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Kinetics of edta-catalysed oxidation of some cycloalkanones by pyridinium chlorochromate

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Cr(IV)edta–cycloalkanone ternary complex decomposes by slow oxidation to the α-ketol followed by fast oxidation to the dione.

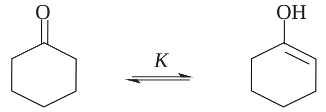
Keywords: Cr(IV)edta-cycloalkanone ternary complex, pyridinium chlorochromate

Edta has the ability to form stable and soluble metal chelates in solution. It has a wide variety of chemical, analytical and industrial applications including water softening, scale removal and preservative action through the suppression of catalytic effects of metal ion impurities.[1] A few kinetic studies of edta oxidation by various oxidants have been reported in the literature. Catalytic activity of transition metal–edta complexes has been observed, especially those of Fe(II), Fe(III),[20-22] Ru(III)[23] and Cr(VI).[24] We have undertaken a systematic study of the oxidation behaviour of Cr(VI) in the presence of edta with a series of cycloalkanones. Differences in reactivity point to an important effect of ring size on chemical behaviour. The mechanistic pathway has been determined based on product assignments and stoichiometry.

Pyridinium chlorochromate (PCC) was synthesised by the method described in the literature.[25] Cycloalkanones (Fluka grade) were used as supplied. Heavy water (99.4%) was supplied by Bhaba Atomic Research Centre, India. Experiments were carried out under pseudo-first-order conditions by keeping the cycloalkanones always in excess over the oxidant. Reactions were followed iodometrically. The estimation of unreacted PCC shows that 4 mol of oxidant is consumed by 3 mol of substrate. The product cyclohexane-1,2-dione was identified by the formation of cyclohexane-1, 2-dione dioxime (white crystals) (m.p. 185–187°C).[26]

The reaction exhibits first order dependence each on oxidant and reductant. The order dependence on $[H^+]$ was < 1 throughout the entire range of acidities studied. The Cr(VI)–edta complex catalyses the reaction and a fractional order dependence on [edta] is oberved. High permitivity of the medium slightly favours the conversion. The k_{D_2O}/k_{H_2O} ratio does not seem to indicate any significant solvent isotope effect. Quite likely, the O–H/O–D isotope effect resulting from labile hydrogen exchange in D_2O may neutralise the rate enhancing effect of deuterium oxide.[33] The lack of solvent isotpe effect excludes the rate-controlling participation of water as a nucleophile.[34] Depressed reactivity is observed in the presence of Mn(II), and in the presence of an excess of Co(III). The rate of conversion did not change in acrylonitrile, ruling out the possibility of a radical mechanism.

It is reasonable to envisage the site of attck as the enol form of the substrate since this would be extremely susceptible to attack by the electrophilic oxidant. Protonation enhances the electrophilic activity of the oxidant. The Cr(VI)edta mononuclear and binuclear complexes have been reported in the literature.[42] The kinetic data in the present investigations can be rationalised by envisaging the formation of a Cr(VI)edta mononuclear complex. We have proposed a π-complex in the present study to explain the kinetic observations. A similar type of π-complex has been proposed concerning the oxidation of alcohols by Heasley *et al.*[41]



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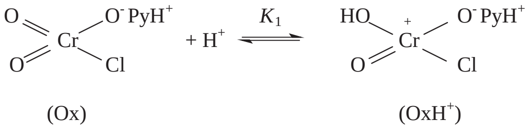
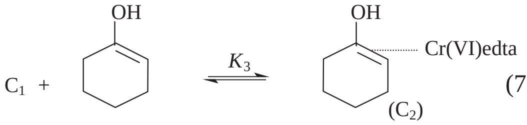


(5)

$$OxH^+ + edta \underset{}{\overset{K_2}{\rightleftharpoons}} \underset{(C_1)}{Cr(VI)edta} \tag{6}$$



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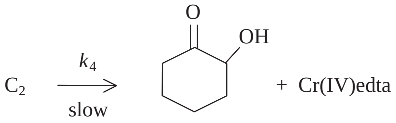

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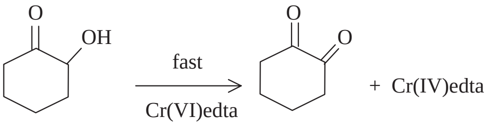
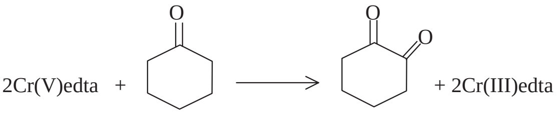


(9)

$$2Cr(IV)edta \longrightarrow Cr(III)edta + Cr(V)edta \tag{10}$$



(11)

After neglecting the higher terms, the conversion can be characterised by the rate equation, where $[Ox]_t$ represents the total Cr(VI) concentration.

$$-\frac{d\,[PCC]}{dt} = \frac{k_4 KK_1K_2K_3[\text{ketone}][\text{edta}][H^+][Ox]_t}{1+K_1[H^+]+K_1K_2[H^+][\text{edta}]} \tag{12}$$

$$[Ox]_t = [Ox] + [OxH^+] + [C_1] + [C_2] \tag{13}$$

where $[Ox]_t$ represents the total Cr(VI) concentration.

The rate law (eqn (12)) is consistent with a mechanism in which a rapid equilibrium exists between the Cr(VI)edta intermediate complex and the enol form of the substrate, and with the ternary complex decomposing through an intramolecular electron transfer at a much smaller specific rate. The mechanism accounts for the fact that conversion of

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Table 4 Rate constants and activation parameters for the oxidation of cycloalkanones

No.	Cycloalkanone	k_{obs} $10^5/s^{-1}$				$\Delta H^\#$ /kJ mol^{-1}	$-\Delta S^\#$ /J K^{-1} mol^{-1}	$\Delta G^\#_{(303\ K)}$ /kJ mol^{-1}	*r*	*s*
		303 K	313 K	323 K	333 K					
1	Cyclopentanone	1.01	2.05	4.19	11.77	64.6	128.4	103.1	0.995	0.124
2	Cyclohexanone	3.17	7.94	15.89	40.52	66.6	111.3	100.2	0.998	0.975
3	Cycloheptanone	0.51	1.30	2.72	8.04	72.0	116.0	104.7	0.997	0.101
4	Cyclooctanone	3.74	8.19	16.32	42.62	63.90	119.4	100.1	0.998	0.050

[Sub] = 3.1×10^{-2} mol dm^{-3} [$HClO_4$] = 1.0×10^{-1} mol dm^{-3}
[PCC] = 2.1×10^{-3} mol dm^{-3} [edta] = 1.0×10^{-4} mol dm^{-3}
AcOH : H_2O = 70:30 (v/v)

cycloalkanone to 1,2-dione would be a 4-electron oxidation. The other possible explanation for the reaction observed is the fast oxidation of an α-ketol partly by Cr(V) produced from Cr(IV) disproportionation. Involvement of a coordinatively stable binuclear Cr(VI) species is not supported by the observed stoichiometry, which shows three moles of ketone oxidised by 4 moles of Cr(VI).

The ternary complex offers the reaction a more favourable pathway and enhances the reactivity. Quite likely, the complexation with edta facilitates the internal electron transfer from substrate to oxidant. The addition of edta and its binding to the Cr would presumably change the redox potential of the oxidant resulting in a faster rection.

The order of reactivity is, $C_8 > C_6 > C_5 > C_7$ (Table 4). The reactivity order clearly shows that even-numbered (C_6, C_8) cyclic ketones react much faster than odd-numbered (C_5, C_7) ketones in this conversion. The higher enolisation constant of the cyclohexanone is one of the most important factors contributing towards greater reactivity of this ketone. The linear Exner plots ($r \approx 0.995$; $s \approx 0.041$) favour a similar mechanism in all the cyclic ketones. Near constancy in $\Delta G^\#$ values further confirms the above view.

Techniques used: Titrimetry, UV

References : 48

Table 1. Effect of reactants on the reaction rate of oxidation at 303 K

Table 2. Effect of $NaClO_4$, dielectric constant and D_2O on the reaction rate at 303 K

Table 3. Effect of Mn(II), Co(III) and acrylonitrile on the reaction rate in the oxidation of cyclohexanone at 303 K

Figures : 4

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