

Kinetics of Chromic Acid Oxidation of Citric Acid and Tartaric Acid (in Lemon and Tamarind, a Comparative Study) in Acetic Acid-Water Medium

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The oxidation of citric acid in lemon and tartaric acid in tamarind (natural form) by chromium(VI) shows that the rates of reaction are first order dependence, each in $[\text{Cr(VI)}]$, [substrate]. The reactions are carried out in aqueous acetic acid medium and sulphuric acid in the temperature range 20 to 50°C.

The reactions are acid catalyzed and presence/absence of water molecule participation in mechanism has been indicated by Hammetts and Bunnett's criteria. The decrease in dielectric constant of the medium increases the rate. Specific salt effect has been observed.

Key Words: Kinetics, Chromic acid, Oxidation, Citric acid, Tartaric acid.

INTRODUCTION

Kinetics of oxidation of some α -hydroxy acids by chromic acid was studied earlier^{1,2}. In this paper tartaric acid in tamarind (natural form) and citric acid in lemon (natural form) are studied and comparative investigations are made.

EXPERIMENTAL

All chemicals were either AR, E. Merck or BDH grade, extra pure quality. The solutions were prepared by using double distilled water. The organic substrate was standardized by titration with a standard alkali. Acetic acid used was 25% (v/v). The rate of consumption of $[\text{Cr(VI)}]$ was followed spectrophotometrically by measuring optical density on a Spectronics-20 spectrophotometer at different intervals at 350 nm. The products, aldehydes/ketones, were identified by preparing their 2,4-dinitrophenyl hydrazine derivative³.

RESULTS AND DISCUSSION

Effect of varying [oxidant]

The rate of $[\text{Cr(VI)}]$ was observed keeping [substrate] and [acid] constant. As the $[\text{Cr(VI)}]$ increased, the value of rate constant decreased in the case of pure citric acid. In the case of tartaric acid reaction rate increases with increasing $[\text{Cr(VI)}]$. In the case of citric acid in lemon reaction rate increases with increasing $[\text{Cr(VI)}]$. It is due to the fact that reactive species of chromium, in this case, may be different and not HCrO_4^- (Table-1, Fig. 1(a) and Fig. 1(b)).

Effect of varying [Substrate]

The rate of reaction increased with increasing [substrate]. The plot $\log K$ vs. [substrate] is found to be 0.9042 and 1.262, showing that reaction is of first order (Table-2 and Fig. 2).

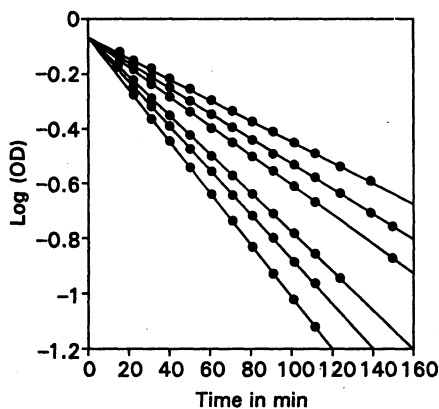
TABLE-1

[Citric acid] = 4.72×10^{-2} M
[H₂SO₄] = 1.0188 M

Temp. = 35°C

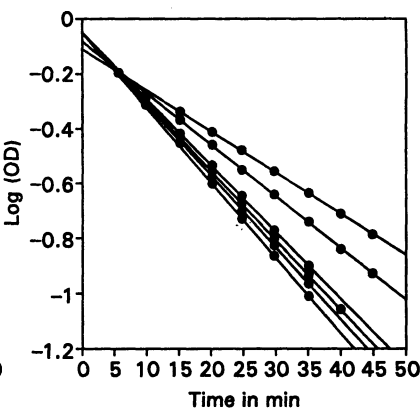
[Tartaric acid] = 4.72×10^{-2} M
[HO-Ac] = 25% v/v

[Cr(VI)]	Natural citric acid (K × 10 ² min ⁻¹)	Natural tartaric acid (K × 10 ² min ⁻¹)
4.48×10^{-4} M	0.9269	3.9690
9.43×10^{-4} M	1.0940	4.5470
2.36×10^{-3} M	1.2240	5.5330
2.83×10^{-3} M	1.6130	5.8390
3.77×10^{-3} M	1.8340	5.9000
4.72×10^{-3} M	2.0030	6.2120



Effect of varying [Oxidant] on rate constant of natural citric acid [Citric acid] = 4.72×10^{-2} M
[H₂SO₄] = 1.0188 M [HO-Ac] = 25% v/v
Temp. 35°C

Fig. 1(a)



Effect of varying [Oxidant] on natural tartaric acid [Tartaric acid] = 4.72×10^{-2} M
[H₂SO₄] = 1.0188 M [HO-Ac] = 25% v/v
Temp. 35°C

Fig. 1(b)

TABLE-2

EFFECT OF VARYING [NATURAL TARTARIC ACID] AND [NATURAL CITRIC ACID] ON RATE CONSTANT

[Cr ^{IV}] = 2.36×10^{-3} M		Temp. = 35°C		[HO-Ac] = 25% v/v		[H ₂ SO ₄] = 1.0188 M	
[Substrate] × 10 ⁻² M	3 + log [substrate]	Natural tartaric acid		Natural citric acid			
		K × 10 ² min ⁻¹	3 + log [K]	K × 10 ² min ⁻¹	3 + log [K]		
1.890	1.2764	3.215	1.5072	0.6253	0.7961		
2.830	1.4518	3.642	1.5613	0.7299	0.8632		
3.770	1.5763	4.991	1.6982	0.9096	0.9588		
4.710	1.6730	5.533	1.7430	1.2260	1.0880		
5.660	1.7528	6.604	1.8198	1.6590	1.2190		
6.600	1.8195	8.234	1.9156	2.0800	1.3100		

TABLE-3
EFFECT OF VARYING SOLVENT COMPOSITION

[Cr(IV)] = 2.36×10^{-3} M Temp. = 35°C [Natural tartaric acid] = 4.72×10^{-2} M
[H₂SO₄] = 1.0188 M [Natural citric acid] = 4.72×10^{-2} M

[HOAc] v/v %	10 ³ /D	Natural tartaric acid		Natural citric acid	
		K ₁ × 10 ² min ⁻¹	log K ₂	K ₂ × 10 ² min ⁻¹	log K ₂
10	8.40	3.980	-1.400116928	0.5611	-2.250959731
20	13.00	4.735	-1.324680017	1.0070	-1.996970529
25	15.15	5.533	-1.257039330	1.2240	-1.912218582
30	17.98	6.518	-1.185885644	1.9920	-1.700710666
40	22.38	7.207	-1.142245478	2.1300	-1.671620397
50	26.70	9.302	-1.031423665	2.8330	-1.547753425

Effect of varying ionic strength

All reactions are ionic dipole type. It was found that the rates increased with increasing ionic strength at lower concentration and at higher concentration of NaCl, the rate remains nearly constant due to ionic association together with the cage effect, which retains dissociation of ion pair Na⁺Cl⁻ effectively

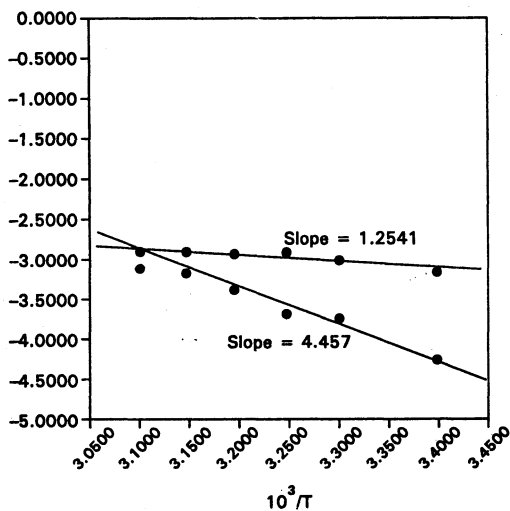
Effect of varying temperature

The first order rate constants were determined at the temperature range 293–313 K and the activation parameters were evaluated.

The rates were calculated from log k vs. 1/T, where linear and heat of activation were calculated from these plots (Table 4, Fig. 4).

[Cr^{VI}] = 2.36×10^{-3} M
[H₂SO₄] = 1.0188 M

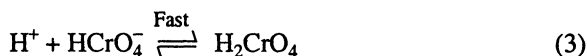
[Natural tartaric acid] = 4.72×10^{-2} M
[Natural citric acid] = 4.72×10^{-2} M



Effect of varying Temperature

Fig. 4

The reactions were characterised by wide range of enthalpy of activation. The transfer of three electrons to Cr(VI) for overall reaction does not take place in single step, either they are transferred one by one or by two-electron transfer process. In acid catalysed reactions proton may either add on to substrate to give protonated substrate followed by reaction of the latter with HCrO_4^- to give products according to steps 1 and 2 or it may be added to HCrO_4^- to give H_2CrO_4 followed by its reaction with substrate according to steps 3 and 4.



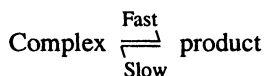
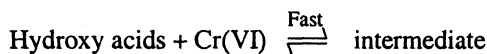
where S is substrate and P* is product

TABLE 4
EFFECT OF VARYING TEMPERATURE

$[\text{Cr(VI)}] = 2.36 \times 10^{-3} \text{ M}$ $[\text{Natural tartaric acid}] = 4.72 \times 10^{-2} \text{ M}$
 $[\text{H}_2\text{SO}_4] = 1.0188 \text{ M}$ $[\text{HO-Ac}] = 25\% \text{ (v/v)}$ $[\text{Natural citric acid}] = 4.72 \times 10^{-2} \text{ M}$

Temp. (K)	1/T 10^3 K^{-1}	Natural tartaric acid		Natural citric acid	
		$K_2 \times 10^{-4} \text{ sec}^{-1}$	Log K_2	$K_2 \times 10^{-4} \text{ sec}^{-1}$	log K_2
293	3.4130	5.127	-3.2901	0.3506	-4.4552
303	3.3003	7.405	-3.1305	1.4050	-3.8523
308	3.2468	9.222	-3.0352	2.0400	-3.6904
313	3.1949	10.030	-2.9987	4.0870	-3.3886
318	3.1447	11.470	-2.9404	6.6000	-3.1805
323	3.0960	12.820	-2.8921	8.5760	-3.0667

The formation of protonated substrate seems unlikely since water is more basic than hydroxy acids



On the other hand, the H_2CrO_4 is highly ionized species and its reaction with hydroxy acid seems unlikely; since plot of $1/K$ v/s. $1/[\text{substrate}]$ is linear passing

through origin, there is formation of intermediate complex between Cr(VI) and hydroxy acids.

The collision numbers of these reactions are not high enough (less than 10^{11}) showing that the reactions are not by molecular type.

α -Hydroxy acids form complexes with divalent and trivalent transition metal ions.

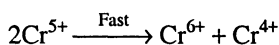
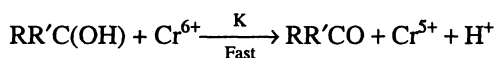
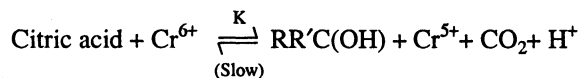
TABLE-5
THERMODYNAMIC PARAMETERS FOR NATURAL TARTARIC ACID

[Cr(VI)] = 2.36×10^{-3} M			[Natural tartaric acid] = 4.72×10^{-2} M						
[H ₂ SO ₄] = 1.0188 M			[HO-Ac] = 25% V/v						
T (K)	1/T $\times 10^3$ M	K $\times 10^{-4}$ (sec ⁻¹)	log K	E (kcal)	ΔH^\ddagger (kcal)	ΔS^\ddagger (eu)	ΔG^\ddagger (kcal)	A (sec ⁻¹)	
493	3.4130	5.127	-3.2901	5.6038443	5.021653	-55.6141	21.31658	7.7517	
303	3.3003	7.405	-3.1305	5.6038443	5.001783	-55.5814	21.84294	8.1507	
308	3.2468	9.222	-3.0352	5.6038443	4.991848	-55.4780	22.07909	8.7277	
313	3.1949	10.03	-2.9987	5.6038443	4.981913	-55.6338	22.39529	8.1990	
318	3.1447	11.47	-2.9404	5.6038443	4.971978	-55.6802	22.67827	8.1319	
323	3.0960	12.82	-2.8921	5.6038443	4.963043	-55.7628	22.97344	7.7930	

TABLE-6
THERMODYNAMIC PARAMETERS FOR NATURAL CITRIC ACID

[Cr(VI)] = 2.36×10^{-3} M			[Natural citric acid] = 4.72×10^{-2} M						
[H ₂ SO ₄] = 1.0188 M			[HO-Ac] = 25% (v/v)						
T (K)	1/T $\times 10^3$ M	K $\times 10^{-4}$ (sec ⁻¹)	log K	E (kcal)	ΔH^\ddagger (kcal)	ΔS^\ddagger (eu)	ΔG^\ddagger (kcal)	A (sec ⁻¹)	
293	3.4130	0.3506	-4.4552	19.997387	19.41520	-11.8206	22.8786422	2.8820×10^{10}	
303	3.3003	1.4050	-3.8523	19.997387	19.39533	-11.3811	22.8438035	3.7179×10^{10}	
308	3.2468	2.0400	-3.6904	19.997387	19.38539	-11.7439	23.0025231	3.1484×10^{10}	
313	3.1949	4.0870	-3.3886	19.997387	19.37546	-11.4322	23.9537296	3.7430×10^{10}	
318	3.1447	6.6000	-3.1805	19.997387	19.36552	-11.5158	23.0275405	3.6466×10^{10}	
323	3.0960	10.2100	-2.9910	19.997387	19.35559	-11.6532	23.1195599	3.4562×10^{10}	

The reaction may be explained on the basis of formation of free radicals, *e.g.*, RR'C(OH) which reacts with Cr(IV) to form stable products ketone and Cr(IV) may be consider as:



The formation of free radicals could not be detected since all experiments are performed in presence of air. [The presence of intermediate valence states of chromium has been indicated by decrease in the reaction rate in the presence of [Mn(II)].

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(Received: 03 July 2003; Accepted: 09 December 2003)

AJC-3273

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