

Evaluation of individual rate constants and activation parameters of acid bromate oxidation of hydroxy acids catalysed by aquachlororuthenium complex

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The oxidation of citric and malic acids by bromate in acidic aqueous solutions is catalysed by aquachlororuthenium complex and the kinetics of the reaction is investigated. The rate law is interpreted by a mechanism involving the oxidation of Ru(III) to Ru(V) by oxidant (K_1), followed by a complex formation (K_c) between Ru(V) and substrate, which decomposes (k_d) to products in a slow rate determining step with regeneration of Ru(III). All individual rate constants are determined at different temperatures and their activation parameters are also evaluated and discussed.

There is no perceptible reaction between pure bromate Br(V) and hydroxy acids. But its oxidation rate increases many folds with the addition of ruthenium trichloride hydrate. Catalytic role of Ru(III) was also observed in the bromate oxidations of organic substrates like alcohols^{1a}, carbonyl compounds^{1b}, amines^{1c} and olefinic acids². Different mechanisms are used to explain catalytic effect of Ru(III) ion, in the above mentioned systems, clearly indicating that the mechanism is solely dependent upon the nature of the substrate. To know the mechanism of Ru(III) ion catalysed bromate oxidation of biologically important hydroxy acids like malic and citric acids, which is hitherto unreported, the present study is carried out in detail and reported.

Materials and Methods

The source of Ru(III) was $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (Johnson and Mathey, England). It was dissolved in dilute perchloric acid and standardised by the method of Houriuchi *et al.*³. All other chemicals were of AnalaR grade and were purified by either distillation or recrystallisation. The stock solutions were prepared either in triply distilled water or 1:1 aq. acetic acid and preserved in the dark. Under subdued light and nitrogen atmosphere, the reaction mixture containing the requisite amount of substrate, Ru(III), acid and mercury(II) acetate were thermostated for an hour at temperature warranted by the experimental conditions. Temperature equilibrated oxidant of required concentration was added to the above reaction mixture. The

kinetics of the reaction was followed by estimating the unreacted bromate iodometrically for two half-lives by withdrawing aliquots of the reaction mixture at regular intervals of time. A Shimadzu multipurpose recording double beam spectrophotometer model MPS-5000 equipped with a temperature controller was used for absorption studies.

All reactions were carried out under pseudo-first order conditions using tenfold excess of [substrate] over [bromate]. The pseudo-first order rate constants (k_1) with respect to Br(V) were computed from linear plots [$r > 0.99$] of $\log[\text{Br(V)}]_t$ against time. The reproducibility of k_1 was within $\pm 3\%$ and mean values are reported.

Results

The data obtained from the study of [bromate] effect on the reaction rate fit well into first order plot. But, the pseudo-first order rate constants (k_1) obtained from the plots of $\log[\text{bromate}]$ against time decrease with increase in initial [bromate] (Table 1). The same trend in k_1 is observed at various [substrate], temperatures and acidities. The pseudo-first order rate constants increase with increase in [substrate] (Table 1). The plot of $\log k_1$ versus $\log[\text{substrate}]$ is linear with slope less than unity. The plots of k_1 against [substrate] are reminiscent to Michaelis-Menten's kinetics. The catalytic effect of Ru(III) is studied in the range $1.90\text{--}22.80 \times 10^{-5} \text{ mol dm}^{-3}$ and the rate constant increases linearly with increase in [Ru(III)], showing first order dependence on [ca-

Table 1—Effect of varying [oxidant] and [substrate] on the rate of reaction at different temperatures

[HClO₄] = 1.0 mol dm⁻³; [Ru(III)] = 7.6 × 10⁻⁵ mol dm⁻³; [Hg(OAc)₂] = 0.005 mol dm⁻³; HOAc-H₂O = 30-70% (v/v)

$10^4 \times [\text{Br(V)}]$ (mol dm ⁻³)	$10^2 \times [\text{substrate}]$ (mol dm ⁻³)	$10^5 \times k_1$ (s ⁻¹)				
		293	298	303	308	313 K
Malic acid						
4.0	1.0	11.60	19.60	31.60	47.60	88.10
6.0	1.0	9.34	15.80	27.00	32.20	76.90
8.0	1.0	7.80	13.40	21.37	31.25	62.50
10.0	1.0	6.75	11.94	19.19	29.93	52.58
12.0	1.0	5.95	10.41	16.60	21.50	47.60
16.0	1.0	5.00	8.95	14.49	17.85	38.46
20.0	1.0	4.21	7.14	12.50	15.15	31.25
10.0	1.5	7.67	13.55	21.80	33.11	60.03
10.0	2.0	8.42	14.90	24.00	38.00	64.60
10.0	4.0	10.62	18.78	30.02	45.70	83.00
10.0	5.0	11.08	19.50	31.50	47.86	89.10
10.0	6.0	11.92	21.07	33.80	51.28	93.32
Citric acid						
4.0	1.0	—	22.72	35.70	49.75	76.92
6.0	1.0	—	19.61	30.30	39.84	64.51
8.0	1.0	—	17.39	26.32	35.71	52.63
10.0	1.0	—	15.70	22.45	30.42	45.67
12.0	1.0	—	14.29	20.00	27.01	40.00
16.0	1.0	—	12.12	16.39	23.50	31.25
20.0	1.0	—	10.25	13.80	17.39	26.31
10.0	1.5	—	18.32	25.20	35.48	52.48
10.0	2.0	—	22.22	30.60	40.60	57.47
10.0	4.0	—	28.74	38.40	50.47	73.91
10.0	6.0	—	30.77	41.50	57.97	86.22
10.0	8.0	—	32.78	44.00	62.94	89.91
10.0	10.0	—	35.71	51.80	68.40	100.02

talyst]. The effect of [HClO₄] on reaction rate, studied in the range 0.05 to 3.0 mol dm⁻³, reveals that k₁ increases with increase in [acid] and reaches a maximum at 0.5 mol dm⁻³. Further increase in [acid] results in a decrease in the rate of reaction (Fig. 1). Increase in polarity of the medium (by varying H₂O-HOAc content in the reaction mixture) decreases the rate suggesting a charge dispersal in the transition state. Oxidation is studied at different temperatures by varying initial reductant as well as oxidant concentrations (Table 2), to evaluate the values of individual rate constants and their activation parameters.

Discussion

In acid medium molecular bromine is expected to be produced by an autocatalytic bromate-bromide (reduction product of bromate) reaction.

Spectroscopic analysis of the reaction mixture also shows an absorption maximum at 373 nm (where Br₂ has a maximum absorbance with ε = 164). When concentration of hydroxy acid is in excess, the plot of log[BrO₃⁻]_t versus time gives a smooth curve, concave upward in contrast to earlier findings of bromate oxidations^{4,5}, wherein a slow reaction followed by a faster one is due to liberated bromine oxidation of the substrate. Under similar conditions, oxidation of hydroxy acids by bromine, studied independently, reveals that the bromine oxidation is much slower in comparison with bromate oxidation. To avoid bromine formation and its interference in the present kinetics, the product bromide ion is trapped by employing a complexing agent like mercury(II) or thallium(III), which binds bromide ions as and when they are formed. The detailed study shows

Table 2—Effect of temperature and individual rate constants: Evaluation of activation parameters at 303 K
 $[\text{Br(V)}] = 0.001 \text{ mol dm}^{-3}$; $[\text{substrate}] = 0.01 \text{ mol dm}^{-3}$; $[\text{Ru(III)}] = 7.6 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{Hg(OAc)}_2] = 0.005 \text{ mol dm}^{-3}$ H_2O -
 $\text{HOAc} = 70\text{-}30\%$ (v/v); $[\text{HClO}_4]/[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$

Temp(K)	293	298	303	308	313	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
Malic acid								
$10^5 \times \text{Overall reaction constant}$ (k_1, s^{-1})	6.75	11.94	19.19 (6.14)	29.93 (10.69)	52.93 (15.14)	74.09 (70.61)	71.82 (93.63)	95.85 (99.00)
$10^{-2} \times \text{Formation constant } (K_f)$	7.25	9.67	16.00	19.04	25.28	41.50	65.90	61.46
Complexation constant (K_c)	711.47	511.11	351.00	300.00	250.00	(-)42.48	353.05	59.41
$10^3 \times \text{Decomposition constant}$ (k_d)	1.52	2.86	4.59	7.31	12.53	74.05	45.42	87.82
Citric acid								
$10^5 \times \text{Overall reaction constant}$ (k_1, s^{-1})	11.13	15.70	22.45 (5.49)	30.42 (9.59)	45.67 (12.28)	52.06 (70.24)	143.20 (94.91)	95.45 (99.05)
$10^{-2} \times \text{Formation constant } (K_f)$	7.36	9.79	15.84	19.20	24.32	41.50	66.01	61.50
Complexation constant (K_c)	363.00	324.40	310.04	248.20	227.45	(-)25.49	281.46	59.79
$10^3 \times \text{Decomposition constant}$ (k_d)	3.68	4.94	6.32	8.22	11.33	37.69	162.79	87.01

(The values in parentheses are in sulphuric acid: The average error limits in values of $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ are $\pm 3 \text{ kJ mol}^{-1}$; $\pm 5 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\pm 4 \text{ kJ mol}^{-1}$ respectively)

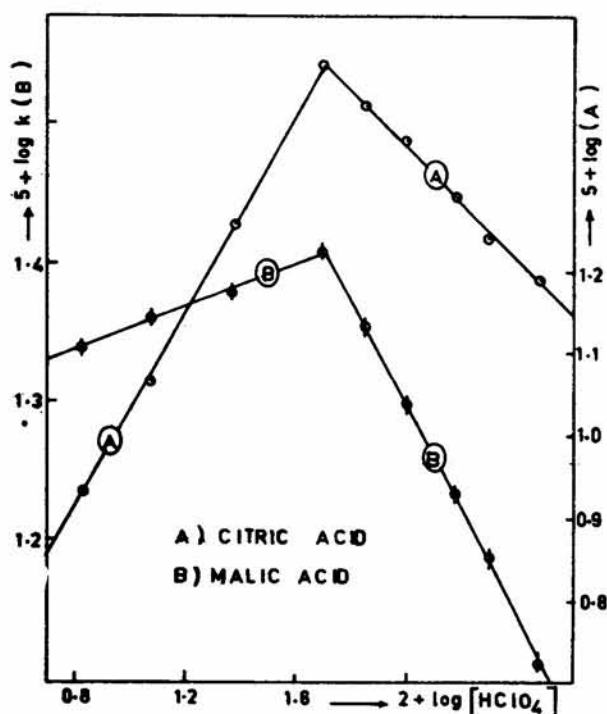


Fig. 1—Plot of $\log k_1$ against $\log [\text{HClO}_4]$. $[\text{Substrate}] = 0.01 \text{ mol dm}^{-3}$; $[\text{bromate}] = 0.001 \text{ mol dm}^{-3}$; $[\text{Ru(III)}] = 7.6 \times 10^{-5} \text{ mol dm}^{-3}$; $\text{HOAc-H}_2\text{O} = 30\text{-}70\%$ (v/v) and temp. = 303 K.

that mercury(II) is more suitable complexing agent than thallium(III), because it plays a single role of complexing bromide ions and thereby eliminates the bromine to be produced, autocatalytically⁵. To keep back all the Br^- ions produced, all reactions are carried out with an optimum concentration of $0.005 \text{ mol dm}^{-3}$ mercuric acetate. Different concentrations of mercuric acetate over a multiple range has no effect on the rate constant. Hence the reported rate constants pertain to pure bromate oxidation only.

The reaction rate is neither accelerated in the presence of benzoyl peroxide nor retarded in the presence of acrylic monomers indicating that the reaction is not proceeding by a free radical pathway. The kinetic behaviour of hydroxy acids studied is similar irrespective of their structures.

The oxidation of hydroxy acids by bromate in the presence of Ru(III) ion may follow any one of the three possible ways: (i) catalyst forms a complex with substrate, which later on interacts with bromate to give rise to an activated complex, which in turn decomposes into products; (ii) the reaction between Br(V) and Ru(III) to form a complex takes precedence over the substrate-catalyst interaction and the activated complex resulting from the reaction of $\text{Ru}^{\text{III}}\text{-Br}^{\text{V}}$ complex

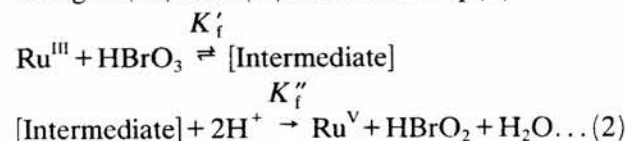
and substrate, decomposes to afford products; and (iii) instead of forming a complex Br(V) oxidises Ru(III) to Ru(V) in acid medium, which in turn converts substrate into products via complexation.

The spectral studies are made involving the substrate, oxidant and catalyst. To know the effect of one on the other, the solutions under study are mixed together and kept for required time before recording the spectrum. A solution of Ru(III) in acetic acid and perchloric acid (1.0 mol dm^{-3}) shows an absorption maximum at 490 nm and the oxidant has no absorption in visible region. It is observed that the substrate presence has no effect on the absorption of RuCl_3 , which leads to the exclusion of substrate-Ru(III) complexation. Addition of Br(V) to a solution of Ru(III), drastically changed the colour of the solution and an absorption is recorded at 690 nm, with a simultaneous disappearance of absorption at 490 nm due to Ru(III). Further release or regeneration of the catalyst has occurred by the addition of substrate to the above solution, which is confirmed not only by restoration of the colour of Ru(III), but also by the shift of absorption from 690 nm to 490 nm. As per these findings reaction may be routed through second or third pathway assumed above. But, the positive influence of $[\text{H}^+]$ on the rate cannot be explained through second pathway. This leaves third alternative as the most probable way by which oxidation is taking place. It is in good agreement with all kinetic results obtained for both the substrates studied.

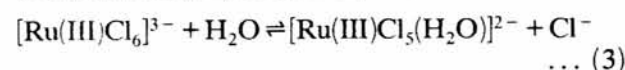
The linear increase in the rate of oxidation with increase in acidity may be due to protonation of BrO_3^- to give HBrO_3 , which is having more oxidising property than its precursor.



Therefore, Br(V) in the form of HBrO_3 is oxidising Ru(III) to Ru(V) as shown in Eq. (2)



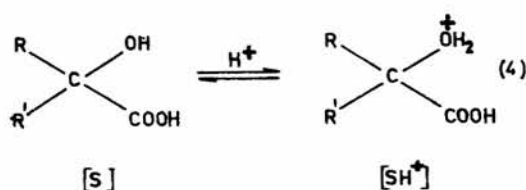
A study on the oxidation states of ruthenium has shown that Ru(III) exists in equilibrium⁶⁻⁸



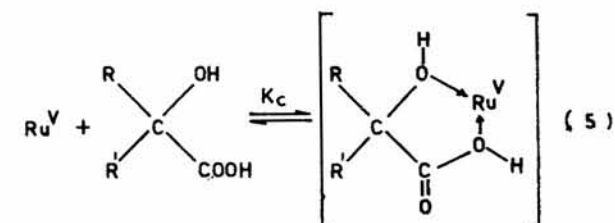
in acid medium.

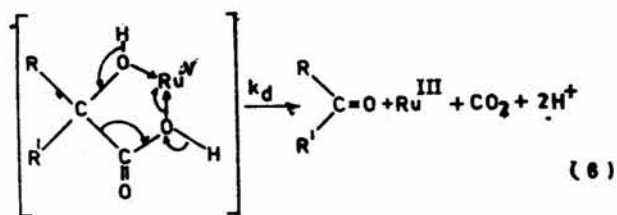
From ion exchange studies, it is confirmed that ruthenium(III) chloride forms $[\text{RuCl}_6]^{3-}$ species in hydrochloric acid⁹, and aquation of this species to $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ takes only a few seconds¹⁰. Therefore, it is assumed that Ru(III) in the form of $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ is taking part in the reaction. Singh *et al.*^{11,12} also employed the above equilibrium in Ru(III) catalysed bromamine-T oxidation of primary alcohols¹¹ in acid medium, also in the glycols oxidation by N-bromoacetamide in HClO_4 medium¹² and in ceric sulphate oxidation of ketones¹³ in sulphuric acid.

Fractional order in [substrate] and a definite intercept in Michaelis-Menten's plot indicates the involvement of substrate in the complex formation prior to breakdown of the complex. As the dissociation constants of malic acid ($K_{a1} = 3.9 \times 10^{-4}$; $K_{a2} = 7.8 \times 10^{-6}$) and citric acid ($K_{a1} = 3.4 \times 10^{-4}$; $K_{a2} = 1.8 \times 10^{-5}$; $K_{a3} = 4.0 \times 10^{-6}$) are very low, the existence of $\text{RH}(\text{OH})\text{COO}^-$ in mineral acid solutions does not arise. In strong acid medium (0.25 to 4.0 mol dm^{-3} , HClO_4) the substrate is expected to be either in neutral [S] or protonated $[\text{SH}^+]$ form. Oxidation step involves removal of H^+ from the α -hydroxy function and the process will be the driving force for decarboxylation. Since the protonated form would have an adverse effect on the rate, the substrate should participate in the reaction in its neutral form only. At higher acid concentration, the decrease in rate may be attributed to SH^+ formation as indicated in Eq. (4).



Therefore, in the light of the above discussion, it is assumed that an intermediate complex is formed by the substrate and Ru(V), which in turn decomposes in a slow step to products as shown in Eq. (5) and (6).





in case of malic acid ($\text{R} = \text{CH}_2\text{COOH}$ and $\text{R}' = \text{H}$) and citric acid (R and $\text{R}' = \text{CH}_2\text{COOH}$).

On the basis of the mechanism envisaged (Eqs 1 to 6), the rate law can be deduced as follows:

$$\text{Rate} = \frac{-d[\text{Br(V)}]}{dt} = k_d [\text{Ru(V)} \dots \text{S}] \quad \dots (7)$$

[Intermediate complex]

$$\begin{aligned} [\text{Intermediate complex}] &= K_c [\text{Ru(V)}][\text{S}] \\ &= K_f K_c K_p [\text{H}^+]^3 [\text{BrO}_3^-][\text{S}] \\ &\quad [\text{Ru(III)}] \quad \dots (8) \end{aligned}$$

(where $K_f = K'_f \cdot K''_f$)

$$\begin{aligned} \text{Therefore, Rate} &= \frac{-d[\text{Br(V)}]}{dt} = k_d K_f K_c K_p [\text{H}^+]^3 \\ &\quad \times [\text{BrO}_3^-][\text{S}][\text{Ru(III)}] \quad \dots (9) \end{aligned}$$

As catalyst exists in different forms, total concentration of Ru(III) is given by

$$\begin{aligned} [\text{Ru(III)}]_T &= [\text{Ru(III)}] + [\text{Ru(V)}] \\ &\quad + [\text{Intermediate complex}] \\ &= [\text{Ru(III)}] + K_f K_p [\text{H}^+]^3 [\text{BrO}_3^-][\text{Ru(III)}] \\ &\quad + K_f K_c K_p [\text{H}^+]^3 [\text{BrO}_3^-][\text{S}][\text{Ru(III)}] \\ &= [\text{Ru(III)}] \{ 1 + K_f K_p [\text{H}^+]^3 [\text{BrO}_3^-] \\ &\quad + K_f K_c K_p [\text{H}^+]^3 [\text{S}] [\text{BrO}_3^-] \} \\ \therefore [\text{Ru(III)}] &= [\text{Ru(III)}]_T / \{ 1 + K_f K_p [\text{H}^+]^3 [\text{BrO}_3^-] \\ &\quad + K_f K_c K_p [\text{H}^+]^3 [\text{S}] [\text{BrO}_3^-] \} \quad \dots (10) \end{aligned}$$

Substituting this value in Eq. (9) we have,

$$\begin{aligned} \frac{-d[\text{Br(V)}]}{dt} &= \frac{k_d K_f K_c K_p [\text{H}^+]^3 [\text{BrO}_3^-][\text{S}][\text{Ru(III)}]_T}{1 + K_f K_p [\text{H}^+]^3 [\text{BrO}_3^-] + K_f K_c K_p [\text{H}^+]^3 [\text{S}][\text{BrO}_3^-]} \quad \dots (11) \end{aligned}$$

Further, bromate is present in protonated and unprotonated forms. Therefore, total bromate concentration is given by

$$\begin{aligned} [\text{Br(V)}]_T &= [\text{BrO}_3^-] + [\text{HBrO}_3] + [\text{H}_2^+\text{BrO}_3] \\ &= [\text{BrO}_3^-] + K_{p1}[\text{H}^+][\text{BrO}_3^-] + K_{p1}K_{p2}[\text{H}^+]^2[\text{BrO}_3^-] \\ [\text{BrO}_3^-] &= [\text{Br(V)}]_T / \{ 1 + K_{p1}[\text{H}^+] + K_{p2}[\text{H}^+]^2 \} \dots (12) \end{aligned}$$

where K_{p1} (0.5) and K_{p2} (0.2) (ref. 14) are the protonation constants of bromate.

All the reactions are carried out under pseudo-first order conditions, where initial [substrate] is ten times greater than initial [bromate] and 130 times than initial [catalyst]. Hence the change in the [substrate] at any instant is negligible (considered to be unaltered), therefore,

$$[\text{S}] \approx [\text{S}]_{\text{Total}} \quad \dots (13)$$

Substituting the values of bromate and substrate in terms of their total concentrations in Eq. (11), we have

$$\begin{aligned} \frac{-d[\text{Br(V)}]}{dt} &= \frac{k_d K_f K_c K_p [\text{H}^+]^3 [\text{S}]_T [\text{Ru(III)}]_T [\text{Br(V)}]_T}{\left\{ 1 + K_{p1}[\text{H}^+] + K_{p1}K_{p2}[\text{H}^+]^2 + K_f K_{p1}[\text{H}^+]^3 \right\} \\ &\quad [\text{Br(V)}]_T + K_f K_c K_p [\text{H}^+]^3 [\text{S}]_T [\text{Br(V)}]_T} \quad \dots (14) \end{aligned}$$

The rate constant of the reaction is given by

$$\begin{aligned} k_1 &= \frac{-d[\text{Br(V)}]/dt}{[\text{Br(V)}]_T} \\ &= \frac{k_d K_f K_c K_p [\text{H}^+]^3 [\text{S}]_T [\text{Ru(III)}]_T}{\left\{ 1 + K_{p1}[\text{H}^+] + K_{p1}K_{p2}[\text{H}^+]^2 + K_f K_{p1}[\text{H}^+]^3 \right\} \\ &\quad [\text{Br(V)}]_T + K_f K_c K_p [\text{H}^+]^3 [\text{S}]_T [\text{Br(V)}]_T} \quad \dots (15) \end{aligned}$$

Taking reciprocal and rearranging Eq. (15), after substituting the values of K_{p1} , K_{p2} and $[\text{H}^+]$ (1.0 mol dm^{-3}).

$$\begin{aligned} \frac{1}{k_1} &= \frac{3.2}{k_d K_f K_c [\text{Ru(III)}]_T [\text{S}]_T} + \frac{[\text{Br(V)}]_T}{k_d K_c [\text{Ru(III)}]_T [\text{S}]_T} \\ &\quad + \frac{[\text{Br(V)}]_T}{k_d [\text{Ru(III)}]_T} \quad \dots (16) \end{aligned}$$

As per Eq. (16), plot of $1/k_1$ against $1/[\text{S}]_T$ at fixed $[\text{Ru(III)}]$ and $[\text{Br(V)}]$ should be linear with an

intercept equal to $\frac{[\text{Br(V)}]_T}{k_d[\text{Ru(III)}]_T}$. The same is reali-

zed. The values of k_d at different temperatures are evaluated from the intercepts of the plots of $1/k_1$ versus $1/[S]_T$ obtained from the study of substrate effect at different temperatures (Table 1). The plot of $1/k_1$ against $[\text{Br(V)}]_T$ is linear with a slope of $\{1 + K_c[S]_T\}/k_d[\text{Ru(III)}]_T$. The values of K_c at different temperatures are also evaluated, with the knowledge of corresponding k_d values. As the slopes of the plots of $1/k_1$ versus $1/[S]_T$ are given

by $\frac{1}{k_d K_c [\text{Ru(III)}]_T} \left\{ 1 + \frac{3.2}{K_f} \right\}$, the values of K_f can

be determined by substituting corresponding values of k_d and K_c evaluated as mentioned above. Thus evaluated individual rate constants and composite rate constants are recorded in Table 2.

The values of K_f for malic and citric acids are almost equal, as this step involves the interaction between oxidant and catalyst in both the cases and is independent of the substrate, supporting the mechanism proposed.

$$\frac{1}{k_1} = \left\{ \frac{3.2}{k_d K_f K_c [S]_T} + \frac{[\text{Br(V)}]_T}{k_d K_c [S]_T} + \frac{[\text{Br(V)}]_T}{k_d} \right\} \frac{1}{[\text{Ru(III)}]_T} \quad \dots (17)$$

The plot of $1/k_1$ versus $1/[\text{Ru(III)}]_T$ is linear at fixed, $[S]_T$ and $[\text{Br(V)}]_T$ passing through the origin.

The slopes of these plots evaluated theoretically by substituting the values of k_d , K_f and K_c obtained from the study of [substrate] and [bromate] effects, are in good agreement with the slopes observed, supporting the mechanism envisaged.

The composite and individual activation parameters are evaluated from least square slopes of $\log(\text{individual/composite rate constant})$ versus $1/T$. Related activation parameters, namely, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ are calculated (Table 2). It is also observed that the sum of enthalpies of activation of individual rate constants is found equal to the enthalpy activation of composite rate constant.

The free energy of activation pertaining to each individual rate constant of citric acid is equal to malic acid, revealing that identical mechanism is operating in the oxidation of both the substrates studied. Enthalpy of activation of the complexation constant is negative in both the cases, inferring the formation of an outer sphere labile com-

plex (ruthenium is having tendency to form only outer sphere complexes) having inverse effect of temperature on its stability. Entropy of activation of all reactions involved in the oxidation of these hydroxy acids are found to be negative, due to the compactness of the transition state as compared to the ground state. Further large entropies of activation are expected for a bimolecular reaction with a high polar transition state.

Under similar conditions the rate of oxidation of citric acid is faster than malic acid which indicates that C-H bond is not involved in reaction, only O-H and C-C bonds are involved in the reaction. The difference between malic and citric acids is -H and -CH₂COOH. The -I effect with -CH₂COOH may be the driving force for faster oxidation of citric acid.

The intermediate CHO CH₂COOH of malic acid, upon oxidation produces a species identified by spot test¹⁵ to be malonic acid which gets oxidised to final product. At the end of the reaction, malonic acid and acetone dicarboxylic acid are the oxidised products of malic and citric acids at low bromate concentrations. However, at higher concentrations of bromate, formic acid is the product for both the substrates. This would essentially involve a number of stable and unstable intermediates which are not easily identifiable. Test for decarboxylation with the reaction mixture used for the kinetic runs is not possible because of large dilution. But CO₂ could be conveniently detected with large amounts of reactants by passing it into a weighed bulb containing KOH solutions, whose weight is found to be increased after lapse of some time. As no induced polymerization is observed with acrylic monomers, the intermediates undergo oxidation through a series of successive two electron transfer steps, leading ultimately to CO₂ and formic acid.

HBrO₂ is a two equivalent oxidant, strong enough to consume many organic substrates. HBrO₂ thus formed in Eq. (2) oxidises intermediate/substrate in fast steps and finally converts to bromide ion.

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