Mechanism of oxidation of \( p \)-nitroaniline by ammonium metavanadate in sulphuric acid medium: A kinetic approach

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The kinetics of ammonium metavanadate oxidation of \( p \)-nitroaniline in sulphuric acid medium has been followed spectrophotometrically. The reaction follows second order kinetics being unity in each of the reactants. The stoichiometry of the reaction has been found to be 1:1. The effect of various parameters viz. [oxidant], [substrate], [H\(^+\)], ionic strength, dielectric constant and added micelles have been investigated and the thermodynamic parameters have been evaluated. \( p \)-Benzquinone has been identified as the main oxidation product by chromatographic and UV spectrophotometric techniques. A suitable mechanism consistent with the experimental results has also been proposed.

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The oxidation of aromatic amines by different oxidants has been investigated by many workers due to the complex behaviour of their mode of oxidation\(^1\). A review of literature reveals that different compounds like Ce(IV) sulphate\(^2\), N-bromothalamide\(^3\), chromic acid\(^4\), N-bromosuccinimide\(^5\), KMnO\(_4\)\(^6\), periodate\(^7\), lead tetraacetate\(^8\), potassium dichromate\(^9\) and potassium bromate\(^10\) have been employed as oxidizing agents to carry out the oxidation of various aromatic amines. Ammonium metavanadate, a versatile oxidizing agent, has also been used to oxidize many organic compounds like hydroxylamine hydrochloride, acetonilides, L-cysteine, glycerol and cyclohexanol\(^11\)-\(^15\). The present study has been carried out with a view to postulate a general mechanism for the oxidation of \( p \)-nitroaniline with ammonium metavanadate in sulphuric acid medium.

**Experimental**

All chemicals and reagents used were of Loba G.R or Merck A R grade. \( p \)-Nitroaniline was used after redistillation/recrystallisation. Doubly distilled water was used throughout. \( p \)-Nitroaniline solution was prepared by dissolving appropriate quantities in absolute alcohol. Ammonium metavanadate solution was prepared by dissolving the calculated amount in \( 2N \) H\(_2\)SO\(_4\) and was standardized with ferrous ammonium sulphate solution using diphenylamine as indicator\(^16\). All the solvents used for spectroscopic and TLC studies were of spectroscopic and CP grade respectively and silica gel G (BDH, AR) was used after activation.

The reaction of \( p \)-nitroaniline and ammonium metavanadate in the sulphuric acid medium produced a yellow colour, which showed maximum absorbance at 386 nm. Hence, the progress of the reaction was followed by measuring the absorbance at 386 nm using a Shimadzu double beam spectrophotometer (UV-160). Studies were kept confined to the period in which the \( \lambda_{\text{max}} \) of the reaction mixture did not change. Initial rates in terms of (\( d\text{A} / dt \)) were used for studying the kinetic behaviour of the reaction\(^17\). Required volumes of the reactants (ammonium metavanadate and \( p \)-nitroaniline) solutions were thermally equilibrated and mixed. The absorbance was measured at a fixed interval of 1 to 2 min, depending upon the rate of reaction for a particular set. In order to prevent precipitation of the products and to keep the reaction mixture homogenous, the reaction was carried out in very dilute solutions.

In addition, the 2 \( \lambda \) method\(^18\) was also used to monitor the reaction kinetics and to eliminate the effect of product on the absorbance. Accordingly, absorbance at two wavelengths i.e. \( \lambda_1=350 \) nm and \( \lambda_2=246.8 \) nm was measured at a fixed interval of time and data thus obtained were used to calculate the rate constants by the integration method. Ionic strength was kept constant i.e. 6.1 mol dm\(^{-3}\) through-out the investigation and all studies were carried out at a constant temperature 300±1 K unless stated otherwise.

The procedure followed for determination of stoichiometry of the reaction consisted of estimating the amount of either unused ammonium metavanadate titrimatically\(^16\) or of amine by the bromination method\(^19\) after refluxing the reaction mixture for 30 min or after keeping the solutions of the reactants in a thermostatic bath for 24 h at room temperature and then by heating the solution for the completion of the reaction. It was found that one equivalent of the substrate consumed one equivalent of ammonium metavanadate.
The reaction mixture containing excess of standard solution of ammonium metavanadate over p-nitroaniline in ethanol sulphuric acid medium was kept at room temperature overnight. Initially, the reaction mixture was yellow in colour and after standing for 24 h it changed to a brown red color. For product analysis, the reaction mixture was filtered after 24 h and the filtrate was extracted with petroleum ether. A yellowish brown compound with a melting point of 116°C was obtained on evaporation of the solvent. The benzene extract on TLC over silica gel using benzene as developer produced a single spot with a Rf value of 0.85 and the absorption spectrum was found to be super imposable on p-benzoquinone i.e. near 285 nm.

Addition of few drops of acrylonitrile under nitrogen atmosphere to the reaction mixture gave white polymeric product, indicating the participation of free radicals in this reaction. The formation of free radical was further confirmed by studying the effect of addition of allylacetate, a free radical scavenger, in the reaction mixture.

Results and discussion

Different oxidation states of vanadium exhibit different colors e.g. \( V^{5+} \) has a yellow colour whereas, \( V^{4+} \) and \( V^{3+} \) exhibit blue and green colours respectively.\(^\text{20}\) When solutions of p-nitroaniline and ammonium metavanadate (yellow) were mixed, a green colour developed within thirty minutes indicating that ammonium metavanadate got reduced from \( V^{5+} \) to \( V^{3+} \) with the simultaneous oxidation of p-nitroaniline.

The initial rates of the reaction were evaluated either by varying p-nitroaniline or ammonium metavanadate while keeping the other parameters constant. The results thus obtained were recorded in Table 1, which showed that the reaction followed second order kinetics being unity in each of the reactants. The plot of \( 1/(a-x) \) against time was linear supporting the second order kinetics. The oxidant has a positive effect on rate of reaction. Under the conditions, \([p\text{-nitroaniline}] = 10^3 \text{ mol dm}^{-3}, [H^+] = 2N \) and \( \mu = 6.1 \text{ mol dm}^{-3} \) at 301 K, \( k_1 \times 10^4 \) increased from 4.43 to 8.54 s\(^{-1}\) when \( 10^4 \text{ [AMV]} \) was increased from 0.833 to 2.00 \text{ mol dm}^{-3}. \) The velocity of reaction also increased linearly with the increase in the [substrate] which is evidenced by the Michaelis Menten plot. The acceleration of reaction rate with increase in \([H^+]\) indicates that the oxidation of p-nitroaniline with ammonium metavanadate is an acid catalysed reaction.

The rate of reaction was found to decrease with increase in the dielectric constant, as measured by conducting various kinetic runs at varying % composition of ethanol-sulphuric acid solvent system ranging from 10-50%. The linear plot of \( \log k \) versus \( 1/T \) (Amis plot) with a slope of \( +14.039 \) suggests that the rate determining step is a reaction between an ion and a dipole. In accordance with Amis’s view\(^\text{21}\) a positive slope suggests that the reacting ion is a cation which may be \( \text{VO}_2^+ \) or \( [\text{V(OH)}_3]^+ \) in the present study. The ionic strength was varied from 6.1 \text{ mol dm}^{-3} \) to 6.6 \text{ mol dm}^{-3} \) using sodium sulphate and \( k_2 \) increased from 9.65 to 13.80 \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}. \) The Bjerrum plot of \( \log k \) versus \( \mu \) suggests that the positive salt effect is of primary linear type, which also supports the fact, that rate determining step should be a reaction between an ion and a dipole.

The reaction was investigated at different temperatures in the range 303-323 K. Various activation parameters were evaluated from the linear Arrhenius plot of \( \log k_2 \) versus \( 1/T \). Calculated values are: \( \Delta E_a = 7.174 \text{ kJ mol}^{-1} \), \( \Lambda = 3.44 \times 10^8 \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1} \), \( \Delta H^\circ = 5.69 \text{ kJ mol}^{-1} \), \( \Delta S^\circ = -97.84 \text{ JK}^{-1} \text{ mol}^{-1} \), \( \Delta G^\circ = 35.50 \text{ KJmol}^{-1} \) at 303 K. A perusal of activation parameters shows that the reaction is characterized by a large negative value of entropy of activation and a low value of energy of activation. The latter is characteristic of a bimolecular reaction in solution whereas, the former is mainly observed in polar sol-
vents and also suggests the formation of a charged and a rigid transition state which is expected to be strongly solvated in the polar solvent employed.

The effect of micelles or surfactant was also found to be very striking. Added anionic surfactant (i.e. lauryl sulphate) accelerated the reaction. When $10^6$ [lauryl sulphate] was increased from 1.0 to 10.0, $k_2$ values increased from 9.73 to $15.41 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$. Whereas, cationic surfactant (i.e. cetyl trimethylammonium bromide) retarded the reaction (for the same range of concentration variation $k_2$ values decreased from 8.53 to 2.83 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$). These trends of

$$\text{VO}_2^+ + \text{H}_3\text{O}^+ \rightarrow \{\text{V(OH)}_3\}^{2+}$$

Scheme 1
micellar effects on the reaction rate are also in accordance with the proposed mechanism. The enhancement of reaction rate by amionic surfactant may due to the coulombic force of attraction between the anionic surfactant and positively charged complex and vice versa.

**Mechanism**

Under the present conditions of study, the reaction follows the rate law

\[
dx/dt = [p-NO_2C_6H_4NH_2] [V(OH)_3]^{2+}
\]

A tentative mechanism may be suggested for the oxidation of \( p \)-nitroaniline by ammonium metavanadate in acidic medium. As reported by Littler and Waters\(^2\) the oxidation by ammonium metavanadate in acidic medium is associated with its yellow cations \( VO_2^+ (aq) \) and \( [V(OH)_3]^{2+} \) which are formed in mineral acid solution.

The observation of colour change of the reaction mixture from yellow to green in very dilute solution indicates that \( V^{5+} \) was reduced to \( V^{3+} \) i.e. it is a two electron transfer reaction. Thus,

\[
V^{5+} + \text{organic compound} \rightarrow V^{3+} + \text{oxidized product} + 2H^+ \text{ (Heterolytic)}
\]

The effect of \([H^+]\) indicates that the reaction rate is proportional to \([H^+]\) and not to the hydrogen ion activity and also is first order with respect to both \([p\text{-nitroaniline}]\) and \([V^{3+}]\). Consequently, the slow reaction involves a complex of \( p \)-nitroaniline and \([V(OH)_3]^{2+}\) which is formed by the reaction of \( V^{3+} \) with a proton and a water molecule as shown in Scheme 1. Formation of charged complex is further supported by non-zero intercept in Michaelis Menten plot, and the intensification of the colour of the reaction mixture is also suggestive of complex formation.

The high negative value of entropy of activation and effect of dielectric constant on rate indicates that the activated complex should be strongly solvated thus supporting the formation of charged intermediate (I) as concluded above. This charged complex oxidized to form \( p \)-benzoquinoneimine was also reported earlier\(^23\)\(^-\)\(^25\) via the formation of transient free radical intermediate (II) as is evidenced by induced polymerization of acrylonitril and is further followed by hydrolysis of nitro group. The \( p \)-benzoquinoneimine so formed is also a transient one and extremely sensitive in acidic solution. Thus, it undergoes hydrolysis in a fast step to produce \( p \)-benzoquinone. In this step imine intermediate (III) undoes a nucleophilic attack on \( \alpha \) carbon by water molecule to form an \( \alpha \) hydroxyl amine (IV) which on further solvolysis forms \( p \)-benzoquinone (V) and ammonia as reported earlier\(^26\).

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**References**