

V(v) Oxidation of Aromatic Ketones

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The Vanadium(v) oxidation of acetophenone and its substituted derivative has been found to be first order with respect to the oxidant, the substrate and the perchloric acid concentration. No effect of the ionic strength has been observed. The oxidation rate is accelerated with increasing acetic acid content in the reaction mixture. The value of 'r' has been computed to be 4.38 to 5.36 Å depending on the ionic nature of the oxidant. The electron donating group is found to retard the reaction with a rho value of +0.12 at 50°. Leffler's energy-entropy relation is found to be obeyed by this oxidation.

OXIDATION of ketones by various oxidants like Mn(III)¹, MnO₄², Ce(IV)³, alkaline Fe(CN)₆⁻³⁴, Cr(VI)⁵ has been carried out by various workers. It has been suggested that all one equivalent oxidants attack the enol tautomer and do not attack the ketone directly. The oxidation with Mn(III) is a ligand dependent process: Mn(III) sulphate oxidation⁶ does not, however, proceed through the enol intermediate. The oxidation of CO(III)⁷, V(v)⁸ of cyclohexanone appear to proceed directly with the ketone. The present work deals with V(v) oxidation of acetophenones in order to evaluate general features of oxidation process and to get information, through substituent effect, regarding the mechanistic picture.

Experimental

AnalaR BDH acetic acid has been used for the purpose. Sulphuric acid, perchloric acid used were of analaR BDH variety. Sodium vanadate was used for V(v). Acetophenones used were purified either by distillation or by crystallisation. The 2:4 dinitrophenyl hydrazones of these acetophenones were prepared and the purity of the ketone and the phenyl hydrazones were checked by t.l.c. on a silica gel t.l.c. plate. Solutions of ketones were prepared in glacial acetic acid. Sodium vanadate solutions were prepared in appropriate concentration of sulphuric or perchloric acid.

25.0 ml. each of reactants were preheated in a thermostat at desired temperature ($\pm 0.1^\circ$) and then mixed. Aliquots of the reaction mixture were withdrawn and the unconsumed V(v) were estimated against Mohr's Salt solution using N-phenylanthranilic acid as indicator. Since the [Ketone] is almost ca. 100 times larger than [V(v)], the first order rate equation,

$$t = \frac{2.303}{K^1} \log \frac{a}{a-x}$$

was employed to derive the first order rate constants (k^1). The bimolecular rate constants (k^2) were evaluated by dividing k^1 with the concentration of ketone. The value of energy of activation and entropy of activation have been calculated by employing Arrhenius and Eyring's equation respectively.

Results and Discussion

The vanadium(v) oxidation of acetophenones has been studied in perchloric acid medium. The concentration of ketone used is always in large excess. The oxidation has been found to be first order with respect to [V(v)] and also to the [ketone]. The ratio of the first order rate constant and the concentration of ketone is constant (Table 1). Plot of $1/k$ vs. $1/[\text{ketone}]$ has been prepared in order to see the possibility of kinetically discernible complexation. No intercept has been obtained (Fig. 1). The oxidation has also been studied at various [HClO₄] and the

TABLE 1. CHANGING CONCENTRATION OF KETONE.

$10^3 [\text{V(v)}] = 4.72M, [\text{HClO}_4] = 0.90M, \text{HOAC} : \text{H}_2\text{O} = 85.15$ Temp. = 40°						
[Acetophenone] in M	0.1	0.2	0.3	0.4	0.45	0.5
$k \times 10^5 \text{ sec}^{-1}$	0.732	1.798	2.60	3.05	3.22	4.21
$k \times 10^5 / \text{Ketone}$	7.32	8.99	8.6	7.6	7.15	8.40

TABLE 2. CHANGING CONCENTRATION OF OXIDANT

[Acetophenone] = 0.5M, [HClO ₄] = 0.90M, HOAC : H ₂ O = 85.15				
$10^3 [\text{V(v)}]$ in M	14.25	9.25	7.85	4.22
$k \times 10^5$ in sec ⁻¹	3.31	3.42	3.86	4.21

results are incorporated in Table 3. The values of $k/[HClO_4]$ are constant and so the reaction is also first order with respect to perchloric acid concentration.

TABLE 3. CHANGE IN PERCHLORIC ACID CONCENTRATION

$10^3 [V(v)] = 47.5M$, $[Acetophenone] = 0.5M$, $HOAC : H_2O = 75.25$
Temp = 40°

$[HClO_4]$ in M	0.45	0.75	0.90	1.16	1.20	1.50
$k \times 10^5 \text{ sec}^{-1}$	1.05	1.37	1.65	2.12	2.73	4.62

At a fixed $[HClO_4]$, perchlorate ion concentration was varied by addition of sodium perchlorate and the rate constant was found to be unaltered (Table 4).

TABLE 4. CHANGING $[ClO_4^-]$ WITH $HClO_4$ CONSTANT.

$[Acetophenone] = 0.5M$, $10^3 [V(v)] = 47.5$, $HClO_4 = 0.9M$
 $HOAC : H_2O = 75.25$ Temp. = 40°

$[ClO_4^-]$ in M	0.90	1.05	1.20	1.35
$K \times 10^5 \text{ in sec}^{-1}$	1.65	1.50	12.60	1.62

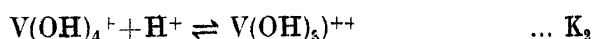
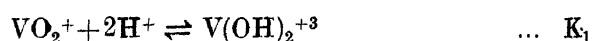
$= k_3 [ketone] [V(v)] [HClO_4]$. Vanadium(v) in aqueous perchloric acid media has been described as

TABLE 5. CHANGING $[HClO_4]$ KEEPING $[ClO_4^-]$ CONSTANT

$[Acetophenone] = 0.5M$, $10^3 [V(v)] \text{ in } M = 47.5$ $[ClO_4^-] = 1.5M$, $HOAC : H_2O = 75.25 (V/v)$, Temp = 40°

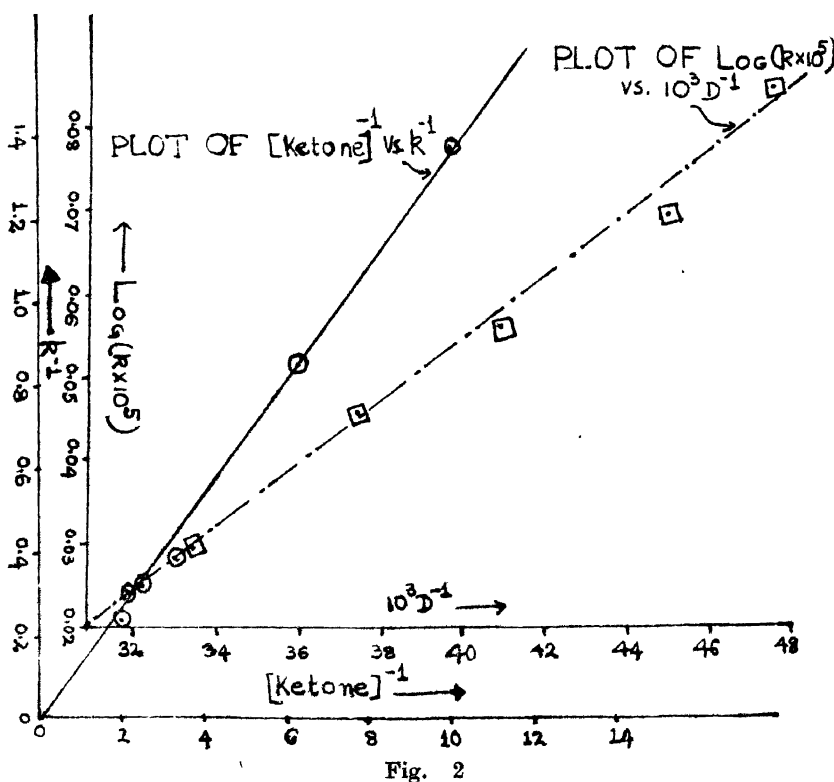
$[HClO_4]$ in M	0.90	1.05	1.20	1.35
$k \times 10^5 \text{ sec}^{-1}$	1.82	2.32	3.41	4.05

$VO_2^+(aq)$ and $V(OH)_4^+$. In perchloric acid solution the following equilibria (K_1 & K_2) exist



Since the rate increases with increasing acidity, the species $V(OH)_2^{+3}$ and $V(OH)_3^{++}$ may be important in the oxidation of acetophenone.

Further, the oxidation has been studied at different acetic-acid water mixtures. Increase in acetic acid concentration increases the rate of reaction (Table 6). A plot of $\log k$ vs. $1/D$ in accordance to the Arris



So V(v) oxidation of acetophenone is unaffected by ionic strength effect. Cristol and coworkers⁸ have also made a similar observation in perchloric acid catalysed reactions. However, at a fixed $[ClO_4^-]$ of $1.5M$ there was a slight enhancement in rate when $[HClO_4]$ was varied (Table 5).

The rate expression for vanadium(v) oxidation of acetophenone, therefore, may be written as, rate

TABLE 6. CHANGE IN PERCENTAGE OF ACETIC ACID.

$[Acetophenone] = 0.5M$, $10^3 [V(v)] = 47.5M$, $[HClO_4] = 1.25M$
Temp. = 40°

%HAC. (V/v)	65	70	75	80	82.5
$k \times 10^5 \text{ sec}^{-1}$	1.98	2.87	3.89	5.04	7.06
$10^3/D$	33.5	37.5	41.0	45.0	47.5

equation⁹, has been prepared and a straight line (Fig. 2) has been obtained, with a slope of 35.4 for $ze\mu/2.303 k T r^2$, where the terms have their usual significance. The value of 'r' has been computed to be 4.38 to 5.36 \AA considering bi- and tri-positive vanadium ion as the oxidising species. The corresponding value of the slope with phenacyl bromide is 45.0 , which appears to be reasonable in view of greater value of μ and lower value of r (due to complexation).

The oxidation has also been studied with substituted acetophenones. The order of reactivity of the substituents is $p\text{-NO}_2 > p\text{-Cl} > \text{-H} > p\text{-OMe}$. This order of reactivity has been observed in most of the Vanadium(v) and Cerium(IV) oxidation of aromatic ketones containing Ar-CO group. The energy and entropy of activation values have been calculated (Table 7). The values of ΔS^\ddagger are highly negative. Since the oxidation takes place by transfer of electrons from the substrate to the oxidant this high negative ΔS^\ddagger value may be due to curtailment of vibrational and rotational degrees of freedom and freezing of solvent molecules¹⁰. A straight line plot of $\log k$ vs. $\log [\text{HClO}_4]$ indicates participation of

The rate data show that the energy of activation values are in reverse order to the reactivity. The plot of ΔH^\ddagger vs. ΔS^\ddagger gives a straight line with ' β ' value of 630°K . The oxidation therefore, is both energy and entropy controlled obeying Leffler's compensation law, supporting the validity of a straight line Hammett plot, with a rho value of $+0.12$ at 50° . This value of rho does not agree at all with that of acid catalysed bromination of acetophenones¹¹, which is known to proceed through an enol intermediate. It appears therefore, that the V(v) oxidation of a ketone takes place directly on the ketone and not on the enol.

The product analysis shows the formation of benzoic acid or substituted benzoic acids. No experimental evidence has been adduced for the formation of a free radical, since polymerisation of acrylonitrile or reduction of mercuric chloride was not affected. Sengupta *et al.*¹² have also made a similar observation.

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TABLE 7. VALUES OF RATE DATA, ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION FOR THE V(V) OXIDATION OF SUBSTITUTED ACETOPHENONES.

[Ketone] = $0.3M$, $10^3[\text{V(v)}] = 43.5$, $[\text{HClO}_4] = 1.5M$.
HOAC : $\text{H}_2\text{O} = 75.25$ (V/v)

Nature of substituent	$k \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$				E in K.cal mole ⁻¹	- ΔS^\ddagger in e.u.
	35°	40°	45°	45°		
H	—	8.33	11.36	15.13	13.36	17.7
p-OMe	2.05	7.20	9.93	—	11.98	19.9
p-Cl	—	10.03	12.91	17.10	14.74	15.4
p-NO ₂	—	10.10	15.10	20.03	18.00	10.2

water molecules in the oxidation. Approximately a loss of 2.2 e.u. can be accounted for by arresting the translational degrees of freedom of a molecule of water. In the reaction a loss of 10 to 20 e.u. has been indicated. Therefore 4 to 8 molecules of water are frozen around the transition state. The validity of this assumption is due to the fact that the oxidation proceeds by an outersphere process and possibly ClO_4^- acts as an electron transport agent.