rate among the cyclanols may also be reconciled with the chromate ester mechanism since the chromate ester formation is likely to be little influenced by the structural change[11,12].

Our sincere thanks are due to Prof. P.S. Radhakrishnamurty, for helpful discussions, and to Dr C.S. Panda for providing a sample of pyridinium chlorochromate. One of the authors (D.D.M.) is thankful to CSIR, New Delhi for the award of a JRF.

References

1. COREY, E. J. & SUGGS, W. J., Tetrahedron lett., (1975), 2647.
2. VENKATARAMAN, K. S., SUNDARAM, S. & VENKATASUBRAMANIAN, N., Indian J. Chem., 16B (1978), 84.
3. BANERJI, K. K., J. chem. Soc., Perkin II, (1978), 639.
4. BANERJI, K. K., J. chem. Res. (M), (1978), 2561.
5. BOWEN, J. B., GRAHAM, S. H. & WILLIAMS, A. J. S., Organic qualitative analysis (University of London Press, London), 1957, 31.
6. WIBERG, K. B., Oxidation in organic chemistry : (Part A) (Academic Press, London), 1965, 69.
7. KUIVILLA, H. G. & BECKER, W. J., J. Am. chem. Soc., 74 (1952), 5329.
8. KWART, H. & FRANCIS, P. S., J. Am. chem. Soc., 81 (1959), 2116.
9. BROWN, H. C., FLETCHER, R. S. & JOHANNESON, R. B., J. Am. chem. Soc., 73 (1951), 252.
10. MARES, F., ROCEK, J. & SICHER, J., Colln. Czech. chem. Commun., 26 (1961), 2355.
11. DENO, N. C. & NEWMAN, M. S., J. Am. chem. Soc., 72 (1950), 3852.
12(a). KLANNING, U. & SYMONS, M. C. R., J. chem. Soc., (1961), 3204.
   (b). KLANNING, U., Acta chem. scand., 11 (1957), 1313.
   (c). KLANNING, U., Acta chem. scand., 12 (1958), 576.

Kinetics & Mechanism of Os(VIII)–catalysed Oxidation of Cyclopentanone, Cyclohexanone & Cycloheptanone by Periodate

M. PRASADA RAO, B. SETHURAM & T. NAVANEETH RAO*,
Department of Chemistry, Osmania University,
Hyderabad 500 007

The rate law for the oxidation of title substrates is found to be: rate=kK_1 [cyclic ketone] [Os(VIII)] [OH⁻], where K_1 is the equilibrium constant for the enolate ion formation from the ketone and k is the rate constant for the slow step, viz., the ester formation between the enolate ion and Os(VIII). This mechanism explains all the kinetic data obtained. Activation parameters are also presented and discussed.

RECENTLY Panigrahi et al.[1] studied the kinetics of Os(VIII)-catalysed and uncatalysed oxidation of aliphatic ketones by periodate and suggested that the enolate ion is the active species. In this note we present our results on the Os(VIII)-catalysed oxidation of some cyclic ketones, viz. cyclopentanone, cyclohexanone and cycloheptanone.

All the chemicals used were of BDH (AR) grade or extra pure quality and purified wherever necessary by standard methods. Cyclic ketone was added to

requisite quantities of periodate, hydroxide and OsO_4 after equilibrating the solutions for 30 min. Unreacted periodate at definite time intervals was estimated iodometrically in phosphate buffer ($pH \approx 5\text{-}5.5$). Under these conditions periodate is reduced to iodate (Eq. 1).

$$IO_4^- + 2H^+ + 2I^- \longrightarrow IO_3^- + H_2O + I_2 \qquad .. \quad (1)$$
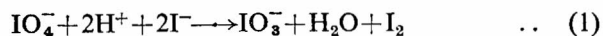
Under the conditions of [periodate]$\gg$[cyclic ketone], three mol of periodate were consumed per mol of cyclic ketone. The products of oxidation were identified as the corresponding dibasic acids as determined by their characteristic tests[2].

The rate of oxidation was found to be independent of initial [periodate] exhibiting zero order kinetics in [periodate] (Table 1). The order in [ketone] and [OsO₄] was found to be one each (Tables 1 and 2). First order in [OH⁻] was obtained at [OH⁻] in the range 0.008-0.038 M beyond which the rate remained unaltered (Table 2).

OsO_4 is known to exist mainly as $[OsO_4 (OH)_2]^{2-}$ in basic medium[3] (Eq. 2).

$$OsO_4 + 2OH^- \rightleftharpoons [OsO_4 (OH)_2]^{2-} \qquad .. \quad (2)$$
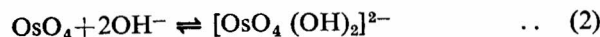
The enol form of cyclic ketone, which will be the most likely species in basic medium, might undergo

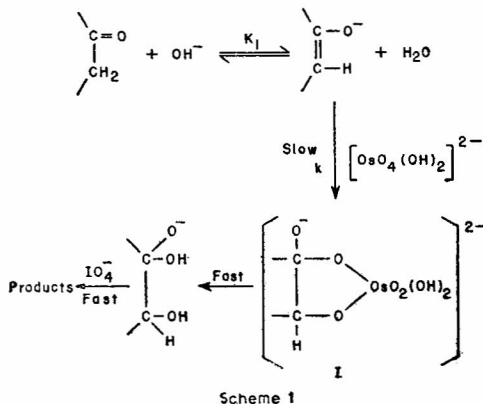TABLE 1—EFFECT OF VARYING [PERIODATE] AND [CYCLOPENTANONE] ON THE RATE

{[OsO₄]=3.94×10^{-6} M;   [OH⁻]=0.016 M; temp.=303 K}

[periodate]×10³ M	[ketone]×10³ M	$k_0 \times 10^5$ (mol litre⁻¹ min⁻¹)	$\dfrac{k_0 \times 10^2}{\text{[ketone]}}$ (min⁻¹)
0.600	1.00	4.62	—
0.800	1.00	4.70	—
1.00	1.00	4.65	—
2.00	1.00	4.67	4.67
4.00	1.00	4.65	4.65
2.00	0.800	3.78	4.73
2.00	2.00	9.25	4.63
2.00	3.00	13.8	4.60
2.00	4.00	18.6	4.65
2.00	6.00	28.2	4.70

TABLE 2 — EFFECT OF VARYING [OsO₄] AND [OH⁻] ON THE RATE OF OXIDATION OF CYCLOPENTANONE

{[periodate] = 2.00×10^{-3} M; [cyclopentanone] = 1.00×10^{-3} M; temp. = 303 K}

[OsO₄]×10⁶ M	[OH⁻]×10² M	$k_0 \times 10^5$ (mol litre⁻¹ min⁻¹]	$\dfrac{k_0 \times 10^{-1}}{\text{[OsO}_4\text{]}}$ (min¹)	$\dfrac{k_0 \times 10^2}{\text{[OH⁻]}}$ (min⁻¹)
1.18	1.60	1.39	1.18	—
1.97	1.60	2.38	1.21	—
7.88	1.60	9.53	1.21	—
3.94	0.800	2.15	—	2.69
3.94	1.20	3.26	—	2.72
3.94	1.60	4.67	—	2.92
3.94	3.80	10.7	—	2.82
3.94	5.80	12.7	—	—
3.94	7.60	14.1	—	—

Scheme 1

The rate constants and activation parameters are presented in Table 3. The higher rate of oxidation of cyclohexanone compared to cyclopentanone and heptanone might probably be due to the higher enolate content of cyclohexanone responsible for the formation of the complex. The large negative $\triangle S\ddagger$ values obtained in all the cases provide support for the formation of a more rigid activated complex (I).

References

1. PANIGRAHI, G.P. & MISRO, PRAFULLA KUMAR, *Indian J. Chem.*, **16A** (1978), 762.
2. FEIGL, F., *Spot tests in organic analysis* (Elsevier, New York), 1966, 213.
3. COTTON, F. A. & WILKINSON, G., *Advanced inorganic chemistry* (Wiley Eastern, New Delhi), 1966, 1007.
4. PANIGRAHI, G. P. & MISRO, PRAFULLA KUMAR, *Indian J. Chem.*, **16A** (1978), 201.
5. CRIEGEE, R., *Liebig's Ann.*, **522** (1936), 75.
6. BELL, R. P. & SMITH, P. W., *J. chem. Soc* (B), (1966), 242.

hydroxylation by Osmium-tetroxide, a well known hydroxylating agent for the unsaturated compounds[4,5]. In view of this a mechanism (Scheme 1) involving initial ester formation (I) between Os(VIII) and the enolate ion in a rate (k) determining step is suggested. The ester then hydrolyses to a glycol type of compound which is further cleaved by periodate in a fast step giving the final product, viz. the corresponding dibasic acid.

From the enolization and rate determining steps the rate expression comes out to be

$$k_0 = -\frac{d[IO_4^-]}{dt} = \frac{k\,K_1\,[\text{ketone}]\,[OH^-]\,[Os(VIII)]}{1 + K_1\,[\text{ketone}] + K_1[OH^-]} \quad .. \ (3)$$

Under similar conditions the equilibrium constant values for the keto-enol-enolate system, i.e.

$$K_E' = [\text{enol}]\,[\text{enolate}]/[\text{keto}] \quad .. \ (4)$$

were calculated by earlier workers[6] for cyclopentanone and cyclohexanone to be of the order of 10^{-5}. The concentrations of cyclic ketone and hydroxide in the present work are of the order 10^{-3} and 10^{-2} M respectively. It is therefore quite possible that the term K_1 [ketone]+K_1[OH$^-$]$\ll$1. The rate expression (3) then reduces to

$$-\frac{d[IO_4^-]}{dt} = k\,K_1\,[\text{ketone}]\,[OH^-]\,[Os(VIII)] \quad .. \ (5)$$

The rate expression (5) satisfactorily explains the results obtained.

Kinetics of Vanadium (V) & Cerium (IV) Oxidations of Deoxybenzoin

B. K. SINHA & G. B. BEHERA*

P. G. Department of Chemistry, Sambalpur University, Burla 768017 (Orissa)

Oxidation of deoxybenzoin has been studied by one-electron oxidants like V(V) and Ce(IV). In general Ce(IV) is found to be a more powerful oxidant than V(V). The oxidaising species during V(V) oxidation has been proposed to be V(OH)$_4^{3+}$ from the acid-dependence on the rate. One mol of deoxybenzoin is found to consume 3.5 mol of V(V) and 6.0 mol of Ce(IV). The products isolated are benzoic acid and benzil.

MISRA et al[1]., Patnaik et al[2]. and Singh et al[3] have investigated the kinetics of oxidation of acetophenone[1,2] and phenacyl bromide[3] using V(V) and Ce(IV) as oxidants. Two mechanisms involving free radical formation at the alkyl group[4] or the carbonyl group[5] have been suggested. We have also suggested a mechanism involving formation of free radical at the carbonyl group for the oxidation of acetophenone[2]. Vanadium(V) and Ce(IV) oxidations of deoxybenzoin have now been carried out with a view to ascertaining the applicability of either of the mechanism.

Deoxybenzoin was crystallised several times from absolute ethyl alcohol before use. Acetic acid was of AR(BDH) variety. Vanadium(V) used was in form of sodium vanadate(AR) in appropriate concentration of perchloric acid. Ceric ammonium sulphate (AR) in appropriate concentration of sulphuric acid was the source of Ce(IV). These were dried before use. The methods of rate measurement have been reported earlier[1,2].

In general Ce(IV) is found to be a more powerful oxidant than V(V). The concentration of the substrate during V(V) oxidation was in large excess and

TABLE 3 — RATE CONSTANTS AND ACTIVATION PARAMETERS

{[OH$^-$] = 0.016 M; [IO$_4^-$] = 2.00 $\times$ 10^{-3} M; [OsO$_4$] = 3.94 $\times$ 10^{-6} M; temp = 303 K}

Substrate	$k_0 \times 10^4$ [S] (sec^{-1})	E_{exp} (kJ mol^{-1})	$\triangle H\ddagger$ (kJ mol^{-1})	$\triangle G\ddagger$ (kJ mol^{-1})	$-\triangle S\ddagger$ (J deg^{-1} mol^{-1})
Cyclopentanone	7.78	41.8	39.3	110	232
Cyclohexanone	19.8	39.1	36.6	108	235
Cycloheptanone	1.42	46.9	44.4	114	231