Asian J. Exp. Sci., Vol. 21, No. 1, 2007, 87-92

Kinetics of the Oxidation of *p*-Nitrotoluene and Aceto *p*-Toluidide by Quinquevalent Vanadium Ion

Suman Malik[1], Bharti Jain[2] and Suparna Ghosh*[1]

1. Department of Chemistry, Sadhu Vaswani College,
   Bairagarh, Bhopal, M.P., India
2. Department of Chemistry, Sarojini Naidu Govt. Girls (Auto.), College,
   Shivaji Nagar, Bhopal, M.P., India

Abstract : Kinetic investigation of oxidation the of p-nitrotoluene and aceto p-toluidide by Vanadium (V) in 40% acetic acid- water (V/V) solution in the presence of 1.5 M H_2SO_4 have been studied in the temperature range of 40°C .Corresponding aldehydes are found to be the oxidation product. The reaction is first order with respect to both vanadium (V) and the substrate. It is observed that rate constant increases with increase in the molarity of sulphuric acid. The linear increase of rate Constant with increase in $[H^+]$ concentration at constant ionic strengths confirms the positive salt effect on reaction rate. The rate increases with acetic acid concentration in the binary mixtures. The magnitude of Arhenius parameter indicates the bimolecular nature of the oxidation reaction. The stoichiometric studies confirm that one mole of substrate requires four mole of the oxidant for complete oxidation.

Key words : p-nitrotoluene, Aceto p-toluidide, Vanadium, Salt effect.

Introduction :

Oxidation of p-nitrotoluene and aceto p-toluidide by vanadium (V) in 1.5 M H_2SO_4 medium has a 1:4 stoichiometry and exhibits first order for both oxidant and substrate. The product of oxidation are reported to be corresponding aldehydes which are analyzed under kinetic conditions using the method of Cullis and Ladburry (1987). The effect of H^+ molarity, ionic strength, dielectric constant and temperature on reaction rate have been studied. Activation parameters have been calculated with respect to the slowest step of the proposed mechanism of reaction.

A survey of literature reveals that vanadium is used for the oxidation of various organic compounds.

The kinetics of the oxidation of phenylphosphinic acid by quinquevalent vanadium ion have been investigated in aqueous perchlorate media under pseudo-first order conditions (phenylphosphinic acid in excess). The reaction has a first order dependence in [V(V)] and [phenylphosphinic acid] and the observed pseudo-first order rate constant k_{obs} is given by $k_{obs} = a + b[H^+]$. The acid-independent path is considered to be due to the reaction between VO_2^+ (aq.) and $C_6H_5P{:}(OH)_2$, the active form of phenylphosphinic acid, while the reaction between $V(OH)_3^{2+}$ (aq.) and $C_6H_5P(O)(OH)H$, the inactive form of phenylphosphinic acid, is considered to explain the acid-dependent path. Phenylphosphinic acid in aqueous acidic

---

* **Corresponding author :** Suparna Ghosh, Department of Chemistry, Sadhu Vaswani College, Bairagarh, Bhopal, Mobile : 09303115005.

solution is known to exist as an equilibrium mixture of the active and inactive forms. The composite activation and thermodynamic parameters associated with the constants *a* and *b* are reported (Mehrotra, 1985). The kinetics of the oxidation of ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid by vanadium(V) was the reaction of first order with respect to V(V) and the complexone. The reaction rate constants were determined and the activation energies of the oxidation processes were calculated (Tishchenko et al., 1973). The oxidation of ethane with molecular oxygen on a well-characterized V[2]O[5]/SiO[2] catalyst produced ethylene and acetaldehyde as the only selective oxidation products. The effects of partial pressures of ethane, oxygen, and water were investigated at 841 K, and it was found that only water had a strong influence on the overall selectivity. The results were described by a simple sequence of steps. Ethylene was the major product, and its oxidation was studied further to determine whether its secondary reaction affected the kinetic results. A first-order analysis of the reaction network indicated that the oxidation of ethylene and acetaldehyde contributed significantly to the observed kinetics (Oyama et al., 1990). Various mechanisms of the selective action of catalysts in the liquid-phase oxidation of organic substances are discussed. It is shown that the high selectivity of the autoxidation of organic substances catalysed by compounds of transition and non-transition elements is due to the interaction of the substrate being oxidised with the peroxide derivative of the element formed via the reaction between oxygen or the hydroperoxide product and the catalyst (Spirina *et al.*, 1987).

No kinetic data is available on the oxidation kinetics of substituted toluenes and toluidide by vanadium (V).

Materials and Methods :

All the chemicals were of AR Grade and double distilled water free from carbon dioxide were used to prepare reaction mixtures and all the solutions. Stock solution of the oxidant was prepared by dissolving accurately weighed amount of ammonium metavandate in 12N sulphuric acid .The stock solution so prepared was standardized against a standard solution of ferrous ammonium sulphate using N-phenylanthranillic acid as indicator. The substrate solution was prepared by dissolving known amounts of p-nitrotoluene and aceto p-toluidide in glacial acetic acid. Stock solution of about 8M H_2SO_4 was prepared and its dilute solution was standardized against 0.1N borax solution using methyl red as indicator for determining its correct strength.

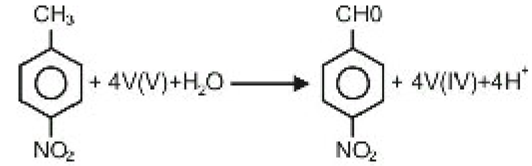
Kinetic Measurement : The reactions were studied under pseudo first order condition taking a known large excess of p-nitrotoluene and aceto p-toluidide over ammonium metavandate. The progress of reaction was measured by estimating ammonium meta vandate volumetrically. The variation of substrate was carried out at 40^o C. The pseudo first order rate constant were calculated using integrated form of first order rate equation and compared with the graphical values obtained from the linear plots of log (a/a-x) against time. To determine the stoichiometry reaction mixture containing excess of ammonium meta vandate (about

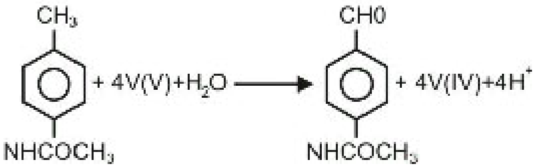
20 times) over p-nitrotoluene and aceto p-toluidide were allowed to equilibrate at 40°C for more than 48 hours to ensure the complete oxidation of the substrate; the amount of unconsumed oxidant was estimated volumetrically.

Results and Discussion :

The reactions were found to be first order with respect to oxidant as well as the substrate. The values of first order rate constants were found to be independent of initial concentration of ammonium meta vandate. This clearly confirms the first order dependence on the oxidant vanadium(v). Rate constant K_1 increases with increase in the initial concentration of substrate (Table 1) and constant K_2 obtained by K_1/[substrate] confirms that reaction follows first order kinetics in substrate. The plot of log K_1 versus log [substrate] gives a straight line with a positive slope of unity, which also confirms the first order dependence in substrate. The reaction rate increases with increase in acid molarity at various constant ionic strength (Table 2). The plot of rate constant versus $[H^+]^2$ was found to be linear. The slopes of these lines increase with the increasing ionic strength confirming the positive salt effect on acid catalysed reaction. Influence of solvent on the oxidation rates of substrate was studied by varying the percentage of acetic acid in reaction mixture and it is observed that the rates increase with the increasing percentage of acetic acid in the $AcOH-H_2O$ mixture up to 60%; thereafter there is a sharp rise in rate with the increasing percentage of acetic acid. To study the effect of temperature, kinetic runs were carried out in the temperature range of 40°C at constant acetic acid concentration (40%v/v). The plot of log K_1 Vs. 1/T gave straight line, which confirms the validity of Arhenius equation (Figures 1, 2). The magnitude of Arhenius parameter indicates the bimolecular nature of the oxidation reaction in each case (Table 3).

The stoichiometric study indicates that one mole of substrate was found to consume four mole of oxidant for complete oxidation. The experimental result leads to the following overall reaction-





Vanadium is distributed extensively in nature. It is a trace element and is present in almost all-living organisms including man. Essentiality of this element in cellular functions is yet to be established. Biological importance of vanadium was originally recognised by its ability to inhibit membrane sodium pump. Its capacity to affect the activities of various other intracellular enzyme systems and to modify physiological processes is now documented. Vanadium is used extensively in various heavy industries. The incidence of exposure to toxic levels of vanadium to industrial workers has been an increasing concern for toxicologists. Disposition of vanadium in specific tissues may be involved in the pathogenesis of certain neurological disorders and cardiovascular diseases. The chemical contribution from

Table 1 : Rate constant for the oxidation of p-nitrotoluene and aceto p-toluidide by ammonium meta vandate at 313K

[Oxidant] $\times 10^{-3}$M	[Substrate] $\times 10^{2}$M	[H_2SO_4] M	[ACOH] percentage	p-nitrotoluene $K_1 \times 10^3$ min^{-1}	Aceto p-toluidide $K_1 \times 10^2$ min^{-1}
0.8	2.0	1.5	40.00	5.92	5.38
1.2	2.0	1.5	40.00	5.85	5.26
1.6	2.0	1.5	40.00	5.42	5.09
2.0	2.0	1.5	40.00	5.39	4.90
2.5	2.0	1.5	40.00	5.74	5.18
3.0	2.0	1.5	40.00	5.54	5.00
0.8	2.0	1.5	40.00	6.06	5.42
0.8	2.5	1.5	40.00	7.53	6.73
0.8	3.0	1.5	40.00	8.91	8.31
0.8	3.4	1.5	40.00	10.14	9.10
0.8	3.8	1.5	40.00	11.24	10.32
0.8	4.5	1.5	40.00	13.62	12.34

Table 2 : Effect of H_2SO_4 variation at constant ionic strength

[H_2SO_4] Molarity	[Na_2SO_4] Molarity	Ionic Strength	p-nitrotoluene $K_1 x 10^3$ min^{-1}	aceto p-toluidide μ $K_1 x 10^2$ min^{-1}
0.25	0.75	1.0	1.143	1.005
0.50	0.50	1.0	1.600	1.390
0.75	0.25	1.0	2.225	2.035
1.00	0.50	1.5	3.425	3.705
1.25	0.25	1.5	4.112	4.584
1.50	0.00	1.5	4.800	5.652
1.25	0.75	2.0	5.046	5.435
1.75	0.25	2.0	7.052	7.728
2.00	0.00	2.0	8.290	8.640

Table 3 : Rate constant and Arrhenius Parameter for vanadium (V) Oxidation of p-nitrotoluene and aceto p-toluidide in Acetic Acid – Water Mixture (1:1) (V/V)

Substrate	303K	313K	323K	ÄE KCal/m	ÄH≠ K.Cal	ÄS≠ e. μ	A min^{-}	ÄF≠ K.Cal
p-nitrotoluene K1 $\times 10^3$ min^{-1}	2.747	5.950	12.133	14.64	14.04	-23.92	1.0×10^8	21.29
Aceto-*p*-toluidide K1 $\times 10^2$ min^{-1}	2.916	5.540	10.519	11.44	10.84	-29.80	$5.2x10^6$	19.87

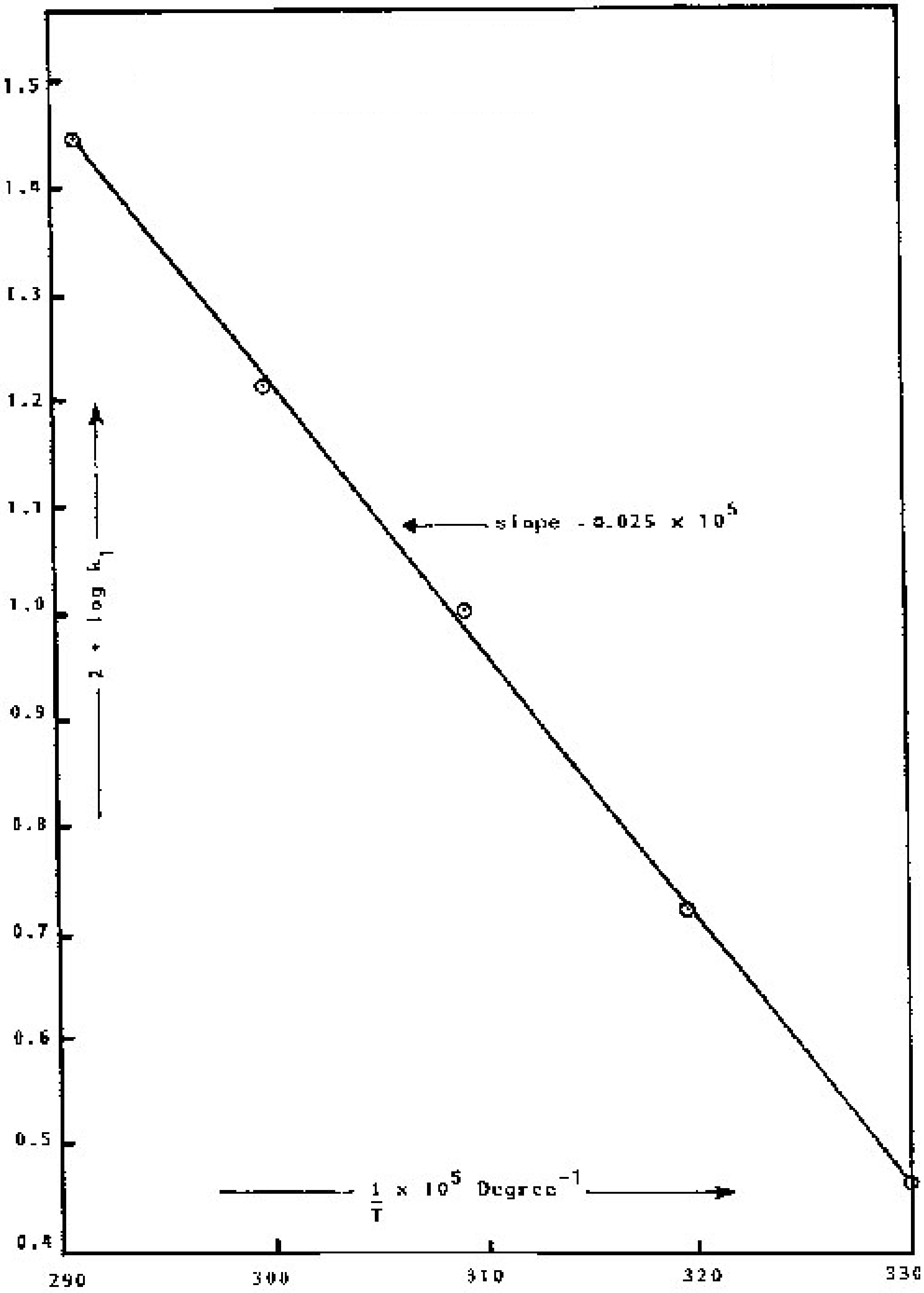


Fig. 1 : Temperature effect on the rate of oxidation of aceto-*p*-toluidide

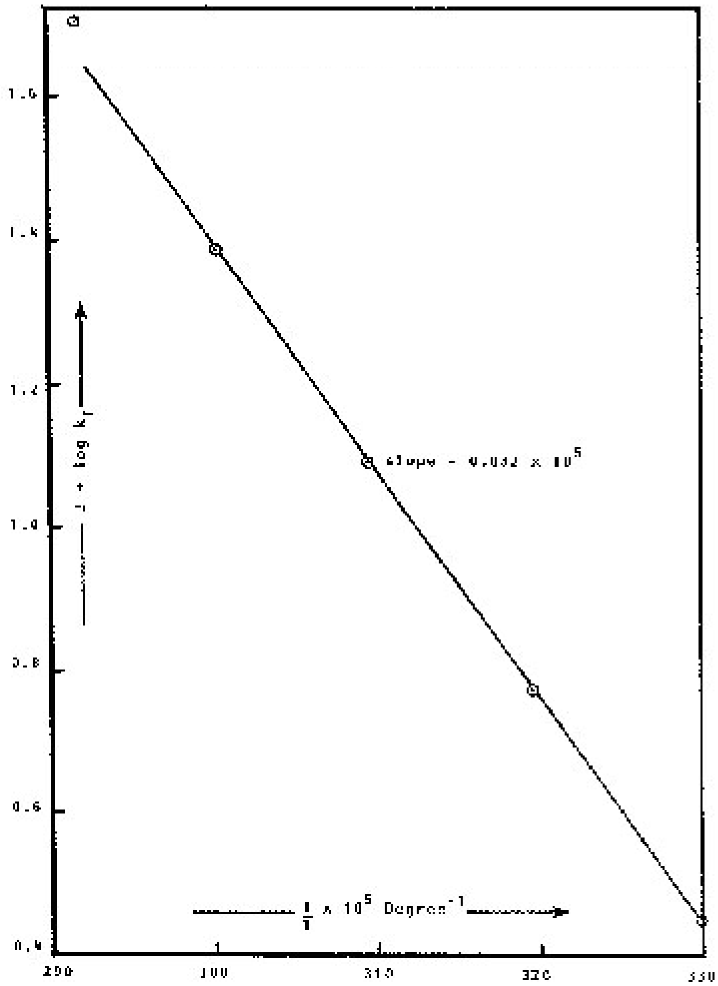


Fig. 2 : Temperature effect on the rate of oxidation of *p*-Nitrotoluene

the outcome of present study is also indicated in various biological/ toxicological actions of vanadium (Venkataraman & Sudha, 2005).

References :

Cullis C.F. and Ladburry J.W. (1987) : *J. Chem. Soc*. 555.

Mehrotra R. N. (1985) : Kinetics and mechanisms of oxidations by metal ions. Part IV. Oxidation of phenylphosphinic acid by aquavanadium(V) ions. *Can. J. Chem./Rev. can. chim*. **63(3),** 663-666.

Oyama S. T., Middlebrook A. M. and Somorjai G. A. (1990) : Kinetics of ethane oxidation on vanadium oxide Journal of physical chemistry . *J. phys. chem*., **94(2),** 5029-5033.

Spirina I. V., Maslennikov V. P. and Aleksandrov Yu A (1987) : The Role of Peroxide Derivatives of the Elements in the Selective Catalytic Oxidation of Organic Substances, *Russ Chem Rev*, **56(7),** 670-681.

Tishchenko R. P. , Pechurova N. I., Martynenko L. I. and Spitsyn, Vikt I. (1973) : Study of the kinetics of the oxidation of complexones by vanadium (V). *J. Russian Chemical Bulletin*. **22,** 1173-1175