Kinetics of Oxidation of Some Substituted 4-Oxanones by Vanadium(V)

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Kinetics of oxidation of r-2, cis-6-diphenyl-4-oxanone(Ia), r-2,trans-6-diphenyl-4-oxanone (II), r-2, cis-6-diphenyl-trans-3-methyl-4-oxanone (Ib), r-2, cis-6-diphenyl-trans-3-ethyl-4-oxanone(Ic) and r-2, cis-6-diphenyl-trans-3, 5-dimethyl-4-oxanone(Id) by V(V) in the presence of sulphuric acid in aq. acetic acid have been investigated. The reaction has been found to be of second order at constant acid concentration, first order each with respect to oxidant and oxanone. The order with respect to sulphuric acid is found to lie between one and two in the [acid] range of 0.2-0.5 M. The oxidation follows a free radical mechanism through an enol intermediate. A tentative mechanism and a corresponding rate equation have been proposed.

KINETICS of the oxidation of ketones, alcohols and hydroxy acids using V(V) as oxidant have been studied extensively[1-6]. In our previous paper the kinetics of oxidation of some substituted 4-piperidones have been reported[7]. We report in this paper the oxidation kinetics of some 4-oxanones using V(V) as the oxidant with a view to correlating the conformation with the reactivity of the substrates.

Materials and Methods

Substituted 4-oxanones Ia-d and II were prepared by known methods[8,9]. Other chemicals and the experimental procedure used were the same as reported earlier[7].

Results and Discussion

The stoichiometry of the reaction was determined by keeping the reaction mixture containing excess of V(V) until the reaction was complete and then estimating the unreacted V(V). It was found that one mole of oxanone consumed two moles of the oxidant.

The pseudo-first order principle was followed to get the rate constants, k_{obs}, by keeping the concentration of oxanone always more than ten-folds
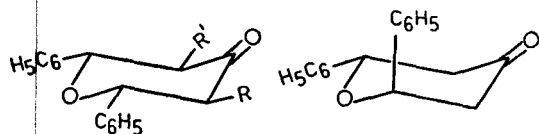
of the [oxidant]. The linear curves obtained by plotting log $(a/a-x)$ versus time suggest the first order dependence on V(V).

Effect of varying substrate concentration — The increase in oxanone concentration at constant [acid] increases the rate. The plot of log k_{obs} versus log [oxanone] gave a linear curve with unit slope thereby indicating the order of reaction with respect

	I		II
Ia	R = R' = H		
Ib	R = CH₃ ; R' = H		
Ic	R = C₂H₅ ; R' = H		
Id	R = R' = CH₃		

TABLE 1 — EFFECT OF VARYING SUBSTRATE CONCENTRATION ON THE PSEUDO-FIRST ORDER RATE CONSTANTS (k_{obs})

[Temp. = 30°; [V(V)] = 0.0025 M; solvent = 80% HOAc(v/v)]

[Substrate] × $10^2 M$	$k_{obs} \times 10^3$ (min^{-1})	$k'' \times 10^2$ (litre mole^{-1} min^{-1})
*r-2, cis-6-*Diphenyl-4-oxanone (Ia), [H₂SO₄] = 0.5 M		
3.389	4.833	14.26
4.051	5.482	13.52
5.044	6.690	13.26
6.233	8.241	13.22
*r-2, trans-6-*Diphenyl-4-oxanone (II), [H₂SO₄] = 0.2 M		
2.472	2.598	10.51
3.413	3.558	10.43
4.089	4.286	10.48
4.798	4.970	10.36
*r-2,cis-6-*Diphenyl-*trans-*3-methyl-4-oxanone(Ib), [H₂SO₄]=0.2M		
3.376	6.031	17.86
4.011	6.976	17.39
5.286	9.436	17.85
6.053	10.760	17.78
*r-2,cis-6-*Diphenyl-*trans-*3-ethyl-4-oxanone(Ic), [H₂SO₄]=0.2M		
3.336	6.031	18.08
4.167	7.306	17.53
5.119	8.661	16.92
6.068	10.670	17.58
*r-2,cis-6-*Diphenyl-*trans-*3,5-dimethyl-4-oxanone(Id), [H₂SO₄]= 0.2M		
Too fast to measure the rate.		

to substrate to be one. The values of second order rate constants (k'') for different oxanones are given in Table 1. They are found to fluctuate within ± 5%.

Effect of varying acid concentration — The increase in acid concentration has been found to increase the rate of reaction (Table 2). The slope of the plot of log k'' versus log [H_2SO_4] gave the order with respect to H_2SO_4. These values for various oxanones are as follows : r-2, cis-6-diphenyl-4-oxanone (Ia) 1.25; r-2,trans-6-diphenyl-4-oxanone (II) 1.25; r-2, cis-6-diphenyl-trans-3-methyl-4-oxanone (Ib) 1.46 and r-2,cis-6-diphenyl-trans-3-ethyl-4-oxanone (Ic) 1.46. Hence the order lies between one and two and varies with the substrate.

There is no kinetic evidence for the complex formation between the reacting species, since the plot of $1/k_{obs}$ versus $1/$ [substrate] gives a linear curve passing through the origin. The presence of free radicals in the reaction mixture was found by the polymerization of acrylamide.

It has been observed that the addition of $NaHSO_4$ enhanced the reaction rate at constant acid and substrate concentrations. Hence the reactive species of V(V) may be taken as [$V(OH)_3HSO_4^+$] (refs 1,6). It has already been reported[1] that the oxidation of some ketones by V(V) proceeds through the attack on enol- as well as keto-form. But, in the present study it appears that the oxidation involves the enol formation as the intermediate step which was confirmed by bromination studies. The bromination rate was found to be faster than the oxidation rate in all the cases. Thus, it is apparent that the intermediate enol forms a short lived complex with the reactive form of vanadium(V), which then gives V(IV) and the radical X. The different steps involved in the oxidation of oxanones are shown in Scheme 1.

$$VO_2^+ + H_2SO_4 + H_2O \overset{K_1}{\rightleftharpoons} V(OH)_3HSO_4^+$$

$$S + H_2SO_4 \overset{K_2}{\rightleftharpoons} Enol$$

$$V(OH)_3HSO_4^+ + Enol \overset{k_s}{\longrightarrow} X + V\ (IV)$$

$$X + V(V) \overset{k_t}{\longrightarrow} Product + V\ (IV)$$
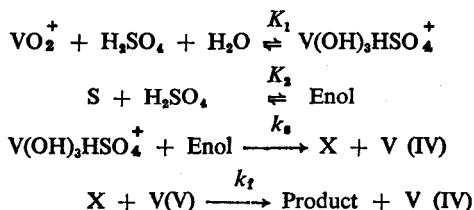
Scheme 1

TABLE 2 — EFFECT OF VARYING H_2SO_4 CONCENTRATION ON THE SECOND ORDER RATE CONSTANT (k'')

[Temp. 30°; [V/V]] = 0.0025 *M*; [substrate] = 0.025 *M*; solvent = 80% HOAc (v/v)]

Substrate	$k'' \times 10^2$ (litre mole^{-1} min^{-1}) at			
	0.2*M*	0.3*M*	0.4*M*	0.5*M*
Ia	4.42	7.42	10.59	13.77
II	10.45	16.10	25.03	32.93
Ib	17.72	34.20	49.88	69.15
Ic	17.53	32.63	49.78	66.32

Thus, the rate of reaction can be calculated as :

$$Rate = \frac{-d[V\ (V)]}{dt} = k_s\,[V(OH)_3HSO_4^+]\,[Enol]$$

$$= k_s\,K_1\,K_2\,[VO_2^+]\,[H_2SO_4]^2\,[S]$$

Replacing [VO_2^+] by [V(V)]$_{total}$, the above equation becomes :

$$Rate = \frac{k_s\,K_1\,K_2\,[V\ (V)]_{total}\,[H_2SO_4]^2\,[S]}{1 + K_1\,[H_2SO_4]} \quad ..(1)$$

This equation at constant vanadium concentration takes the form of Eq. (2) as given below.

$$k_{obs} = \frac{k_s\,K_1\,K_2\,[H_2SO_4]^2\,[S]}{1 + K_1\,[H_2SO_4]}$$

$$\frac{1}{k_{obs}} = \frac{1}{[S]}\left\{\frac{1}{k_s\,K_1\,K_2\,[H_2SO_4]} + \frac{1}{k_s\,K_2\,[H_2SO_4]}\right\}$$
$$..(2)$$

Hence, the plot of $1/k_{obs}$ versus $1/$ [S] should be linear and passing through the origin as has been obtained. At constant substrate and vanadium concentrations, Eq. (1) becomes :

$$\frac{1}{k''} = \frac{1}{k_s\,K_1\,K_2\,[H_2SO_4]^2} + \frac{1}{k_s\,K_2\,[H_2SO_4]}$$

That is,

$$\frac{[H_2SO_4]^2}{k''} = \frac{1}{k_s\,K_1\,K_2} + \frac{[H_2SO_4]}{k_s\,K_2} \quad ..(3)$$

The plots of [H_2SO_4]$^2/k''$ versus [H_2SO_4] were constructed and were found to be linear with a positive intercept. We also define a hypothetical rate constant (k''') for a particular substrate as :

$$\frac{k''}{[H_2SO_4]^x} = k''' \quad ..(4)$$

where x is the order of reaction with respect to H_2SO_4. The values of k''' calculated from Eq.(4) for various oxanones are given in Table 3 and were found to fluctuate within ± 5%.
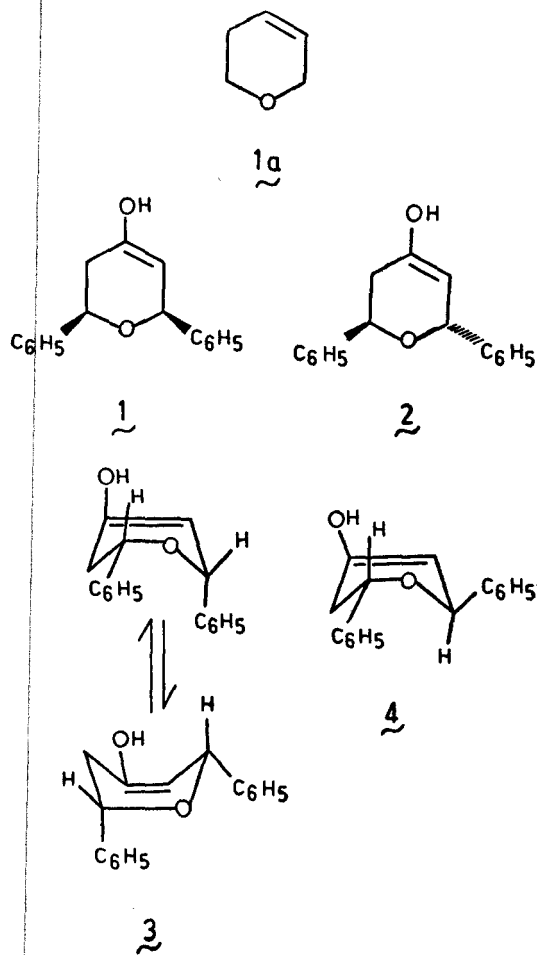
The slope value obtained at constant [acid] for the linear plot of $1/k_{obs}$ versus $1/[S]$ has also been calculated employing the slope and intercept values obtained from the plot of [H_2SO_4]$^2/k''$ versus [H_2SO_4] of Eq. (3). These values are given in Table 4, and there is an excellent agreement between the calculated and observed slopes supporting the proposed rate equation and Scheme 1.

Structure and reactivity — Examination of data in Table 3 shows that r-2, trans-6-diphenyl-4-oxanone (II) reacts at a faster rate as compared to r-2, cis-6-diphenyl-4-oxanone (Ia). The observed order with respect to H_2SO_4 and bromination rates suggest that the oxidation possibly involves the intermediate formation of an enol. Examination of the drieding stereo model shows that the most stable conformation of 5,6-dihydro-2H-oxanone ring (Ia) is quasiboat. The enols 1 and 2 adopt quasiboat conformations 3 and 4, respectively. The trans-enol 2 will have both phenyl groups in equatorial positions as in 4.

TABLE 3 — RATE CONSTANTS (k'') FOR VARIOUS OXANONES AT DIFFERENT ACID CONCENTRATIONS

[Temp. = 30°; [(V (V)] = 0.0025M; [substrate] = 0.025M; solvent = 80% HOAc (v/v)

Substrate	k'' (Hypothetical) at			
	0.2M	0.3M	0.4M	0.5M
Ia	33.07	33.40	33.29	32.75
II	77.99	72.52	78.69	78.33
Ib	185.74	198.38	190.09	190.23
Ic	183.77	189.24	189.69	182.45

TABLE 4 — COMPARISON OF CALCULATED AND OBSERVED SLOPE VALUES FOR THE PLOT OF $1/k_{obs}$ VERSUS 1/[substrate]

Substrate	Intercept and slope from Eq. (3)		Slope value for Eq. (2)	
	Intercept	Slope	Obs.	Calc.
Ia	0.3004	3.031	7.28	7.26
II	0.1323	1.259	9.50	9.60
Ib	0.1301	0.465	5.66	5.58
Ic	0.1284	0.492	5.56	5.67

rate. Baxter and Whiting have also observed that the formation of enol from a similarly constituted trans-2,6-diphenyl-4-thianone is faster than its epimer[8].

The values in Table 3 also reveal that 3-alkyl-4-oxanones (Ib and Ic) react faster than the unsubstituted 4-oxanones (Ia and II). Also, under identical experimental conditions, the oxidation kinetics of r-2, cis-6-diphenyl-trans-3,5-dimethyl-4-oxanone (Id) was found to be too fast to follow. This may be due to the stabilisation of the enol-form by the inductive effect of the alkyl groups. Nevertheless, there is not much difference between the rates of 3-ethyl (Ic) and 3-methyl-4-oxanones (Ib). The nearby equal reaction rate for the ethyl compared with the methyl substituted oxanone may be due to the contribution of steric factor of the ethyl group.

Acknowledgement

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However, the cis-enol 1 has one phenyl in axial position and the other in equatorial as in 3. Hence, it is likely that the trans-enol 2 is more stable that the cis-intermediate 1 and the formation of trans-enol is more rapid than that of the cis-form Therefore, the equilibrium constant K_2 will have a higher value for the trans-enol 2 and hence the higher