



A kinetic approach to the oxidation of some primary perfumery alcohols using ammonium metavanadate in acidic medium

Harichandra A. Parbat* and D. V. Prabhu

Department of Chemistry, Wilson College (aff. University of Mumbai), Mumbai-400 007, India

E-mail: dvprabhu48@gmail.com

Manuscript received online 30 November 2019, revised and accepted 06 January 2020

Literature survey shows several reports of the oxidation of a variety of alcohols to the corresponding carbonyl compounds. But there are relatively few reports of the kinetic and thermodynamic aspects of oxidation of alcohols.

This paper reports the kinetics of oxidation of primary perfumery alcohols, Nerol, Citronellol and Geraniol by ammonium metavanadate in acidic medium under first order kinetic conditions with respect to the inorganic oxidant. The oxidation was monitored by titrimetric estimation of the unreacted oxidant at regular intervals in the temperature range 303–318 K. K_2SO_4 was used to determine the effect of ionic strength on the oxidation rates of alcohols. The thermodynamic activation parameters have been interpreted in terms of the molecular dynamics and reaction mechanism suggested for the oxidation process.

Literature study indicates extensive use of costly catalysts like Os(viii), Cr(vi) and Ru in different oxidation states. In the present study, relatively less expensive transition metal ions of the first series, Mn(II), Co(II) and Ni(II) have been effectively used to catalyze the oxidation reaction.

The sequence of oxidation rates of alcohols, Nerol > Citronellol > Geraniol has been explained on the basis of their steric, structural and isomeric features. The catalytic efficiency of metal ions follows the sequence, Mn(II) > Co(II) > Ni(II) for all the primary alcohols studied.

Keywords: Primary perfumery alcohols, ammonium metavanadate, oxidation, kinetics, thermodynamic activation parameters, transition metal ions, homogeneous catalysis.

Introduction

The quantitative conversion of alcohols to the corresponding aldehydes/ketones has been exhaustively reported in literature^{1–6}. There are few reports of the kinetic studies of oxidation of aliphatic alcohols^{7,8}, allyl alcohol using KIO_4 oxidant⁹, cyclic alcohols^{10,11} and Cr(III) catalyzed oxidation of ethane-1,2-diol and propane-1,2-diol using Ce(IV) oxidant¹². The mechanism of the oxidation of primary alcohols using mild to strong oxidizing agents has also been reported¹³.

In our laboratory, we have studied the kinetics of oxidation of some industrially important alcohols and phenols using inorganic and organic oxidizing agents^{14–19}. Herein, we report the kinetic and thermodynamic aspects of the oxidation of the primary perfumery alcohols, Nerol, Citronellol and Geraniol using ammonium metavanadate in H_2SO_4 medium.

The effects of alcohol and oxidant concentrations, ionic strength and temperature on the oxidation rates of alcohols have been determined. The sequence of oxidation rates has been interpreted in terms of steric, structural and isomeric characteristics of the alcohols. Transition metal ions have been used to catalyze the oxidation of alcohols and the sequence of their catalytic activity determined for each alcohol.

Experimental

Materials:

The primary perfumery alcohols were obtained from Shaivi Industries, Lucknow and distilled before use. All other chemicals and reagents used were of AR analytical grade.

Method:

The oxidation of alcohols was studied under first order

kinetic conditions with respect to ammonium metavanadate i.e. $[\text{oxidant}] \ll [\text{alc.}]$. The solutions of alcohol and oxidant in required amounts were allowed to equilibrate in a previously adjusted thermostat (accuracy $\pm 0.1^\circ\text{C}$). After the temperature equilibrium was attained, the solutions were mixed to start the reaction. Aliquots of the reaction mixture were withdrawn at regular time intervals and the unreacted oxidant was estimated iodometrically. The rate constants (k) were determined from the linear plots of \log (unreacted oxidant) versus time. The energy of activation (E) and other thermodynamic activation parameters were determined from the Arrhenius graphs of $\log k$ versus T^{-1} .

The effect of ionic strength on the oxidation rates of alcohols was determined in dilute solution in the range $\mu = 5$ to $25 \times 10^{-2} \text{ mol dm}^{-3}$ at 313 K in accordance with Bronsted-Bjerrum equation,

$$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$$

Using a similar procedure, the catalytic effect of transition metal ions on the oxidation rates of primary alcohols was determined.

Results and discussion

Kinetics of oxidation of primary alcohols:

The primary alcohols were oxidized to the corresponding aldehydes by ammonium metavanadate in acidic medium. For all the alcohols, the oxidation rate increased with $[\text{alc.}]$ but decreased with $[\text{oxidant}]$ (Table 1, Fig. 1).

Table 1. Rate constant data for the oxidation of primary perfumery alcohols by ammonium metavanadate: $[\text{H}_2\text{SO}_4] = 0.1 \text{ mol dm}^{-3}$, temperature = 303 K

$[\text{Alc.}] \times 10^1$ (mol dm^{-3})	$[\text{NH}_4\text{VO}_3] \times 10^3$ (mol dm^{-3})	Nerol $k \times 10^4 (\text{s}^{-1})$	Citronellol $k \times 10^4 (\text{s}^{-1})$	Geraniol $k \times 10^4 (\text{s}^{-1})$
0.25	5.00	5.52	4.14	1.84
0.50	5.00	5.60	4.21	2.53
0.63	5.00	5.98	4.60	2.76
0.75	5.00	7.06	4.69	3.68
0.88	5.00	8.75	5.29	4.83
1.00	5.00	9.48	5.98	5.07
1.00	2.50	5.62	4.60	5.29
1.00	5.00	4.83	3.91	4.14
1.00	10.00	3.68	3.22	2.50
1.00	15.00	2.07	2.76	2.30
1.00	20.00	1.92	1.15	1.80
1.00	25.00	1.77	0.90	1.38

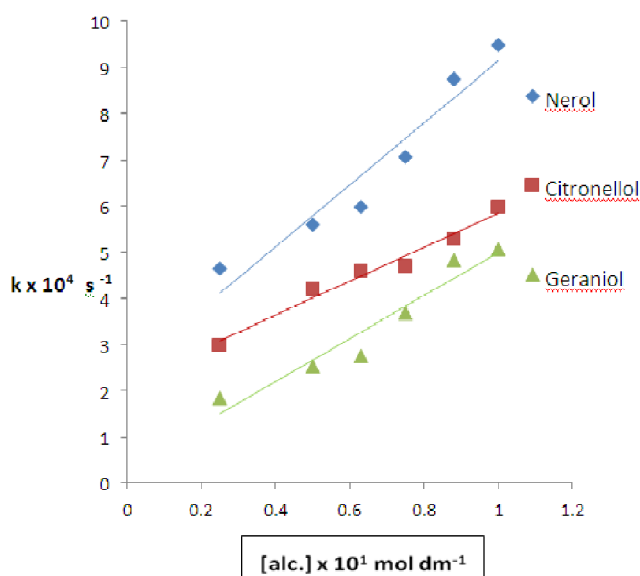
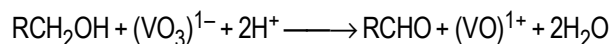


Fig. 1. Variation of rate constant of oxidation of primary perfumery alcohols with $[\text{alc.}]$

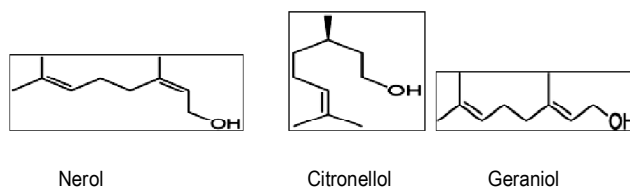
Reaction mechanism of oxidation of primary alcohols:

In acidic medium, ammonium metavanadate NH_4VO_3 forms vanadic acid which is a strong acid and strong oxidant. For a primary alcohol, the oxidation reaction can be shown as



The oxidation product i.e. aldehyde was identified by 2,4-dinitrophenyl hydrozone test and further confirmed by TLC.

The oxidation rates follow the sequence: Nerol > Citronellol > Geraniol



The oxidation rates of the primary alcohols are consistent with their steric hindrance effects on the oxidation. Nerol has the least hindered alpha hydrogen hence its oxidation is the fastest.

Effect of ionic strength on the oxidation rates of primary alcohols:

The effect of ionic strength on the oxidation of alcohols

Table 2. Effect of ionic strength on the oxidation rates of primary perfumery alcohols by ammonium metavanadate in acidic medium: [Alc.] = 0.1 mol dm⁻³, [H₂SO₄] = 2.5 × 10⁻² mol dm⁻³, [Amm. metavanadate] = 2.5 × 10⁻³, temperature = 313 K

μ (mol dm ⁻³)	$\sqrt{\mu}$	Nerol k × 10 ⁴ (s ⁻¹)	Citronellol k × 10 ⁴ (s ⁻¹)	Geraniol k × 10 ⁴ (s ⁻¹)
0.00	0.00	4.96	2.08	2.51
0.05	0.22	5.15	2.05	2.52
0.10	0.32	4.91	2.02	2.50
0.15	0.39	5.00	2.07	2.53
0.20	0.45	5.08	2.11	2.49
0.25	0.50	4.95	2.10	2.47

was studied in the range,

$$\mu = 5 \text{ to } 25 \times 10^{-2} \text{ mol dm}^{-3} \text{ at } 313 \text{ K (Table 2).}$$

The graphs of log *k* versus $\sqrt{\mu}$ were straight lines parallel to the $\sqrt{\mu}$ axis indicating that ionic strength has no effect on the rate of oxidation of alcohols (Fig. 2). This observation is supported by the reaction mechanism suggested for the oxidation of alcohols which involves participation of a neutral species viz. alcohol.

Variation of oxidation rates of primary alcohols with temperature:

From the variation of oxidation rates with temperature

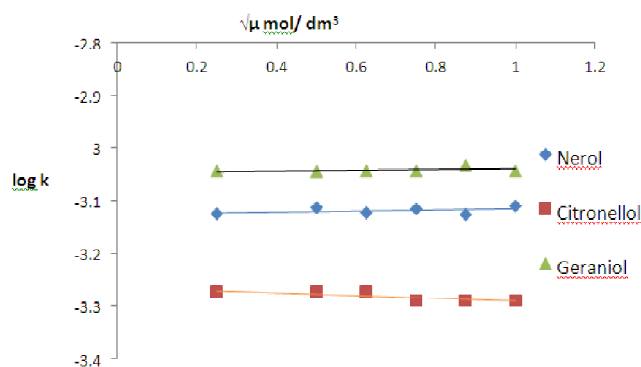


Fig. 2. Effect of ionic strength on rate constant of oxidation of primary perfumery alcohols.

(303–318 K), the thermodynamic activation parameters were evaluated (Table 3). The negative values of entropy of activation ΔS^* indicate a decrease in the rotational and vibrational degrees of freedom of the reacting system due to the formation of a rigid short lived activated complex during the course of the reaction followed by reorientation of water molecules around the activated complex^{20,21}.

Kinetics of transition metal ion catalyzed oxidation of primary alcohols:

The primary perfumery alcohols were oxidized to the cor-

Table 3. Thermodynamic activation parameters of the oxidation of primary perfumery alcohols by ammonium metavanadate in acidic medium: [Alc.] = 0.1 mol dm⁻³, [H₂SO₄] = 0.1 mol dm⁻³

Temp. (K)	k × 10 ⁴ (s ⁻¹)	E (kJ mol ⁻¹)	K* × 10 ¹⁷	ΔH^* (kJ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	ΔS^* (kJ K ⁻¹ mol ⁻¹)
Nerol:						
303	2.53	20.45	4.05	17.95	94.16	-0.2540
308	2.76	20.45	4.34	17.91	95.55	-0.2545
313	3.68	20.45	5.70	17.87	96.41	-0.2538
318	5.52	20.45	8.41	17.83	96.95	-0.2511
Citronellol:						
303	1.29	21.67	2.06	19.17	95.84	-0.2550
308	1.38	21.67	2.17	19.13	97.61	-0.2560
313	3.45	21.67	5.34	19.09	96.58	-0.2500
318	3.67	21.67	5.29	19.05	98.17	-0.2510
Geraniol:						
303	1.38	21.94	2.21	19.44	95.69	-0.2540
308	1.61	21.94	2.53	19.40	96.91	-0.2541
313	1.84	21.94	2.85	19.36	98.20	-0.2543
318	3.45	21.94	5.26	19.32	98.15	-0.2500

responding aldehydes by ammonium metavanadate in acidic medium using transition metal ion catalysts in the range $[M(II)] = 2.5$ to $4.5 \times 10^{-3} \text{ mol dm}^{-3}$. For each of the metal ion catalysts, the oxidation rates of all alcohols increase with $[M(II)]$ (Table 4, Figs. 3a, 3b and 3c).

Table 4. Catalytic effect of transition metal ions on the oxidation of primary perfumery alcohols by ammonium metavanadate in acidic medium: $[Alc.] = 0.1 \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.1 \text{ mol dm}^{-3}$, $[Amm. \text{ metavanadate}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, temperature = 303 K

$[M(II)] \times 10^3$ (mol dm^{-3})	Mn(II) $k \times 10^4 \text{ (s}^{-1}\text{)}$	Co(II) $k \times 10^4 \text{ (s}^{-1}\text{)}$	Ni(II) $k \times 10^4 \text{ (s}^{-1}\text{)}$
Nerol:			
0.00	2.30	2.30	2.30
2.50	4.79	4.14	3.68
3.50	5.83	5.29	4.72
4.50	8.06	6.98	7.59
Citronellol:			
0.00	2.07	2.07	2.07
2.50	6.21	4.14	3.22
3.50	6.67	4.37	3.91
4.50	7.59	6.90	4.83
Geraniol:			
0.00	0.90	0.90	0.90
2.50	5.06	4.60	2.05
3.50	7.02	6.44	4.15
4.50	8.06	6.67	5.06

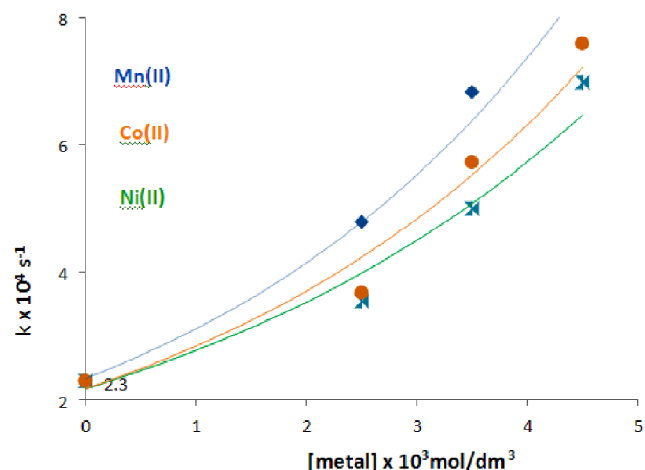


Fig. 3a. Variation of rate constant of oxidation of Nerol with $[M(II)]$ sequence of catalytic activity: $Mn(II) > Co(II) > Ni(II)$.

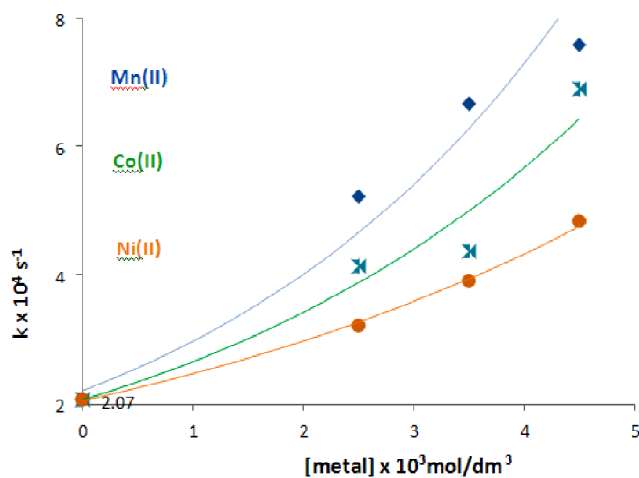


Fig. 3b. Variation of rate constant of oxidation of Citronellol with $[M(II)]$ sequence of catalytic activity: $Mn(II) > Co(II) > Ni(II)$.

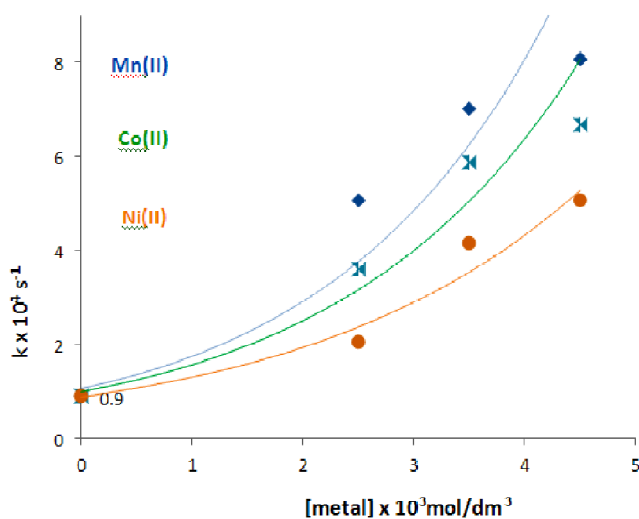
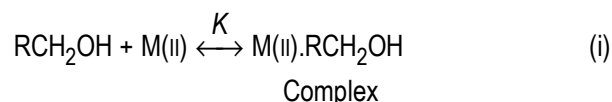


Fig. 3c. Variation of rate constant of oxidation of Geraniol with $[M(II)]$ sequence of catalytic activity: $Mn(II) > Co(II) > Ni(II)$.

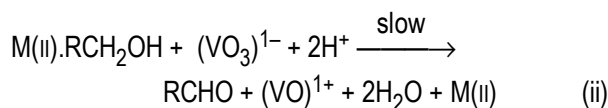
Reaction mechanism of transition metal ion catalyzed oxidation of primary alcohols:

For a primary alcohol, the first step is the formation of a short lived complex between the substrate and $M(II)$ ions.



In the second step, the complex reacts with the vanadate ion in the presence of acid to yield aldehyde

Parbat *et al.*: A kinetic approach to the oxidation of some primary perfumery alcohols using ammonium etc.



The catalytic efficiency of metal ions is inversely proportional to the stability of their transient complexes formed during the course of a reaction which in turn depends largely on the charge density of the metal ions. The stability order for the complexes of the metal ions under study is expected to be Ni(II) > Co(II) > Mn(II)^{22,23}. Consequently the catalytic activity of metal ions is expected to follow the sequence, Mn(II) > Co(II) > Ni(II). All the primary alcohols under study show this expected sequence of catalytic activity.

Conclusions

The oxidation rates of primary perfumery alcohols follow the sequence, Nerol > Citronellol > Geraniol. The oxidation reaction is unaffected by ionic strength in dilute solution and is accompanied by decrease in entropy of activation. The oxidation of primary alcohols is catalyzed by relatively less costly metal ions, Mn(II), Co(II) and Ni(II) in acidic medium.

Acknowledgement

Authors are thankful to Principal, Dr. Anna Pratima Nikalje of Wilson College, Mumbai for providing laboratory facilities, help and guidance at all times.

References

1. J. C. Collins and W. W. Hess, *Org. Synth.*, 1972, **5**, 42.
2. E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.
3. E. J. Corey and D. L. Bayer, *Tetrahedron Lett.*, 1978, 240.
4. E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 399.
5. F. S. Guizec and F. A. Luzzio, *Synthesis*, 1980, 691.
6. G. Piancatelli, A. Scettri and M. D. Auria, *Synthesis*, 1982, 245.
7. P. K. Choudhary, P. K. Sharma and K. K. Banerjee, *Intl. J. Chem. Kinetics*, 1979, **31**, 469.
8. P. K. Sharma and Manju Baghmar, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 2001, **113**, 139.
9. S. T. Nandibewoor *et al.*, *J. Indian Chem. Soc.*, 1998, **75**, 363.
10. Sheila Srivastava *et al.*, *J. Indian Chem. Soc.*, 2009, **86**, 58.
11. Sheila Srivastava *et al.*, *Asian J. Chem.*, 2008, **20**, 4776.
12. Asim K. Das, *J. Indian Chem. Soc.*, 2000, **77**, 225.
13. K. P. Herlily, *Aust. J. Chem.*, 1938, **36**, 203.
14. D. V. Prabhu, M. A. Tandel and H. A. Parbat, Proceedings of the Fourth International Congress of Chemistry and Environment (Chemical Society of Thailand and Research Journal of Chemistry and Environment, India) Ubonratchathani, Thailand, 2010, pp. 169-172.
15. D. V. Prabhu, *J. Indian Chem. Soc.*, 2007, **84**, 1135.
16. D. V. Prabhu, *Oriental J. Chem.*, 2008, **24**, 163.
17. D. V. Prabhu, M. A. Tandel and H. A. Parbat, *Asian J. Chem.*, 2014, **26**, 6669. doi.10.14233/ajchem.2014.17431.
18. D. V. Prabhu, M. A. Tandel, H. A. Parbat and Himanshu Gupta, *Rasayan J. Chem.*, 2015, **8**, 138.
19. D. V. Prabhu and Chetana Rana, *Rasayan J. Chem.*, 2017, **10**, 385, doi.10.7324/RJC.2017.1021649.
20. G. L. Eichhorn and I. M. Trachtenberg, *J. Am. Chem. Soc.*, 1954, **76**, 5184.
21. E. S. Amis, "Kinetics of chemical change in solution", The Macmillan Co., New York, 1948, pp. 108, 110.
22. H. Irving and R. J. P. Williams, *J. Am. Chem. Soc.*, 1953, 3192.
23. D. P. Mellor and L. Maley, *Nature*, 1947, **158**, 370.

