

KINETICS OF OXIDATION OF TARTARIC ACID BY Ce(IV) IN PRESENCE OF SULPHURIC ACID

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Oxidation of tartaric acid by Ce(IV) in sulphuric acid has been studied. The reaction is found to be of the first order in initial stages (~40% of the completion of reaction), but to a major extent it is of second order. Second order rate constant increases with the increase in pH from 1.8 to 3.6. Effect of ionic strength indicates $Z_A \cdot Z_B = +2.05$. Value of energy of activation, frequency factor and entropy are 11.65 Kcal; 2×10^7 litre mol⁻¹ sec⁻¹ and -19.06 e.u. respectively. The results can be explained on the basis of the formation of a complex between tartarate and Ce(IV) ions which decomposes to give a free radical.

Introduction

Kinetics of the oxidation of tartaric acid by Ce(IV) have not been reported in the literature. G.V. Bakore and Rama Shankar,¹ and Bhale *et al.*² have studied the oxidation of tartaric acid by acid permanganate. The present investigation was, therefore, undertaken to study the mechanism of oxidation of tartaric acid by Ce(IV) and compare the results with those obtained by the acid permanganate oxidation.

Experimental

Materials: All reagents used were of Analar quality.

Instruments: Ultrathermostat maintained at a temperature constant to $\pm 0.01^\circ\text{C}$. Cambridge pH-meter (Mains operated).

Procedure

In the course of preliminary experiments it was observed that when tartaric acid and ceric sulphate solutions were of equal strength and of the same pH the reaction was too fast to be studied quantitatively in the temperature range of 15° - 25°C . Hence the standard solutions of the two reactants of different strengths and different pH were used in this investigation.

The pH of tartaric acid solutions was adjusted with standard sulphuric acid solutions at 2.5 and 3.1. The ionic strength of these solutions were maintained constant by adding required amount to potassium sulphate. The pH of ceric sulphate was adjusted at 0.33 by addition of dilute H_2SO_4 .

50 ml. of tartaric acid and 50 ml. of ceric sulphate solutions of known concentration were kept at a

fixed temperature in a thermostat for one hour. Then the two solutions were mixed and 10 ml. of the reaction mixture were withdrawn after definite intervals of time and were chilled by ice to stop the reaction. The amount of unreacted Ce(IV) was estimated by titration with a standard Mohr's salt solution using ferroin as indicator.

Stoichiometry of the reaction was studied in the dark and sun-light by reacting a known volume of standard tartaric acid solutions with an excess of ceric sulphate solution of known concentration and determining the unreacted oxidant by the above procedure.

Results

Order of Reaction.—The reaction has been found to be of the first order in respect of Ce(IV) ion concentration in initial stages for about 40% completion of the reaction (Table 1). The rate of reaction is also found to be of the first order initially with respect to tartarate ion concentration (Table 2 and Fig. 1). The initial rates of reactions, where necessary, were measured by mirror and scale device.³

TABLE I.—VARIATION OF INITIAL RATE OF REACTION WITH Ce(IV) CONCENTRATION.

[Ce(IV)] $\times 10^2\text{M}$	K_1 (Initial rate) Sec ⁻¹ $\times 10^4$	Initial rate Ce(IV)
1.4	7.48	5.34
1.24	6.86	5.53
1.07	5.93	5.59
0.98	5.44	5.55
0.805	4.48	5.56

[Tartaric Acid], $2.05 \times 10^{-3}\text{M}$; (pH, 3.1); [Ce(IV)] (pH, 0.33); temperature, 18°C .; μ , 0.87.

TABLE 2.—VARIATION OF INITIAL RATE OF REACTION WITH TARTARIC ACID CONCENTRATION.

Tartaric Acid × 103 M	$K_I \times 10^{-3}$ Sec ⁻¹	$\left(\frac{1}{T. Acid}\right) \times 10^{-3}$	$\frac{1}{K_I} \times 10^3$	$\frac{1}{K_I} \frac{1}{K_C} \times [Acid]$
9.4	1.68	0.106	0.595	5.217
7.4	1.29	0.148	0.775	5.432
5.4	0.998	0.185	1.002	5.195
3.8	0.733	0.262	1.364	5.031
1.65	0.297	0.606	3.367	5.489

[Ce(IV)], $1.26 \times 10^{-2}M$; [pH, 0.33]; [Tartaric Acid], (pH, 2.5); temperature, 18°C.; μ , 0.0047M.

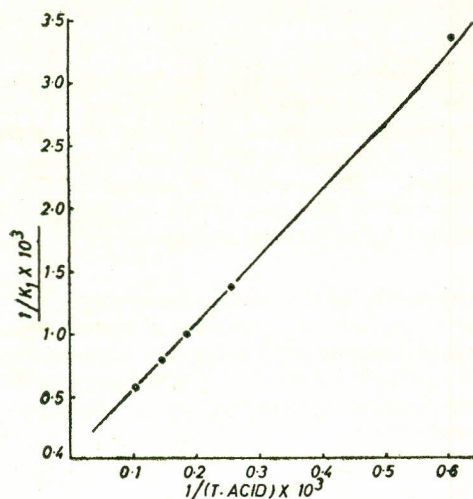


Fig. 1.—Showing variation of initial rate of reaction with tartaric acid concentration.

Induced Reduction of Mercuric Chloride.—Induced reduction of mercuric chloride has been observed in the course of oxidation of tartaric acid by Ce(IV) suggesting the formation of a reducing intermediate i.e. a free radical.⁴

Effect of pH.—Effect of increase of pH on the second order rate constant is shown in Table 3 and Fig. 2.

TABLE 3.— VARIATION OF THE RATE OF REACTION WITH pH.

pH	K_2 moles litre ⁻¹ min ⁻¹	log K_2
1.0	1.220	0.0862
1.8	1.246	0.0945
2.6	1.296	0.1127
3.1	1.351	0.1308
3.6	1.410	0.1490

[Tartaric Acid], $2.0 \times 10^{-3}M$; [Ce (IV)], $8.4 \times 10^{-3}M$; (pH, 0.8) temperature, 18°C.

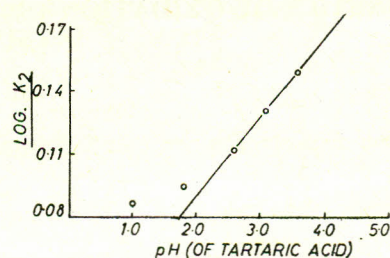


Fig. 2.—Showing variation of reaction rate with pH.

The rate constant increases from pH 1.8 to 3.6 and induction period is observed below pH 1.8.

Effect of Ionic Strength.—Second order rate constant was found to increase with ionic strength. Variation of rate constant with ionic strength at various temperatures is shown in Table 4 and Fig. 3.

TABLE 4.—VARIATION OF REACTION RATE WITH IONIC STRENGTH AT DIFFERENT TEMPERATURES.

μ	$\sqrt{\mu}$	K_2 moles litre ⁻¹ min ⁻¹			
		15°C.	18°C.	20°C.	23°C.
0.0012	0.0346	1.67	2.058	2.386	2.893
0.0429	0.2071	1.73	2.135	2.445	2.996
0.1121	0.3480	1.80	2.220	2.548	—
0.1746	0.4178	1.82	2.245	2.575	3.152
0.2427	0.4926	1.86	2.295	—	—
0.3144	0.5607	1.89	2.330	2.676	3.273
0.3801	0.6165	1.91	—	—	—
0.4488	0.6691	—	2.371	—	3.330
0.5178	0.7194	1.95	2.405	2.760	—

Ce(IV), $1.365 \times 10^{-2}M$; (pH, 0.8); [Tartaric Acid], $2.0 \times 10^{-3}M$; (pH, 3.1).

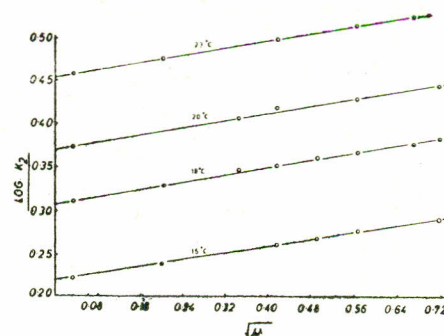


Fig. 3.—Showing variation of reaction rate with ionic strength at various temperatures.

Effect of Fluoride Ion Concentration.—Addition of fluoride ion decreases the initial rate to some extent (Table 5), suggesting that Ce(IV) ions are primarily involved in the reaction. Addition of F⁻ ions decreases the concentration of Ce(IV) by complex formation.

TABLE 5.— VARIATION OF INITIAL RATE WITH VARYING FLUORIDE ION CONCENTRATION.

NaF(M)	-1×10^{-2}	2×10^{-2}	3×10^{-2}	5×10^{-2}
(initial rate)				
Sec ⁻¹ × 10.4	6.860	6.850	6.840	6.835

[Tartaric Acid], 2.0×10^{-3} M; (pH, 3.1); [Ce(IV)], 1.365×10^{-2} M; (pH, 0.8); temperature, 20°C.; μ , 1.2×10^{-3} M.

Effect of Temperature.—A plot of $1/T$ against $\log K_0$ (where K_0 =extrapolated values of K_2 to zero ionic strength at various temperatures, computed from Fig. 3, shows a straight line (Fig. 4).

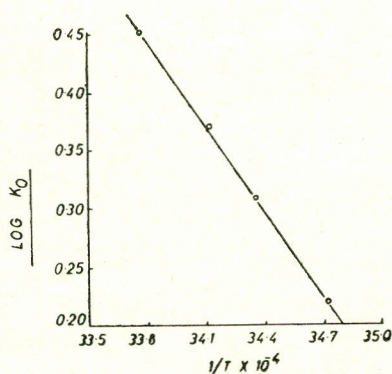


Fig. 4.—Showing variation of temperature with $\log K_0$

From the values of ΔE at 20°C., obtained from the slope of the curve, frequency factor (pz) and entropy of activation ΔS^\ddagger have been evaluated (Table 6).

TABLE 6.— THERMODYNAMIC DATA FOR THE REACTION.

T	$\log K_0$	ΔE Kcals.	$pz \times 10^7$ litre mole ⁻¹ Sec ⁻¹	ΔS^\ddagger e.u. (cal deg ⁻¹ mole ⁻¹)
288	0.220	—	—	—
291	0.309	—	—	—
293	0.370	11.65	2.0	(-19.065)
296	0.450	—	—	—

[Ce (IV)], 1.365×10^{-2} M; (pH, 0.8); [Tartaric Acid], $2. \times 10^{-3}$ M; (pH, 3.1); μ , 1.2×10^{-3} M.

Discussion

Tartaric acid has been found to be oxidised through free radical formation as mercuric chloride is reduced when tartaric acid is oxidized by Ce(IV) in its presence.³

The initial Order of reaction with respect to tartarate ion concentration can be expressed by the expression.

$$d[\text{Ce(IV)}] / dt = k [(\text{Acid})] [\text{Ce(IV)}] / [a + \text{Acid}]$$

where "a" = $1/K$ and is a measure of the stability of the complex formed. The value of "a" (=0.188) was determined from the slope of the curve obtained from the plot of $1/[\text{Acid}]$, Vs. $1/K_1$ (Fig. 1).

The validity of the above equation has been verified by obtaining a linear relationship between $1/[\text{Tartaric Acid}]$ and $1/K_1$ (Fig. 1) and from the constancy of the values of $1/K_1 - 1/K_0 \times \text{Acid}$ (Table 2), where $1/K_0$ is the value of $1/K_1$ extrapolated to zero $1/[\text{Acid}]$ concentration. This indicates that a complex is formed between tartarate and Ce(IV) ions which subsequently decomposes to give CO_2 and a free radical.

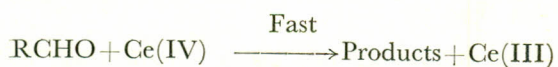
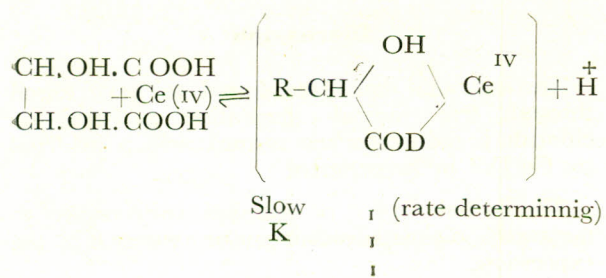
A similar mechanism has been observed by Bakore *et al.* (Loc. cit) in the oxidation of tartaric acid by acid permanganate.

The stoichiometry of the reaction between tartaric acid and Ce(IV) has been found to be 1:7.9 moles, which is comparable to the value of 6.1 obtained for lactic acid oxidation by Ce(IV) by Bhargava *et al.*⁵

The average value of Z.A.Z.B obtained from the slope of the straight lines of Fig. 3 ($\sqrt{\mu}$ Vs $\log K_2$) is found to be +2.05, which shows that the step involves the reaction between two ions of similar charges i.e. tartarate ion and a complex anion of ceric sulphate-sulphuric acid.

The values of frequency factor, pz and entropy of activation, ΔS^\ddagger are 2×10^7 litre mole⁻¹ sec⁻¹, and -19.06 cal deg⁻¹ mole respectively. The value of ΔS^\ddagger computed from the expression $\Delta S^\ddagger = 10 \text{ Z.A.Z.B}$ is -20.05 e.u., which is in fair agreement with the experimental value of ΔS^\ddagger obtained from the energy of activation (ΔE). This also shows that the reaction is not entirely uni-molecular but to a major extent it is of second order as for a unimolecular reaction $\Delta S^\ddagger = 0$.

In the light of the results presented in this paper the following mechanism seems to be plausible for the oxidation of tartaric acid by Ce(IV).



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