

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

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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. NaClO_4 has practically no effect on the rate, NaHSO_4 increases the rate and Na_2SO_4 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 substrates¹⁻⁵. The oxidation of methyl ethyl ketone (MEK) by alkaline hexacyanoferrate(III) ion⁶, chloramine-T⁷ and Cr(VI)⁸ 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. H_2SO_4 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 Fe^{2+} against standard dichromate using N-phenylanthranilic acid as the indicator. All the experiments were conducted at $30^\circ \pm 0.1^\circ$ unless otherwise stated.

Stoichiometry and product analysis—The stoichiometry of the reaction was determined by keeping reaction mixtures 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 in 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 $\log [\text{MEK}]$, 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 1.5M and [V(V)] from 1.5×10^{-2} to $5.0 \times 10^{-2} \text{M}$. With higher and lower concentrations, there is some deviation. The rate increases with increase in $[\text{H}_2\text{SO}_4]$. Due to the difficulties in maintaining the ionic strength constant in H_2SO_4 , HClO_4 was used instead of H_2SO_4 and NaClO_4 was added to keep the ionic strength constant. A plot of $\log k_1$ vs $\log [\text{HClO}_4]$ 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 NaClO_4 has negligible effect on the rate of the reaction (Table 1). Sodium bisul-

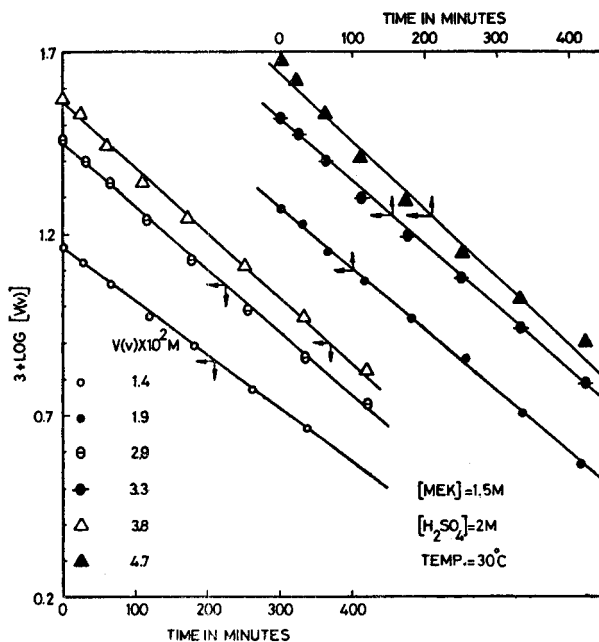


Fig. 1 — First order plots with respect to V(V)

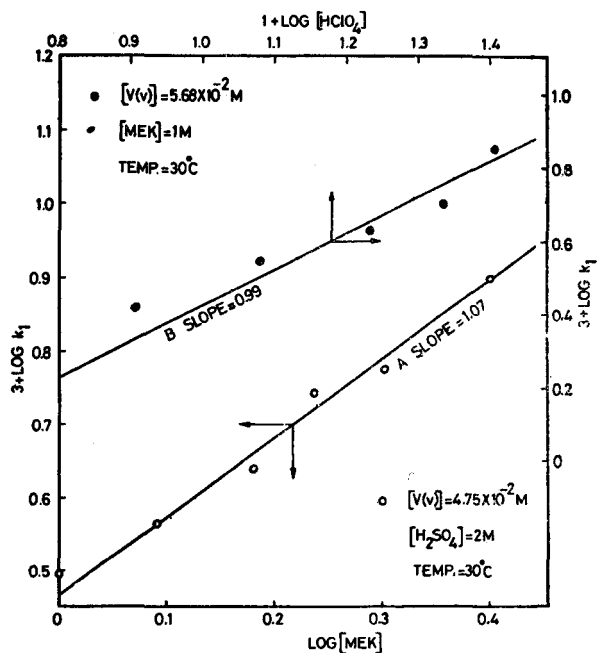


Fig. 2 — (A) First order plots with respect to MEK. (B) First order dependence in acid

phate when added under constant ionic strength (NaClO_4 was added to keep the ionic strength constant) showed increase in the rate whereas Na_2SO_4 is found to decrease the rate (Table 2).

Comparison of rates in HClO_4 and H_2SO_4 — In 1M acid, the rate is similar in both acids. At higher concentrations, the reaction is faster in HClO_4 indicating that in HClO_4 a more active form of the oxidizing agent is present (Table 3). Similar results have been obtained by Mehrotra⁹ in the oxidation of 2-hydroxy-2-methylpropanoic acid by V(V).

Acid catalysis — The fact that the rate increases with increase in HClO_4 at constant ionic strength clearly shows that the reaction is acid-catalysed. The plots of $\log k_1$ vs $-H_0$ were reasonably linear in the case of H_2SO_4 and HClO_4 . The values of $-H_0$ are those given by Paul and Long¹¹. The slopes of the linear plots are much less than unity being 0.5 and 0.6 in H_2SO_4 and HClO_4 respectively (Fig. 3). These results are comparable to the results reported by Mehrotra for the oxidation of citric acid by V(V)¹².

Littler and Waters³ have shown that a dependence of $\log k_1$ on H_0 , the Hammett acidity function, rather than a dependence on $[\text{H}_3\text{O}^+]$ can be taken as an indication for the formation of a cyclic transition state. In the present case, there is a depen-

TABLE 1 — EFFECT OF ADDITION OF NaClO_4 ON THE REACTION RATE

$[\text{MEK}] = 1.0M$; $[\text{V(V)}] = 1.19 \times 10^{-2}M$; $[\text{H}_2\text{SO}_4] = 2.0M$; temp. 30° ; ionic strength was not kept constant

$[\text{NaClO}_4], M$	0	0.2	0.4	0.7	0.85	1.0
$k_1 \times 10^3, \text{min}^{-1}$	2.82	2.55	2.60	2.53	2.75	2.36
Correlation coeff.	0.995	0.997	0.997	0.999	0.997	0.995

TABLE 2 — EFFECT OF ADDITION OF SALTS UNDER CONSTANT IONIC STRENGTH

(a) $[\text{V(V)}] = 2.05 \times 10^{-2}M$; $[\text{MEK}] = 1.0M$; $[\text{H}_2\text{SO}_4] = 2.0M$; temp. $= 30^\circ$

$[\text{NaHSO}_4], M$	0	0.3	0.5	0.6	0.7	0.8
$[\text{NaClO}_4], M$	1.0	0.7	0.5	0.4	0.3	0.2
$k_1 \times 10^3, \text{min}^{-1}$	2.92	3.04	3.34	3.52	3.63	3.76
Correl. coeff.	0.999	0.999	0.999	0.999	0.999	0.999

(b) $[\text{V(V)}] = 2.01 \times 10^{-2}M$; $[\text{MEK}] = 1.0M$; $[\text{H}_2\text{SO}_4] = 2.0M$; temp. $= 30^\circ$

$[\text{Na}_2\text{SO}_4], M$	0	0.2	0.4	0.6	0.8	1.0
$[\text{NaClO}_4], M$	3.0	2.4	1.8	1.2	1.6	0
$k_1 \times 10^3, \text{min}^{-1}$	4.28	3.61	3.23	2.65	2.26	1.99
Correl. coeff.	0.997	0.999	0.999	0.999	1.000	1.000

TABLE 3 — COMPARISON OF THE RATES OF THE REACTION AT THE SAME CONCENTRATION OF HClO_4 AND H_2SO_4

$\{[\text{V(V)}] = 1.42 \times 10^{-2}M$; $[\text{MEK}] = 1M$; temp. $= 30^\circ\}$

$[\text{Acid}] M$	H_2SO_4		HClO_4	
	$k_1 \times 10^3, \text{min}^{-1}$	Correl. coeff.	$k_1 \times 10^3, \text{min}^{-1}$	Correl. coeff.
1.2	1.62	0.992	1.33	0.975
2.1	2.27	0.998	2.43	0.998
3.0	3.89	1.000	4.81	0.995
3.9	5.51	0.999	8.90	0.999
4.8	9.75	0.999	13.97	0.999
5.7	16.98	0.999	20.25	0.996

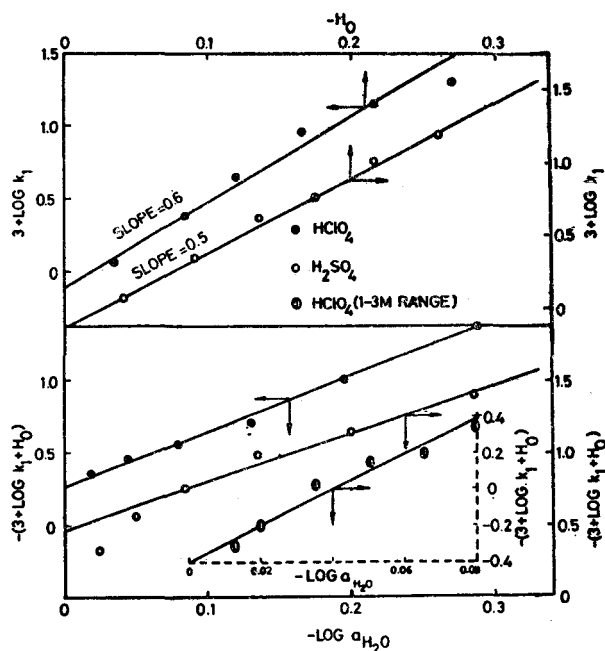
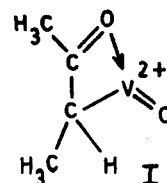


Fig. 3 — Plots of rate constants versus acidity (H_0) functions and activity of water ($a_{\text{H}_2\text{O}}$)



dence of $\log k_1$ on H_0 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 Bunnett¹³, the plots of $\log(k+H_0)$ against $\log a_{H_2O}$ 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 $-(\log k_1+H_0)$ vs $-\log a_{H_2O}$ 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 $[HClO_4] > 3M$, the w values obtained from the linear plots were 3.0 for H_2SO_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.

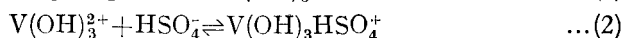
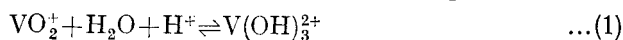
The UV spectrum of the reaction mixture showed a very small optical exaltation around 240 nm indicating some complex formation. A plot of $1/k_{obs}$ vs $1/[MEK]$ at constant V(V) was linear with a small intercept on the Y-axis, offering kinetic support for complex formation (Fig. 4).

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_{obs}) is calculated by conducting the reaction at temperatures of 30° , 35° , 40° , 45° and 50° . From the slope of the plot of $\log k_{obs}$ against $1/T$ the energy of activation is found to be 16.6 ± 0.3 kcal/mole. The values of ΔG^\ddagger and ΔS^\ddagger are 21.5 kcal/mole and -16.5 e.u. respectively. k_{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_2SO_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 $0.05M^{10}$. The marked colour of the H_2SO_4 solutions of V(V) suggests that one HSO_4^- ion may be incorporated in the active species² as shown in Eqs. (1) and (2).



Since the rates are different in $HClO_4$ and H_2SO_4 and increase with increase in H_2SO_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_2SO_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 $V(OH)_3^{2+}$ 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^{14,15}, ceric^{15,16} and manganic salts¹⁵ 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, mercuric and permanganate salts¹⁷ and for manganic pyrophosphate¹⁸. 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 intermediate⁸. 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

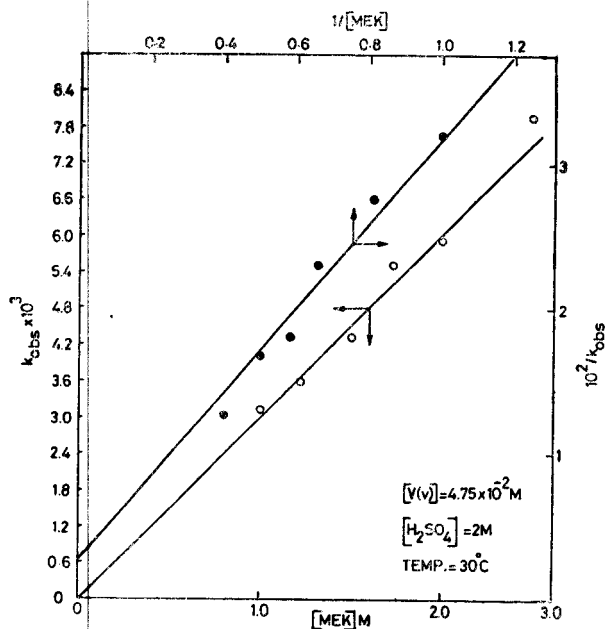
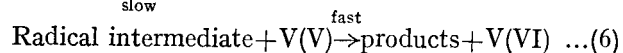
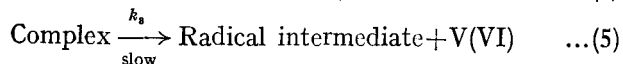
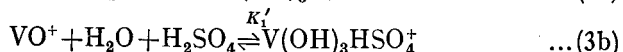
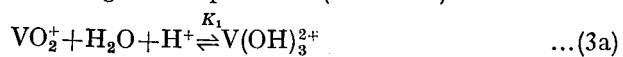


Fig. 4 — Plot of $1/[MEK]$ versus k_{obs} and $[MEK]$ versus k_{obs}

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



Scheme 1

It is assumed that $\text{V}(\text{OH})_3^{2+}$ and $\text{V}(\text{OH})_3\text{HSO}_4^+$ are the respective active species in perchloric and sulphuric acids¹² respectively.

$$\begin{aligned} \text{Rate} &= k_3[\text{complex}] \\ &= k_3K_2[\text{MEK}][\text{V}(\text{OH})_3\text{HSO}_4^+] \\ &= k_3K_2K_1'[\text{MEK}][\text{VO}_2^+][\text{H}_2\text{SO}_4] \quad \dots(7) \end{aligned}$$

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

$$\text{Rate} = \frac{k_3K_2K_1'[\text{MEK}][\text{H}_2\text{SO}_4][\text{V(V)}]_{\text{T}}}{1 + K_1'[\text{H}_2\text{SO}_4] + K_2K_1'[\text{MEK}][\text{H}_2\text{SO}_4]} \quad \dots(8)$$

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

$$k_{\text{obs}} = \frac{k_3K_2K_1'[\text{MEK}][\text{H}_2\text{SO}_4]}{1 + K_1'[\text{H}_2\text{SO}_4] + K_2K_1'[\text{MEK}][\text{H}_2\text{SO}_4]} \quad \dots(9)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{[\text{MEK}]} \left\{ \frac{1}{k_3K_2K_1'[\text{H}_2\text{SO}_4]} + \frac{1}{k_3K_2} \right\} + \frac{1}{k_3} \quad \dots(10)$$

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

If K_1' is very small compared to k_3K_2

$$\frac{1}{k_3K_2K_1'[\text{H}_2\text{SO}_4]} + \frac{1}{k_3K_2} = \frac{1}{k_3K_2K_1'[\text{H}_2\text{SO}_4]} \quad \dots(11)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{[\text{MEK}]} \frac{1}{k_3K_2K_1'[\text{H}_2\text{SO}_4]} + \frac{1}{k_3} \quad \dots(12)$$

From the slope and intercept values, k_3 and K_2K_1' are calculated to be equal to 0.137 and 1.14×10^{-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_1' are found to be sufficiently small, to be neglected.

$$k_{\text{obs}} = k_3K_2K_1'[\text{MEK}][\text{H}_2\text{SO}_4] \quad \dots(13)$$

and at constant concentration of the acid,

$$\begin{aligned} k_{\text{obs}} &= k_3K_2K_1'[\text{MEK}] \\ &= k'[\text{MEK}] \end{aligned}$$

A plot of k_{obs} vs $[\text{MEK}]$ 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 $1/[\text{MEK}]$ (Eq. 10) when $[\text{H}_2\text{SO}_4]$ is kept constant at 2M agrees well with that calculated from the plot of k_{obs} vs $[\text{MEK}]$ (Eq. 13, $k_3 = 0.143$). By using the slope and intercept of these two plots, K_1' value is calculated and is found to be equal to 1.28×10^{-2} which is seen to be negligible compared to the calculated value of $k_3K_2 = 0.125$, supporting the line of argument proposed.

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