

Kinetics of Os(VIII) Catalysed Chromic Acid Oxidation of Maleic, Fumaric, Acrylic & Cinnamic Acids

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Received 23 June 1981; revised and accepted 10 August 1981

Kinetics of Os(VIII) catalysed chromic acid oxidation of maleic, fumaric, acrylic and cinnamic acids have been studied in aqueous and aq. acetic acid media in the presence of perchloric acid. Maleic acid and cinnamic acid exhibit zero order dependence in oxidant at lower concentrations of the oxidant and first order dependence at higher concentrations of the oxidant. Acrylic acid shows zero order dependence in oxidant in the total range of [oxidant] studied while a fractional order dependence in oxidant is observed in the case of fumaric acid. The dependence on substrate is unity for all the compounds studied. First order dependence on catalyst has been observed in the case of fumaric and acrylic acids in a wide range of [oxidant]. First order dependence on catalyst in the case of cinnamic and maleic acids is observed at zero order concentration ranges of the oxidant. In the first order range of [oxidant] in the case of cinnamic and maleic acids, the dependence on catalyst is fractional. The effect of acidity is marginal and with increase in the percentage of acetic acid the rate decreases.

THE title investigation is in continuation of earlier works from our laboratory^{1,2} on the Os(VIII) catalysed periodate and Ce(IV) oxidations of unsaturated compounds.

Materials and Methods

All the reagents used were of extra pure quality (either BDH or E. merck). Perchloric acid (BDH, AR) was used. OsO₄ solution was used after proper dilution allowing necessary correction for the alkali present in it.

The kinetics of the reactions, in aqueous and aq. acetic acid media in the presence of perchloric acid were followed by estimating the unreacted Cr(VI) iodometrically against standard thiosulphate using starch as indicator. The rate constants are reproducible within $\pm 3\%$ error.

Results and Discussion

(A) *Oxidation of maleic and cinnamic acids* — The significant features of the investigations are listed below :

(i) The oxidation of maleic and cinnamic acids shows zero order and first order dependences in oxidant at different oxidant concentration ranges (see Table 1). The first order dependence at high [oxidant] is further supported by the linear plots of log [Cr(VI)] versus time. (ii) Increase in the concentration of substrate both at the zero order and first order ranges of oxidant concentration increases the rate of oxidation (Table 2). The plots of log k_0 versus log [substrate] and log k_1 versus log [substrate] are linear with unit slopes indicating unit dependence in substrate both at zero order and first order ranges of [oxidant]. (iii) The rate constants at various concentrations of Os(VIII) at both the ranges of [oxidant] are given in Table 3. While the plots of

log k_0 versus log [Os(VIII)] are linear with unit slopes indicating first order dependence with respect to Os(VIII), the plots of log k_1 versus log [Os(VIII)] are linear with slopes less than unity indicating fractional dependence with respect to Os(VIII). The results clearly proved that (I) the catalyst exhibits first order dependence when the dependence on [oxidant] is zero and (II) it exhibits fractional order dependence when the dependence on [oxidant] is unity. (iv) Increase in the concentration of perchloric acid from 0.05M to 0.30M slightly increases the reaction rate ($k_0/[S] \times 10^4 \text{ min}^{-1}$) from 0.88 to 1.38 for maleic acid and from 4.20 to 6.20 in case of cinnamic acid at zero order ranges of [oxidant] and from 2.05 to 3.76 ($10 \times k_1/[S] \text{ litre mol}^{-1} \text{ min}^{-1}$) in case of maleic acid at first order range of [oxidant]. (v) Increase in the percentage of acetic acid of the reaction medium decreases the rate of oxidation. The plots of log k_0 versus 1/D are linear with negative slopes indicating these reactions to be dipole-dipole type. (vi) The reaction has been carried out at different temperatures in the range 50°-70° and the total second order rate constants at 50°, 60° and 70° for maleic acid are 2.09, 4.41 and 7.02 M⁻¹ min⁻¹ respectively. The Arrhenius activation parameters have been computed from the linear plot of log k_2 versus 1/T and found to be $E_a = 47.84 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 45.11 \text{ kJ mol}^{-1}$, $\log_{10} A = 3.08$ and $\Delta S^\ddagger = -195.1 \text{ JK}^{-1} \text{ mol}^{-1}$.

(B) *Oxidation of acrylic and fumaric acids* — The salient features observed in case of acrylic acid oxidation are :

(i) The oxidation is zero order with respect to oxidant in a wide range of [Cr(VI)] (Table 5). (ii) The plot of log k_0 versus log [substrate] is linear with unit slope indicating first order dependence with respect to substrate (Table 5). (iii) The plot of log

TABLE 1 — EFFECT OF VARYING [Cr(VI)] ON THE REACTION RATE

[HClO₄]=0.1M; [Os(VIII)] = 3.93 × 10⁻⁵M; solvent = aq. medium; temp. = 60°C

[Substrate] M	10 ⁴ [Cr(VI)] M	10 ⁶ × k ₀ mol litre ⁻¹ min ⁻¹	10 ³ × k ₁ min ⁻¹
Maleic acid 0.005	2.66	1.07	4.56
	2.80	0.904	3.68
	5.47	1.01	2.11
	10.5	2.06	2.24
	21.4	3.73	1.98
42.3	6.43	1.73	
*Cinnamic acid 0.01	3.0	5.0	18.5
	5.5	5.0	11.77
	9.74	5.4	8.37
	25.86	6.8	3.64
	36.56	11.8	4.12
44.88	14.7	4.18	

*Reaction carried out in 10% aq. HOAc (v/v)

TABLE 2 — EFFECT OF VARYING [SUBSTRATE] ON THE REACTION RATE

[HClO₄] = 0.1M; [Os(VIII)] = 3.93 × 10⁻⁵ M; solvent = aq. medium; temp.=60°C

Range	10 ³ × [S] M	10 ⁶ × k ₀ mol litre ⁻¹ min ⁻¹	10 ³ × k ₁ min ⁻¹	10 ⁴ × k ₀ /[S] min ⁻¹	10 × k ₁ /[S] litre mol ⁻¹ min ⁻¹
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MALEIC ACID

Zero order [Oxidant]=0.0003M	2.77	0.53	1.93
	5.10	0.90	1.78
	10.27	1.83	1.78
	18.0	3.06	1.70

First order [Oxidant]=0.001M	3.0	1.26	4.20
	5.19	2.24	4.30
	10.0	3.71	3.71
	18.2	6.91	3.82

*CINNAMIC ACID

Zero order [Oxidant]=0.0005M	2.55	1.24	4.86
	5.25	2.50	4.76
	10.0	5.00	5.00
	18.4	8.50	4.62

First order [Oxidant]=0.003M	3.05	1.29	4.23
	4.90	1.90	3.88
	9.64	3.80	3.94
	20.2	7.74	3.83

*Reaction carried out in 10% aq. HOAc (v/v)

k₀ versus log [Os(VIII)] is linear with unit slope confirming first order dependence with respect to Os(VIII) (Table 5). (iv) Increase in the percentage of acetic acid decreases the rate of reaction and the plot of log k₀ versus 1/D is linear with negative slope indicating the nature of reaction to be dipole-dipole type (Table 4). (v) Effect of acid is

TABLE 3 — EFFECT OF VARYING [Os(VIII)] ON THE REACTION RATE

[HClO₄] = 0.1M; solvent = aq. medium; temp. = 60°C

Range	10 ⁵ × [Os(VIII)] M	10 ⁴ × k ₀ /[S] min ⁻¹ litre mol ⁻¹	10 × k ₁ /[S] min ⁻¹
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[MALEIC ACID] = 0.005 M

Zero-order [Oxidant]=0.0003 M	1.96	1.08	
	3.93	2.18	
	7.86	3.59	
	11.78	5.03	

First-order [Oxidant] = 0.001M	1.96	3.27	
	3.93	4.42	
	7.86	7.17	
	11.78	9.74	

[CINNAMIC ACID]* = 0.01M

Zero-order [Oxidant] = 0.0005M	0.98	1.28	
	1.96	2.30	
	3.93	5.00	
	7.86	9.36	

First-order [Oxidant] = 0.003M	0.98	2.0	
	1.96	2.85	
	3.93	3.77	
	5.90	5.60	

*Reaction carried out in 10% aq. HOAc (v/v)

TABLE 4 — EFFECT OF VARYING SOLVENT COMPOSITION ON THE REACTION RATE

[Cr(VI)] = 0.0005M; [S] = 0.005M; [HClO₄] = 0.1M; temp. = 60°C

Substrate	10 ⁴ × k ₀ /[S] values in aq. HOAc containing HOAc %			
	10	20	30	40
Maleic acid	1.50	1.23	1.07	
Cinnamic acid*	5.0	3.10	2.35	1.72
Acrylic acid†	4.93	4.35	3.26	
	10 ³ × k ₁ /[S] values			
Fumaric acid	3.38	2.36	1.65	1.25

*Reactions carried out with [substrate] = 0.01 M

†Reactions carried out with [Cr(VI)] = 0.001M

marginal (Table 5). (vi) The reactions have been carried out at temperatures 50, 60 and 70°C and the rates constants (k₀/[S]) are 3.33, 5.75 and 10.14 min⁻¹ respectively. The plot of log k₁ (k₀/[S]) versus 1/T is linear. The activation parameters have been calculated and found to be E_a = 47.86kJ mol⁻¹, ΔH‡ = 45.11 kJ mol⁻¹, log₁₀A = 1.96, ΔS‡ = -216.7 JK⁻¹ mol⁻¹.

(C) Oxidation of fumaric acid — The salient features observed in case of fumaric acid oxidation are as follows :

(i) The zero order rate constant gradually increases with the increase in [oxidant]. Similarly the first order rate constant gradually decreases with the increase in [oxidant]. This clearly indicates that these

TABLE 5 — EFFECT OF VARYING [Cr(VI)], [SUBSTRATE], [Os(VIII)], [HClO₄] ON THE REACTION RATE

Solvent : aq. medium; temp. = 60°C

10 ⁴ [Cr(VI)] M	10 ³ [Acrylic acid] M	10 ³ [Os(VIII)] M	[HClO ₄] M	10 ⁶ × k ₀ mol litre ⁻¹ min ⁻¹	10 ⁴ × k ₀ /[S] min ⁻¹
2.99				3.3	
5.80				3.22	
10.97	5.0	3.93	0.1	3.6	
21.2				4.15	
37.1				3.4	
	3.61			2.34	6.48
	6.08			3.60	5.92
10.00	24.80	3.93	0.1	13.90	5.61
	54.00			30.00	5.55
		1.96			4.13
		3.93			5.92
10.00	5.00	5.90	0.1		9.82
		7.86			12.58
			0.05		6.3
			0.1		5.92
10.00	5.0	3.93	0.2		7.0
			0.3		7.2

 TABLE 6 — EFFECT OF VARYING [Cr(VI)], [SUBSTRATE], [Os(VIII)], [HClO₄] ON THE REACTION RATE

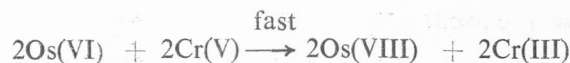
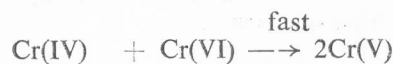
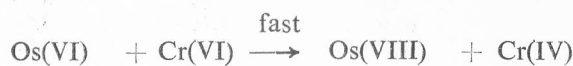
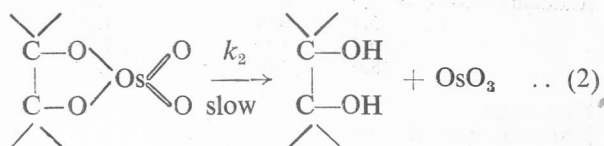
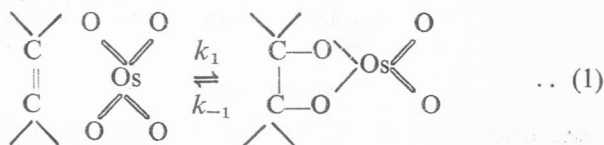
Solvent : 10% HOAc; temp. = 60°C

10 ⁴ [Cr(VI)] M	10 ³ [Fumaric acid] M	10 ³ [Os(VIII)] M	[HClO ₄] M	10 ⁴ × k _{1/2} mol ^{1/2} litre ^{-1/2} min ⁻¹	10 ² × k _{1/2} /[S] mol ^{-1/2} litre ^{1/2} min ⁻¹
3.01				1.58	
5.94				1.69	
11.05	5.0	3.93	0.1	1.56	
20.76				1.53	
40.73				1.42	
	2.63			0.59	2.25
	5.20			1.11	2.15
5.0	9.43	3.93	0.1	2.0	2.16
	19.68			3.58	1.82
		1.96			1.44
		3.93			3.38
5.0	5.0	7.86	0.1		4.30
		11.78			7.62
			0.05		3.35
			0.10		3.40
			0.20		3.20
			0.30		3.21

(vi) The reaction has been carried out at different temperatures in the range 50-70°C. From the linear plot of log k_{3/2} versus 1/T the Arrhenius parameters have been computed and found to be : E_a = 47.86 kJ mol⁻¹, ΔH‡ = 45.11 kJ mol⁻¹, log₁₀A = 3.49 and ΔS‡ = -187.4 JK⁻¹ mol⁻¹.

Mechanism—Kinetic features observed in the present investigation indicate that the reaction is not routed through identical mechanisms in all the substrates studied. The rate determining step in the reaction is dependent on the concentration of the oxidant. This complex dependence on oxidant needs rationalisation. As reported earlier^{3,4}, the unsaturated compounds can form complexes with the catalyst to give intermediate complexes. These complexes then disproportionate in a rate determining step, to give Os(VI) which is oxidised in a fast step by Cr(VI) leading, as observed experimentally at lower [oxidant], to zero order dependence with respect to oxidant. But at higher [oxidant], the oxidant forms complexes with the substrates and the resultant complexes disproportionate in presence of catalyst in a rate determining step leading to first order dependence with respect to oxidant.

The zero order, first order and fractional dependences with respect to oxidant have been noticed. To account for this behaviour in oxidant Schemes 1 and 2 are proposed.



Scheme 1

reactions are not routed through a single path. But the fractional order rate constant computed with the formula $2/t \{a^{1/2} - (a-x)^{1/2}\}$ are almost constant at different concentrations of oxidant indicating fractional dependence with respect to oxidant (Table 6). (ii) The plot of log k_{1/2} versus log [substrate] is linear with unit slope indicating first order dependence with respect to substrate. (iii) The plot of log k_{1/2} versus log [Os(VIII)] is linear with unit slope indicating unit dependence with respect to catalyst. (iv) Increase in the percentage of acetic acid decreases the rate of oxidation (Table 4). The plot of log k_{1/2} versus 1/D is linear with negative slope as observed in the case of other unsaturated compounds. (v) The effect of perchloric acid is marginal (Table 6).

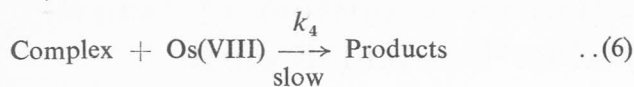
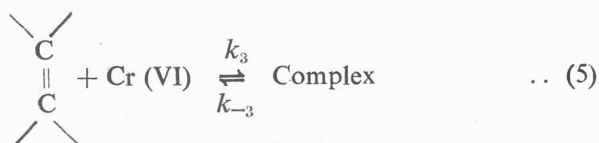
Postulating steady state treatment for the complex formed in step 1, the rate-law is given by Eq. (3)

$$\begin{aligned} \text{Rate} &= k_2 [\text{Complex}] \\ &= \frac{k_1 k_2 [S] [\text{Os(VIII)}]_{\text{T}}}{k_{-1} + k_2 + k_1 [S]} \quad \dots (3) \end{aligned}$$

As the dependence on substrate is unity, the term k₁[S] in the denominator can be neglected. The rate assumes the form (4)

$$-\frac{d[\text{Cr(VI)}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [S] [\text{Os(VIII)}]_{\text{T}} \quad \dots (4)$$

where [Os(VIII)]_T = [Os(VIII)] + [Complex]



Scheme 2

$$\begin{aligned} \text{Rate} &= k_4 [\text{Complex}] [\text{Os(VIII)}] \\ &= \frac{k_3 k_4 [\text{S}] [\text{Os(VIII)}] [\text{Cr(VI)}]_{\text{T}}}{k_{-3} + k_4 [\text{Os(VIII)}] + k_3 [\text{S}]} \end{aligned}$$

As the dependence on substrate is unity the term $k_3 [\text{S}]$ in the denominator can be neglected.

$$\frac{d[\text{Cr(VI)}]}{dt} = \frac{k_3 k_4 [\text{S}] [\text{Os(VIII)}] [\text{Cr(VI)}]_{\text{T}}}{k_{-3} + k_4 [\text{Os(VIII)}]} \quad \dots (7)$$

Combining equations (4) and (7)

$$\begin{aligned} - \frac{d[\text{Cr(VI)}]}{dt} &= \frac{k_1 k_2}{k_{-1} + k_2} [\text{S}] [\text{Os(VIII)}]_{\text{T}} \\ &\quad \text{(A)} \\ &+ \frac{k_3 k_4 [\text{S}] [\text{Os(VIII)}] [\text{Cr(VI)}]_{\text{T}}}{k_{-3} + k_4 [\text{Os(VIII)}]} \\ &\quad \text{(B)} \quad \dots (8) \end{aligned}$$

Equation (8) explains all the observed facts. The operation of first term(A) explains the zero order in oxidant in the concentration range $2.5 \times 10^{-4} M$ to $5.5 \times 10^{-4} M$ of the oxidant in the case of cinnamic acid and maleic acid.

The operation of second term (B) explains the first order dependence on oxidant in the concentration range $1.0 \times 10^{-3} M$ to $4.5 \times 10^{-3} M$ of oxidant for cinnamic and maleic acid.

In the case of acrylic acid in the total range studied term (A) alone operates giving rise to zero order dependence on oxidant.

In the case of fumaric acid in the total range studied terms (A) and (B) both operate simultaneously leading to fractional dependence on oxidant.

Acknowledgement

One of the authors (B. K. P.) is thankful to the UGC for the award of a teacher fellowship.

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