $\geq 2.0M$  (ref. 8).

After substituting the terms for  $\text{Co(III)}_T$  where it is the sum of all the species of Co(III) ions in Eqs. (1), (2) and (5), and rewriting Eq. (6) we obtain

$$1/k_0 = \frac{1 + K_h[\text{H}^+]^{-1}}{2\beta_1[k_1 + k_3K_2[\text{H}^+]^{-1}]L} + \frac{1 + K_2(\text{H}^+)^{-1}}{2[k_1 + k_3K_2(\text{H}^+)^{-1}]}$$

or

$$[L]/k_0 = \frac{1 + K_h[\text{H}^+]^{-1}}{2\beta_1[k_1 + k_3K_2[\text{H}^+]^{-1}]} + \frac{[1 + K_2(\text{H}^+)^{-1}]L}{2[k_1 + k_3K_2[\text{H}^+]^{-1}]} \quad \dots(7)$$

Thus a plot of  $1/k_0$  against  $[L]$  should be linear with a slope

$$\frac{1 + K_2[\text{H}^+]^{-1}}{2[k_1 + k_3K_2[\text{H}^+]^{-1}]} \text{ and intercept } \frac{1 + K_h[\text{H}^+]^{-1}}{2\beta_1[k_1 + k_3K_2[\text{H}^+]^{-1}]}$$

Fig. 1 shows the linearity of such plots. Writing above intercept as  $I$  we can relate

$$0.5[1 + K_h[\text{H}^+]^{-1}]I^{-1} = \beta_1[k_1 + k_3K_2[\text{H}^+]^{-1}] \quad \dots(8)$$

A plot of left-hand side against  $[\text{H}^+]^{-1}$  is linear (Fig. 2) having intercept as  $\beta_1k_1$  and slope  $\beta_1k_3K_2$ . Similarly slopes ( $S$ ) and intercepts from Eq. (7) can be related as

$$S/I = \frac{1 + K_2[\text{H}^+]^{-1}}{1 + K_h[\text{H}^+]^{-1}}$$

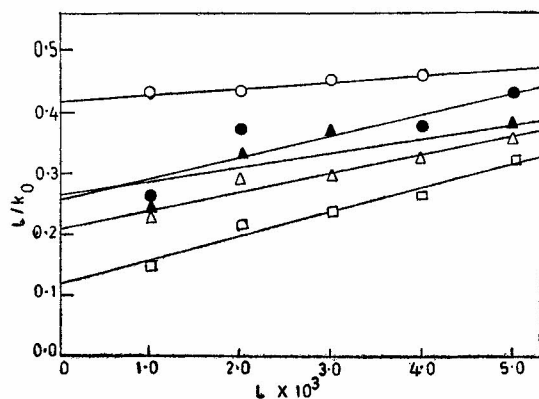


Fig. 1 — Plots of  $1/k_0$  against  $L \times 10^3$  at  $25^\circ$  ( $\mu = 5M$ )  $\{[\text{H}^+] = 5M$  (O),  $4M$  (●),  $3M$  (▲),  $2M$  (Δ),  $1M$  (□)

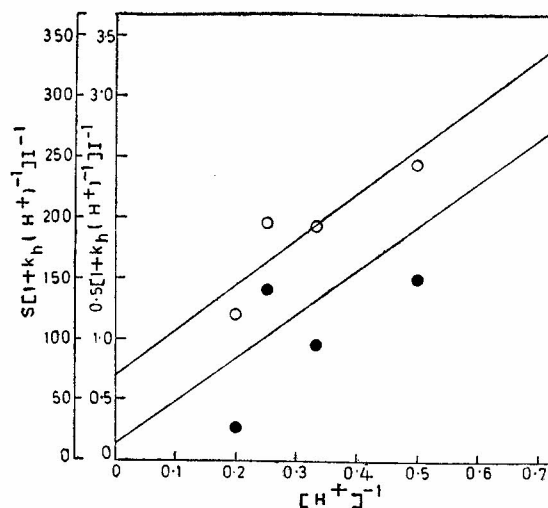


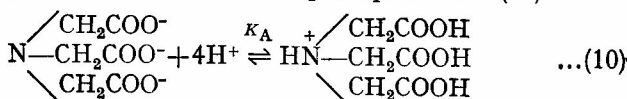
Fig. 2 — Plots at  $25^\circ$  ( $\mu = 5M$ ) of  $0.5 [1 + K_h[\text{H}^+]^{-1}]I^{-1}$  against  $[\text{H}^+]^{-1}$  (O) and  $S[1 + K_h[\text{H}^+]^{-1}]I^{-1}$  against  $[\text{H}^+]^{-1}$  (●)

or

$$S[1 + K_h[\text{H}^+]^{-1}]I^{-1} = \beta_1[1 + K_2[\text{H}^+]^{-1}] \quad \dots(9)$$

The plot of the left-hand side against  $[\text{H}^+]^{-1}$  is linear (Fig. 2) having intercept as  $\beta_1$  and slope  $\beta_1K_2$ . Thus all terms  $\beta_1$ ,  $K_2$ ,  $k_1$  and  $k_3$  can be calculated for various temperatures. Values for  $K_h$  are calculated from data of Sutcliffe and Weber<sup>9</sup>. Values for these constants are collected in Table 4.

(ii) Mechanism of oxidation of NTA between acidities  $5M$  and  $7M$  — The reactive species is proposed to involve the pre-equilibrium (10)



and in all subsequent equations, viz. 11-14 this species is represented as  $L'$ .

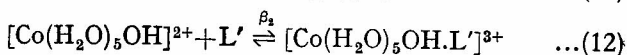
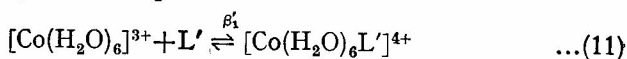
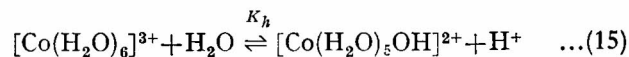
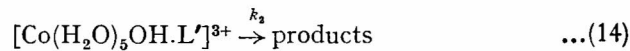


TABLE 4—VALUES FOR  $\beta_1$ ,  $k_1$ ,  $k_3$  AND  $K_2$  AT  $[\text{HClO}_4] = 1.5M$  AND  $\mu = 5M$ 

Temp. °K	$\beta_1/$ mole <sup>-1</sup>	$k_1 \times 10^3$ (sec <sup>-1</sup> )	$k_3 \times 10^3$ (sec <sup>-1</sup> )	$K_2/$ mole <sup>-1</sup>	$10^3 \times K_h/$ mole <sup>-1</sup>
293	185.70	6.95	12.07	0.82	10.14
296	95.40	10.65	5.42	2.55	12.05
298	12.53	55.61	10.25	28.79	13.49
300	12.13	132.80	4.38	60.11	15.07

$\Delta E$  for  $k_1 = 76.1$  kcal and  $\Delta S^*$  (298°) = 190.14 e.u.  
 $\Delta E$  for  $k_3 = -19.42$  kcal and  $\Delta S^*$  (198°) = -130.80 e.u.



Thus the rate is given by Eq. (16).

$$-\frac{d[\text{Co(III)}]_T}{dt} = nK_A \text{Co(III)}_{aq} \text{L}' [k_1 \beta_1' \text{H}^+ + k_2 \beta_2 K_h] \quad \dots(16)$$

Substituting for  $\text{Co(III)}_T$  and rewriting

$$k_0 = \frac{n[\text{X}]}{\beta_1' \text{H}^+ + K_h \beta_2} - \frac{k_0}{\text{L}'} \cdot \frac{1 + K_h (\text{H}^+)^{-1}}{nK_A [\text{X}]} \quad \dots(17)$$

where  $[\text{X}] = [k_1 \beta_1' \text{H}^+ + k_2 \beta_2 K_h]$ .

Thus a plot of  $k_0$  against  $k_0/[\text{L}']$  should be linear having a slope  $-\frac{1 + K_h [\text{H}^+]^{-1}}{nK_A [\text{X}]}$  and intercept

$\frac{n[\text{X}]}{\beta_1' [\text{H}^+] + K_h \beta_2}$ . Such plots are shown in Fig. 3.

Writing slope as  $S$  as before we get,

$$[1 + K_h [\text{H}^+]^{-1}] S^{-1} = nK_A [\text{X}] = nK_A [k_1 \beta_1' [\text{H}^+] + k_2 \beta_2 K_h] \quad \dots(18)$$

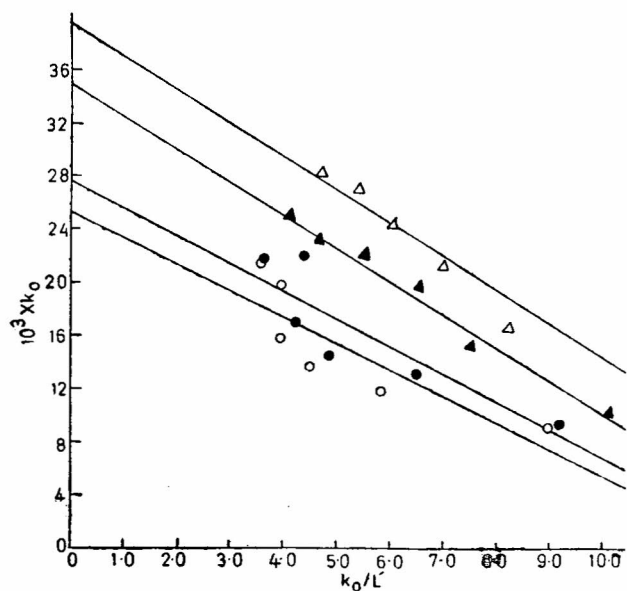


Fig. 3—Plots of  $k_0 \times 10^3$  against  $k_0/\text{L}'$  at 25° ( $\mu = 7M$ )  $\{[\text{H}^+] = 5M$  (○), 5.5M (●), 6M (▲), 6.5M (△)

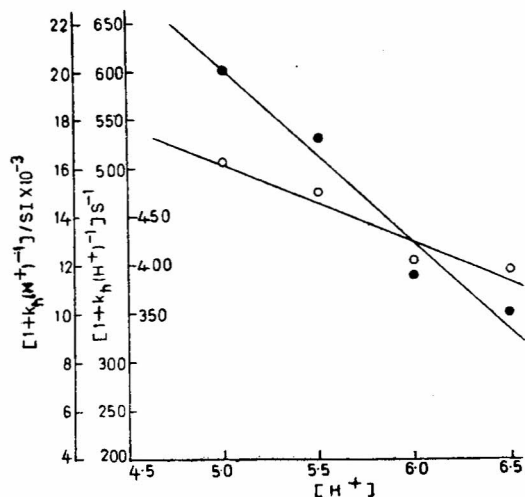


Fig. 4—Plots at 25° ( $\mu = 7M$ ) of  $[1 + K_h [\text{H}^+]^{-1}] S^{-1}$  against  $[\text{H}^+]$  (○) and  $10^3 \times [1 + K_h [\text{H}^+]^{-1}] / SI$  against  $[\text{H}^+]$  (●)

The plot of left-hand side against  $[\text{H}^+]$  is linear (Fig. 4) having slope  $= nK_A k_1 \beta_1'$  and intercept  $= nK_A k_2 \beta_2 K_h$ . From slope and intercept ( $I$ ) of Eq. (17) we have

$$IS = \frac{n[\text{X}]}{\beta_1' [\text{H}^+] + K_h \beta_2} \cdot \frac{1 + K_h [\text{H}^+]^{-1}}{nK_A [\text{X}]} = \frac{1 + K_h [\text{H}^+]^{-1}}{K_A [\beta_1' [\text{H}^+] + K_h \beta_2]}$$

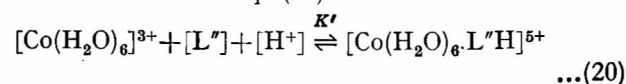
or

$$\frac{1 + K_h [\text{H}^+]^{-1}}{IS} = K_A [\beta_1' [\text{H}^+] + K_h \beta_2] \quad \dots(19)$$

The linear plot of the left-hand side expression against  $[\text{H}^+]$  (Fig. 4) gives a slope  $K_A \beta_1'$  and intercept  $K_A \beta_2 K_h$ .

Thus the terms  $\beta_1'$ ,  $\beta_2$ ,  $k_1$  and  $k_2$  can be found knowing the values of  $K_A$  (ref. 10) and  $K_h$ . These terms are collected in Table 5. In this case also  $\text{Co(III)}$  ion was assumed to be monomeric and hence  $n = 2$ .

(iii) *Alternative mechanism of oxidation of NTA at acidities 5M-7M*—It has been found that the plots of  $1/k_0$  against  $1/[\text{NTA}]$  are linear making positive intercepts of different magnitudes at different acidities (Fig. 5). This phenomenon may have some bearing on the rate of decomposition of the  $\text{NTA-Co(III)}$  complex. It is probable that there is little or no hydrolysis of  $\text{Co(III)}$  species at such high acidities and moreover, rates of decomposition of both the hydrolysed and unhydrolysed species might be indistinguishable as the decomposition rate of the corresponding complexes are very fast. Thus it may be supposed that the only complex between  $\text{NTA}$  and cobalt(III) is that between a protonated  $\text{NTA}$  molecule and the cobalt(III) hexaaquo molecule as shown in Eq. (20).



where  $\text{L}''$  represents protonated  $\text{NTA}$ .

The complex then rapidly decomposes into products in a rate determining step (21). The rate is thus given by Eq. (22).

TABLE 5 — VALUES FOR  $\beta'_1$ ,  $\beta_2$ ,  $k'_1$  AND  $k_2$  AT  $[\text{HClO}_4] = 5\text{-}7M$  AND  $\mu = 7M$ 

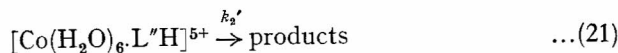
Temp. °K	$\beta'_1 \times 10^6$ mole <sup>-1</sup>	$\beta_2 \times 10^6$ mole <sup>-1</sup>	$k'_1 \times 10^3$ sec <sup>-1</sup>	$k_2 \times 10^3$ sec <sup>-1</sup>
293	2.85	20.86	3.18	4.44
298	1.60	9.24	5.68	8.18
300	1.57	7.45	9.26	11.12

$\Delta E^\ddagger$  for  $k'_1 = 26.83$  kcal and  $\Delta S^\ddagger$  (298°) = 19.22 e.u.  
 $\Delta E^\ddagger$  for  $k_2 = 23.80$  kcal and  $\Delta S^\ddagger$  (298°) = 9.80 e.u.

 TABLE 6 — VALUES FOR  $k'_2$  AND  $K'$  AT  $\mu = 7M$ 

$[\text{H}^+]$ $M$	$k'_2 \times 10^3$ sec <sup>-1</sup>	$K'$ mole <sup>-1</sup>
TEMP. 293°K		
5.0	6.52	100.35
5.5	9.02	58.86
6.0	9.28	55.96
6.5	15.76	39.95
7.0	19.32	47.23
TEMP. 298°K		
5.0	11.97	112.41
5.5	13.35	92.46
6.0	17.38	67.97
6.5	19.07	64.95
7.0	61.31	15.15
TEMP. 300°K		
5.0	15.33	77.84
5.5	15.27	104.26
6.0	22.00	73.84
6.5	30.65	16.32

$\Delta E^\ddagger$  at  $[\text{H}^+] = 5.0M = 23.43$  kcal and  $\Delta S^\ddagger$  (298°) = 23.07 e.u.  
 $\Delta E^\ddagger$  at  $[\text{H}^+] = 6.0M = 23.74$  kcal and  $\Delta S^\ddagger$  (298°) = 24.81 e.u.



$$\text{Rate} = nk'_2 K' [\text{Co}(\text{III})_T] [\text{L}^n] [\text{H}^+] \quad \dots(22)$$

If  $\text{Co}(\text{III})_{aq}$  exists as a monomer, Eq. (22) can be rearranged as

$$k_0 = \frac{2k'_2 K' [\text{L}^n] [\text{H}^+]}{1 + K' [\text{L}^n] [\text{H}^+]}$$

or

$$\begin{aligned} 1/k_0 &= \frac{1}{2k'_2 K' [\text{L}^n] [\text{H}^+]} + \frac{1}{2k'_2} \\ &= \frac{[\text{H}^+]^{-1}}{2k'_2 K' [\text{L}^n]} + \frac{1}{2k'_2} \quad \dots(23) \end{aligned}$$

The values of  $k'_2$  and  $K'$  are thus obtained from the intercepts and slopes respectively of the linear plots of  $1/k_0$  against  $1/[\text{L}^n]$  at a fixed acidity. These values and the corresponding activation parameters are collected in Table 5. Fig. 6 shows the applicability of this pathway.

**Energies and entropies of activation** — The values for  $\beta_1$ ,  $K_2$ ,  $k_1$  and  $k_3$  were calculated using the plots of  $0.5 [1 + K_h(\text{H}^+)^{-1}]I^{-1}$  and  $S [1 + K_h(\text{H}^+)^{-1}]I^{-1}$  against  $[\text{H}^+]^{-1}$  for acid range  $1M\text{-}5M$  at ionic strength

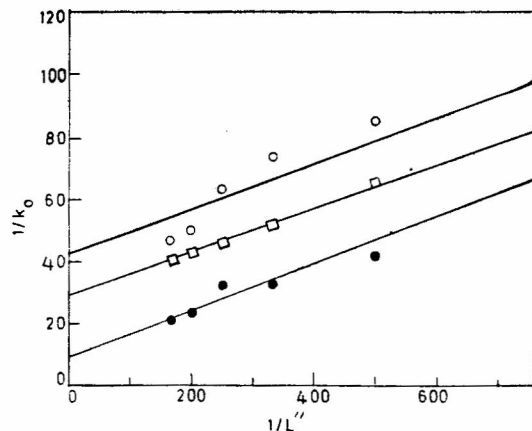


Fig. 5 — Plots of  $1/k_0 \times 10^3$  against  $1/L^n$  at 25° ( $\mu = 7M$ ),  $\{[\text{H}^+] = 5M (\text{O}), 6M (\text{□}), 7M (\bullet)\}$

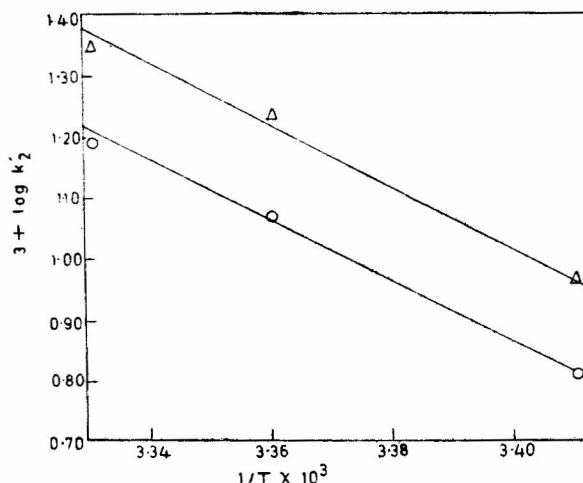


Fig. 6 — Plots of  $3 + \log k_2$  against  $1/T \times 10^3$  at  $[\text{H}^+] = 5M$  (O) and  $[\text{H}^+] = 6M$  ( $\Delta$ )

adjusted to  $5M$ . The plots of  $\log k_1$  and  $\log k_3$  against  $1/T$  are linear (Fig. 7), which supports the above mechanism and rate law. The overall energies of activation and entropies at 25° are included in Table 4. Similarly the values of  $\beta'_1$ ,  $\beta_2$ ,  $k_1$  and  $k_2$  are obtained from linear plots of  $[1 + K_h[\text{H}^+]^{-1}]S^{-1}$  and  $[1 + K_h[\text{H}^+]^{-1}]/SI$  against  $[\text{H}^+]$  in the acidity range  $5M\text{-}7M$ , the ionic strength being adjusted to  $7M$ . The corresponding Arrhenius plots (Fig. 8) give the overall energies and entropies of activation (Table 5).

The overall  $\Delta E$  value (76.41 kcal) corresponding to  $k_1$  is quite high. This is obvious from the fact that the corresponding equilibrium constant  $\beta_1$  is high. A high equilibrium constant arises from rather a stable complex, which is expected of  $\text{Co}(\text{III})_{aq}$  and the trisodium salt of NTA at the acidity range involved. On the other hand  $\Delta E$  value (26.82 kcal) corresponding to  $k'_1$  at high acidity range is fairly low since the equilibrium constant  $\beta'_1$  in this case is exceedingly small. Still this value could be much lower if the pre-equilibrium in Eq. (10) were not involved.

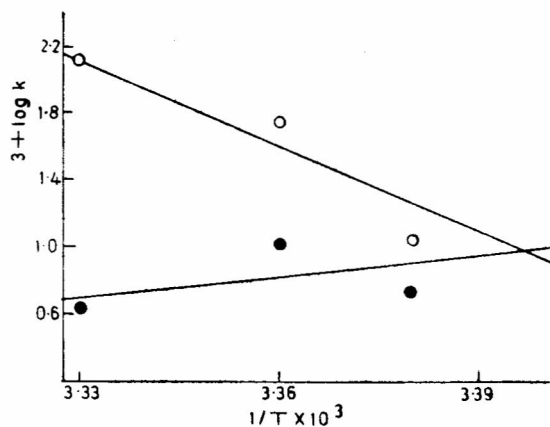


Fig. 7 — Plots of  $3 + \log k_1$  against  $1/T \times 10^3$  (○) and  $3 + \log k_3$  against  $1/T \times 10^3$  (●)

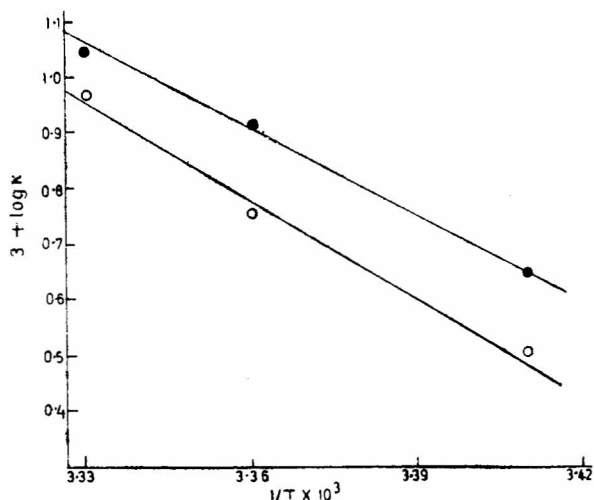


Fig. 8 — Plots of  $3 + \log k_1'$  against  $1/T \times 10^3$  (○) and  $3 + \log k_2$  against  $1/T \times 10^3$  (●)

The large negative energy of activation ( $-19.42$  kcal) corresponding to  $k_3$  may be reflected by the decomposition rate of the hydroxy complex as the value of corresponding equilibrium constant  $K_2$  becomes higher at higher temperatures with the decomposition rate  $k_3$  becoming lower. The large negative value of energy of activation is obviously due to instability of the hydroxy complex as reflected from the data ( $K_2$ ) in Table 4. This value could be positive if the shape of the Arrhenius plot for  $k_3$  were not as in Fig. 7. It is notable that the hydroxy complex at this stage is proposed to be positive, which may undergo a ligand substitution in the coordination shell. It is interesting that this complex is seen to be more stable at higher temperatures. It is however, an accepted phenomenon that a negative entropy of activation as has been found in the present case, arises from a less probable activated complex<sup>11</sup>. But the overall  $\Delta E$  ( $23.8$  kcal) corresponding to  $k_2$  is quite low as can be expected from the gradually low equilibrium constant ( $\beta_2$ , Table 5) at higher temperatures.

A high positive entropy of activation ( $190.14$  e.u.) has been obtained for the decomposition of the

NTA-Co(III) complex. This may be due to the fact that a fairly strong complex is formed with the metal ion in this case, as it is more probable that NTA behaves as a tridentate ligand towards cobaltic ion.

The large positive entropy does account for appreciable orientations of solvent molecules from the vicinity of the reactants towards the products in the activated complex. The entropy increase should also arise from the fact that the oxidation of NTA corresponding to Eqs. (1) and (3) is a reaction between two almost oppositely charged ions, where NTA has a greater tendency to behave as a negatively charged ion, since the values for  $\beta_1$  becomes smaller as the temperature rises. Other factors such as steric hindrance should also be considered for the products to be formed from a crowded activated complex such as NTA-hexaquo cobaltic ion.

The negative entropy corresponding to  $k_3$  clearly arises from the slower rate of decomposition at higher temperatures, where the equilibrium constant gradually rises, and in which case there is more likelihood of the oxidation process to involve a reaction between two ions of like charges. The entropy factors for the decomposition rates at acidity range  $5M-7M$  can be similarly accounted for, where the situation becomes more clear keeping in mind that the rates corresponding to  $k_1'$  and  $k_2$  become faster as the temperature rises.

Assuming the single complex of hexaquo cobalt(III)-NTA as the only species at the activated stage leading to products in high acidity range the overall energy of activation corresponding to  $k_2'$  at  $[H^+] = 5.0M$  ( $\mu = 7.0M$ ) has been found to be  $23.43$  kcal, which is comparable with the value corresponding to  $k_1'$  ( $26.83$  kcal) of the hexaquo cobalt(III)-NTA complex. This is, however, almost the same value as obtained for  $k_2$  ( $23.80$  kcal) corresponding to the decomposition of the pentaquo hydroxy cobalt(III)-NTA complex. The  $\Delta E$  value at  $[H^+] = 6.0M$  is also of the same order and almost similar to those obtained corresponding  $k_1'$  and  $k_2$ . These similarities may account for the applicability of alternative pathway for the reaction at the high acid range. This may also suggest for the thermodynamic indistinguishability between the unhydrolysed and the hydrolysed complexes of Co(III)-NTA.

The entropies of activation corresponding to  $k_2'$  at acidities  $5.0M$  and  $6.0M$  are also low as those for  $k_1'$  and  $k_2$  ( $19.22$  and  $9.80$  e.u. respectively). This situation is encountered for reactants having similar charges (in this case, positive charge) and accompanied by increasing instability of the complex with rise in temperature.

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