ORIGINAL RESEARCH PAPER

Volume-6 | Issue-9 | September-2017 | ISSN No 2277 - 8179 | IF : 4.176 | IC Value : 78.46

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

UNCATALYSED OXIDATION OF AROMATIC ALCOHOLS BY CERIUM(IV) IN NON-AQUEOUS ACIDIC MEDIUM-A KINETIC AND MECHANISTIC STUDY

Chemistry

Dashrath Singh Rathore Research Scholar ,Department of Chemistry, Pacific University, Udaipur, India

B. K. Dangarh Department of Chemistry, Govt. P. G. College, Neemuch, India

ABSTRACT

The oxidation of aromatic alcohols to carbonyl compounds and carboxylic acids is a very important organic transformation that is extensively used in the manufacture of a wide range of products. The oxidation of Benzyl alcohol and 2-Hydroxy benzyl alcohol by ceric ammonium nitrate has been studied spectrophotometrically, in the presence of glacial acetic acid, in acetonitrile as solvent. The reaction is first order with respect to oxidant and [H+]. Michaelis-Menten type kinetics is observed. The reactions exhibit positive polymerization test. The activation parameters have been evaluated.

KEYWORDS

Kinetics, alcohols, CAN, oxidation.

Introduction-

Ceric ammonium nitrate (CAN) and ceric ammonium sulfate (CAS), in addition to other cerium salts, have been extensively studied as organic compoundoxidants.[1–7].Alcohols and diol oxidation by Ce(IV) was not extensively studied in a preparative way. Ce(IV) chemical oxidation of alcohols is largely dependent on structural effects. Several kinetic investigations on redox reactions involving Ce(IV)and different organic and inorganic compounds including different alcohols have been carriedout[8-14].Kinetic study on the oxidations of ethanol by Ce(IV) in perchloric acid media have been reported. Oxidation of malonic acid, aliphatic ketones and aldehydes, isobutyric acid and 3-bromopropanoic acid has been studied. Various investigations are also made on Ce(IV) in aqueous H_2SO_4, where it forms strong sulphate complex[15]. Trahanovsky et al.[16] studied the oxidation of benzyl alcohol in high yields to benzaldehyde. Oxidation of benzyl alcohol to benzaldehyde in 1-ethyl-3-methylimi dazoliumtriflate was studied by in-situ FTIR spectroscopy and ^{13}C NMR spectroscopy on carbon-13-labeled benzyl alcohol17 .CAN converts benzylic alcohols into carbonyl compounds[18].

Materials and Method:-

Benzyl alcohol and 2-Hydroxy benzyl alcohol were commercial products of the highest purity available. CAN was prepared by method described by Smith et al[19]. Acetonitrile was purified by method given in literature[20]. Due to the non-aqueous nature of the medium, acetic acid (AcOH) was used as a source of hydrogen ions.

The pseudo-first order conditions were attained by keeping a large excess of the alcohol over CAN. The temperature was kept constant to ± 0.1 K. The reactions progress was followed by monitoring the decrease in the concentration of CAN spectrophotometrically at 390 nm up to 80% of the reaction.

Product and Stoichiometry:-

Products of oxidation are corresponding carbonyl compounds. Products of the reaction were also confirmed by extracting the reaction mixture with ether (3 x 15 ml). Tandon et. al.[21] observed that stretching peaks of the hydroxyl group as well as carbonyl group >C=O were shifted to lower wave numbers. There may be intramolecular hydrogen bonding between hydroxyl group and the carbonyl oxygen which may be reason for shifting of peaks to the lower wave numbers[22]. The stoichiometry of the reaction is found to be 2:1 for Ce(IV) and substrate.

RESULTS AND DISCUSSION:-

Effect of oxidant:-

When alcohols were in excess, the disappearance of CAN followed the first-order rate law. The first-order rate constants are independent of the initial concentration of the [CAN] when varied in the range (2 to 7) ×10 –3mol/dm-3 at 303 K

Effect of Substrate:-

At constant [CAN], the rate constants for oxidation were calculated at different initial concentration of alcohols and found to increase linearly with the increase in concentration of alcohols (2x10-^{2}M to 6x10-^{2}M), (Table-1). A plot of log kobsversus log[subs.] gives a straight line with slope nearly one revealed that the rate of oxidation is first order with respect to the substrate. It has been found that plot of $[1/k_i]$ versus (1/[substrate]) is straight line with an intercept on the rate ordinate, indicating the oxidation of both the alcohols follow Michaelis–Menten type kinetics and proceeds through the formation of a complex between the oxidant and the substrate.

Effect of H^+ Ion:-

To study effect of hydrogen ion, glacial acetic acid was used. The rate of oxidation was studied from [H+] = 2 to 5 x10-^{2} M. It was observed that rate increases with increase in hydrogen ion concentration. Plot of log k_{obs}versus log $[H^+]$ is a straight line in both the alcohols show first order dependence of $[H^+]$ on rate. The results are summarized in (Table 1).

Effect of Solvent composition:-

Effect of solvent was studied by changing proportion of water and acetonitrle percentage composition was varied from 10 to 50 % acetonitrle v/v. We have calculated dielectric constant using law of mixture and data for pure acetonitrle and water[23,24] assuming a linear realtionship in the limited range. Wieberg and Evans[25] have made a similar approximation with regard to the same binary solvent system. Looking to the nature of reaction, it can be either ion-dipole or dipole-dipole[26].

It was observed that log kobs versus1/dielectric constant is straight line for both the alcohols with the positive slope. This indicates that reaction is ion - dipolar and further by positive slope, we can say it is cation-dipole interaction in rate dertermining step[27]. Result are summarized in (Table-1).

Effect of Temperature:-

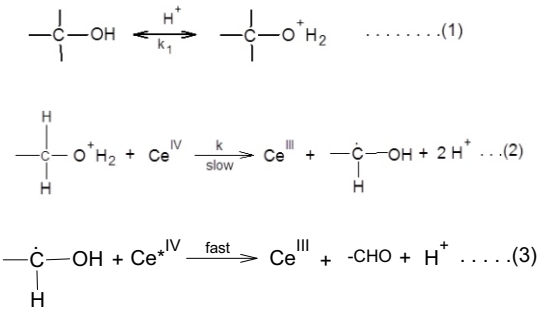
Rate of oxidation increases with increase in temperature. Rate of reactions were determined at different temperature (303 to 323 K) (Table- 2). In case of both the alcohols, a plot of log k_{obs} versus 1/T is straight line. This shows that Arrhenius equation is valid for this oxidation. The energy of activation is 57.44 and 63.36 kJ mol-^{1} respectively. The entropy values are negative and high suggesting that the transition state is more rigid. The negative entropy also suggests the formation of cyclic intermediate from acyclic species. Thermo dynamic parameters have been calculated (Table-3).

Conclusion:-

Oxidative transformation of Benzyl alcohol and 2-Hydroxy benzyl alcohol is first order with respect to oxidant and $[H^+]$.Glasston[28]has pointed out that if entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow. In this case, the negative values of entropy of activation come under a category of slow reactions. In these oxidation reaction negative values of entropy suggest either formation of cyclic struture from non-cyclic

structure or the activated state is more polar than the reactants. Polymerization of the monomer acrylonitrile by reaction mixture was observed. This is in contradiction with Nayak et. al.[29]There fore reaction involve free radicals.Kemp and Water[30] also suggest that C-H fission must occur with Ce(IV). Thus the overall mechanism is proposed to involve the formation of a complex in a fast pre-equilibrium and then a decomposition of the complex in a subsequent slow step via cyclic concerted symmetrical transition state leading to the product.

The kinetic data represents Michaelis-Menten type of kinetics suggesting protonation of alcohol in acid media indicating involvement of H^+ in the reaction in equilibrium step. Ce^{IV} has been found kinetically active in this study with generation of free radical in the reaction.



In equation (3) Ce*(IV) represents any species of Ce^{IV}.

TABLE- 1 Effect of [Substrate], [H^+] and [Solvent] [CAN] = 3 x 10^{-3} M T = 308 K

[Substrate]X 10^2 M	[ACETIC ACID] x 10^2 M	Percentage of H_2O [In Acetonitrile-Water Mix.]	k_{obs} x 10^5 sec-1	
			Benzyl alcohol	2-Hydroxy Benzyl alcohol
2.0	2.0	0	10.48	5.25
3.0	2.0	0	13.43	8.73
4.0	2.0	0	15.91	12.48
5.0	2.0	0	18.04	16.95
6.0	2.0	0	20.73	22.03
2.0	2.0	0	10.48	5.25
2.0	2.5	0	19.11	6.78
2.0	3.0	0	30.14	8.50
2.0	3.5	0	43.37	9.94
2.0	4.0	0	64.29	12.81
2.0	4.5	0	88.38	15.36
2.0	5.0	0	123.21	18.68
2.0	2.0	0	10.48	5.25
2.0	2.0	10	9.56	4.38
2.0	2.0	20	8.73	3.69
2.0	2.0	30	7.84	3.07
2.0	2.0	40	6.91	2.59
2.0	2.0	50	6.34	2.13

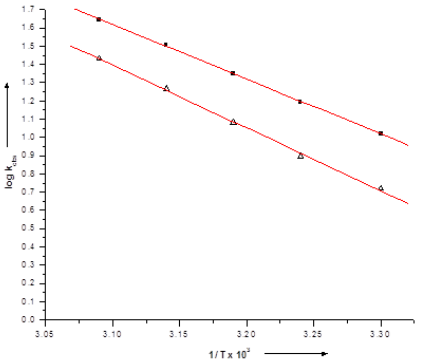
Table- 2 VARIATION OF RATE WITH TEMPRATURE [SUBSTRATE] = 2.0 X 10^{-2}[ACETIC ACID] = 2 X10^{-2}M [CAN] = 3 X10^{-3} M

Temperature in K	k x 10^5 sec-1	
	Benzyl alcohol	2-Hydroxy Benzyl alcohol
303	10.48	5.25
308	15.65	7.88
313	22.43	12.06
318	32.18	18.51
323	44.05	27.36

Table-3 Thermodynamic Parameters

Alcohol	log A	Energy of activation E# kJ mol-1	Entropy of activation S# JK-1 mol-1	Free energy of activation G# kJ mol-1	Enthalpy of activation H kJ mol-1
Benzyl Alcohol	7.32	57.44	-108.76	54.92	87.74
2-Hydroxy Benzyl Alcohol	8.56	63.36	-85.07	63.84	89.61

Figure-1 VARIATION OF RATE WITH TEMPRATURE 1/ T v/s log k_{obs}
■ BENZYL ALCOHOL Δ 2-HYDROXY BENZYL ALCOHOL



REFERENCES

1. Zongsen Y., Minbo C.: Rare Earth Elements and Their Applications, Metallurgical Industry Press, Pequim; (1995).
2. Solderquist J.A.: Aldrichim. Acta.; (1991), 24, 15.
3. T.L. Ho, in: W.J. Mijs, C.R.H.I de Jonge (Eds.): OrganicSynthesis by Oxidation With Metal Compounds, Plenum,New York; (1986), 569.
4. Baciocchi E., Ruzziconi R.: Free radicals in synthesis and biology, in: F. Minisci (Ed.), Mathematical and Physical Sciences, Series C 260 Kluwer Academic Publisher; (1989).
5. Ho T.L.: Synthesis; (1973), 347.
6. Kagan H.B., Namy J.L.: Tetrahedron; (1986), 42, 6600.
7. G.A. Molander: Chem. Rev.; (1992), 92, 29.
8. Willard H.H. and Young P.J.: Am. Chem. Soc.; (1928), 50, 1322.
9. Willard H.H. and Young P.J.: Am. Chem. Soc.; (1930), 52, 132.
10. Yadav R.L. and Bhagwat B.V.: J. Indian chem. Soc.; (1964), 41, 389.
11. Shorter J. and Hinshelwood C.N.: J. Chem Soc.; (1950), 3277.
12. Shorter J.: J. Chem. Soc.; (1950), 3425.
13. Singh B., Richards M., Shukla R.K. and Krishna B.: Indian J. Chem. Soc. L(iii); (1976), 751.
14. Singh B., Saxena P.K., Shukla R.K. and Krishna B.: Indian J. Chem. Soc. L(iv); (1977), 378.
15. Hardwick J. and Hobertson N.: Can, J. Chem; (1951), 29, 828.
16. Young L.B. and Trahanovsky W.S.: J. Am. Chem. Soc.; (1969), 91, 5060.
17. Hasan Mehdi, Andrea Bodor, Diana Lantos, Istvan T.Horvath, Dirk E. DeVos and Koen Binnemans: J. Org. Chem.; (2007), 72 (2) 517-524.
18. (a) Trahanovsky W. S., Cramer J.: JOC; (1971), 36, 1890. (b)Trahanovsky W. S., Fox N. S.: JACS; (1974), 96, 7968. (c) Ho T. L.: S; (1978), 936.
19. Banerji K.K., Kumbhat V. and Sharma P.K.: Int. J. Chem. Kinet.; (2002), 34,248.
20. Perrin D.D., Armarego W.L. and Perrin D.R.: Purification of Organic Compounds, Pergamon Press, Oxford;(1966).
21. Tondon P.K., Khanam S.Z. and Singh S.B.: The open Catalysis Journal; (2012), 5, 1-7.
22. Silverstein R.M., Bassler G.C. and Morill T.C.: Spectrometric identification of organic compounds, 4th ed.; John wiley New York; (1981), 120.
23. Zimmermans H.E.: Physico-Chemical Constants of Pure Organic Comp. Elsevir Pub.;(1950), 383.
24. Le Fever: Trans Faraday Soc.;(1938), 34.1127.
25. Wieberg K.B. and Evans T.R.: J.Am. Chem. Soc.;(1958), 80, 3019.
26. Amis: J. Chem. Educ.; (1953),30, 351.
27. Bakore G.V. and Narain S.: Z Physik. Chem. (Leipzig); (1964), 8,227.
28. Glasston S., Laidler K.J. and Eyring H. : The Theory of Rate Processes, Mc Graw Hill New York; (1947).
29. Nayak B.B., Sahu S, Patel S., Dash S. and Mishra B.K.: Indian Journal of Chemistry; (2008), 47 A, 1486-1490, 10.
30. Kemp T. J. and. Waters W. A: J. Chem. Soc.; (1964), 1192.