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Oxidation of *ortho*-Substituted Benzyl Alcohols by Phenyliodoso Acetate

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Oxidation of benzyl alcohol and some *ortho*-substituted benzyl alcohols by phenyliodoso acetate in *t*-butyl alcohol:water medium (50:50) leads to the formation of corresponding benzaldehyde. The stoichiometry of the reaction is found to be 1:1. The reaction is first order each in substrate and oxidant concentrations. This reaction is studied at four different temperature and the activation parameters are calculated. Correlation analysis is carried out using Chartons Triparametric equation. The reaction is subjected to steric retardation by the *ortho*-substituents. The % of steric and resonance calculated. A suitable mechanism has been proposed.

Key Words: Oxidation, *o*-Substituted benzyl alcohols, Phenyliodoso acetate.

INTRODUCTION

Pausaucker *et al.*[1] have studied that the oxidation of primary and secondary alcohols by phenyliodoso acetate (PIA) is not facile. Vaidyanathan and Venkatasubramaniam[2] reported the oxidation of α-hydroxy acids by phenyliodoso acetate in acetic acid medium and they found in aqueous medium only free radical and ionic mechanism is possible. The oxidation of various organic compounds by phenyliodoso acetate was studied[3-9].

Phenyliodoso acetate is found to be a good oxidizing agent in the synthesis of isoflavan quinones[10]. Redox properties of marine natural products are studied by phenyliodoso acetate[11]. This communication deals with the kinetics and mechanism of oxidation of *o*-substituted benzyl alcohols by phenyliodoso acetate in *tert*-butyl alcohol-water medium. Phenyliodoso acetate acts as a good oxidizing agent and the mechanism followed is found to be complex formation type.

EXPERIMENTAL

Benzyl alcohol and *ortho*-substituted benzyl alcohols were purified by repeated distillation and recrystallization. Phenyliodoso acetate (PIA) was prepared by the reported method[12].

All the kinetic measurements were carried out in a glass stoppered iodine flask protected from light and thermostated to within ± 0.1 °C. Reactions were carried out in *tert*-butyl alcohol-water medium at 30 °C in the presence of 2.5×10^{-3} M sulphuric acid unless otherwise stated. The course of the reaction was followed iodometrically.

Stoichiometry and product analysis: Stoichiometry of the reaction was found to be 1:1. The product analysis was carried out by mixing equimolar mixture of benzyl alcohol and phenyliodoso acetate and kept at room temp for 24 h under the kinetic conditions employed. Then the mixture was poured into a china dish and concentrated to a small volume by spontaneous evaporation. It was extracted with ether and the ether extract was dried over anhydrous sodium sulphate. Then the ether evoprated to get the liquid product. From IR and UV spectra, the extracted mixture was analyzed and it showed that the sole product was benzaldehyde.

RESULTS AND DISCUSSION

The oxidation of benzyl alcohol by phenyliodoso acetate (PIA) has been conducted in 50:50 *tert*-butyl alcohol:water medium in presence of 2.5×10^{-3} M sulphuric acid. The rate data observed is given in Table-1.

The reaction is found to be first order with respect to [PIA]. A plot of log k_{obs} *vs.* log [BzOH] gave a straight line with unit slope indicating first order with respect of [BzOH]. In order to know the role of H_2SO_4 the reaction was carried out in the absence of H_2SO_4 It has been observed that the rate of the reaction increases with increase in H_2SO_4.

A plot of log k_{obs} *vs.* log [PIA] is a straight line and passes through the origin. The effect of varying the solvent composition was studied by following the rate of the reaction by increase the % of *tert*-butyl alcohol. Rate of oxidation increases with decrease in dielectric constant of the medium. The addition of sodium perchlorate has no significant effect on the reaction rate showing the absence of primary salt effect.

TABLE-1
EFFECT OF VARYING [BzOH], [PIA], [H$^+$] AND THE SOLVENT COMPOSITION ON THE REACTION RATE AT 303 K

[PIA] × 10^4 mol dm^{-3}	[BzOH] × 10^3 mol dm^{-3}	[H$^+$] × 10^3 mol dm^{-3}	% *t*-BuOH-H_2O	k_{obs} ×10^3 (s^{-1})
1.0	1.0	2.5	50-50	3.78
1.0	2.0	2.5	50-50	7.51
1.0	3.0	2.5	50-50	11.40
1.0	4.0	2.5	50-50	15.10
1.0	5.0	2.5	50-50	19.00
0.5	2.0	2.5	50-50	7.21
1.0	2.0	2.5	50-50	7.51
1.5	2.0	2.5	50-50	7.62
2.0	2.0	2.5	50-50	7.80
2.5	2.0	2.5	50-50	7.82
1.0	2.0	1.5	50-50	4.50
1.0	2.0	2.0	50-50	6.10
1.0	2.0	2.5	50-50	7.51
1.0	2.0	3.0	50-50	9.00
1.0	2.0	3.5	50-50	10.50
1.0	2.0	2.5	30-70	3.88
1.0	2.0	2.5	40-60	5.49
1.0	2.0	2.5	50-50	7.51
1.0	2.0	2.5	60-40	9.32
1.0	2.0	2.5	70-30	11.10

Mechanism and rate law: Phenyliodoso acetate is the active oxidizing species at low concentration of acid [H$^+$] 2.5 × 10^{-3} M.

$$\text{BzOH} + \text{PIA} \xrightleftharpoons{\textbf{K}} \text{Complex} \qquad (1)$$

$$\text{Complex} + \text{H}^+ \xrightarrow[\substack{\textbf{slow and rate}\\ \textbf{determining}}]{\mathbf{k_1}} \text{Products} \qquad (2)$$

The rate law derived is as follows:

$$\text{Rate} = -d[\text{PIA}]/dt = k_1[\text{Complex}]\,[\text{H}^+]$$

$$\text{Complex} = [\text{BzOH}]\,[\text{PIA}]$$

$$-d[\text{PIA}]/dt = [\text{BzOH}]\,[\text{PIA}]\,[\text{H}^+]$$

Correlation analysis of reactivity: Eight *o*-substituted benzyl alcohols have been subjected to oxidation by phenyliodoso acetate at four different temperatures in similar conditions for the parent compound. The rate constants along with the activation parameters for the reaction of *o*-substituted benzyl alcohols with phenyliodoso acetate are given in Table-2.

A linear isokinetic relationship[13] has been observed by plotting $\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$. Thus a common mechanism may be responsible for oxidation of all the substituted benzyl alcholos[14] under investigation. The rate data of *ortho*-substituted benzyl alcohols was analyzed by Charon's method[15] in terms of DSP equations[16,17] using σ_I, $\sigma_R\nu$ values compiled by Chapman *et al.*[17]. The results of this correlation are given in Table-3. The statistical parameters, standard deviation (SD), coefficient of multiple correlations (R) and the parameters for precision[18,19] (f and φ) are also presented in Table-3.

From Table-3 it is clear that the rate data for *o*-substituted benzyl alcohols correlates well with Taft's σ_I,σ_R and Charton's ν values in which the -NO_2 and -COOH group is considered as orthogonal.

The regression coefficients of σ_I and σ_R are negative indicating that electron releasing groups accelerate the reaction. Also the negative regression coefficient for the steric term ν points out that the reaction is subject to steric retardation by the *ortho*-substituents.

The contribution of resonance parameters to the total effect of the *ortho*-substituents have also been determined at four temperatures. These values are given in Table-4. The values of % R are in the range of 39 to 42 % and the values of steric are in the range of 20 to 23 %.

TABLE-2
k_{obs} × 10^3 (s^{-1})

Substituents	293 K	303 K	313 K	323 K	$\Delta H^{\neq}$	$\Delta S^{\neq}$	R
-H	90.00	181.33	378.67	786.67	54.38	-79.55	0.999
-OCH_3	75.00	163.30	330.00	690.00	55.37	-17.50	0.999
-CH_3	41.00	96.00	205.00	440.00	59.46	-68.48	0.999
-C_2H_5	36.00	88.10	296.00	445.00	63.12	-57.13	0.999
-F	28.00	67.29	155.00	344.00	63.25	-58.81	0.999
-Cl	16.00	43.45	100.60	255.00	69.43	-42.32	0.999
-Br	16.00	45.70	106.60	260.00	69.94	-40.39	0.999
-I	14.00	36.36	94.62	225.00	70.55	-39.10	0.999
-NO_2	5.30	16.00	40.00	100.00	74.07	-35.45	0.999
-COOH	10.29	33.96	78.10	166.10	69.55	-43.79	0.996

TABLE-3

Substituent constants	λ	ρ_I	ρ_R	ν	R	SD	F	φ
$\sigma_I\sigma_R$	-1.0526	-1.1293	-0.937	–	0.9174	0.1471	0.1173	0.1311
$\sigma_{I\nu}$	-0.7062	-0.8841	–	-0.512	0.8320	0.1339	0.1068	0.1197
$\sigma_{R\nu}$	-0.8072	–	-1.0207	-0.582	0.8411	0.1999	0.1594	0.1782
$\sigma_I\sigma_{R\nu}$	-0.8652	-0.9790	-0.8392	-0.552	0.9921	0.0751	0.0598	0.0669
$\sigma_I\sigma_{R^\circ\nu}$	-0.8184	-0.9815	-0.9912	-0.462	0.9909	0.0579	0.0987	0.1119
$\sigma_I\sigma_R^{(BA)}{}_\nu$	-0.8389	-1.0214	-0.7916	-0.525	0.9884	0.0653	0.0848	0.0962
$\sigma_I\sigma_R^{-\nu}$	-0.7903	-0.8667	-0.6244	-0.525	0.9812	0.0829	0.0674	0.1217
$\sigma_I\sigma_R^{+\nu}$	-0.8387	-0.9717	-0.5324	-0.502	0.9828	0.0795	0.0825	0.0955

TABLE-4
TEMPERATURE DEPENDENCE OF THE REACTION CONSTANTS FOR THE OXIDATION OF *ortho*-SUBSTITUED BENZYL ALCOHOLS BY PHENYLIODOSO ACETATE

Temp. (K)	ρ_I	ρ_R	ν	SD	F	φ	P_R	P_S
293	-1.1323	-1.1910	-0.6963	0.0673	0.0383	0.0434	39.44	23.05
303	-0.9815	-0.9912	-0.5526	0.0579	0.0457	0.0496	39.25	21.85
313	-0.8933	-0.9183	-0.4845	0.0558	0.0585	0.0585	39.98	21.09
323	-0.7982	-0.8883	-0.4335	0.0612	0.1024	0.1024	41.90	20.40

REFERENCES

1. K. Pausaucker, *J. Chem. Soc.*, 107 (1953).
2. K. Vaidyanathan and N. Venkatasubramanian, *Indian J. Chem.*, **11**, 1146 (1973).
3. K. Rangarajan and I.M. Mathai, *Indian. J. Chem.*, **16B**, 1097 (1978).
4. P.S. Radhakrishnamurthi and H.P. Panda, *Gazz. Chem.*, **109**, 637 (1979).
5. C. Subas and B.P. Patil, *Dev. Phys. Chem.*, **26**, 176 (1981).
6. M. Uma and C.S. Kalavathi, *Curr. Sci.*, **51**, 412 (1982).
7. N. Bhavani and K. Lilly, *Oxid. Commun.*, **20**, 87 (1997).
8. K. Karunakaran, R. Gurumurthy and K.S. Narayanan, *Oxid. Commun.*, **16**, 351 (1993).
9. K. Karunakaran, S. Nagarajan, D. Kanagavel and T. Jegadish, *Oxid. Commun.*, **20**, 576 (1997).
10. G.A. Kraus and I. Kim, *Tetrahedron*, **59**, 7935 (2003).
11. R. Weizhong and D. Little, *Tetrahedron*, **65**, 10784 (2009)
12. J. Boeskan and G.C.C.C. Schneider, *J. Prakt. Chem.*, **131**, 285 (1931).
13. O. Exner, *Coll. Czech. Chem. Commun.*, **29**, 1094 (1964).
14. C. Srinivasan, S. Chellamani and A. Rajagopal, *J. Org. Chem.*, **50**, 1201 (1985).
15. K. Ganapathy and S. Kabilan, *Int. J. Chem. Kinet.*, **21**, 423 (1989).
16. S.K. Dayal, S. Ehrenson and R.W. Taft, *J. Am. Chem. Soc.*, **94**, 113 (1974).
17. C.G. Swain, S.H. Unger, N.R. Rosenquist and M.S. Swain, *J. Am. Chem. Soc.*, **105**, 492 (1985).
18. S. Ehrenson, R.T.C. Brownlee and R.W. Taft, *Progr. Phy. Org. Chem.*, **10**, 3 (1973).
19. O. Exner, *Coll. Czech. Chem. Commun.*, **31**, 3222 (1966).