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Kinetics of Oxidation of Cyclohexanone, Cyclopentanone, Cyclooctanone & Cycloheptanone by V(V) in Acid Medium

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The order of reactivity is cyclohexanone > cyclopentanone > cyclooctanone > cycloheptanone. Added Mn(II) retards the rate significantly. This may be attributed to the interaction of V(V) with Mn(II) consequently reducing the oxidant ineffective in aq. acetic acid and aq. dioxan eat varying [H_2SO_4]. Salt effects are traced to specific salt influences. On the basis of the available evidence it is suggested that the preferential mechanistic route for the V(V) oxidation of cyclanones in acid medium is through their keto forms by single electron transfer in the rate determining step.

THE kinetics of oxidation of cyclohexanone by vanadium (V) has been studied by Littler and Waters[1]. In the present paper which deals with the kinetics and mechanism of V(V) oxidation of a series of cyclic ketones, an attempt has been made to correlate conformation and reactivity and to throw light on the mechanism of oxidation.

Materials and Methods

All the cyclic ketones were of Analar (BDH) grade. Acetic acid (BDH), Analar was refluxed with CrO_3 and acetic anhydride (equivalent to the amount of water present in acetic acid) and distilled neglecting large head and tail fractions, b.p. 118°. Ammonium metavanadate (AR grade) was approximately weighed and dissolved in a known amount of H_2SO_4 (AR) by slight warming. The solutions thus obtained after sufficient cooling was made up with the appropriate solvent mixture, taking care to see that the solution was of the required acidity.

Procedure — Both the V(V) solutions from the oxidant flask before mixing and the aliquots from the reaction mixture were analysed as follows. 5 ml of the V(V) solution was poured into a known excess of acidified standard ferrous ammonium sulphate solution and the residual Fe(II) was titrated against standard potassium dichromate solution using N-phenyl anthranilic acid as indicator.

Results and Discussion

The reactions are first order each in oxidant and substrate at constant acidity. The second order rate constants in aq. acetic acid and aq. DMSO are given in Table 1.

The reactivity order of the various cyclanones is similar to that observed in the hexacyanoferrate oxidation of cyclanones[2], i.e. cyclohexanone > cyclopentanone > cyclooctanone > cycloheptanone.

Solvent effect — The reaction rate is slowest in 10%(v/v) acetic acid-water and increasing proportion of acetic acid accelerates the rate (Table 2). Such an increase in the rate with the decrease in dielectric constant of the medium for reactions involving an ion and a dipole has been predicted by Frost and Pearson[3] and by Laidler and Eyring[4]. The oxidation in 10% DMSO at the same acidity is slightly faster than in 10% aq. acetic acid. The higher reactivity is due to the specific geometry of DMSO[5].

TABLE 1 — EFFECT OF AQ. ACETIC ACID AND AQ. DMSO ON REACTION RATE

([V(V)] = 0·005*M*; temp.= 60°)

Acidity *M*	$k_2 \times 10^2$ litre $mole^{-1}$ min^{-1}			
	Cyclohexanone	Cyclopentanone	Cyclooctanone	Cycloheptanone
	10% HOAc (v/v)			
1·0	29·00	8·06	7·21	5·97
1·5	58·39	18·10	17·19	12·84
2·0	114·20	32·23	29·59	20·14
	10% DMSO (v/v)			
1·0	32·82	13·45	9·27	6·57
1·5	64·89	22·05	18·42	13·53
2·0	134·45	37·18	30·23	23·86

Nature of the oxidizing species — Waters[6] has formulated that in perchloric acid solutions the active oxidizing species might by $V(OH)_3^{2+}$ and a sulphate complex in sulphuric acid solutions. The red solutions in sulphuric acid together with the kinetic evidence clearly establish the existence of a charged sulphate complex such as $V(OSO_3H_3)_3^{2+}$ or $VO(OSO_3H)^{2+}$ or $V(OH_3)HSO_4^+$ of enhanced oxidizing power.

TABLE 2 — EFFECT OF SOLVENT COMPOSITION ON THE REACTION RATE

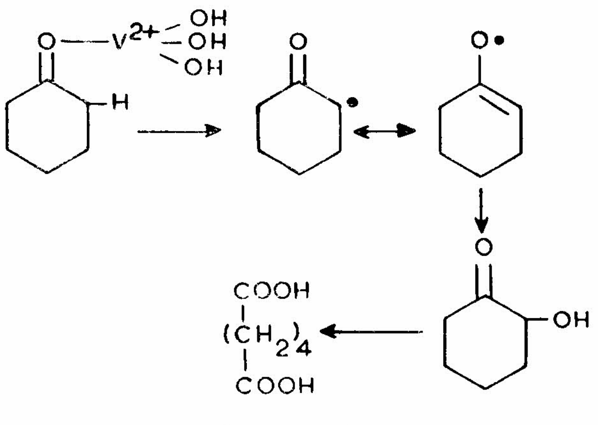
([V(V)] = 0·005M; [H_2SO_4] = 1M; temp. = 60°)

HOAc (%, v/v)	$k_2 \times 10^2$ litre mole^{-1} min^{-1}			
	Cyclohexanone	Cyclopentanone	Cyclooctanone	Cycloheptanone
10	29·00	8·06	7·21	5·97
20	52·96	13·03	12·75	11·24
30	74·76	18·08	17·60	14·37

TABLE 3 — EFFECT OF [$MnSO_4$] ON THE REACTION RATE

(Substrate: Cyclohexanone, [H_2SO_4] = 1M; HOAc = 10% (v/v); temp. = 60°)

[$MnSO_4$]M	$k_2 \times 10^2$ litre mole^{-1} min^{-1}	[$MnSO_4$]M	$k_2 \times 10^2$ litre mole^{-1} min^{-1}
0·005	23·68	0·015	23·81
0·01	21·23	0·02	20·13



Scheme 1

Effect of acidity — Dependence on acidity is unity. Zücker-Hammett slope for all the cyclic ketones is one. A plot of $\log_{10} k_2$ versus [H^+] is linear but a consideration of the effect of water composition in the solvent on the rate of reaction suggests that H_0 is a more suitable measure than the stoichiometric concentration of the acid. The plots of ($\log k_2 + H_0$) versus $\log a_{H_2O}$ are linear indicating in general the applicability of Bunnett treatment.

Effect of added Mn(II) — The data in Table 3 show a retardation in the rate on addition of Mn^{++}. This is probably the first report of Mn(II) retardation in the oxidation of cyclic ketones by V(V). The retardation of the rate by Mn(II) in the Mn(III) pyrophosphate oxidation of malonic acid, formic acid and cyclohexanol has earlier been observed[7]. The retardation has been rationalized by the effect of Mn(II) on the reversible equilibria:

(a) $CH_2(COOH)_2 + Mn(H_3P_2O_7)_2 \rightleftharpoons \dot{C}H(COOH)_2 + Mn(II) + H^+$

(b) $2Mn(III) \rightleftharpoons Mn(II) + Mn(IV)$
$Mn(IV) + 2H_2O \rightarrow MnO_2 + 4H^+$

On an analogy of the effect of Mn(II) in the Ce(IV) oxidation of cyclanols[8] it is likely that Mn(II) interacts with V(V) giving Mn(III) which dismutates to Mn(IV). This interaction of V(V) and Mn(II) consequently renders the oxidant ineffective. This interpretation finds support in Cr(VI) oxidation studies[9] in which Cr(VI) is reported to interact with Mn(II)

Salt effects — There is acceleration of oxidation rate on the addition of $(NH_4)_2SO_4$, NH_4-OAc and $CoSO_4$ indicating that the rate differences are not due to changes in ionic strength but due to specific salt effects. The rate of oxidation of cyclohexanone at 60° increase from 29×10^{-2} litre mole^{-1} min^{-1} in the absence of $(NH_2)_4SO_4$ to 45×10^{-2} litre mole^{-1} min^{-1} in the presence of 0·005M $(NH_4)_2SO_4$.

Effect of addition of organic bases — There is acceleration in the rate of oxidation of cyclohexanone at 60° {(V(V) = 0·005M; (H_2SO_4) = 1M; Solvent: aq. HOAc (10%)} on the addition of bases. The order of acceleration is dipyridyl ($40·20 \times 10^{-2}$) > pyridine ($61·37 \times 10^{-2}$) > *o*-phenanthroline ($31·75 \times 10^{-2}$). It is surprising that there is minimum acceleration with *o*-phenanthroline inspite of the fact that it is a bidentate ligand.

Mechanism — The general mechanism postulated for the oxidation of ketones is through the enolate form followed by electron transfer in all oxidations by the transition metal oxidants. In the alkaline medium oxidation there is absolutely no difficulty in picturing the enolate anion but the difficulty arises only in the oxidation in acid medium. One has to decide whether it is through the enolate form or through the keto form. The kinetic isotopic effect and solvent isotopic effect[10] help in deciding between the two possibilities, whether it is reacting through the enol form or keto form.

The primary kinetic isotope effect is significant only when the ketone is attacked directly. The earlier observation that the rate of oxidation of ketones is slower than the enolization rate (loc.cit) also points out to the fact that C-H cleavage is, important in these oxidations. The solvent isotope effect (rates in D_2O and H_2O) being same rules out the possibility of enolization in the rate determining step in these ketone oxidations. Hence it can be safely argued that all the cyclic ketones react through their keto forms. The mechanism shown in Scheme 1 is consistent with the results.

The species has been represented as $V(OH)_3^{2+}$ for convenience though actually it is a sulphate complex as the study has been made in the presence of aq. H_2SO_4.

It is therefore clear that the enol form does not provide the easiest route for one electron oxidation of a ketone in the acid medium. Attack on either ketone or enol could give the same mesomeric free radical and the low concentration of enol would preclude that the reaction is through the enol and it is the oxidation of the ketone that is significant. The oxygen of the enol molecule is less nucleophilic and a substrate-oxidant complex can easily be visualized in the case of ketone. This mode of preferential attack on the ketone is only in the acid medium.

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