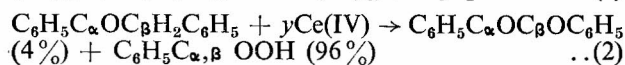
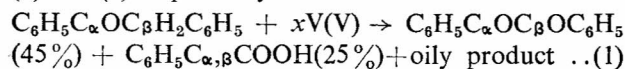


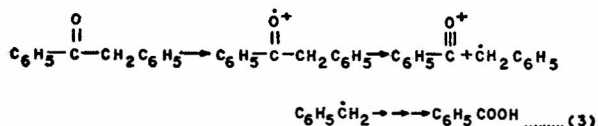
SCHEME - 1

V(V) and 6 mol of Ce(IV). The products isolated from both V(V) and Ce(IV) oxidations are benzoic acid and benzil, as characterised by TLC and spectral data. In V(V) oxidation benzil and benzoic acid are obtained in 45% and 25% yields, whereas in Ce(IV) oxidation the corresponding yields are 4% and 96%. The stoichiometric equations for both V(V) and Ce(IV) oxidations can be represented by Eqs. (1) and (2) respectively.



A comparison of the rate data of oxidation of acetophenone², phenacyl bromide³ ($k_{\text{Ce(IV)}} = 26.8 \times 10^{-4}$ $k_{\text{V(V)}} = 2.15 \times 10^{-4}$ litre mol⁻¹ sec⁻¹, and deoxybenzoin reveals that more active the methylene group greater is the rate of oxidation. This indicates that the radical is perhaps first formed at the alkyl group. Carbonyl radical may be formed first if the methylene group is not active, i.e. in case of acetophenone.

Therefore the mechanism given in Scheme 1, can be proposed for the oxidation of deoxybenzoin.



According to this scheme oxidation number of (C_α, C_β) system changes by four units during conversion to benzil and six units during conversion to benzoic acid. Since product ratio during the Ce(IV) oxidation is 4% benzil and 96% benzoic acid, the value of 'y' in the stoichiometric Eq. (2) is calculated to be $4 \times 0.04 + 6 \times 0.96 = 5.92$ which is in conformity with our experimental observation. The formation of a radical at the methylene group results in its oxidation first followed by a C—C cleavage (mechanism suggested), whereas electron abstraction from the >C=O group would cleave the C—C bond first followed by the oxidation of the methylene group (Eq. 3).

The former process seems more likely in view of the reduced electron density on C—C bond in benzil whereas in the other process the C—C bond has a

greater double bond character. Therefore the mechanism involving free radical formation at the alkyl group appears to take place with greater preference in deoxybenzoin.

With V(V) as the oxidant, the stoichiometric calculation needs about 0.2 mol of the oxidant for the formation of the oily material. Since the products obtained are the same as in Ce(IV) oxidation, it is presumed that the mechanism for V(V) oxidation of deoxybenzoin is similar to that of Ce(IV) oxidation.

Thanks are to the UGC, New Delhi for the award of a research grant to one of them (G.B.) Thanks are due to Dr A. Nayak, Louisiana State University, Baton Rouge, USA for analysis of the mixture of products by preparative TLC and for the spectra.

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

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The oxidation of 4-methylpentan-2-one by V(V) in dilute sulphuric acid is found to be first order in V(V) and 0.8 in the ketone. The reaction follows both acid dependent and independent paths and the order in acid is one. At concentration of V(V) > 1.5×10^{-2} M, while the order in acid remains unchanged, the order in V(V) is two and that in ketone is one. Taking into account the formation of free radicals during the reaction, a mechanism involving a one-electron transfer process is suggested.

IN continuation of our earlier studies on the oxidation of ketones by V(V) in acid media^{1,2}, the oxidation kinetics of 4-methylpentan-2-one by V(V) in dil. sulphuric acid are reported in this paper.

The ketone was purified by distillation and its solutions in acetic acid were used. Ammonium metavanadate (AR, Hungary) was dissolved in dilute sulphuric acid. The kinetics of the reaction was studied at 40° and 55°C, following the decrease in the concentration of V(V) as a function of time, as reported earlier^{1,2}.

The stoichiometry of the oxidation is found to be 2 g ion of V(V) to one mole of the ketone, 2-methylpropanal being the product.

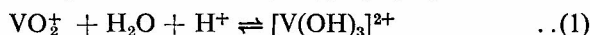
At constant [ketone] (0.4M) and [H₂SO₄] (2M), the oxidation is first order in V(V) at low concentrations (<1 × 10⁻²M), the first order rate constant *k*_{obs} decreasing slightly with increase in the initial [V(V)]. At higher concentrations (>10⁻²M) of V(V), the order in V(V) is two, and the value of the second order rate constant *k*_{2(obs)}, also seems to decrease with an increase in the initial [V(V)]. Similar observations have been reported for Cr(VI)³, Tl(III)⁴ and chloramine-T⁵ oxidations. This decrease may be due to the formation of unreactive V(V) species, such as polymers of V(V)⁶.

At low [V(V)] the order in the ketone is found to be 0.8 from the slope of the log-log plots of *k*_{obs} against [ketone]. The fractional order in ketone is due to complex formation between the ketone and V(V), as evidenced by a linear plot of 1/*k*_{obs} against 1/[ketone], with a positive intercept and slope. At high [V(V)], the order in the ketone is one.

Sulphuric acid is considered a strong monobasic acid⁷ and NaClO₄ is added to keep the ionic strength constant. A plot of *k*_{obs} or *k*_{2(obs)} against [H₂SO₄] is linear with an intercept indicating the presence of an acid-independent path and that the acid-catalysed path is first order in sulphuric acid, both at low and high [V(V)].

With increase in the proportion of acetic acid, the rate of the reaction increases under both the conditions. The decrease in the rate of oxidation with an increase in the polarity of the medium may be due to increase in the solvation of the reactants, compared to the less polar transition state.

Addition of NaHSO₄, NaCl and NaClO₄ to the reaction mixture increases the rate. Na₂SO₄ when added decreases the rate sharply. Though V(V) is amphoteric, it exists as a cation in solutions of acidity greater⁸ than 0.05M, i.e. as VO₂⁺ (ref. 8). At slightly higher acid concentrations VO₂⁺ is believed to be in equilibrium with V(OH)₃²⁺ (Eq. 1).



The active species may be represented as V(OH)₄⁺ (ref. 9), or V(OH)₄.OH₂⁺ (ref. 10) or V(OH)₃²⁺ (ref. 11). The marked colour of the sulphuric acid solutions of V(V) suggests that one HSO₄⁻ ion may be incorporated in the active species¹², which may be represented as V(OH)₃HSO₄⁺. The effect of addition of NaHSO₄ and Na₂SO₄ lends support to the above suggestion.

The addition of HgCl₂ increases the rate of the reaction slightly whereas the addition of Mn(II) almost stops the reaction. Methyl methacrylate and acrylonitrile when added undergo polymerization. Since V(V) or the ketone as such does not induce polymerization, these results suggest that the reaction involves the formation of free radicals and V(V) acts as a one-electron oxidant. V(IV) does not have any effect on the rate of the reaction.

The above results suggest the following rate expressions :

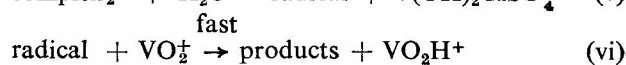
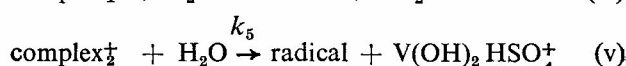
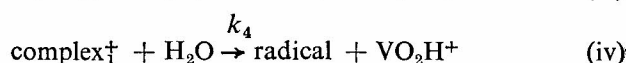
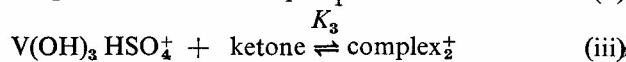
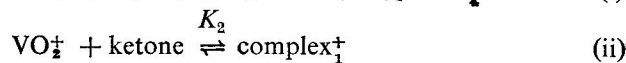
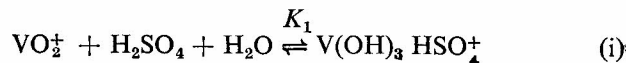
(i) At low concentrations of V(V) :

$$\text{Rate} = \frac{k [\text{V}(\text{V})] [\text{ketone}] [1 + b (\text{H}_2\text{SO}_4)]}{1 + a [\text{ketone}]} \quad \dots(2)$$

(ii) At high concentrations of V(V) :

$$\text{Rate} = k' [\text{V}(\text{V})]^2 [\text{ketone}] (1 + b' [\text{H}_2\text{SO}_4]) \quad \dots(3)$$

At low concentrations of V(V), the uncatalysed path is due to the unprotonated V(V) species, i.e. VO₂⁺ and the catalysed path is due to the protonated bisulphate complex, V(OH)₃HSO₄⁺ as shown in Scheme 1.



Scheme 1

$$\text{Rate} = \frac{-d[\text{V}(\text{V})]_{\text{T}}}{dt} = \frac{(k_4 K_2 + k_5 K_3 K_1 [\text{H}_2\text{SO}_4]) [\text{ketone}] [\text{V}(\text{V})]_{\text{T}}}{1 + K_2 [\text{ketone}] + K_1 [\text{H}_2\text{SO}_4] (1 + K_3 [\text{ketone}])} \quad \dots(4)$$

According to Wells and Kuritsyn¹³ the equilibrium constant for the formation of V(OH)₃²⁺, is very much less than one and so *K*₁ may also be assumed to be less than one. At constant [V(V)]_T, Eq. (4) becomes,

$$\frac{\text{Rate}}{[\text{V}(\text{V})]_{\text{T}}} = k_{\text{obs}} = \frac{(k_4 K_2 + k_5 K_3 K_1 [\text{H}_2\text{SO}_4]) [\text{ketone}]}{1 + K_2 [\text{ketone}]} \quad \dots(5)$$

$$1/k_{\text{obs}} = 1/X [\text{ketone}] + K_2/X \quad \dots(6)$$

where *X* = *k*₄*K*₂ + *k*₅*K*₃*K*₁ [H₂SO₄], at constant concentration of H₂SO₄. When [H₂SO₄] = 2M, from the slope of the plot of 1/*k*_{obs} vs 1/[ketone] [Eq. (6)], *X* can be calculated. *K*₂, being the ratio of the intercept to the slope, has been calculated to be 1.45 at 40°C and 2.91 at 55°C.

At constant concentration of ketone (=0.4 M) Eq. (5) becomes,

$$k_{\text{obs}} = (k_4 K_2 + k_5 K_3 K_1 [\text{H}_2\text{SO}_4]) 0.253 \quad \dots(7)$$

A plot of *k*_{obs} vs [H₂SO₄] (Eq. 7) is found to be linear with a slope of 7.03 × 10⁻⁴ and an intercept of 9.14 × 10⁻⁴ at 40°C. These values can be compared with those obtained from the plot according to Eq. (6), provided the former values which are for a different ionic strength are corrected. A comparison of the observed rate constants for the same concentration of ketone and H₂SO₄ shows that the values of rate constants for different [H₂SO₄] and at constant [ketone] are approximately 1.5 times higher than the values of rate constants obtained in the experiments varying the concentration of ketone and keeping

[H₂SO₄] constant. Hence the values of the slope and intercept obtained at different [H₂SO₄] and constant [ketone] are divided by 1.5 for comparing with those calculated from the plot according to Eq. (6). From the plot according to Eq. (7), using the corrected values, $k_4K_2=2.42 \times 10^{-3}$ and $k_5K_3K_1=1.86 \times 10^{-3}$. The values of X calculated from Eq. (6) are 5.8×10^{-3} at 40°C and 2.3×10^{-2} at 55°C. From Eq. (7) the values of X at 40°C and 55°C are 6.14×10^{-3} and 3.4×10^{-2} respectively. The reasonably good agreement between the values of X supports the proposed mechanism.

At high concentrations of V(V), apart from the active V(V) species proposed earlier, other dimeric V(V) species are also proposed. These are [V₂O₄.H₂SO₄]²⁺ for the acid-catalysed path and [V₂O₄]²⁺ for the acid-independent path. Since there is no kinetic evidence for complex formation, the proposed mechanism at high [V(V)] involves a concerted oxidation of the ketone by the V(V) species to give free radicals in slow steps. K_6 and K_7 are equilibrium constants for the formation of [V₂O₄]²⁺ and [V₂O₄.H₂SO₄]²⁺ respectively. k_8 is the slow step for the acid-independent path and k_9 is that for the acid-catalysed path, both giving rise to radicals and V(IV). The mechanism leads to the composite rate expression accounting for the acid-catalysed and acid-independent paths. This gives rise to the rate expression (8) Rate = (K_7k_9 [H₂SO₄] + K_6k_8) [ketone] [V(V)]_T² ..(8)

$$\frac{\text{Rate}}{[\text{V(V)}]_T^2} = k'_{\text{obs}} = (K_7k_9 [\text{H}_2\text{SO}_4] + K_6k_8) [\text{Ketone}] \quad \dots(9)$$

At constant [H₂SO₄] (=2M), Eq. (9) becomes,

$$k'_{\text{obs}} = Y [\text{ketone}]$$

where $Y=(2K_7k_9 + k_8K_6)$. A plot of k'_{obs} vs [ketone] (Eq. 9) under these conditions is linear with a positive slope (Y) of 0.14 at 40°C and 1.2 at 55°C. At constant [ketone] (=0.4 M), Eq. (9) becomes,

$$k'_{\text{obs}} = 0.4K_6k_9[\text{H}_2\text{SO}_4] + 0.4 K_6k_8 \quad \dots(10)$$

A plot of k'_{obs} vs [H₂SO₄] (Eq. 10) should be linear with a positive slope equal to 0.14 K_6k_9 and a positive intercept equal to 0.4 K_6k_8 . As explained earlier, these values also have to be corrected for the effect of ionic strength and compared with the values obtained from Eq. (9). From the corrected values of K_6k_8 and K_7k_9 , Y has been calculated to be 0.136 at 40°C and 1.21 at 55°C from Eq. (10). The values of Y from Eq. (9) at 40° and 55°C are 0.14 and 1.2 respectively. The good agreement between the values of Y supports the suggested mechanism.

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Nickel(II) Complexes Derived from New Tridentate Ligands

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Tridentate ligands derived from isonitrosoketone and 2-aminomethylpyridine (denoted as HRR'T) form high-spin nickel(II) complexes, Ni(HRR'T)₂X₂ (X = ClO₄, NO₃). The electronic spectra ($Dq \sim 1280 \text{ cm}^{-1}$), conductivity (1 : 2 electrolytes in nitromethane solution), magnetic moments (~ 3.1 B.M.) and infrared spectra point out to an octahedral NiN₆ coordination sphere.

CHAKRAVORTY and coworkers have extensively reported¹⁻⁷ on nickel and iron complexes of ligand systems having oxime-amine groups. We wish to report here some of the results on nickel(II) complexes of new tridentate ligands (1) obtained by the replacement of amino nitrogen of type (2) by pyridine nitrogen. The chemical and electrochemical studies of nickel(III) and nickel(IV) complexes of 1 are under progress. These studies have revealed that the ligands containing two oximato groupings^{2,3,5,8} can stabilise nickel(IV) in a better way than nickel(III). On the other hand ligands containing one oximato group⁷ form complexes with nickel(III) with greater ease than with nickel(IV).

Isonitrosoketones were synthesised by similar procedures reported elsewhere^{9,10}. HMe₂T was prepared by a procedure reported elsewhere¹¹. HETMeT (m.p. 421K) and HMeEtT (m.p. 424K) were synthesised by a similar procedure. Ni(HMe₂T)₂X₂ (X = ClO₄, NO₃) Ni(HETMeT)₂(ClO₄)₂ and Ni(HMeEtT)₂(ClO₄)₂ were synthesised by a method described⁵ for Ni(HRRT)₂X₂, i.e. by reacting the ligands and NiX₂ in 2:1 molar ratio. Ni(HPhMeT)₂(ClO₄)₂ and Ni(HMePhT)₂(ClO₄)₂ were prepared by *in situ* reaction of NiX₂ with appropriate iso-

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