

Kinetics of Oxidation of Cyclic Ketones by Periodate Catalysed by Os(VIII), Ru(III) & Os(VIII) + Ru(III) Mixture

N SWARNALAKSHMI, V UMA, B SETHURAM* & T NAVANEETH RAO

Department of Chemistry, Osmania University, Hyderabad 500 007

Received 29 August 1986; accepted 21 October 1986

The kinetics of oxidation of cyclic ketones by periodate in the presence of Ru(III), Os(VIII) and Ru(III) + Os(VIII) mixture have been studied in alkaline medium under identical conditions. The catalytic efficiency is in the order: Ru(III) < Os(VIII) < Ru(III) + Os(VIII). The product of oxidation in all the cases is dicarboxylic acid. The stoichiometry is the same in all the three catalysed reactions, i.e. $[\text{IO}_4^-]:[\text{cyclic ketone}] = 3:1$. Probable mechanisms have been proposed and discussed.

In some recent publications from our laboratory, it was shown that a mixture of two metal ions such as Os(VIII) + Ru(III) functions as an efficient catalyst in the oxidation of organic substrate by different oxidants¹⁻⁵. The Os(VIII)-catalysed oxidation of cyclic ketones by periodate in alkaline medium has already been reported⁶. We have observed that Ru(III) also catalyses the above reaction. A comparative study of Os(VIII), Ru(III) and Os(VIII) + Ru(III) catalysed oxidations of cyclic ketones by periodate has now been undertaken in alkaline medium in order to interpret the mechanisms.

Materials and Methods

Alicyclic ketones, viz cyclopentanone, cyclohexanone and cycloheptanone (all AR reagents) were distilled just before use. An aqueous solution containing cyclic ketone and requisite amounts of base and metal ion (s) were thermostated at the desired temperature. To this was added a known con-

centration of pre-equilibrated periodate solution and the progress of the reaction followed by estimating unreacted periodate iodometrically at regular time intervals.

Results and Discussion

Os(VIII)-catalysed oxidation

Under the conditions $[\text{IO}_4^-] \ll [\text{cyclic ketone}]$ the order in $[\text{IO}_4^-]$, $[\text{Os(VIII)}]$, $[\text{ketone}]$ were zero, one and one respectively. Increase in $[\text{OH}^-]$ increased the rate of reaction (Table 1).

Dicarboxylic acid was the product of oxidation, the stoichiometry being $[\text{IO}_4^-]:[\text{cyclic ketone}] = 3:1$. The enol, which is the most likely species in alkaline medium is assumed to undergo hydroxylation by OsO_4 (ref. 7). The formation of ester type complex between Os(VIII) and enolate ion is shown to be the rate-controlling step. The rate law derived for the disappearance of periodate is given by Eq. (1).

Table 1—Effect of Varying $[\text{OH}^-]$ in Metal Ion(s) Catalysed Oxidation of Cyclohexanone by Periodate in Basic Medium
 $[\text{IO}_4^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{cyclohexanone}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Os(VIII)}]^a = 1.56 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{Ru(III)}]^b = 2.29 \times 10^{-6} \text{ mol dm}^{-3}$; Temp = 303°K

A ^b		B ^a		C ^c	
$[\text{OH}^-] \times 10^3$ (mol dm ⁻³)	$k_0 \times 10^6$ (mol dm ⁻³ min ⁻¹)	$[\text{OH}^-] \times 10^3$ (mol dm ⁻³)	$k_0 \times 10^6$ (mol dm ⁻³ min ⁻¹)	$[\text{OH}^-] \times 10^3$ (mol dm ⁻³)	$k_0 \times 10^6$ (mol dm ⁻³ min ⁻¹)
1.10	2.00	1.30	3.0	1.10	6.50
2.20	6.50	2.20	10.5	2.20	20.0
3.30	12.5	3.10	18.5	3.30	28.0
4.40	18.5	4.00	25.5	4.40	39.0
5.50	23.5	4.90	30.0	5.50	51.0
11.0	25.5	5.50	32.0	11.0	60.0
22.0	27.0	11.0	36.2	22.0	63.5
44.0	29.0	22.0	39.0	44.0	64.0
		44.0	40.1	55.0	65.5

(A) Ru(III), (B) Os(VIII) and (C) Ru(III) + Os(VIII) catalysed oxidations; c = a + b

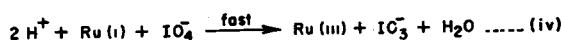
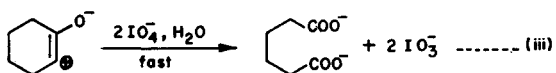
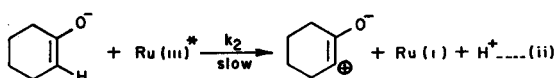
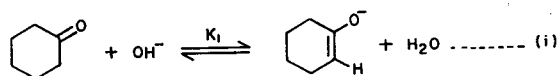
$$\frac{-d[\text{IO}_4^-]}{dt} = k_0 = \frac{k_1 K_1 [\text{ketone}] [\text{Os(VIII)}] [\text{OH}^-]}{1 + K_1 [\text{ketone}] + K_1 [\text{OH}^-]} \quad \dots (1)$$

Since the enolisation constant⁸ (K_1) is known to be of the order of 10^{-5} , the term $K_1 [\text{ketone}] + K_1 [\text{OH}^-]$ is probably very much less compared to one and hence neglected. The resulting rate law satisfactorily explains all the observed kinetic results.

Ru(III)-catalysed oxidation

In Ru(III)-catalysed oxidation also the order in $[\text{IO}_4^-]$ and $[\text{Ru(III)}]$ were found to be zero and one respectively as in Os(VIII)-catalysed reaction. However, the order in [substrate] was fractional. The rate increased with increasing $[\text{OH}^-]$ (Table 1). The product of oxidation was dicarboxylic acid and the stoichiometry was found to be $[\text{IO}_4^-]: [\text{cyclic ketone}] = 3:1$.

Keeping these points in view the mechanism taking cyclohexanone as a typical example is shown in Scheme 1.



SCHEME 1

Increase in rate with increase in $[\text{OH}^-]$ indicates that both the hydroxylated species of Ru(III)⁹ and the enolate ion of the cyclic ketone are the reactive species in the reaction (step-i of Scheme 1). Since $[\text{OH}^-] \gg [\text{Ru(III)}]$ it is assumed that all Ru(III) is present as hydroxylated species (shown as Ru(III)^* for simplicity). The slow step (k_2 step) involves interaction of hydroxylated species of Ru(III) with the enolate ion resulting in the formation of Ru(I) and an intermediate (II) probably a carbonium ion. Formation of intermediate could be via a hydride ion transfer to Ru(III), since the latter is known to be a good hydride

ion abstractor^{5,10}. However, in view of the very low concentration of Ru(III) used, no kinetic evidence could be obtained for the formation of Ru(I). The intermediate carbonium ion is assumed to undergo oxidation by periodate to yield the final product, viz. adipic acid. The catalyst Ru(III) is regenerated in a subsequent step.

The rate law derived for the above mechanism is given by (Eq. 2)

$$\frac{-d[\text{IO}_4^-]}{dt} = \frac{k_2 K_1 [\text{Cyclic ketone}] [\text{OH}^-] [\text{Ru(III)}]}{1 + K_1 \{[\text{Cyclic ketone}] + [\text{OH}^-]\}} \quad \dots (2)$$

This rate law satisfactorily explains all the observed kinetic features.

Oxidation catalysed by Os(VIII) + Ru(III) mixture

In this system also the order in [periodate] was zero excluding the possibility of Ru(V) formation. In cyclohexanone oxidation the order in $[\text{Os(VIII)}]$, $[\text{Ru(III)}]$ and [cyclohexanone] were 0.41, 0.40 and 0.69 respectively (Table 2). A similar fractional order dependence was observed in cyclopentanone oxid-

Table 2—Effect of Varying [Ketone] in Metal Ion(s) Catalysed Oxidation of Cyclic Ketones by Periodate

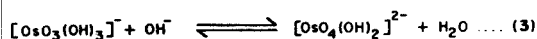
$[\text{IO}_4^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{KOH}] = 2.20 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Ru(III)}]^a = 2.29 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{Os(VIII)}]^b = 1.56 \times 10^{-6} \text{ mol dm}^{-3}$; $\{[\text{Ru(III)}]\} = 2.29 \times 10^{-6} \text{ mol dm}^{-3} + [\text{Os(VIII)}] = 1.56 \times 10^{-6} \text{ mol dm}^{-3}\}^c$; temp. = 303 K

[Ketone] × 10 ² mol dm ⁻³	$k_0 \times 10^6 (\text{mol dm}^{-3} \text{ min}^{-1})$ catalysed by		
	Ru(III) ^a	Os(VIII) ^b	Ru(III)+Os(VIII) ^c
Cyclopentanone			
1.00	4.25	6.00	18.5
2.00	7.50	10.5	33.5
3.00	10.0	17.0	41.5
4.00	12.5	22.0	50.0
5.00	15.5	29.5	56.8
Cyclohexanone			
1.00	6.50	10.2	33.3
2.00	11.0	20.4	55.0
3.00	12.5	30.0	76.0
4.00	18.0	41.1	98.0
5.00	25.0	50.9	108.0
Cycloheptanone			
1.00	1.25	2.00	4.50
2.00	3.05	4.40	9.00
3.00	3.75	6.30	12.7
4.00	4.40	8.00	17.0
5.00	5.00	10.2	21.0

ation. However in cycloheptanone oxidation the order in [Os(VIII)] and [Ru(III)] were 0.65 and 0.45 respectively while the order in [cycloheptanone] was one. The rate increased with increase in [OH⁻] and reached limiting values at higher concentrations of [OH⁻] (Table 1). The product of oxidation and stoichiometry were similar to Os(VIII) or Ru(III) catalysed oxidations.

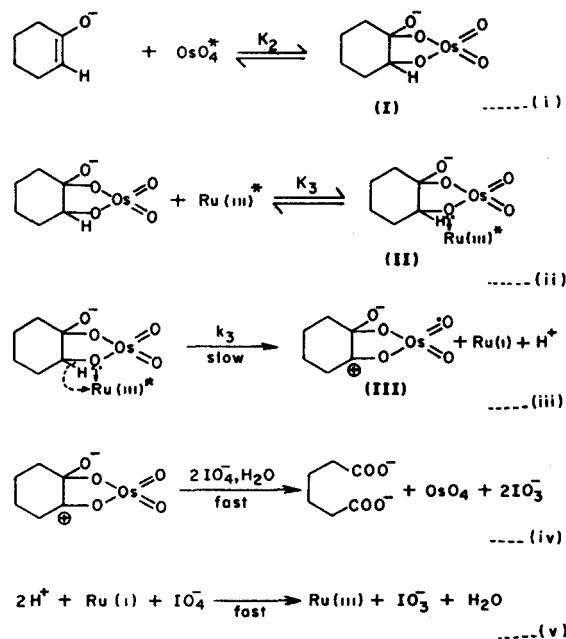
The probable mechanism shown in Scheme 2 for cyclohexanone oxidation envisages the formation of an initial complex between Os(VIII) and enolate ion of cyclohexanone, followed by interaction with Ru(III) to give a reactive intermediate which finally rearranges in a slow step to give the products.

In alkaline solutions OsO₄ is known to exist^{11,12} as [OsO₃(OH)₃]⁻. Since the rate of oxidation increased with increase in [OH⁻] it is quite reasonable to assume the equilibrium



Under the condition [OsO₄] ≪ [OH⁻], it can be presumed that OsO₄ exists mostly as [OsO₄(OH)₂]²⁻. This dihydroxy species is considered to be the reactive species which is represented as OsO₄* in reaction Scheme 2. In alkaline solutions Ru(III) is mostly present as hydroxylated species (shown as Ru(III)* for simplicity). The enol form of the ketone is taken as the reactive species since it is well known that the keto-enol equilibrium is set up rapidly in alkaline solutions⁸. Moreover OsO₄ is known to react across olefinic double bonds, as it is a well known agent for *cis*-hydroxylation⁷. The formation of an enol which creates a carbon-carbon double bond facilitates the attack by Os(VIII). Also the removal of a hydride ion from an anion is reported to be more facile according to Farkas *et al.*¹³ in their work on the oxidation of alcohols by bromine. The fractional order dependence of rate on [substrate], [Os(VIII)] and [Ru(III)] shows that all these are involved in complex formation before the rate-determining step.

The formation of complex (I) between the enolate ion of ketone and OsO₄* is envisaged as the initial step. This complex (I) in the presence of Ru(III)* could form another reactive intermediate (II) (step-ii, of Scheme 2) which is then assumed to rearrange in a slow step (iii) via hydride ion abstraction by Ru(III) resulting in the formation of Ru(I) and intermediate (III). The subsequent fast steps involve the formation of dicarboxylic acid and OsO₄ in the presence of two mol of periodate and water. Ru(III) is formed by the interaction of another periodate with Ru(I) thus



accounting for the stoichiometry of 3 mol of periodate for every mol of ketone reacting.

The rate law based on Scheme 2 is given by Eq. (4)

$$\frac{-d[\text{IO}_4^-]}{dt} = \frac{k_3 K_1 K_2 K_3 [\text{cyclohexanone}] [\text{OH}^-] [\text{Os(VIII)}] [\text{Ru(III)}]}{\{1 + K_3 [\text{Ru(III)}]\} \{1 + K_1 [\text{OH}^-]\} + K_1 [\text{Cyclohexanone}] \{1 + K_2 [\text{OH}^-]\} + K_3 [\text{Os(VIII)}]} \quad (4)$$

The rate law (4) satisfactorily explains the observed kinetic results. In the case of cycloheptanone, however, it is possible that $K_1 [\text{cyclic ketone}] \ll 1$ so that the order in [cycloheptanone] is one.

The order of reactivity of the catalysts is Ru(III) < Os(VIII) < Os(VIII) + Ru(III) (Table 3). The Ru(III)-catalysed reaction is the slowest probably due to the inability of Ru(III) to act across a double bond. The abstraction of a hydride ion by Ru(III), also appears difficult in the presence of a double bond. Os(VIII)-catalysed reaction is, however, reasonably fast in view of the readiness of Os(VIII) to act across a double bond. Formation of this type of complex is probably responsible for the increase in hydride ion abstracting ability of Ru(III) when Os(VIII) and Ru(III) are taken together. This is considered to be responsible for the highest catalytic activity of Os(VIII) + Ru(III) mixture.

The reactivity order of cyclic ketones in all the three catalysed reactions is: cyclohexanone > cyclopentanone > cycloheptanone (Table 2). This trend has been observed during the oxidation of these ketones by phenyl iodosoacetate¹⁴, BrO₃⁻ (ref. 15) and hexacyanoferrate(III)¹⁶. The higher enolisation constant of

Table 3—Effect of Varying [Catalyst] in Metal Ion(s) Catalysed Oxidation of Cyclic Ketones by Periodate in Basic Medium
 $[IO_4^-] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; [cyclic ketone] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$; $[Os(VIII)]^a = 1.5 \times 10^{-6} \text{ mol dm}^{-3}$; $[Ru(III)]^b = 2.29 \times 10^{-6} \text{ mol dm}^{-3}$ [KOH] = $2.20 \times 10^{-3} \text{ mol dm}^{-3}$ Temp. = 303 K

A		B		C			
$[Ru(III)] \times 10^6$ (mol dm ⁻³)	$k_0 \times 10^6$ (mol dm ⁻³ min ⁻¹)	$[Os(VIII)] \times 10^6$ (mol. dm ⁻³)	$k_0 \times 10^6$ (mol dm ⁻³ min ⁻¹)	$[Ru(III)] \times 10^6$ (mol. dm ⁻³) at constant $[Os(VIII)]^a$	$k_0 \times 10^6$ (mol. dm ⁻³ min ⁻¹)	$[Os(VIII)] \times 10^7$ (mol. dm ⁻³) (at constant $[Ru(III)]^b$)	$k_0 \times 10^6$ (mol. dm ⁻³ min ⁻¹)
Cyclopentanone							
2.29	2.75	1.56	6.00	1.14	13.0	7.80	12.5
4.58	5.00	3.14	10.5	2.29	16.0	15.6	18.5
8.02	9.50	4.70	17.0	3.42	21.0	22.4	21.0
10.3	12.5	6.28	21.0	5.73	27.5	31.2	24.5
11.5	13.8	7.80	25.0	8.02	31.0	39.2	31.5
Cyclohexanone							
1.14	3.70	0.780	5.50	1.14	15.0	3.90	12.0
2.29	7.50	1.56	10.1	3.42	21.0	7.80	15.0
4.58	12.2	2.34	14.7	5.73	30.0	15.6	21.0
5.73	18.5	3.12	21.0	8.02	35.0	22.4	24.0
9.17	28.1	3.92	24.5	11.5	39.0	39.2	33.0
Cycloheptanone							
2.29	0.35	1.56	1.00	2.29	4.60	15.6	2.40
4.58	0.75	2.24	1.50	3.42	5.50	22.4	3.25
8.02	1.75	3.90	2.70	5.73	6.50	39.2	4.70
11.5	2.50	5.46	3.75	8.02	7.50	59.6	6.25
16.0	3.05	8.58	6.00	11.5	8.75	85.8	8.00

(A) Ru(III)-catalysed oxidation; (B) Os(VIII)-catalysed oxidation; (C) Ru(III) + Os(VIII) catalysed oxidation

cyclohexanone, is probably the most important factor contributing towards greater reactivity of this ketone compared to the other two ketones. In step (i) (Scheme 2) there is a change in the hybridization in the ketone from sp^2 to sp^3 at the site of attack. The conversion from sp^2 into sp^3 is most favoured when it is a six-membered ring and least favoured when it is seven-membered ring¹⁷. This trend can be seen in the rate data reported in Table 2.

References

- Ram Reddy M G, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **16A** (1978) 591.
- Uma V, Sethuram B & Navaneeth Rao T, *React Kinet & Catal Lett*, **18** (1981) 283.
- Ram Reddy M G, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **17A** (1979) 378.
- Anand Rao M, Adinarayana M, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **16A** (1978) 440.
- Uma V, Sethuram B & Navaneeth Rao T, *React Kinet Catal Lett*, **18** (1981) 283.
- Prasad Rao M, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **19A** (1980) 582.
- Criegee, *Leibis Ann*, **522** (1936) 75.
- Bell R P & Smith P W, *J chem Soc*, **B** (1966) 242.
- Cotton F A, Wilkinson G, *Advanced Inorg Chemistry*, Wiley Eastern, New Delhi (1966) 153.
- Uma V, Sethuram B & Navaneeth Rao T, *Indian J Chem*, **22A** (1983) 65.
- Griffith W P, *J chem Soc*, (1964) 245.
- Mohan D & Gupta Y K, *J chem Soc*, Dalton (1977) 1085.
- Farkas L, Perlmutter B & Schachter O, *J Am Chem Soc*, **71** (1949) 2829.
- Swain C G, Wiles R A & Bader R F W, *J Am Chem Soc*, **83** (1961) 1945.
- Pati S C & Dev B R, *Indian J Chem*, **17A** (1979) 92.
- Radhakrishnamurthy P S & Mahapatro D K, *Indian J Chem*, **18A** (1979) 53.
- Radhakrishnamurthy P S & Sushila Devi, *Indian J Chem*, **10** (1972) 496.
- Elieil E L, *Stereochemistry of Carbon Compounds* Tata McGraw-Hill, New Delhi 266.