RJC

RASĀYAN *J. Chem.*
Vol. 8 | No.4 |459 - 464 | October - December | 2015
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

A COMPARATIVE STUDY OF THE OXIDATION RATES OF PERFUMERY PHENOLS USING INORGANIC OXIDANTS

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ABSTRACT

The quantitative conversion of phenols to quinones has been extensively studied and reported but there are few reports about the kinetic and thermodynamic investigations of the oxidation of phenols. In this paper we report the kinetics of the oxidation of the perfumery isomeric phenols, Eugenol and Isoeugenol using KIO_4 and $K_2S_2O_8$ in acidic medium. The oxidation was studied under first order kinetic conditions with respect to the inorganic oxidants and the rate of oxidation of phenols was monitored by iodometric estimation of the unreacted oxidants at regular time intervals. The oxidation rate increased with [phenol] but decreased with increasing [oxidant]. K_2SO_4 was used to study the effect of ionic strength on the oxidation rate of phenols. The oxidation rates were found to be independent of ionic strength as borne out by the reaction mechanism suggested. The thermodynamic activation parameters were evaluated from the variation of oxidation rate of phenols with temperature (303-318K). The observed negative values of the entropy of activation were ascribed to the formation of a rigid activated complex during the course of the reaction and reorientation of the solvent molecules around the activated complex. This greatly curtailed the degrees of freedom of the reacting system resulting in decrease in entropy. The oxidation rates followed the sequence: Isoeugenol>Eugenol, which has been explained on the basis of isomeric and structural features of the perfumery phenols under study. $K_2S_2O_8$ was found to be a stronger oxidising agent than KIO_4 for oxidation of perfumery phenols in acidic medium.

Keywords: perfumery phenols, inorganic oxidants, first order kinetics, ionic strength, entropy of activation, conjugation

INTRODUCTION

The kinetics of various types of reactions including oxidation , reduction and hydrolysis using different experimental techniques has been reported.[1-11]We have studied the kinetics of oxidation of phenols using organic and inorganic oxidants.[12,13] This paper deals with the kinetics of oxidation of Eugenol (4-Allyl-2-methoxy phenol) and Isoeugenol (2-methoxy-4(prop-1-en-1-yl)phenol) by KIO_4 and $K_2S_2O_8$ in acidic medium. These isomeric phenols are found in the Indian spices, clove (*Syzygium Aromaticum*) and nutmeg (*Myristicafragrans HOUTT*) and are extensively used in the preparation of perfumes, fragrances and flavouring agents.

The effects of phenol and oxidant concentrations, ionic strength and temperature on the oxidation rates of phenols have been studied and suitable reaction mechanisms have been suggested. The sequence of oxidation rates of phenols has been explained on the basis of their isomeric and structural characteristics.

EXPERIMENTAL

The perfumery phenols were procured from Shaivi Industries, Lucknow and purified by distillation before use. All other chemicals and reagents used were of ANALAR Grade. The oxidation of phenols was studied under first order kinetic conditions with respect to the inorganic oxidant i.e. [oxidant] << [phenol]. Aliquots of the reaction mixture were withdrawn at regular time intervals, the reaction was arrested using ice and the unreacted oxidant was estimated iodometrically. The first order rate constants were determined from the straight line plots of log (unreacted oxidant) versus time. The effect of ionic strength (μ) on the oxidation rate was studied using K_2SO_4 in dilute solution in the range, μ = 5 to 25 x

10^{-2}mol dm^{-3}. From the Arrhenius plots of log k versus 1/T, the energy of activation and other thermodynamic activation parameters were evaluated and interpreted.

RESULTS AND DISCUSSION

The perfumery phenols, Eugenol and Isoeugenol were oxidised to the corresponding o-quinones.The oxidation rate increased with phenol concentration but decreased with oxidant concentration (Tables-1 and 2). The oxidation of Isoeugenol by KIO_4 in acidic medium was found to be too fast to be measured by titrimetric estimation.

Reaction mechanism of oxidation of phenols

KIO_4 as oxidant in acidic medium

In acidic medium, KIO_4 rapidly forms periodic acid, HIO_4 which is a strong acid and also a strong oxidising agent.[14,15] The oxidation of phenol results in the formation of the hypohalite ion, IO^-.

$$\text{Phenol} + 2IO_4^- + 13H^+ \rightarrow o\text{-Quinone} + IO^- + CH_3I + 7\,H_2O$$

The unreacted oxidant was estimated iodometrically, as-

$$IO_4^- + I^- + 8H^+ \rightarrow I_2 + 4H_2O$$

The liberated iodine was titrated against standard $Na_2S_2O_3$ using starch as indicator.

$K_2S_2O_8$ as oxidant in acidic medium

In acidic medium $K_2S_2O_8$ forms $H_2S_2O_8$ which is a strong acid and strong oxidising agent.[16,17]

$$2\,\text{Phenol} + S_2O_8^{=} \rightarrow 2\ o\text{-Quinone} + (CH_3)_2SO_4 + H_2SO_4$$

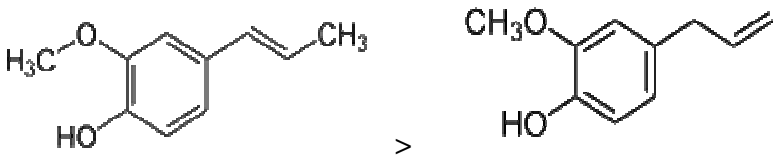
The unreacted oxidant was estimated iodometrically, as-

$$S_2O_8^{=} + 2I^- + 4H^+ \rightarrow I_2 + 2\,H_2SO_4$$

The oxidation product ,o-quinone was identified and confirmed by TLC.

The oxidation rates of phenols by $K_2S_2O_8$ in acidic medium followed the sequence(Table-2, Figure-1):

Isoeugenol > Eugenol



In Isoeugenol, conjugation extends outside the aromatic ring hence the oxidation product obtained is more stable. However in Eugenol there is no such extended conjugation hence its oxidation product is less stable.[18] This explains the higher rate of oxidation of Isoeugenol as compared to that of Eugenol. $K_2S_2O_8$ was found to be a stronger oxidant than KIO_4 for the oxidation of the perfumery phenols under study (Tables-1and 2, Figure-1).

Table-1: Rate constant data for the oxidation of perfumery phenol by KIO_4 in acidic medium.
[H2SO4] =1M, Temperature =303K

[phenol] x10^1 mol dm^{-3}	[KIO_4] x 10^3 mol dm^{-3}	Eugenol k x 10^3 s^{-1}
1.00	2.50	1.84
1.00	5.00	1.38
1.00	10.00	1.84

1.00	15.00	1.61
1.00	20.00	1.38
1.00	25.00	1.12
0.25	5.00	1.38
0.50	5.00	1.61
0.63	5.00	1.61
0.75	5.00	1.73
0.88	5.00	1.82
1.00	5.00	1.84

Table-2: Rate constant data for the oxidation of perfumery phenols by $K_2S_2O_8$ in acidic medium.
$[H_2SO_4]$ =1M, Temperature =303K

[phenol] x10^1 mol dm^{-3}	$[K_2S_2O_8]$ x 10^3 mol dm^{-3}	Eugenol k x 10^3 s^{-1}	Isoeugenol k x 10^3 s^{-1}
1.00	2.50	-	-
1.00	5.00	-	3.16
1.00	1.00	3.29	2.97
1.00	15.00	3.13	2.88
1.00	20.00	3.04	2.69
1.00	25.00	2.58	2.37
0.25	5.00	2.21	4.97
0.50	5.00	4.54	6.47
0.63	5.00	5.23	7.77
0.75	5.00	5.53	7.92
0.88	5.00	6.54	6.91
1.00	5.00	6.84	4.63

Effect of ionic strength on oxidation rates of phenols

K_2SO_4 was used to study the effect of ionic strength on the oxidation rates of phenols in the range μ = 5 to 25 x 10^{-2}mol dm^{-3} at 303K(Tables-3 and 4).

The graphs of logk versus √μ were found to be straight lines parallel to the √μ axis indicating that the oxidation rates are independent of ionic strength as borne out by the reaction mechanism suggested.

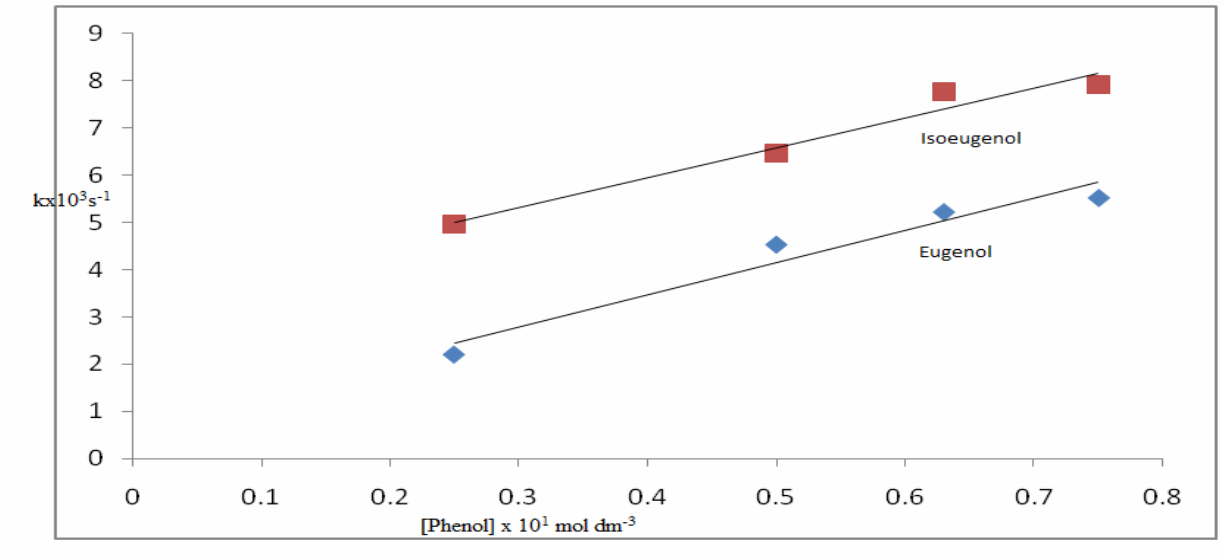


Fig.-1 : Variation of rate constant of oxidation of perfumery phenols with [phenol] using $K_2S_2O_8$ as oxidant in acidic medium.

Table-3: Effect of ionic strength on oxidation rate of perfumery phenol using KIO4 as oxidant.
[Phenol] = 0.1M, $[KIO_4]$ =5 x 10^{-3}M
$[H_2SO_4]$ =0.5M Temperature = 303K

$[K_2SO_4]$ μ x 10^2 mol dm^{-3}	Eugenol k x 10^3 s^{-1}
0	3.29
5.00	3.92
10.00	4.01
15.00	3.92
20.00	3.45
25.00	3.85

Table-4: Effect of ionic strength on oxidation rate of perfumery phenol using $K_2S_2O_8$ as oxidant.
[Phenol] = 0.1M, $[K_2S_2O_8]$ =5 x 10^{-3}M
$[H_2SO_4]$ =0.5M Temperature = 303K

$[K_2SO_4]$ μ x 10^2 mol dm^{-3}	Eugenol k x 10^3 s^{-1}	Isoeugenol k x 10^3 s^{-1}
0.00	3.16	3.90
5.00	3.04	5.37
10.00	3.22	3.75
15.00	3.34	3.89
20.00	3.98	3.96
25.00	4.74	5.73

Table-5: Thermodynamic activation parameters of the oxidation of perfumery phenol, Eugenol by KIO_4 in acidic medium. $[H_2SO_4]$ = 1M

Temp. K	Rate constant k x 10^3 s^{-1}	E kJ mol^{-1}	K*x 10^{15}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ $K^{-1}mol^{-1}$
303	9.51	16.20	1.51	13.68	85.99	-0.2386
308	10.89	16.20	1.70	13.64	87.11	-0.2385
311	11.31	16.20	1.75	13.61	87.88	-0.2388
313	12.62	16.20	1.93	13.60	88.11	-0.2382
318	12.97	16.20	1.96	13.56	89.99	-0.2403

Table-6: Thermodynamic activation parameters of the oxidation of perfumery phenols, Eugenol and Isoeugenol by $K_2S_2O_8$ in acidic medium.$[H_2SO_4]$ = 1M

(a.) Eugenol

Temp. K	Rate constant k x 10^3 s^{-1}	E kJ mol^{-1}	K*x 10^{16}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ $K^{-1}mol^{-1}$
303	3.18	56.79	5.03	54.27	88.75	-0.1138
308	3.20	56.79	4.98	54.22	90.24	-0.1169
311	3.22	56.79	4.97	54.20	91.11	-0.1186
313	6.40	56.79	9.81	54.18	89.94	-0.1142
318	8.46	56.79	12.77	54.14	90.68	-0.1149

(b.) Isoeugenol

Temp. K	Rate constant	E kJ mol^{-1}	K*x 10^{16}	ΔH* kJ mol^{-1}	ΔG* kJ mol^{-1}	ΔS* kJ $K^{-1}mol^{-1}$

	$k \times 10^3 s^{-1}$					
303	3.62	38.44	5.73	35.92	88.42	-0.1766
308	4.56	38.44	7.10	35.87	89.33	-0.1735
311	4.95	38.44	7.64	35.85	90.00	-0.1741
313	5.19	38.44	7.95	35.83	90.49	-0.1745
318	7.67	38.44	11.57	35.80	87.46	-0.1624

Variation of oxidation rates of phenols with temperature

The oxidation was studied at different temperatures in the range 303-318K and the different thermodynamic activation parameters were determined (Tables-5,6a and 6b). Some of the important inferences from the thermodynamic study are:

1. The rate constant of oxidation of phenols is inversely proportional to the energy of activation and increases with temperature.
2. The equilibrium constant K* for the formation of the activated complex from the reactants also increases with temperature and hence is a function of temperature.
3. The entropy of activation ΔS* is constant at all temperatures indicating that the site of oxidation i.e. phenolic –OH group is the same at all temperatures.
4. The negative values of ΔS*indicate decrease in the degrees of freedom of the reacting system due to the formation of a rigid activated complex and reorientation of solvent molecules around the activated complex. This greatly curtails the vibrational and rotational motions of the reacting molecules resulting in decrease in entropy.[19,20]

CONCLUSIONS

1. The oxidation rates of perfumery phenols using $K_2S_2O_8$ oxidant follow the sequence :Isoeugenol>Eugenol.
2. The oxidation of Isoeugenol by KIO_4 in acidic medium was found to be too fast for accurate determination by titrimetric estimation.
3. The oxidation of perfumery phenols is independent of ionic strength in dilute solution. $K_2S_2O_8$ is a stronger oxidising agent for the phenols under investigation than KIO_4 in acidic medium.

ACKNOWLEDGEMENT

One of the authors (Chetana Rana) is grateful to Principal Dr Anjali Kulkarni and Dr N T Nirgude, Head, Department of Chemistry, N. B. Mehta Science College, Bordi, Maharashtra for providing laboratory facilities, constant help and encouragement at all times.

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[RJC-1284/2015]