Kinetics & Mechanism of Oxidation of Methyl Ethyl Ketone by Vanadium(V) in Dilute Sulphuric Acid

G. CHITHAMBARATHANU PILLAI, J. RAJARAM & J. C. KURIACOSE
Department of Chemistry, Indian Institute of Technology, Madras 600036

Received 25 September 1976; accepted 17 January 1977

The oxidation of methyl ethyl ketone (MEK) by V(V) in the presence of sulphuric or perchloric acid, is first order each in MEK, V(V) and the acid, the reaction being slower in the former acid. NaClO₃ has practically no effect on the rate, NaHSO₄ increases the rate and Na₂SO₄ decreases the rate. The proposed mechanism involves a free radical intermediate, whose presence has been established by induced polymerization of acrylonitrile.

Vanadium(V) has been investigated as an oxidizing agent for many organic and inorganic substrates. The oxidation of methyl ethyl ketone (MEK) by alkaline hexacyanoferrate (III) ion, chlorine-T and Cr(VI) has been investigated, but no detailed kinetic study has so far been made of its oxidation by V(V). The results of a detailed study of the oxidation of MEK by V(V) are presented here.

Materials and Methods

MEK was distilled and its purity checked by GLC. Ammonium metavanadate (AR, Hungary) dissolved in dil. H₂SO₄ was used for the preparation of V(V) solutions. The rate of the reaction was followed by quenching an aliquot of the reaction mixture in a measured excess of ferrous ammonium sulphate and back titrating the unreacted Fe²⁺ against standard dichromate using N-phenylanthranilic acid as the indicator. All the experiments were conducted at 30±0.1°C unless otherwise stated.

Stoichiometry and product analysis — The stoichiometry of the reaction was determined by keeping reaction mixture containing excess of V(V) until the reaction was complete and then determining the unreacted V(V). The stoichiometry is found to be 2 g ions of V(V) to one mole of the ketone. The presence of formic acid after distillation of the reaction mixture was indicated by GLC. Carbon dioxide was not one of the products.

Results and Discussion

Using a 20-100 fold excess of MEK in comparison with V(V), the reaction was found to be pseudo-first order in V(V) (Fig. 1). There is very little variation in the pseudo first-order rate constants calculated for the different sets of experiments, indicating that first-order rate constants are independent of the initial [V(V)].

The order of MEK was found to be one by keeping the initial V(V) concentration constant and changing the ketone concentration, the latter being always in excess. When the logarithm of the rate constants are plotted against log [MEK], a linear plot with a slope of unity is obtained (Fig. 2A), indicating first order in MEK. This kinetics is observed when [MEK] is varied from 0.8 to 1.5 M and [V(V)] from 1.5×10⁻² to 5.0×10⁻² M. With higher and lower concentrations, there is some deviation. The rate increases with increase in [H₂SO₄]. Due to the difficulties in maintaining the ionic strength constant in H₂SO₄, HClO₄ was used instead of H₂SO₄ and NaClO₄ was added to keep the ionic strength constant. A plot of log kₜ vs log [HClO₄] gave a slope of 0.99 showing first order dependence in acid (Fig. 2B).

Effect of added salts — Change in ionic strength by the addition of NaClO₄ has negligible effect on the rate of the reaction (Table 1). Sodium bisul-
Table 1 — Effect of Addition of NaClO₃ on the Reaction Rate

<table>
<thead>
<tr>
<th>[MEK] = 1.0 M; [V(V)] = 1.15 X 10⁻² M; [H₂SO₄] = 2.0 M; temp. 30°C</th>
<th>kₓ X 10⁻³ min⁻¹</th>
<th>Correlation coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₃, M</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>kₓ X 10⁻³ min⁻¹</td>
<td>2.82</td>
<td>2.55</td>
</tr>
<tr>
<td>Correlation coeff.</td>
<td>0.995</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Comparison of rates in HClO₄ and H₂SO₄ — In 1 M acid, the rate is similar in both acids. At higher concentrations, the reaction is faster in HClO₄ indicating that in HClO₄ a more active form of the oxidizing agent is present (Table 3). Similar results have been obtained by Mehrotra in the oxidation of 2-hydroxy-2-methylpropanoic acid by V(V).

Acid catalysis — The fact that the rate increases with increase in HClO₄ at constant ionic strength clearly shows that the reaction is acid-catalysed. The plots of log kₓ vs -Hₒ were reasonably linear in the case of H₂SO₄ and HClO₄. The values of -Hₒ are those given by Paul and Long. The slopes of the linear plots are much less than unity being 0.5 and 0.6 in H₂SO₄ and HClO₄ respectively (Fig. 3). These results are comparable to the results reported by Mehrotra for the oxidation of citric acid by V(V).

Littler and Waters have shown that a dependence of log kₓ on Hₒ, the Hammett acidity function, rather than a dependence on [H₃O⁺] can be taken as an indication for the formation of a cyclic transition state. In the present case, there is a depend-
dence of log \( k \) on \( H_\text{a} \) and hence the formation of a complex of the type (I) may be envisaged. The negative value of the gross entropy of activation may be considered to support this idea.

According to Bunnett, the plots of log (\( k + H_\text{a} \)) against log \( \sigma_\text{g} \) are generally linear and the slopes define a parameter \( w \). A \( w \) value of -2.5 to 0 indicates non-participation of water in the transition state, a value between +1.2 and +3.3 indicates that water acts as a nucleophile and a value >3.3 indicates that water acts as a proton transfer agent. In the present case, the plots of \(-\log k + H_\text{a} \) vs \(-\log \sigma_\text{g} \) were not linear in the entire acid range used. Up to 3M HClO\(_4\) the slope of the Bunnett plot was nearly 10 indicating that water may be acting as a proton transfer agent. At \[ [\text{HClO}_4] > 3M \] the \( w \) values obtained from the linear plots were 3.4 for H\(_2\)SO\(_4\) and 3.8 for HClO\(_4\) (Fig. 3). Such borderline values do not permit a clear-cut assignment of a role for water.

**Intermediates** — Induced polymerization of acrylonitrile during the reaction between V(V) and MEK and the absence of polymerization of the monomer by V(V) or MEK indicated the formation of a free radical intermediate.

The UV spectrum of the reaction mixture showed a very small optical exaltation around 240 nm indicating some complex formation. A plot of 1/\( k_{\text{obs}} \) vs 1/[MEK] at constant V(V) was linear with a small intercept on the Y-axis, offering kinetic support for complex formation (Fig. 4).

**Thermodynamic parameters** — The orders in V(V), MEK and HClO\(_4\) are independent of temperature in the range of 30° to 50°. The pseudo first-order rate constant (\( k_{\text{obs}} \)) is calculated by conducting the reaction at temperatures of 30°, 35°, 40°, 45° and 50°. From the slope of the plot of log \( k_{\text{obs}} \) against 1/T the energy of activation is found to be 16.6 ± 0.3 kcal/mole. The values of \( \Delta G^\circ \) and \( \Delta S^\circ \) are 21.5 kcal/mole and -165.5 e.u. respectively. \( k_{\text{obs}} \) is actually a product of a rate constant and two equilibrium constants.

**Reactive V(V) species** — The difference in the rates between the reactions for the same acid concentrations of H\(_2\)SO\(_4\) and HClO\(_4\) indicates the presence of two different active species in these acids.

Though V(V) is amphoteric it exists as a cation in solutions of acidity greater than 0.05M. The marked colour of the H\(_2\)SO\(_4\) solutions of V(V) suggests that one HSO\(_4^+\) ion may be incorporated in the active species as shown in Eqs. (1) and (2).

\[
\begin{align*}
\text{V}^3+ + \text{H}_2\text{O} \rightarrow \text{V(OH)}^+ + \text{HSO}_4^- \quad \text{... (1)}
\end{align*}
\]

\[
\begin{align*}
\text{V}^3+ + \text{HSO}_4^- \rightarrow \text{V(OH)}^+ + \text{H}_2\text{SO}_4^+ \quad \text{... (2)}
\end{align*}
\]

Since the rates are different in HClO\(_4\) and H\(_2\)SO\(_4\) and increase with increase in H\(_2\)SO\(_4\), the reactive species may contain the sulphate or bisulphate group. The sulphate complex is not a probable active species since addition of sulphate ion decreases the rate. So V(OH)_3HSO_4 can be the reactive V(V) species in H\(_2\)SO\(_4\) medium. In HClO\(_4\) no such complex formation is probable since NaClO\(_4\) when added, causes negligible effect or decreases the rate slightly and hence V(OH)_3^+ may be the active oxidant in HClO\(_4\).

**Mechanism** — In oxidation reactions ketones can react either directly or through the enol form. Oxidation rates faster than the rate of enolization have been observed with cobaltic, ceric and permanganate salts as oxidants, indicating that the ketones react directly. All of these oxidants undergo one-electron reduction and the reaction takes place through a free radical mechanism. Oxidation involving enol intermediate is proposed for thallic, manganic and permanganate salts and for manganic pyrophosphate. In all these cases, the formation of the enol is the rate determining step and the reactions are therefore zero order in the oxidant with the rates of oxidations and enolizations being equal. An unambiguous indication of the form in which the ketone reacts can be obtained only when the rate of oxidation is greater than the rate of enolization. Bromination of ketone is considered to take place through an enol intermediate. In the present system the rate of enolization measured by bromination is much greater than the rate of oxidation. Under identical experimental conditions, the bromination is over within 2 min whereas oxidation takes around 400 min for completion.

Since the enolization is very rapid, the ketone could be reacting through an enol intermediate under the experimental conditions. The enol-V(V) complex may be subsequently disintegrating to give the products. However, a direct attack of V(V) species on the ketone and the subsequent decomposition of the ketone-V(V) complex cannot be ignored. In the absence of zero order kinetics with respect to the oxidant, it is immaterial which form of the substrate is considered as taking part in the reaction.

One may visualize the reaction as taking place through the formation of an intermediate complex between the ketone and the V(V) species in an
PILLAI et al.: OXIDATION OF METHYL ETHYL KETONE BY V(V)

equilibrium step followed by its rapid transformation to give the products (Scheme 1)

\[
\begin{align*}
\text{VO}_2^+ + \text{H}_2\text{O} + \text{H}^+ & \rightleftharpoons \text{V(OH)}_2^+ \quad \ldots \quad (3a) \\
\text{VO}^+ + \text{H}_2\text{O} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{V(OH)}_2\text{HSO}_4^+ \quad \ldots \quad (3b)
\end{align*}
\]

\[\text{V(OH)}_2\text{HSO}_4^+ + \text{MEK} \rightleftharpoons \text{Complex} \quad \ldots \quad (4)\]

Complex \[\xrightarrow{\text{fast}}\] Radical intermediate \[\xrightarrow{\text{slow}}\] + V(VI)

Radical intermediate + V(V) \[\rightarrow\] products + V(VI).

Scheme 1

It is assumed that \(\text{V(OH)}_2^+\) and \(\text{V(OH)}_2\text{HSO}_4^+\) are the respective active species in perchloric and sulphuric acids\(^{12}\) respectively.

Rate = \(k_\text{a}[\text{complex}]\)

\[
= k_\text{a}K_1[\text{MEK}][\text{VO}_2^+][\text{H}_2\text{SO}_4] \quad \ldots \quad (7)
\]

Substituting for \([\text{V(V)}]_{\text{T}}\) and \([\text{VO}_2^+]\),

\[
\text{Rate} = k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4][\text{V(V)}]_{\text{T}} \ldots \quad (8)
\]

At constant \([\text{V(V)}]_{\text{T}}\),

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4]} + \frac{1}{k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4]} \quad \ldots \quad (9)
\]

A plot of the reciprocal of observed rate constant \(k_{\text{obs}}\) against \(1/[\text{MEK}]\) is linear with a slope=321 and an intercept=7.32.

If \(K_1\) is very small compared to \(k_\text{a}K_2\)

\[
\frac{1}{k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4]} + \frac{1}{k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4]} \quad \ldots \quad (11)
\]

\[
1 + \frac{1}{k_\text{a}K_1K_2K_3[\text{MEK}][\text{H}_2\text{SO}_4]} \quad \ldots \quad (12)
\]

From the slope and intercept values, \(k_3\) and \(K_2K_3\) are calculated to be equal to 0.137 and 1.14 \(\times\) 10\(^{-2}\) respectively, the \([\text{H}_2\text{SO}_4]\) being 2M.

Since in the denominator of expression (9), compared to (1) \(K_1\) and \(K_2K_3\) are found to be sufficiently small, to be neglected.

\[k_{\text{obs}} = k_3k_2K_3[\text{MEK}][\text{H}_2\text{SO}_4] \quad \ldots \quad (13)\]

and at constant concentration of the acid,

\[k_{\text{obs}} = \frac{k_2K_3[\text{MEK}]}{k_3[\text{MEK}]} \quad \ldots \quad (13a)\]

A plot of \(k_{\text{obs}}\) vs [MEK] should be linear passing through the origin (Fig. 4).

\(k_3\) value (0.137) calculated from the value of the intercept of the plot of \(1/k_{\text{obs}}\) vs \([\text{MEK}]\) (Eq. 10) when \([\text{H}_2\text{SO}_4]\) is kept constant at 2M agrees well with that calculated from the plot of \(k_{\text{obs}}\) vs [MEK] (Eq. 13, \(k_3 = 0.143\)). By using the slope and intercept of these two plots, \(K_3\) value is calculated and is found to be equal to 1.28 \(\times\) 10\(^{-2}\) which is seen to be negligible compared to the calculated value of \(k_2K_3 = 0.125\), supporting the line of argument proposed.

References