Indian Journal of Chemistry
Vol. 23A, September 1984, pp. 766-768

Kinetics of Os(VIII) Catalysed Vanadium(V) Oxidation of a Few Unsaturated Acids

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Received 19 *March* 1983; *revised* 23 *April* 1984; *accepted* 7 *May* 1984

Os(VIII) catalysed oxidation of maleic, fumaric, acrylic and cinnamic acids by vanadium(V) in aqueous acetic acid and sulphuric acid media follows zero order kinetics in V(V) and first order in Os(VIII). The order in substrate is unity except in the case of acrylic acid which exhibits a fractional order. A change in the concentration of sulphuric acid has marginal effect on zero order rate constants. Increase in the proportion of acetic acid retards the rate pointing to a dipole-dipole reaction. The activation parameters have been computed and mechanism has been discussed.

The title investigation is in continuation of earlier reports from this laboratory on OsO_4 catalysed oxidation of unsaturated systems by a variety of oxidants like IO_4^- (ref. 1), Ce(IV)[2] and Cr(VI)[3].

Oxidation of maleic, fumaric, acrylic and cinnamic acids by vanadium(V) is sluggish but the oxidation reaction becomes amenable to kinetic investigation in the presence of catalytic amount of Os(VIII).

All the reagents were of AR grade. Ammonium metavanadate (Riedel) was used as such. Pre-equilibrated solutions of the reactants in water (aqueous acetic acid) were mixed and the aliquots from the reaction mixture were analysed for V(V) as follows: an aliquot (5 ml) of the reaction mixture was added to a known excess of ferrous ammonium sulphate in the presence of 4 *N* H_2SO_4 and the excess ferrous ammonium sulphate was titrated against standard dichromate using N-phenylanthranilic acid as an indicator.

The stoichiometry has been found to be 1:8 under the condition [V(V)] $\gg$ [substrate] and the product is formic acid for the oxidation of fumaric, maleic and acrylic acids. For the oxidation of cinnamic acid the stoichiometry is found to be 1:6 and the products are benzaldehyde and formic acid.

The kinetic results can be summarised as follows: (i) The reaction is zero order in V(V) as found from the linear plot of percentage of reaction versus time and a fair constancy of k_0 (min^{-1}) values (Table 1) at different initial [oxidant]. (ii) The order in substrate in cases of fumaric, maleic and cinnamic acids is one as revealed by the linear plots with unit slope of log k_0 versus log [substrate]. k_1 (min^{-1}) values ($=k_0$/[substrate]) are constant for each substrate at varying [substrate] (Tables 1 and 2). Though the plot of log k_0 versus log [substrate] for acrylic acid is linear it has a slope of 0.5 pointing to a fractional order in acrylic acid. The plot of $1/k_0$ versus 1/[substrate] for acrylic acid is also linear with a finite intercept in the inverse rate axis indicating complex formation. For fumaric, maleic and cinnamic acids such plots pass through the origin. (iii) The reaction is first order in [Os(VIII)], since the plot of log k_0 versus log [Os(VIII)] is linear with unit slope. (iv) Varying [H_2SO_4] has only marginal effect on the zero order rate constants (Tables 1 and 2). Under such conditions of acidity the dissociation of weak acid is negligible and only the undissociated acid molecules are the active species. (v) An increase in the proportion of acetic acid in the reaction medium decreases the rate for all the substrates. The plots of log k_0 versus $1/D$ (D = dielectric constant) are linear with negative slopes indicating the reaction to be of dipole-dipole type. (vi) The reactions have been carried out at 50°, 60° and 70°C and the plots of log k_1 versus $1/T$ are linear. In the case of acrylic acid the effect of varying [substrate] on the reaction rate has also been studied at 50°, 60° and 70°C and the decomposition constants of the complex (k_D) have been found from the plots of $1/k_0$ versus 1/[S] at each temperature. The plot of log k_D versus $1/T$ is also found to be linear. The activation parameters are reported in Table 3.

Under identical conditions fumaric acid reacts six-times faster than maleic acid. The same order of reactivities has been observed by Taylor *et al.*[4] in the OsO_4 catalysed oxidation by chlorate and by Simandi *et al.*[5] in the oxidation of maleic and fumaric acids by permanganate. Cinnamic acid reacts faster than acrylic acid due to extended conjugation with the aromatic ring (rate constants for cinnamic acid $= 2.76 \times 10^{-5}$ mol dm^{-3} min^{-1} and that of acrylic acid $= 1.56 \times 10^{-5}$ mol dm^{-3} min^{-1}) which outweighs the possible steric hindrance that might be present due to the bulky phenyl group in cinnamic acid in place of hydrogen in acrylic acid.

The zero order in oxidant in the present investigation clearly shows that the vanadium species in whatever form it may be (see refs 6 and 7) is not participating in a slow step. As such, it is envisaged that the catalyst Os(VIII) forms a complex with the substrate. The resultant complex then breaks down in a slow step to form the product, and Os(VI) thus generated is reoxidised to Os(VIII) by V(V) in fast steps

Table 1—Effect of Varying [Reactants] on Rate Constant

[Solvent = Aq medium; Temp. = 60°C]

10^2 [substrate] (mol dm^{-3})	10^3 [V(V)] (mol dm^{-3})	10^5 [Os(VIII)] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^5 \times k_0$ (mol dm^{-3} min^{-1})	$10^3 \times k_0$/[substrate] (min^{-1})
		Acrylic acid			
2.5	2.46	3.93	0.18	1.64	
	5.1			2.10	
	10.65			2.24	
1.35	5.0	3.93	0.18	1.43	
2.6				2.10	
5.15				3.35	
9.7				4.20	
2.5	5.0	1.96	0.18	1.14	
		3.93		2.10	
		7.86		4.31	
2.5	5.0	3.93	0.18	2.46	
			0.45	2.49	
			0.90	2.10	
		Maleic acid			
2.0	10.0	3.93	0.18	0.76	0.38
5.0				1.92	0.38
9.0				2.95	0.32
25.0				8.90	0.35
5.0	10.0	1.96	0.18	1.05	0.21
		3.93		1.92	0.38
		7.86		3.20	0.64
		11.70		5.50	1.10
5.0	10.0	3.93	0.18	1.92	0.38
			0.36	1.55	0.31
			0.90	1.42	0.28

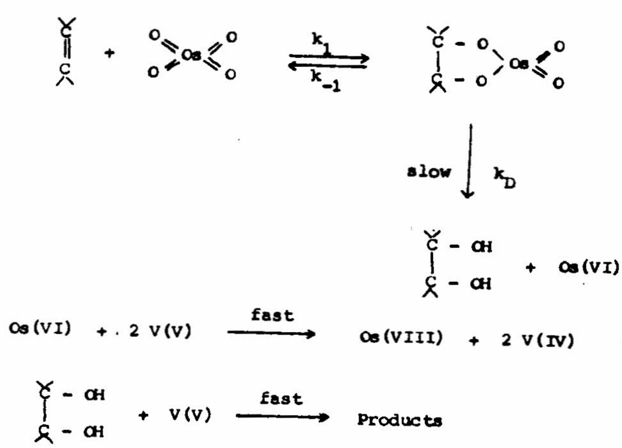
Table 2—Effect of Varying [Reactants] on Rate Constant

[Solvent = 25% aq HOAc (v/v), temp. = 60°C]

10^2 [substrate] (mol dm^{-3})	10^3 [V(V)] (mol dm^{-3})	10^5 [Os(VIII)] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^5 \times k_0$ (mol dm^{-3} min^{-1}]	$10^3 \times k_0$/[substrate] (min^{-1})
		Fumaric acid			
2.5	3.3	3.93	0.18	2.48	
	5.02			2.76	
	9.6			2.93	
1.00	5.0	3.93	0.18	1.06	1.06
2.45				2.74	1.12
4.97				5.07	1.02
2.5	5.0	1.96	0.18	1.15	0.46
		3.93		2.80	1.12
		7.86		5.05	2.02
2.5	5.0	3.93	0.18	2.76	1.12
			0.90	2.12	0.85
		Cinnamic acid			
2.5	3.3	3.93	0.18	2.48	
	5.02			2.76	
	9.6			2.76	
1.01	5.0	3.93	0.18	1.11	1.10
2.5				2.76	1.10
4.99				5.20	1.05
2.5	5.0	1.96	0.18	1.00	0.40
		3.93		2.80	1.12
		7.86		4.55	1.82

Table 3—Activation Parameters at 60°C

Substrate	$\Delta E\ddagger$ (kJ mol^{-1})	$\Delta H\ddagger$ (kJ mol^{-1})	$\log_{10}A$	$\Delta S\ddagger$ (J K^{-1} mol^{-1})
Fumaric acid	57.4	54.6	4.6	−172
Cinnamic acid	57.4	54.6	4.6	−172
Maleic acid	59.6	57.1	4.2	−173
Acrylic acid	54.2	52.5	2.7	−202



Scheme 1

(Scheme 1). Such type of complex formation between Os(VIII) and unsaturated compounds in an equilibrium step and the rate-determining decomposition of such complexes have been invoked earlier[4].

Applying steady state treatment to the complex one arrives at the rate law,

$$\text{Rate} = -\frac{d[\text{V(V)}]}{dt} = k_0$$

$$= \frac{2\,K k_D[\text{substrate}][\text{Os(VIII)}]_T}{1 + K[\text{substrate}]} \quad \ldots (1)$$

where $K = k_1/k_{-1}$

When the formation constant, K, is small the second term in the denominator is negligible as compared to unity. The rate law then takes the form (2).

$$\text{Rate} = -\frac{d[\text{V(V)}]}{dt} = k_0$$

$$= 2\,k_D K[\text{substrate}][\text{Os(VIII)}]_T \quad \ldots (2)$$

Table 4—Comparison of Calculated and Observed Rate Constants

$[\text{V(V)}] = 0.005$ mol dm^{-3}; $[\text{Os(VIII)}] = 3.93 \times 10^{-5}$ mol dm^{-3}; $[\text{H}^+] = 0.18$ mol dm^{-3}; solvent = aqueous medium; temp. = 60°C

10^3[Acrylic acid] (mol dm^{-3})	$10^5 k_0$(mol dm^{-3} min^{-1}) Obs.	Calc.
1.35	1.43	1.41
2.60	2.10	2.24
5.15	3.35	3.25
9.70	4.20	4.16

However for acrylic acid the formation constant appears to be large and the rate law (1) holds. To verify the above rate law for acrylic acid Eq. (1) could be put in the form (3)

$$\frac{1}{k_0} = \frac{1}{2\,K k_D[\text{Os(VIII)}]_T} \times \frac{1}{[\text{substrate}]} + \frac{1}{2\,k_D[\text{Os(VIII)}]_T} \quad \ldots (3)$$

The plot of $1/k_0$ versus $1/[\text{substrate}]$ has been found to be linear with a finite intercept in the inverse rate axis and from the intercept the value of k_D is found to be 0.771 min^{-1} at 60°C. The formation constant as calculated from slope comes out to be ~22.5. Utilizing these values the computed rate constants are found to be in fair agreement with the observed values (Table 4).

One of the authors (BKP) is thankful to the UGC, New Delhi for the award of a teacher fellowship.

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