MECHANISTIC STUDIES ON THE OXIDATION OF BUTANONE AND BENZYL BY VANADIUM (V) IN DILUTE MINERAL ACID – DMF MEDIA

By

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CHAPTER VI

SUMMARY AND CONCLUSIONS

In the oxidation reactions of butanone and benzil, in dilute sulphuric acid-DMF and dilute perchloric acid-DMF media, the reaction proceeds through the formation of free radicals. This indicates that V(V) acts as a one electron oxidising agent in these reactions. It has been found that the effect of V(IV) and other products is negligible in both the systems.

Oxidation of butanone by Vanadium(V):

With both sulphuric acid and perchloric acid, the reactions are acid catalysed and the order with respect to butanone, V(V) and acid are one. The product of the reaction is the same in both. The effect of increasing the proportion of DMF is to increase the rate of the reaction in the case of both the acids, though the increase is more pronounced in dilute perchloric acid medium.

Butanone in dilute sulphuric acid medium:

The reaction proceeds by both acid catalysed and uncatalysed paths. The Lineweaver-Burk plot gave kinetic evidence for the formation of a complex involving the ketone molecule and the V(V) species. An active species of V(V), $V(OH)_3HSO_4^+$, formed in sulphuric acid medium is considered to be interacting with the ketone molecule to form the complex. A composite rate expression of the type

$$rate = (a + b[H_2SO_4])[Butanone][V(V)]_T$$

is obtained which is explained by a mechanism involving the formation of two complexes, one between the unprotonated VO_2^+ and the ketone molecule and the other between $V(OH)_3HSO_4^+$ and the ketone molecule. The complexes decompose to give free radicals in slow steps. These free radicals then get oxidised in fast steps to give the products.

Butanone in dilute perchloric acid medium:

The reaction is acid catalysed and the Lineweaver-Burk plot gave evidence for complex formation between the V(V) species and the acid. The complex formed is probably the protonated V(V) species, $V(OH)_3^{2+}$. The Lineweaver-Burk plot did not give any evidence for the ketone participating in complex formation.

The rate expression is

$$\text{rate} = \frac{k[\text{Butanone}][HClO_4][V(V)]_T}{1 + a[HClO_4]}$$

A mechanism involving the interaction of the protonated V(V) species with a ketone molecule in a slow step to give the free radicals is proposed. These free radicals give the products in fast steps.

Comparison of rates in dilute sulphuric and perchloric acids:

The kinetics in perchloric acid differs from that observed in sulphuric acid in three aspects.
1. There is only an acid catalysed path.
2. There is no evidence for complex formation between the ketone molecule and the V(V) species.

3. The effect of increasing the proportion of DMF in the solvent mixture is more pronounced than that in sulphuric acid.

Under identical conditions, catalysis by sulphuric acid is stronger than that by perchloric acid, both in aqueous medium and aqueous DMF medium. This is probably because the bisulphate complex in sulphuric acid medium is more effective as an oxidising agent than the protonated species of Vanadium(V) formed in perchloric acid.

The observation that the effect of increasing the solvent composition with respect to DMF is more pronounced in perchloric acid is explained on the basis of the difference in acid strengths of these two acids in dipolar aprotic solvents.

Oxidation of Benzil in dilute H_2SO_4-DMF and dilute $HClO_4$-DMF media:

With both the acids, the reaction follows an acid independent path. The absence of acid catalysis shows that the ketone is very susceptible to oxidation. In all cases studied, the order with respect to the oxidant and the substrate is one. There is kinetic evidence for complex formation between the V(V) species and benzil.

The effect of increasing the proportion of DMF is to decrease the rate of the reaction with both the acids, but the decrease in rate constant is almost negligible in dilute perchloric acid. In this reaction too, the

envisaged transition state is less polar compared with the reactants. This is supported by the increase in entropy of activation as the solvent composition is varied from 40 to 75% DMF(v/v). Based on this, it is reasonable to expect an increase in the rate constant.

The observed decrease in rate constant could be rationalised as follows. Owing to the limited solubility of benzil in aqueous DMF, the reaction has been studied only in solvent mixtures containing relatively greater proportion of DMF. Increasing the proportion of DMF will not only affect the solvation of the reactants or transition state, but also modifies the dissociation of acids. Even in the case of butanone-V(V) reaction, it was observed that beyond 50% DMF, the rate of the reaction tends to decrease, the Amis plot showing deviation from linearity.

Considering the above facts it may be concluded that the decrease in rate constant observed in Benzil-V(V) reaction, which has been studied in solvent mixtures contain-ing larger proportion of DMF, is not anything peculiar to this system.

The objective of this study, as stated in the introduc-tion, has been i) to understand the nature of the V(V) species and ii) to study the effect of an aprotic solvent on the rate of the reaction with emphasis on solvent polarity.

With regard to the first objective, we have found that the results of our studies can be explained on the basis of

the active V(V) species that has been proposed by previous authors. The active V(V) species suggested in dilute sulphuric acid medium is the bisulphate complex $V(OH)_3HSO_4^+$. In dilute perchloric acid, the simple protonated species $V(OH)_3^{2+}$ is suggested. In cases where the reaction proceeds by an acid independent path, VO_2^+, the unprotonated species is proposed.

With regard to the second objective, as far as the oxidation studies of ketones by V(V) are concerned, this is the first attempt to study the effect of an aprotic solvent on the rate of the reaction.

In order to explain the effect of solvent polarity on the rate of the reaction, the dielectric constants of $DMF-H_2O$ mixtures were measured at the experimental temperatures, that is, at 35° and $50^\circ C$. Dielectric constant values for $DMF-H_2O$ mixtures at $25^\circ C$ are available in literature.[136]

The explanations offered to account for the observed kinetics in the two systems studied, are in conformity with either the predictions or observations of earlier workers.

The arguments advanced are based on the difference in acid strengths in dipolar aprotic solvents, in terms of solvation and dielectric constant effect.

The present study confirms the conclusions of previous authors, that the lack of H-bonding donor property of aprotic solvents has a significant effect on the reaction rate.

Our studies lead us to the conclusion that in mixed solvent media involving aprotic solvent and water the

oxidation of ketone by V(V) proceeds through both an acid catalysed and uncatalysed path. The transition state appears to be a less polar entity than the reactants.

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