

close to (although somewhat lower than) the interfacial tension.

This suggests that when one measures the interfacial tension at the oil-surfactant-oil interface, all that is being measured is the contribution of the hydrogen bonding and, to the extent that there is no such contribution from the other oil phase in which surfactant is not dissolved (or that it is quite small), the total interfacial energy arises from the hydrogen bonding term in the ethylene glycol solution of the surface active agent.

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### Kinetics & Mechanism of Os(VIII)-catalysed Oxidation of Cyclohexanone by Periodate in Alkaline Medium

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Os(VIII)-catalysed periodate oxidation of cyclohexanone has been studied. Unit dependence each in [cyclohexanone],  $[\text{OsO}_4]$ ,  $[\text{OH}^-]$  and zero order dependence in  $[\text{IO}_4^-]$  is observed. The rate levels off at higher  $[\text{OH}^-]$ . Interestingly, it is found that the  $\text{OsO}_4$ -catalysed  $\text{IO}_4^-$  and  $\text{Fe}(\text{CN})_6^{3-}$  oxidations have essentially the same reaction rate and this has been rationalized.

THE oxidation of active methylene compounds like malonic acid<sup>1,2</sup>, cyclohexane-1,3-dione and cyclopentane-1,3-dione<sup>3</sup> by periodate has received considerable attention. Shiner has reported the kinetics of oxidation of biacetyl, benzil and camphorquinone<sup>4</sup> by  $\text{IO}_4^-$  in a wide pH range. Kinetics of oxidation of simple enolizable ketones like cyclohexanone have not been hitherto attempted probably because of the reason that facile periodate oxidations require active methylene groups. The present work deals with the kinetics of  $\text{OsO}_4$  catalysed  $\text{IO}_4^-$  oxidation of cyclohexanone in alkaline medium.

Cyclohexanone (BDH) was distilled before use. All other chemicals used were of extra pure quality.

**Kinetic run**—Periodate solution (100 ml) containing the required amount of alkali and  $\text{OsO}_4$  and the substrate (100 ml) were equilibrated for 2 hr. The reactants (50 ml each) were then mixed and aliquots (5 ml each) of the mixture withdrawn at regular time intervals. The estimation of periodate in the aliquots was carried out iodometrically in the presence of a suitable amount of  $\text{KH}_2\text{PO}_4$  solution<sup>5</sup>

TABLE 1—RATES OF OXIDATION OF CYCLOHEXANONE BY  $\text{IO}_4^-$  UNDER VARIOUS EXPERIMENTAL CONDITIONS

( $\text{KCl} = 2.5 \times 10^{-2}M$ ; temp. = 35°)

$10^3$ [substrate] <i>M</i>	$10^4$ [ $\text{IO}_4^-$ ] <i>M</i>	$10^3$ [ $\text{OH}^-$ ] <i>M</i>	$10^6$ [ $\text{OsO}_4$ ] <i>M</i>	$10^5$ $k_0$ <i>M</i> , $\text{min}^{-1}$	$10^3 k_0 / [\text{S}]$ $\text{min}^{-1}$
0.19	3.2	1.2	3.93	3.2	1.66
0.42	8.1	1.2	3.93	7.0	1.65
0.41	15.7	1.2	3.93	6.8	1.65
0.41	26.3	1.2	3.93	7.3	1.75
0.08	7.6	1.2	3.93	1.37	1.72
0.15	7.6	1.2	3.93	2.70	1.73
0.38	7.3	1.2	3.93	6.3	1.63
0.30	7.3	1.2	3.93	5.2	1.70
0.22	7.3	1.2	3.93	3.8	1.70
0.41	7.3	1.2	1.96	3.06	0.74
0.41	7.6	1.2	5.90	9.5	2.3
0.19	6.5	1.2	7.87	5.4	2.8
0.38	7.8	0.06	3.93	0.48	0.13
0.38	9.6	0.17	3.93	1.26	0.33
0.38	7.4	0.53	3.93	3.92	1.04
0.20	7.5	2.5	3.93	3.74	1.85
0.20	7.0	5.2	3.93	4.6	2.31

S = [substrate].

so that the pH does not exceed 5 to 5.5. In this pH range  $\text{IO}_3^-$ , a reduction product of  $\text{IO}_4^-$ , does not liberate  $\text{I}_2$ .

It is observed that three moles of  $\text{IO}_4^-$  per mole of the ketone were consumed rapidly in about 1 hr, followed by a slow uptake of 2 moles of  $\text{IO}_4^-$  over the next 24 hr. In this experiment the reaction temperature was maintained at 35°. Adipic acid (m.p., m.m.p. 155°) has been isolated as the product of oxidation of cyclohexanone under our experimental conditions. The consumption of additional 2 moles of  $\text{IO}_4^-$  in the next 24 hr (2nd stage) is rather unusual in view of the known stability of adipic acid towards further oxidation. But interestingly, it was found that  $\text{IO}_4^-$ , in the presence of  $\text{OsO}_4$  oxidizes adipic acid slowly.

The reactions are first order in [ketone] and  $[\text{OsO}_4]$  and zero order in  $[\text{IO}_4^-]$ . Consumed  $[\text{IO}_4^-]$  vs time plots are linear. Zero order rate constants ( $k_0$   $M \text{ min}^{-1}$ ) have been computed from the slopes of these linear plots. This is further confirmed by varying  $[\text{IO}_4^-]$ . It yields the same value of  $k_0$ .  $k_0$  values are given in Table 1.

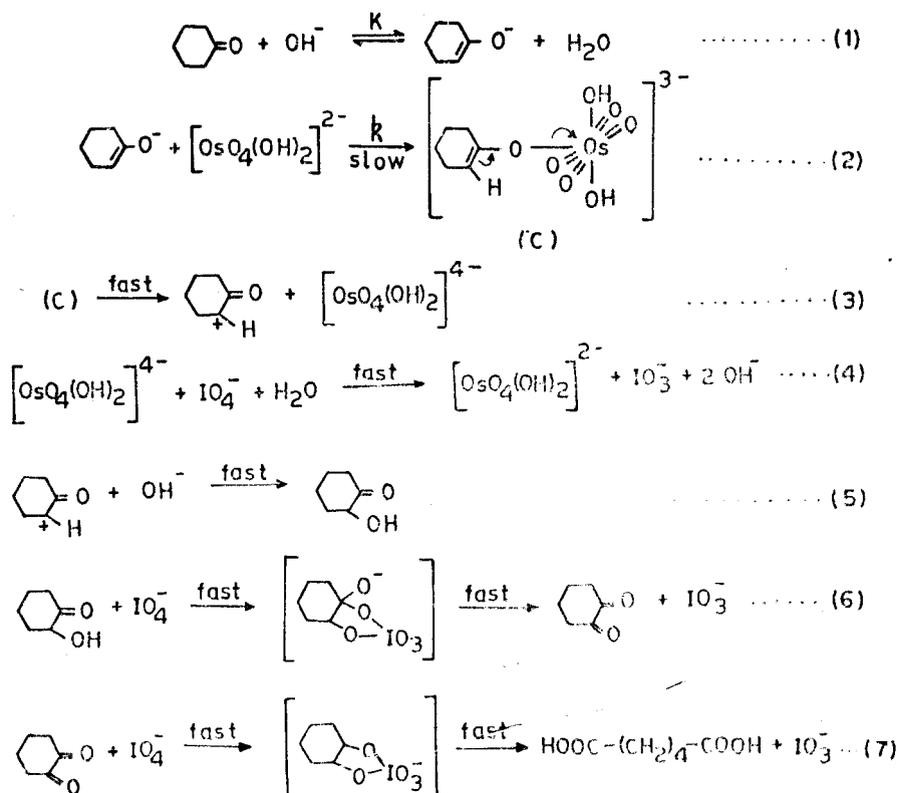
In the  $[\text{OH}^-]$  range of  $6.5 \times 10^{-4}$  to  $1.2 \times 10^{-2}M$ , clear first order dependence on  $[\text{OH}^-]$  is observed and the rate levels off when  $[\text{NaOH}] = 1.2 \times 10^{-2}M$ .

The first order dependence on  $[\text{OH}^-]$  points to the importance of enolic form from which electron transfer occurs (Scheme 1).  $\text{OsO}_4$  in alkaline medium exists as  $[\text{OsO}_4(\text{OH})_2]^{2-}$ , which is responsible for catalysis.

The rate expression can be written as

$$-\frac{d[\text{IO}_4^-]}{dt} = \frac{Kk}{\text{H}_2\text{O}} [\text{Cyclohexanone}][\text{OH}^-][\text{Os(VIII)}] \\ = k_0(\text{obs}) [\text{Cyclohexanone}][\text{OH}^-][\text{Os(VIII)}]$$

Os(VIII)-catalysed hexacyanoferrate(III) oxidation of enolizable ketones like acetone and ethyl methyl



## SCHEME 1

ketones have been reported<sup>6</sup>. The oxidation of cyclohexanone by OsO<sub>4</sub>/hexacyanoferrate(III) has the same kinetic features as the OsO<sub>4</sub>/IO<sub>4</sub><sup>-</sup> oxidation, i.e. zero order dependence on [IO<sub>4</sub><sup>-</sup>] and [hexacyanoferrate(III)]. Since hexacyanoferrate(III) and IO<sub>4</sub><sup>-</sup> participate in a fast step to oxidize Os(VI) to Os(VIII), a change in the oxidant would not be expected to bring out any profound difference in the kinetics. This is revealed by the data in Table 2.

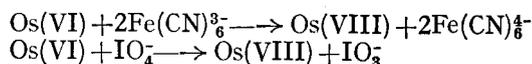
TABLE 2 — COMPARISON OF OsO<sub>4</sub>-CATALYSED PERIODATE AND HEXACYANOFERRATE(III) OXIDATIONS

[IO<sub>4</sub><sup>-</sup>] = 1.0 × 10<sup>-3</sup> M; Fe(CN)<sub>6</sub><sup>3-</sup> = 1.0 × 10<sup>-3</sup> M; KCl = 2.5 × 10<sup>-2</sup> M, pH = 10; OsO<sub>4</sub> = 7.87 × 10<sup>-6</sup> M; temp. = 35°

10 <sup>2</sup> [substrate]	10 <sup>5</sup> k <sub>0</sub> M min <sup>-1</sup>	10 <sup>2</sup> k <sub>1</sub> min <sup>-1</sup>
PERIODATE OXIDATION		
0.2010	0.195	0.097
0.4132	0.4820	0.1166
1.331	1.477	0.110
2.696	2.178	0.080
5.287	4.6	0.087
HEXACYANOFERRATE(III) OXIDATION		
0.41	1.36	0.0878
1.53	1.391	0.0910
2.62	2.34	0.0893
5.57	5.10	0.0884

A discussion on the Littler's work<sup>7</sup> on the kinetics of oxidation of cyclohexanone by two-electron oxidants, such as I<sub>2</sub>, Br<sub>2</sub>, Hg<sup>2+</sup>, Tl(III) and MnO<sub>4</sub><sup>-</sup> where there is rate limiting enolization zero order dependence on the oxidant is relevant. Rate of enolization was measured by iodination. Littler believed that stoichiometry of the fast step is an important factor, the zero order iodination rate was divided by a statistical factor of 2 (two moles of iodine are consumed to give diiodocyclohexanone) so that the iodination rate will be nearly equal to the rate of Tl(III) oxidation.

We have essentially a similar kinetic situation. The stoichiometries of the fast steps are as follows:



If Littler's postulates were correct, this would have resulted in a zero order rate constant for the hexacyanoferrate(III) oxidation, which is twice faster than the zero order rate constant for IO<sub>4</sub><sup>-</sup> oxidation under identical conditions. To us it appears that the correlation between the iodination rate and rate of cyclohexanone oxidation by Hg<sup>2+</sup>, Tl(III), etc. by a statistical factor of 2 may be just a coincidence and it does not appear to be general case as claimed by Littler.

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TABLE 1 — ORDER OF THE REACTION BETWEEN Ce(IV) AND THE SUBSTRATES

Substrate	Temp. °C	[Substrate], M	$k_{\text{obs}}^{(a)} \times 10^4 \text{ sec}^{-1}$	Slope(b)
Acetic acid	50	0.4335	$0.562 \pm 0.022$	0.79
Propionic acid	50	0.4335	$1.45 \pm 0.13$	0.77
Isobutyric acid	40	0.0661	$0.341 \pm 0.017$	0.82
Pivalic acid	35	0.065	$1.20 \pm 0.01$	0.82
Formic acid	50	0.153	$0.252 \pm 0.03$	0.86
Phenylacetic acid				0.98(c)

(a) Varying  $[\text{Ce}^{4+}]$ ;  $\text{HClO}_4 = 1.0M$ ,  $\mu = 1.2$ .(b) Slope of  $\log k_{\text{obs}}$  vs  $\log [\text{RCOOH}]$  when  $[\text{Ce}^{4+}]$ ,  $\mu$  and  $[\text{H}^+]$  are kept constant.(c) 30%  $\text{CH}_3\text{CN}$ .

### Oxidation of Formic, Acetic, Propionic, Isobutyric, Pivalic & Monochloroacetic Acids by Cerium(IV) Perchlorate

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Kinetics of oxidation of formic, acetic, propionic, isobutyric, pivalic and monochloroacetic acids proceed by an inner sphere mechanism. The stoichiometries for the oxidation of formic, acetic, propionic, isobutyric and pivalic acids are near to 2, 6, 6, 4 and 2 respectively in 1.0M perchloric acid. The Hammett plot using  $k_t$  values versus  $\sigma^*$  gives a  $\rho$  of  $-5.28$ . This indicates that a carboxylic acid yielding a more stabler cation is more easily oxidizable. The radical stabilization may be of importance in the oxidation of phenylacetic and diphenylacetic acids.

IN the oxidative decarboxylation of formic<sup>1</sup>, acetic<sup>2</sup>, oxalic<sup>3</sup>, malonic<sup>4</sup>, phenylacetic<sup>5</sup>, aliphatic<sup>6</sup> and aromatic<sup>7</sup> hydroxy acids by cerium(IV) perchlorate in perchloric acid or by ceric ammonium nitrate (CAN) in perchloric or nitric acid, complex formation precedes electron transfer reaction. Further, in perchloric acid media an increase in  $[\text{H}^+]$  decreases the rate of oxidation of  $\alpha$ -hydroxy acids while it increases the rate of oxidation of carboxylic acids. For 3-bromopropionic acid oxidation in aqueous nitric acid solutions, no effect of  $[\text{H}^+]$  was noted<sup>8</sup>. Both spectrophotometric and kinetic evidences for the formation of intermediate complex were presented in the oxidation of acetic, malonic and hydroxy acids. Absorbancy index measurements indicate the complex formation between  $(\text{CeOH})^{3+}$  and acetic acid<sup>9</sup>. In the thermal oxidative decarboxylation of cerium(IV) carboxylates the formation of alkyl radical occurs<sup>10</sup>.

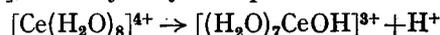
We report in this note the results of the kinetics of oxidation of propionic, isobutyric and pivalic acids by cerium(IV) perchlorate in perchloric acid. A comparative study of these acids with acetic, chloroacetic, phenyl and diphenylacetic acids is also made.

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The effect of various parameters such as  $[\text{HClO}_4]$ ,  $[\text{RCOOH}]$  and temperature at constant ionic strength on the rate and mechanism has been investigated. All kinetic experiments were performed under pseudo-first order conditions using excess of the substrate. Stoichiometries of the reaction were determined separately for the acids. Where the products are further oxidized as in the case of isobutyric and phenylacetic acids, stoichiometries are found greater than the calculated values. Experimental procedure is the same as reported earlier<sup>2</sup>.

The order with respect to  $[\text{Ce(IV)}]$  is one as evidenced by the linearity of the plot of  $\log [\text{Ce(IV)}]$  vs time and also by the constancy of the rate constant for different  $[\text{Ce(IV)}]$  when  $[\text{RCOOH}]$ ,  $[\text{H}^+]$  and ionic strength are kept constant (Table 1). But the order with respect to  $[\text{RCOOH}]$  is fractional. Plots of  $\log k_{\text{obs}}$  vs  $\log [\text{RCOOH}]$  are linear and the slopes vary from 0.77 to 0.82 for the different aliphatic acids. On increasing  $[\text{H}^+]$ , the rate increased in all cases. The predominant species below 2.0M  $\text{HClO}_4$  is  $[\text{CeOH}^{3+}]$ . Since the rate depends on  $[\text{H}^+]$ , the hydrolytic equilibrium is important



and the reported equilibrium constants are between 4.8 and 7.2 (ref. 11). In a freshly electrolytically prepared cerium(IV) perchlorate in perchloric acid, only the monomeric species is present and the concentration is governed by a set of hydrolysis constants<sup>12</sup>.

The plot of  $1/k_{\text{obs}}$  versus  $1/[\text{RCOOH}]$  is linear with an intercept on  $1/k_{\text{obs}}$  axis at constant ionic strength,  $[\text{Ce(IV)}]$  and temperature (Table 2). The presence of the intercept and deepening of the yellow colour of  $\text{Ce(IV)}$  on the addition of the organic acid, HA indicate the formation of  $\text{Ce}^{4+}$ -acid complex which undergoes deprotonation followed by electron transfer, resulting in the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . Spectral measurements cannot distinguish the actual species  $[\text{Ce}(\text{OH})\text{HA}]^{3+}$  or  $[\text{Ce}(\text{HA})]^{4+}$  or  $[\text{CeA}]^{3+}$  present.

The redox potential values of  $\text{Ce(III)/Ce(IV)}$  couple in acetic acid-perchloric acid system depends on  $[\text{CH}_3\text{COOH}]$  and on  $[\text{HClO}_4]$ . The fact that the  $k_{\text{obs}}$  increases with  $[\text{H}^+]$  indicates that  $[\text{Ce}(\text{H}_2\text{O})_8]^{4+}$  is the reactive species. Hence the reaction Scheme 1 is pictured for the oxidation of acids.