

## Cu(II)-catalysed Oxidation of Cyclohexanone & Lactic Acid by Vanadium(V) in HCl Medium

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The rate of oxidation of cyclohexanone and lactic acid by V(V) in HCl medium increases significantly in the presence of  $\text{Cu}^{2+}$  ions. The order with respect to  $[\text{V}^{5+}]$  is strictly one both in the presence and absence of  $\text{Cu}^{2+}$  ions while the order in  $[\text{cyclohexanone}]$  or  $[\text{lactic acid}]$  is fractional in the presence of  $\text{Cu}^{2+}$ . Acid catalysis observed both in the presence and absence of  $\text{Cu}^{2+}$  is found to be  $[\text{H}_3\text{O}^+]$  dependent. A mechanism involving the formation of  $(\text{Cu}^{2+}\text{-substrate})$  adduct in the initial step, followed by the reaction with  $\text{V}^{5+}$  in a rate determining step to form  $(\text{Cu}^{3+}\text{-substrate})$  adduct which subsequently undergoes internal oxidation to yield the products has been suggested to explain the results. Thermodynamic parameters both in the presence and absence of  $\text{Cu}^{2+}$  are also presented and discussed.

It is generally known that all redox reactions proceed in a number of stages. Reactions using V(V), Ce(IV) and Co(III) as oxidants have been studied in great detail<sup>1</sup>. The oxidation of organic substrates by V(V) involves initial complex formation followed by a rate determining decomposition of this complex. However, not much work seems to have been done on the catalysed oxidation of organic substrates by V(V). Catalysis by Mn(II) in the oxidation of malonic and oxalic acids by V(V) was reported by Kemp and Waters<sup>2</sup>. Radhakrishnamurti *et al.*<sup>3</sup> reported a three-fold increase in the rate of oxidation of toluenes by V(V) in the presence of Mn(II).

In the course of the work on the oxidation of cyclohexanone (CHN) and lactic acid (LA) by V(V), it was observed by us that the presence of  $\text{Cu}^{2+}$  ions increased the rate considerably. In the present work, the kinetic data in the oxidation of cyclohexanone and lactic acid by V(V) in HCl medium in the presence and absence of  $\text{Cu}^{2+}$  ions are presented and possible mechanisms discussed.

### Materials and Methods

All the chemicals used were of AR grade and wherever necessary further purification was done by standard methods. The rates of oxidation were followed by quenching the reaction mixture at different intervals of time in a known excess of  $\text{Fe}^{2+}$  and titrating the unreacted ferrous against standard V(V) solution using barium diphenylaminosulphonate as indicator.

### Results and Discussion

The order with respect to  $[\text{V}^{5+}]$  was strictly one in the oxidation of cyclohexanone and lactic acid. The order with respect to  $[\text{substrate}]$  was fractional in the presence of Cu(II) ions (0.8 in the case of cyclohexanone and 0.3 for lactic acid). The plots  $1/k'$  vs  $1/[\text{substrate}]$  were linear with an intercept (Fig. 1). Increase of  $[\text{Cu}^{2+}]$  increased the reaction rates (Tables 1 and 2).

The kinetic data obtained for the oxidation of cyclohexanone or lactic acid in the presence of  $\text{Cu}^{2+}$  are essentially same as in its absence, except for the significant increase in rate in the presence of the latter and decrease in the order of  $[\text{substrate}]$ . It was shown by us in an earlier communication that  $\text{V}(\text{OH})_3\text{Cl}^+$  is the active species in HCl medium<sup>4</sup>.

The fractional order in  $[\text{cyclohexanone}]$  in the presence of  $\text{Cu}^{2+}$  indicates that the substrate is involved in complex formation with V(V) or Cu(II). In the concentration ranges of the substrate used in the present study, there was no evidence of complex formation between V(V) and cyclohexanone either from kinetic or spectrophotometric data.

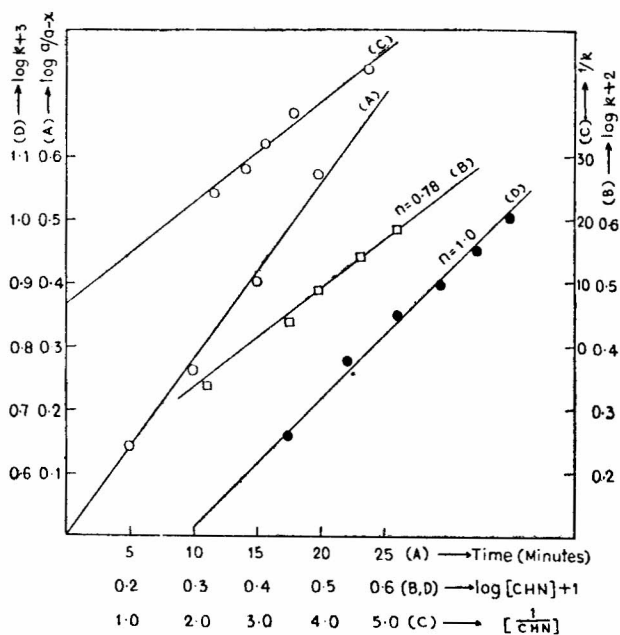


Fig. 1 — Plots of  $1/k'$  versus  $1/[\text{cyclohexanone}]$  and other relevant to the kinetic study of the oxidation of cyclohexanone by V(V) in the presence of Cu(II)

TABLE 1 — EFFECT OF [Cu<sup>2+</sup>] ON *k'* IN THE OXIDATION OF CYCLOHEXANONE BY V<sup>5+</sup>

{[V<sup>5+</sup>]=0.018*M*; [cyclohexanone]=0.24*M*; temp.=48°;  
μ=1.395}

[Cu <sup>2+</sup> ] <i>M</i>	<i>k</i> × 10 <sup>3</sup> min <sup>-1</sup> at [H <sup>+</sup> ] =0.85 <i>M</i>	<i>k</i> <sub>Cu</sub> / <i>k</i> <sub>0</sub> *	<i>k</i> × 10 <sup>3</sup> min <sup>-1</sup> =0.38 <i>M</i>	<i>k</i> <sub>Cu</sub> / <i>k</i> <sub>0</sub> at [H <sup>+</sup> ] =0.38 <i>M</i>
Nil	4.83	—	4.14	—
0.004	6.91	1.43	5.06	1.22
0.008	9.45	1.96	5.27	1.27
0.016	12.67	2.62	5.99	1.45
0.024	16.12	3.26	6.45	1.56
0.032	19.00	3.95	6.91	1.67
0.040	20.70	4.30	—	—

\*At [H<sup>+</sup>]=0.85*M*.TABLE 2 — EFFECT OF [Cu<sup>2+</sup>] ON *k'* IN THE OXIDATION OF LACTIC ACID BY V<sup>5+</sup>

{[V<sup>5+</sup>]=0.004*M*; [lactic acid]=0.21*M*; [H<sup>+</sup>]=0.0256*M*;  
temp.=45°}

[Cu <sup>2+</sup> ] <i>M</i>	<i>k</i> × 10 <sup>2</sup> min <sup>-1</sup>	<i>k</i> <sub>Cu</sub> / <i>k</i> <sub>0</sub>
Nil	1.01	—
0.02	2.09	2.04
0.04	3.22	3.18
0.05	4.84	4.78
0.06	6.56	6.57

Therefore, it is probable that cyclohexanone is involved in an adduct formation with Cu<sup>2+</sup> before oxidation by V<sup>5+</sup>. Also, Cu(II)-cyclohexanone adduct could be a better reductant than simple Cu(II) which may be the reason for the catalysis observed in the presence of Cu(II). From a study of the solvent isotope effects on the oxidation of cyclohexanone by V(V) in sulphuric acid medium, Best *et al.*<sup>5</sup> have concluded beyond doubt that V(V) attacks the ketonic form of the cyclohexanone directly. Therefore, it is assumed that in the present study also, the ketonic form of the cyclohexanone is involved.

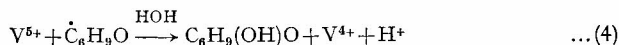
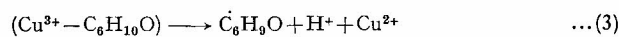
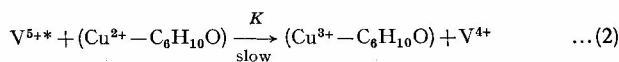
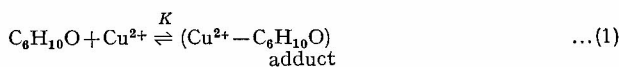
If the formation of Cu<sup>2+</sup>-cyclohexanone adduct is taken as the first step, the probable mechanism of oxidation in the presence of Cu<sup>2+</sup> could be written as shown in Scheme 1.

Under the conditions [cyclohexanone] ≫ [V<sup>5+</sup>] the rate law comes out to be

$$\frac{-d[V^{5+}]}{dt} = \frac{kK[Cu^{2+}][cyclohexanone][V^{5+}]}{1 + K[cyclohexanone] + K[Cu^{2+}]}$$

The above rate equation explains well the first order dependence of rate on [V<sup>5+</sup>] and the fractional order on [Cu<sup>2+</sup>] and [cyclohexanone]. Evidence for the existence of Cu<sup>3+</sup> was obtained through positive Beck's test<sup>6</sup> suggesting that the mechanism proposed is probably correct.

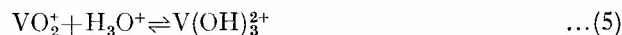
Though the effect of increasing [Cu<sup>2+</sup>] was one of increase in rate constant values (Table 1), the catalytic effect measured in terms of *k*<sub>Cu</sub>/*k*<sub>0</sub> ratios was less marked at low [H<sup>+</sup>] (Table 2). This could



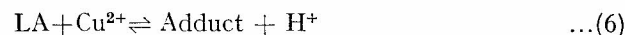
Scheme 1

(\*The chloride complex is written as V<sup>5+</sup> for simplicity).

probably be due to the decreased availability of the protonated species of V<sup>5+</sup>, viz. V(OH)<sub>3</sub><sup>2+</sup> according to the equilibrium (5):



A mechanism similar to the one given for the oxidation of cyclohexanone may be proposed for lactic acid oxidation. However, the effect of [H<sup>+</sup>] on the oxidation of lactic acid by V<sup>5+</sup> needs separate consideration in view of the following observations. Though *k*<sub>Cu</sub> and *k*<sub>0</sub> increased with increase in [H<sup>+</sup>] their ratios decreased (Table 3). It is probable that the adduct formation between lactic acid and Cu<sup>2+</sup> results in a decrease in *p*H, as a result of release of H<sup>+</sup> from the reaction (6),



and the effect of increase in [H<sup>+</sup>] would then be to decrease [adduct] and hence, the rate. However, an increase in [H<sup>+</sup>] increases the concentration of protonated species of V<sup>5+</sup>, thereby resulting in an acceleration of rate, as mentioned earlier. Thus, the adduct formation (Eq. 6) and acid catalysis (Eq. 5) oppose each other in so far as the effect of [H<sup>+</sup>] on the rate of oxidation of lactic acid is concerned. The increase in *k*<sub>Cu</sub> and *k*<sub>0</sub> values with increase in [H<sup>+</sup>] may be explained as due to the shift in equilibrium (5), i.e. formation of larger amounts of protonated species. But the decrease in their ratios (*k*<sub>Cu</sub>/*k*<sub>0</sub>) with increase in [H<sup>+</sup>] indirectly supports the existence of the equilibrium (6). The decrease in catalytic activity is probably due to decrease in concentration of Cu<sup>2+</sup>-lactic acid adduct.

Considerable decrease in entropy of activation values (Table 4) in the presence of Cu<sup>2+</sup> suggests a

TABLE 3 — EFFECT OF [H<sup>+</sup>] ON *k'* IN V<sup>5+</sup>-LACTIC ACID REACTION CATALYSED BY Cu<sup>2+</sup>

{[V<sup>5+</sup>]=0.004*M*; [lactic acid]=0.21*M*; [Cu<sup>2+</sup>]=0.04*M*;  
temp.=45°}

[H <sup>+</sup> ] <i>M</i>	<i>k</i> <sub>0</sub> × 10 <sup>3</sup> min <sup>-1</sup>	<i>k</i> <sub>Cu</sub> × 10 <sup>3</sup> min <sup>-1</sup>	<i>k</i> <sub>Cu</sub> / <i>k</i> <sub>0</sub>
0.018	6.70	30.1	4.52
0.026	10.01	32.2	3.18
0.056	20.05	34.4	1.67
0.079	29.90	36.8	1.29

TABLE 4 — ACTIVATION PARAMETERS

	Cyclohexanone		Lactic acid	
	(A)	(B)	(C)	(D)
$k^{11} \times 10^2$ , litre mol <sup>-1</sup> sec <sup>-1</sup>	4.43	33.67	4.81	15.32
$\Delta E^\ddagger$ , kcal mol <sup>-1</sup>	17.8	14.2	21.2	12.4
$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	17.3	13.7	20.8	11.3
$\Delta G^\ddagger$ , kcal mol <sup>-1</sup>	20.6	19.3	20.5	19.8
$\Delta S^\ddagger$ , e.u.	-8.7	-16.2	0.9	-26.7

A and C refer to uncatalysed reaction and B and D to catalysed reaction.

Error limits:  $k \pm 2\%$ ;  $\Delta E^\ddagger \pm 0.9$  kcal;  $\Delta S^\ddagger \pm 2.7$  e.u.

more rigid structure for the activated complex as could be expected if Cu<sup>2+</sup>-substrate adduct is oxidized in the rate determining step. The decrease in energy of activation values explains well the increase in rate in the presence of Cu<sup>2+</sup> ions.

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