A Kinetic Study of the Effect of Aquo-Propan-1-ol on the Rate and Mechanism of Solvolysis of Phenyl Benzoate

Kumar Ravi Ranjan[1], Kumar Kaushalenra[2] and R. T. Singh
1. *Research Scholar, Department of Chemistry, V. K. S. University, Ara*
2. *HOD, Department of Chemistry, J. J. College, Ara*
3. *Professor & Formerly HOD Chemistry and the Dean of the Faculty of Science, V. K. S. University, Ara*
email: singhramtawakya@gmail.com

ABSTRACT

Phenyl benzoate is used as preservative in cosmetics. It is suitable only for industrial use or research purpose and typically are not suitable for human consumption or therapeutic use.

The kinetics of alkali catalysed hydrolysis of phenyl benzoate has been carried in aquo-propan-1-ol media in order to highlight the effect of dipolar aprotic solvent effect on the industrial uses of the said ester.

Effect of aquo-propan-1-ol reaction media on the rate and mechanism, activation energies (Iso-composition and Iso-dielectric), thermodynamic activation parameters and solvent-solute interaction has been studied.

The rate of reaction has been found to decrease with increasing concentration of propan-1-ol (from 20 to 80%) in the reaction media at all the five temperatures from 20 to 40^0C at which the reaction was carried out.

The number of water molecules associated with the activated complex were found decreasing from 0.848 to 0.155 with increasing temperature from 20°C to 40°C and from this it has been inferred that in water-propan-1-ol media, structure of water is being changed from its bulky from to its dense from and the mechanistic pathways of the reaction is changed from unimolecular to bicomolecular in presence of propan-1-ol (protic solvent) in the reaction media.

KEYWORDS: Phenyl benzoate, Bulky and dense form of water, uni and bimolecular mechanistic pathways, cosmetic, Solvent-solute interaction.

INTRODUCTION

Various kineticists[1-2] have reported about the "solvent effect" on the various types of solvolysis reaction, but less works on the solvent effect on the rate and mechanism of the solvolysis of Phenyl benzoate have been reported so far. Hence, for highlighting the above noted untouched research, the kinetics of alkali catalysed hydrolysis of Phenyl benzoate in water-propan-1-ol media having varying concentrations (from 20 to 80%) was studied, as it was thought important for the cosmetic industrial points of views.

EXPERIMENTAL:

The kinetics of alkali catalysed hydrolysis of Phenyl benzoate in water-

propan-1-ol media was studied by keeping the concentration of alkali and ester M/10 and M/20 respectively following the method reported by Ojha & Singh *et al.*[3] and Laxmi & Singh *et al.*[4]. The specific rate constant values of the reaction were calculated using second order kinetic equation and have been tabulated in Table-I. Variation of log k values on the specific rate constants of the reaction has been shown in Table–II. log k and log [H_2O] values of the reaction and reaction media respectively have been recorded in Table-III and number of water molecules associated with the activated complex of the reaction have been mentioned in Table-IV.

Results and Discussion

Solvent Effect on the rate of Reaction:

In order to study the variation in specific rate constant values of the reaction with increasing concentration of propan-1-ol in the reaction media, the log k values have been plotted against mol% of propan-1-ol. Variation of log k values with mol% of propan-1-ol have been mentioned in Table – II.

From the plots of log k versus mol% of propan-1-ol, it is apparent that the rate of the reaction go on decreasing with different slopes due to two interacting straight line in the plots at about 19.0 mol% of propan-1-ol in the reaction media. This also gives in information that with increase in temperature of the reaction the extent of depletion becomes slower (shallow in nature). Such nature of depletion in the rate with increasing organic content in the reaction media and also with increasing temperature of the reaction is not new, but a number of kineticists like Laidler and Landskroener[5] and recently Rahul & Singh et al.[6] and Lal & Singh et al.[7] have also reported similar observations and their interpretations.

Though these findings are against the view of Hughes and Ingold[8] however our findings and their interpretations have been found in support of the earlier report of Singh et al.[9] and also of the recent report of Sunita & Singh et al.[10] and Singh Atulit[11]. In our views, the decrease in the rate is attributed partly due to the effect of dielectric constant of the media and partly also due to the change in structure of water as a result of solvation change taking place in the reaction media.

Participation of Solvent (water) molecules with the activated complex and mechanism of the reaction:

Participation of water molecules of water-propan-1-ol media in the formation activated complex of the reaction was studied for knowing the effect of change in composition of reaction media on the rate and mechanism of the reaction. The number of water molecules associated with the activated complex were evaluated by plotting log k values against log [H_2O] values, mentioned in Table - III following the equation proposed by Robertson[12] which is as:

$$\log k = \log k_0 + n \log[H_2O]$$

where 'n' is the solvation number which tells about the criterion for studying about the mechanism of the reaction. From the slopes of plots of

log k against log [H_2O], the number of water molecules associated with the activated complex were found to vary with temperature of the reaction as mentioned in Table - IV.

Form the plots of log k versus log [H_2O] and also from Table-IV, it is apparent that before and after log [H_2O] value 1.51 which corresponds to 58.20% of water in the reaction media the values of the slopes of the two intersecting straight lines are different.

Before log[H_2O] value 1.51 which corresponds to 58.20 % of water in the reaction media the value of solvation number (n) i.e. the number of water molecules associated with the activated complex of the reaction decreases from 0.634 to 0.155 with rise in temperature of the reaction from 20 to 40°C.

Similarly in case of above 58.20% water concentration in the reaction media the number of water molecules associated with the activated complex decreases from 0.848 to 0.381 with rise in temperature of the reaction from 20 to 40°C.

Overall, it may be inferred that the number of water molecules associated with the activated complex of the reaction decreases from 0.848 to 0.155 with rise in temperature of the reaction from 20 to 40°C.

From the above recorded findings, in the light of guidelines of Robertson et. al.[13] from the decreasing number of water molecules from 0.848 to 0.155 associated with the formation of activated complex of the reaction it may be opined that the mechanistic path way followed by the reaction is changed from unimolecular to bimolecular with increasing propan-1-ol content in the reaction media and also with increasing temperature of the reaction from 20 to 40°C.

From the values of the number of water molecules associated with the activated complex which decrease from 0.634 to 0.155 when log [H_2O] value is below 1.51 and from 0.848 to 0.381 when log [H_2O] value is above 1.51, it is inferred that with rise of the temperature, water in the water-propan-1-ol media changes its structure from bulky to dense form.

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

As the number of molecules of water associated with activated complex is decreasing with rise in temperature, hence it is inferred that in presence of propan-1-ol in the reaction media, the unimolecular of the mechanism of the reaction is changed to bimolecular in the similar way as observed by Packer and Tomilinson[14]. Our such inferences have also found in support of the recent findings of Parween & Singh et al[6], Sushma & Singh *et al.*[16], Narendra & Singh *et al.*[17] and Srivastava & Singh *et. al.*[18].

References:

1. Singh, L., Singh, R. T. and Jha, R. C.: J. Indian Chem. Soc., **55**, 37, 1978
2. Tauheed, Sarwat, Haider, S. R. and Singh, R. T.: ARJ Phys. Sci., **10**, No. (1-2), 201, 2007
3. Ojha Rishiraj, Singh Y.Prasad and Singh R.T.: Wutan Huatan Jisuan

Jishu, **XVIII**, No(III), 108-118, March 2022
4. Laxmi, R., K., Kumud, and Singh, R. T.: Gradiva Review Journal, **8**, No. (III), 131-140, Nov., 2022
5. Laidler, K. J. and Landskroener, P. A.: Trans. Farady Soc, **52**, 200, 1956
6. K., Rahul and Singh, R.T. : IJESM, **6**, No. (7), 569-591, Nov., 2017
7. Lal, V. K., Kishor, K., K. Raghaw and Singh, RT: Wutan Huatan Jisuan Jishu, **XVI**, No. (IX), 141-160, Sept., 2020
8. Hughes, E. D. and Ingold C. K.: J. Chem. Soc., 255, 244, 1935
9. Singh, A. K., Singh, A., Santosh, P. K. and Singh, R. T.: NIRJ Sci., **4**, 55-60, 2010
10. Kumari Sunita, Kumar, S. and Singh, R. T.: Wutan Huatan Jisuan Jishu, **XVI**, No. (IX), 111-124, Sept., 2020
11. Singh, Atulit: Aut. Aut. Reseach Journal, **XI**, No. (XI), 255-259, Nov., 2020
12. Robertson R.E. : Prog. Phy. Org. Chem., **4**, 213, 1967
13. Robertson R.E, Heppolitile R. L. and : Canad J. Chem Soc., **37**, 803, 1959
14. Packer K. J. and Tomilionson D. J. : Trans. Faraday Soc., **67**, 1302, 1971
15. Parween Zeba and Singh R.T. : IJESM, **7**, No(1), 543-552, Jan 2018
16. K. Sushma, Abhay, Ashutosh, Singh, R. and Singh, R. T.: IJAEMA, **XII**, No. (1), 3345-3363, Jan, 2020
17. K., Narendra and Singh, R. T.: Strad Research Journal, **9**, No. (6), 73-86, 2022
18. Srivastava, P, Singh, Y. P. and Singh, R. T.: Gradiva Review Journal, **8**, No. (11), 113-123, Nov., 2022

Table – I

Specific rate constant values of Alkali Catalysed Hydrolysis of Phenyl Benzoate in Water-Propan-1-ol media

$\mathbf{k \times 10^2} \boldsymbol{in}\ (\boldsymbol{dm})^3\ \boldsymbol{mol}^{-1}\ \mathbf{min}^{-1}$

Temp in ^{0}C	% of Propan-1-ol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20^{0}C	91.03	81.71	72.83	64.83	57.31	46.57	33.95
25^{0}C	172.78	157.69	141.32	128.59	115.11	97.70	75.89
30^{0}C	329.76	288.93	279.32	254.16	233.51	205.16	169.47
35^{0}C	598.00	557.44	521.43	483.62	451.44	408.41	361.24
40^{0}C	1086.68	1023.00	981.97	922.51	877.20	830.04	767.71

Table – II

Variation of log k values of the specific rate constants of the reaction with mol% of propan-1-ol in water-propan-1-ol of reaction media

% of Propan-1-ol (v/v)	Mole % of Propan-1-ol	3 + log k values				
		20^{0}C	25^{0}C	30^{0}C	35^{0}C	40^{0}C
20%	05.66	1.9592	2.2375	2.5180	2.7767	3.0361
30%	09.33	1.9123	2.1978	2.4608	2.7462	3.0141
40%	13.79	1.8623	2.1502	2.4461	2.7172	2.9921
50%	19.35	1.8118	2.1092	2.4051	2.6845	2.9650
60%	26.67	1.7582	2.0611	2.3683	2.6546	2.9431
70%	35.90	1.6681	1.9899	2.3121	2.6111	2.9191
80%	48.98	1.5308	1.8802	2.2291	2.5578	2.8852

Table – III
Variation of log k values of the reaction with log [H_2O] values in water-Propan-1-ol (media)

% of Propan-1-ol	% of H_2O	log [H_2O]	2 + log k values				
			20^{0}C	25^{0}C	30^{0}C	35^{0}C	40^{0}C
20%	80%	1.6478	1.9592	2.2375	2.5182	2.7767	3.0361
30%	70%	1.5898	1.9123	2.1978	2.4608	2.7462	3.0141
40%	60%	1.5229	1.8623	2.1502	2.4461	2.7172	2.9921
50%	50%	1.4437	1.8118	2.1092	2.4051	2.6845	2.9650
60%	40%	1.3468	1.7582	2.0611	2.3683	2.6546	2.9431
70%	30%	1.2218	1.6681	1.9899	2.3121	2.6111	2.9191
80%	20%	1.0458	1.5308	1.8802	2.2291	2.5578	2.8852

Table – IV

Evaluated Values of number of water molecules associated with the activated complex of the reaction media in water-Propan-1-ol media

Temp. in ^{0}C	Slope – I where log [H_2O] is below 1.510	Slope – II when log [H_2O] is above 1.510
20^{0}C	0.634	0.848
25^{0}C	0.581	0.787
30^{0}C	0.455	0.697
35^{0}C	0.306	0.510
40^{0}C	0.155	0.381