# Kinetics & Mechanism of Oxidation of 4-Methylpentan-2-one by Vanadium(V) in Dilute Perchloric Acid Medium

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The oxidation of 4-methylpentan-2-one by vanadium(V) in dil. perchloric acid medium is first order each in V(V) and the ketone. The reaction is acid-catalysed and first order in acid. NaHSO₄, NaClO₄, NaCl and Na₂SO₄ have a specific effect on the reaction which takes place through a free radical mechanism. A mechanism involving the formation of two types of complexes is suggested.

**V**ANADIUM(V) has been investigated as an oxidizing agent for many organic and inorganic substrates[1-5]. The oxidation of 4-methylpentan-2-one by Mn(III)[6] has been reported. But no detailed kinetic study has been carried out on the oxidation of this ketone by V(V). The results of such a study in perchloric acid medium are presented.

## Materials and Methods

4-Methylpentan-2-one (BDH) was purified by distillation and its purity checked by GLC. Ammonium metavanadate (Hungary) dissolved in dil. perchloric acid was used for the preparation of V(V) solutions. The ketone being insoluble in water, 25% aq. acetic acid was used for dissolving it. The rate of the reaction was followed as reported earlier[8]. All the studies were carried out under pseudo-first order conditions; [ketone] $\gg$ [V(V)]. All the experiments have been carried out at $40° \pm 0.1$ and $55° \pm 0.1$.

The stoichiometry of the reaction is found to be 2 g ions of V(V) to one mole of the ketone. 2-Methylpropanal was found to be the product, by the peak enhancement method using an authentic sample of the aldehyde.

## Results and Discussion

In the concentration range of $2.0 \times 10^{-3}$ to $6.0 \times 10^{-2}M$, the reaction is first order in V(V) as revealed by the linear plots of log [V(V)] vs time $[HClO_4] = 2.5M$ and [ketone] $= 0.4M$. The values of the apparent first order rate constants are independent of the initial concentration of V(V), both at 40° and 55°.

Keeping the ionic strength of the system constant at 4.1, the first order plots for different initial concentrations of ketone (0.1, 0.2, 0.3 and 0.4M) are all linear at a V(V) concentration of $7.5 \times 10^{-3}M$ and perchloric acid concentration of 2M. A plot of $k_{obs}$ vs [ketone] is linear (Fig. 1) indicating that the order in ketone is one. At a V(V) concentration of $6.3 \times 10^{-2}M$ and a ketone concentration of 0.4M, the concentration of acid is changed, keeping the

ionic strength constant. The plots of the first order rate constant $k_{obs}$ vs $[HClO_4]$ are also linear at 40° and 55° with positive intercepts indicating that the order in acid is one and an acid uncatalysed path is also operating (Fig. 2).

Though the plot of log $k_{obs}$ against $-H_0$ (taken from the tables of Paul and Long[7]) is linear with a slope of 0.3 as in the case of the oxidation of butan-2-one[8], a plot of $k_{obs}$ versus $[HClO_4]$ gives a better correlation, which according to Waters[3], indicates the absence of a chelate complex between the ketone and V(V). A plot of (log $k_{obs}$) $+ H_0$ against log $a_{H_2O}$ is linear with a $w$ value of 6.0, indicating that water acts as a proton transfer agent in the rate-determining step[9].

As the proportion of acetic acid is altered, even though a plot of log $k_{obs}$ vs $1/D$ is linear (corr. coeff. $= 0.984$), a better correlation is observed between the rate constant and mole fraction of
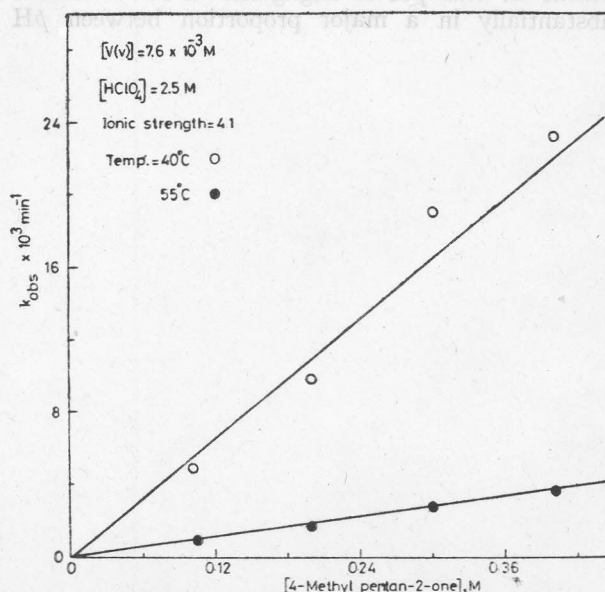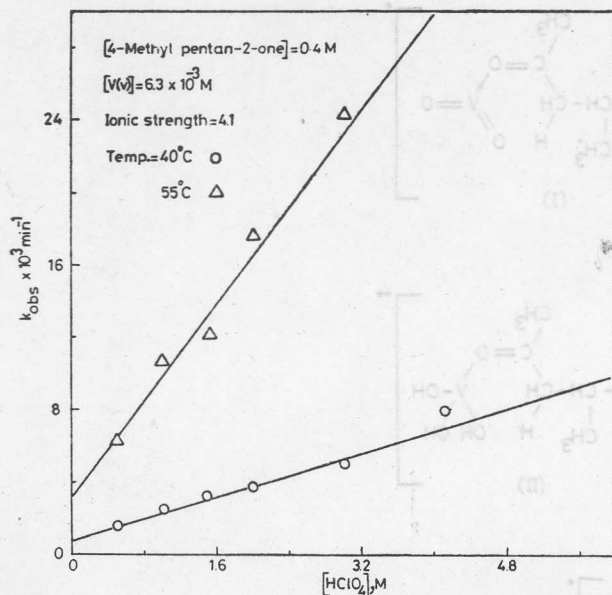


Fig. 1 — Plots of $k_{obs}$ against (Ketone) at 40° and 55°

[4-Methyl pentan-2-one] = 0.4 M

[V(V)] = 6.3 × 10⁻³ M

Ionic strength = 4.1

Temp. = 40°C  ○

55°C  △

Fig. 2 — Plots of $k_{obs}$ against [HClO₄] at 40° and 55°

water (corr. coeff. = 0·999). The present reaction between the ketone molecule, a dipole and the V(V) species $V(OH)_3^{2+}$, an ion, leads to an activated complex in the transition state which is less polar than the initial state on account of a greater dispersal of charge in the transition state. The decrease in the rate of oxidation on the addition of more polar water can be explained as due to the progressive and preferential increase in solvation of the reactants.

The results for reactions in the presence of salts like sodium perchlorate, sodium bisulphate, sodium chloride and sodium sulphate are given in Table 1. The specific effect of these salts indicates the formation of different active V(V) species. In pure perchloric acid medium[11], $V(OH)_3^{2+}$ is considered to be the active species of V(V) which interacts with the ketone in the oxidation reaction since perchlorate ion is not known to form any complex with V(V) ion.

When methyl methacrylate is added to the reaction mixture, polymerization occurs indicating that the reaction involves the formation of free radicals. The addition of V(IV) is found not to have any effect on the rate of the reaction. As in the case of butan-2-one[8] it is not possible to unambiguously determine whether the ketone is reacting through the enol form.

*Mechanism* — From the results obtained, the rate expression should be of the form

$$\text{Rate} = (a + b[\text{HClO}_4])[\text{V(V)}][\text{ketone}]$$

The proposed mechanism involves the formation of two types of complexes of the ketone, one with $VO_2^+$ ion and the other with the protonated $V(OH)_3^{2+}$ ion.
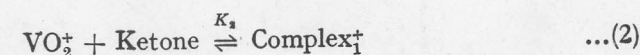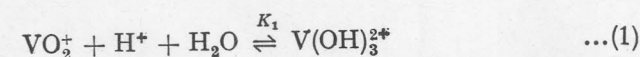
$$VO_2^+ + H^+ + H_2O \overset{K_1}{\rightleftharpoons} V(OH)_3^{2+} \qquad \text{...(1)}$$

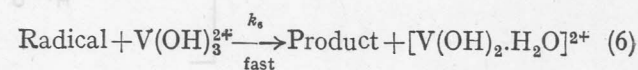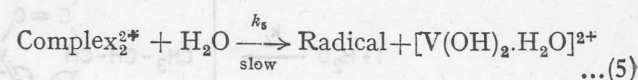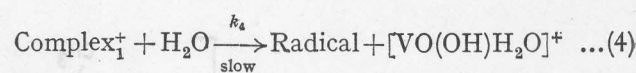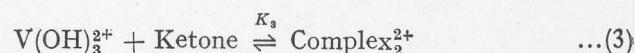$$VO_2^+ + \text{Ketone} \overset{K_2}{\rightleftharpoons} \text{Complex}_1^+ \qquad \text{...(2)}$$

TABLE 1 — EFFECT OF ADDITION OF SALTS ON THE RATE OF REACTION

{[4-Methylpentan-2-one] = 0·4*M*; [V(V)] = 8·3 × 10⁻³ *M*; [HClO₄] = 0·5*M*; μ = 2·0; temp. = 40°}

(a) [NaHSO₄] + [NaClO₄] = 2*M*

| [NaHSO₄], *M* | 0·0 | 0·4 | 0·8 | 1·2 | 1·6 | |
|---|---|---|---|---|---|---|
| $k_{obs}$ × 10³ min⁻¹ | 0·93 | 1·37 | 1·42 | 1·50 | 1·67 | |

(b) [NaCl] + [NaClO₄] = 2*M*

| [NaCl], *M* | 0·0 | 0·4 | 0·8 | 1·2 | 1·6 | 2·0 |
|---|---|---|---|---|---|---|
| $k_{obs}$ × 10³ min⁻¹ | 0·93 | 1·06 | 1·11 | 1·03 | 1·07 | 0·94 |

(c) μ = 3·0

| [Na₂SO₄], *M* | 0·0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 |
|---|---|---|---|---|---|---|
| $k_{obs}$ × 10⁴ min⁻¹ | 12·8 | 9·9 | 5·9 | 3·0 | 2·6 | 1·1 |

$$V(OH)_3^{2+} + \text{Ketone} \overset{K_3}{\rightleftharpoons} \text{Complex}_2^{2+} \qquad \text{...(3)}$$

$$\text{Complex}_1^+ + H_2O \overset{k_4}{\underset{\text{slow}}{\longrightarrow}} \text{Radical} + [VO(OH)H_2O]^+ \quad \text{...(4)}$$

$$\text{Complex}_2^{2+} + H_2O \overset{k_5}{\underset{\text{slow}}{\longrightarrow}} \text{Radical} + [V(OH)_2.H_2O]^{2+} \qquad \text{...(5)}$$

$$\text{Radical} + V(OH)_3^{2+} \overset{k_6}{\underset{\text{fast}}{\longrightarrow}} \text{Product} + [V(OH)_2.H_2O]^{2+} \quad (6)$$

Hence

$$\text{Rate} = \frac{(k_4 K_2 + k_5 K_3 K_1[\text{HClO}_4])[\text{Ketone}][\text{V(V)}]_T}{1 + K_1[\text{HClO}_4](1 + K_3[\text{Ketone}])}$$

$$\text{...(7)}$$

Wells and Kuritsyn[12] have considered that the value of $K_1$ is negligible when compared to 1. Hence considering all the terms in the denominator of Eq. (7) except 1 to be negligible, the rate is given by Eq. (8).

$$\text{Rate} = (k_4 K_2 + k_5 K_3 K_1[\text{HClO}_4])[\text{Ketone}][\text{V(V)}]_T \quad \text{...(8)}$$

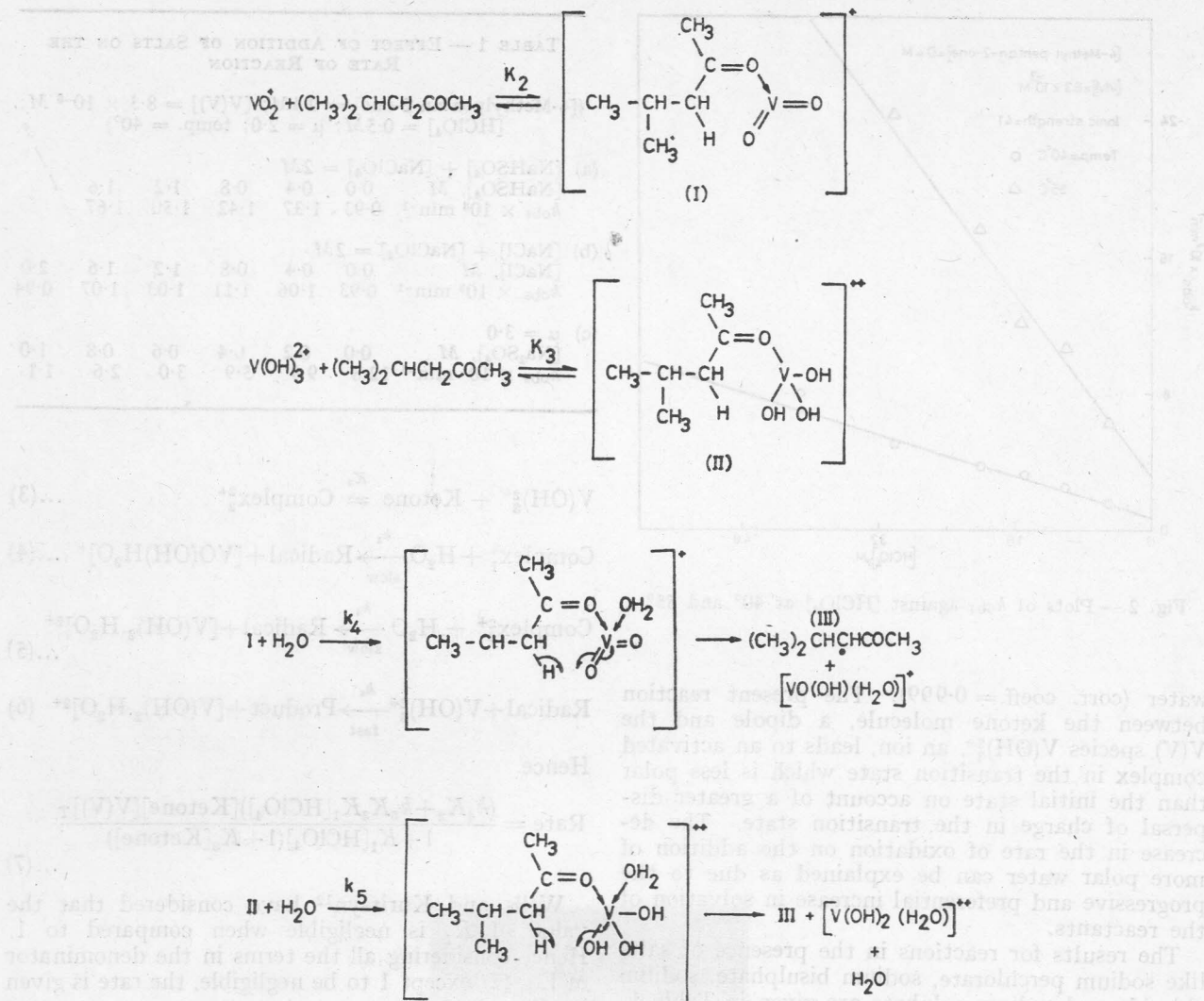$$k_{obs} = (k_4 K_2 + k_5 K_3 K_1[\text{HClO}_4])[\text{Ketone}] \qquad \text{...(9)}$$
$$= [X][\text{Ketone}]$$

At constant [HClO₄], a plot of $k_{obs}$ vs [Ketone] is linear with a slope of 8·9×10⁻³ at 40° and 6·2×10⁻² at 55° (Fig. 1), when [HClO₄] = 2·5*M*. This slope is equal to X. When the concentration of ketone is kept constant at 0·4*M*, Eq. (9) will be

$$k_{obs} = 0·4 k_4 K_2 + 0·4 k_5 K_3 K_1[\text{HClO}_4] \qquad \text{...(10)}$$

According to Eq. (10) a plot of $k_{obs}$ vs [HClO₄] is expected to be linear with a positive slope and intercept. This is found to be so (Fig. 2).

|  | 40° | 55° |
|---|---|---|
| Slope | 1·3×10⁻³ | 6·6×10⁻³ |
| Intercept | 1·0×10⁻³ | 3·2×10⁻³ |
| $k_4 K_2$ | 2·5×10⁻³ | 8·0×10⁻³ |
| $k_5 K_3 K_1$ | 3·3×10⁻³ | 1·6×10⁻² |

$k_4 K_2 + 2·5\ k_5 K_3 K_1 = X = 10·7×10⁻³$ at 40°
$= 4·9×10⁻²$ at 55°

The values of X, obtained, 8·9×10⁻³ and 10·7 ×10⁻³ at 40° and 6·2×10⁻² and 4·9×10⁻² at 55°C

$$VO_2^+ + (CH_3)_2CHCH_2COCH_3 \underset{}{\overset{K_2}{\rightleftharpoons}} \left[ \text{(I)} \right]^+$$

$$V(OH)_3^{2+} + (CH_3)_2CHCH_2COCH_3 \underset{}{\overset{K_3}{\rightleftharpoons}} \left[ \text{(II)} \right]^{++}$$

$$I + H_2O \xrightarrow{k_4} \left[ \right]^+ \longrightarrow (CH_3)_2\overset{\bullet}{C}HCHCOCH_3 \quad \text{(III)} \\ + \\ \left[ VO(OH)(H_2O) \right]^+$$

$$II + H_2O \xrightarrow{k_5} \left[ \right]^{++} \longrightarrow III + \left[ V(OH)_2(H_2O) \right]^{++} + H_2O$$

**Scheme 1**

by both plots i.e. $k_{obs}$ vs $[HClO_4]$ and $k_{obs}$ vs [Ketone] respectively are in good agreement, which lends support to the proposed mechanism. The mechanistic scheme may be visualized as shown in Scheme 1.

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