Iridium(III) Catalyzed Oxidation of Benzyl Alcohol by Cerium(IV) Sulphate: A Kinetic and Synthetic Study

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Abstract: Oxidation of benzyl alcohol by cerium(IV) sulphate catalyzed by iridium(III) chloride was studied both from the kinetic and synthetic point of views. In the kinetic study reaction followed direct proportionality with respect to catalyst concentrations while first order kinetics at low concentrations becoming to zero order at higher concentrations of both oxidant and organic substrate was observed. Rate decreases sharply with increasing concentrations of H^+, Ce^{III} and Cl^- ions. Potential of cerium(IV)-iridium(III) system in synthesis was checked by changing the concentrations or conditions of various factors, which affect the yield of benzaldehyde. After a certain point increase in the duration of experiment or the concentration of oxidant and catalyst does not increase the yield and under the experimental conditions it was only the temperature, which may further increase the yield. Product was identified by various means.

Keywords: Cerium(IV)-iridium(III) system, benzyl alcohol, oxidation, benzaldehyde, oxidation product.

INTRODUCTION

Cerium(IV), an unusually strong one electron oxidant has been frequently used from the synthetic point of view [1]. Out of many salts of cerium(IV), ceric ammonium nitrate has specially been used for the synthesis of various organic compounds. Generally in the synthetic studies, use of transition metal ions as catalysts under homogeneous conditions has not been attended properly. Similar is the case with the use of cerium(IV) sulphate in synthetic work in which little attention has been paid to use transition metal ions as homogeneous catalysts. In the oxidation of organic compounds, use of iridium(III) chloride as a homogeneous catalyst has been given little attention due to its sluggish catalytic activity in alkaline medium [2,3]. To the contrary, during the kinetic studies it was observed by us [4-8] that iridium(III) chloride is a more efficient catalyst compared to even ruthenium(III) chloride or osmium teroxide. Moreover, when used in conjunction with cerium(IV) sulphate, iridium(III) chloride is capable of enhancing the oxidation of benzyl alcohol both from the synthetic as well as from the kinetic point of views. This prompted us to study the oxidation of benzyl alcohol with cerium(IV)-iridium(III) system from the kinetic point of view and these results were compared with the conditions under which maximum yield of product under synthetic conditions was obtained.

EXPERIMENTAL

Cerium(IV) sulphate (E. Merck) dissolved in 1:1 sulphuric acid, was titrated against the standard ferrous ammonium sulphate solution using ferroin as an internal indicator. Sodium hexachloroiridate(III) (Johonson Matthay & Co.) was dissolved in minimum amount of analytical grade HCl. Final concentrations of acid and the catalyst were 0.62×10^{-2}

M and 3.35×10^{-3} M respectively. All other chemicals used were of analytical grade or chemically pure substances. As aromatic alcohols are insoluble in aqueous medium therefore acetic acid was used as a solvent to make the system homogeneous. Considering the insolubility of aromatic alcohols in aqueous medium, stock solution of benzyl alcohol (Fluka A.G.) was dissolved in minimum amount of acetic acid and was diluted to the desired volume. Concentration of acetic acid was kept constant in all the variations except while studying the effect of acetic acid concentration on the rate. Ferrous ammonium sulphate solution was standardized with potassium dichromate (E. Merck) using N-phenyl anthranilic acid as an internal indicator. Progress of the reaction was measured (constant temperature $\pm 0.1°$ C) at different intervals of time by transferring 5.0 ml aliquot of reaction mixture to a fixed amount of ferrous ammonium sulphate solution (in slight excess to cerium (IV) sulphate initially taken) and estimating the residual ferrous ammonium sulphate with a standard cerium(IV) sulphate solution using ferroin as an internal indicator. In all kinetic runs concentration of aromatic aldehyde was kept in excess. For studying the reaction from the synthetic point of view, all reactants were taken in a round bottom flask kept in a water bath at a desired temperature for the desired time. After performing the reaction, contents were extracted with diethyl ether (3×25 ml). Organic part was washed three times with cold water to remove the excess of acetic acid and was again extracted with ether. After evaporating the solvent, hydrazone of the product was prepared by standard method [9]. Yellow precipitate of hydazone was filtered off and was weighed after proper drying. The product was identified with various methods.

KINETIC STUDY

In the case of oxidant variation $-dc/dt$ values were calculated at a fixed initial time in the individual plots, while in all other cases values were calculated at a fixed initial concentration. Rate values ($-dc/dt$) were obtained from the initial slopes of individual time plots. First order rate constants for molar concentrations were calculated by dividing $-dc/dt$ val-

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ues with the concentration of oxidant (k), organic substrate (k') or the catalyst (k"). Tables and figures contain initial concentrations of the reactants. Study could not be made at constant ionic strength of the medium due to large volumes of potassium chloride required to keep the ionic strength constant. However, effect of µ on the rate was studied separately with the help of a standard solution of potassium chloride. Product study was performed after ensuring complete oxidation of organic substrate by taking the oxidant in different ratios. After completion of the reaction, reaction mixture was extracted with diethyl ether (5 × 25 ml) and the solvent evaporated under reduced pressure. After re-crystallization with ethanol oxidation products was identified with the help of spot test method [10], chromatographic technique [11] and also by taking IR spectra of the product. Mp. of hydrazone of the product was found to be 239 °C (reported 241 °C). NMR (^{1}H NMR, Xeol 400 MHz in CdCl$_3$ with TMS as internal standard) signals were obtained at δ 11.3 (1H, s), δ 9.1 (2H, d), δ 8.1-8.3 (2H, m) and δ 7.2-7.9 (5H, m) (supplementary material).

First order plots between log of remaining concentration of oxidant versus time for the consumption of cerium(IV) sulphate show straight lines. However, at higher concentrations of the oxidant, probably due to the formation of complex, deviations in the later part of the reaction were pronounced. In the case of oxidant and substrate both (Table **1**), –dc/dt values increase proportionately and the first order rate constants for molar concentration (k and k' values respectively) show fair constancy at low concentrations, while at higher concentrations increase in –dc/dt values becomes less prominent and k and k' values start decreasing. On plotting –dc/dt versus [oxidant] or [organic substrate] (in the case of oxidant and the organic substrate both) (Fig. **1**), straight lines passing through the origin become parallel to x-axis at higher concentrations. All these facts collectively confirm that the rate shows direct proportionality with respect to oxidant and organic substrate both only at their low concentrations and tends to become independent of concentration at
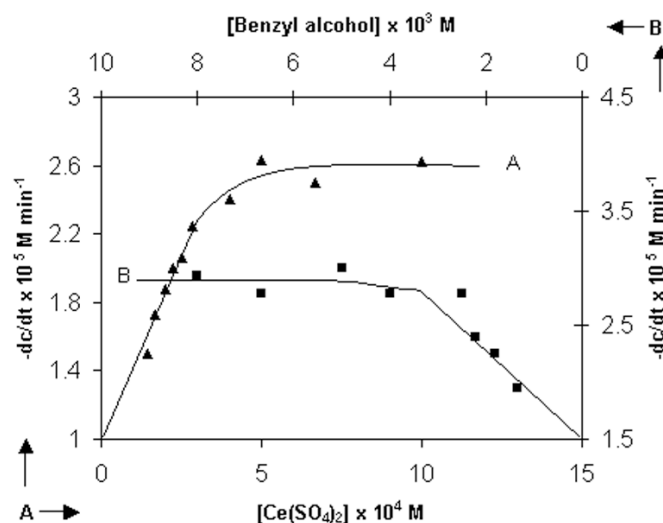

Fig. (1). Effect of variation of [Ce^{IV}] and [Benzyl alcohol] on the rate at 35 ^{0}C.

Variation of [Cerium(IV) sulphate] (A- Primary x-y axis)

[Benzyl alcohol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [CH$_3$COOH] = 0.10 M, [IrCl$_3$] = 1.0×10^{-6} M.

Variation of [Benzyl alcohol] (B- Secondary x-y axis)

[Ce(SO$_4$)$_2$] = 2.5×10^{-4} M, [H$_2$SO$_4$] = 1.0 M, [CH$_3$COOH] = 0.10 M, [IrCl$_3$] = 1.0×10^{-6} M.

higher concentrations of oxidant and organic substrate. Study at still lower concentrations in the case of organic substrate could not be performed because reaction becomes too slow to be measured properly, yet the trend of line can be obtained clearly. In the case of catalyst variation, straight line passing through the origin on plotting –dc/dt values versus [IrCl$_3$] (Fig. **2**), slope value of 1.00 on plotting double logarithmic graph between the rate and concentration of catalyst and constancy in k" values (18.13 ± 1.62) indicate that the reaction follows first order kinetics with respect to iridium(III)

Table 1.   Effect of Variation of [cerium(IV)], [Benyl alcohol] and [IrCl$_3$] on the Rate at 35°C

[Ce^{IV}] × 10^3 M	-dc/dt × 10^5 M min^{-1}	k = (-dc/dt/ [Ce^{IV}]) min^{-1}	[Benzyl Alcohol] × 10^3 M	-dc/dt × 10^5 M min^{-1}	k' = (-dc/dt / [Benzyl alcohol]) × 10^2 min^{-1}	[IrCl$_3$] × 10^6 M	-dc/dt × 10^5 M min^{-1}	k" = (-dc/dt / [IrCl$_3$]) min^{-1}
1.43	1.50	0.10	1.33	1.95	1.50	0.40	0.51	12.75
1.67	1.73	0.10	1.82	2.25	1.20	0.60	0.94	15.66
2.00	1.88	0.09	2.22	2.40	1.10	0.80	1.40	17.50
2.22	2.00	0.09	2.50	2.78	1.10	1.00	1.95	19.50
2.50	2.06	0.07	2.86	3.01	1.10	1.20	2.06	17.16
2.86	2.25	0.08	4.00	2.78	0.70	1.40	2.44	17.42
4.00	2.40	0.06	5.00	3.00	0.60	1.60	3.09	19.21
5.00	2.63	0.05	6.66	2.78	0.40	1.80	3.75	20.83
6.66	2.50	0.04	8.00	2.93	0.30	-	-	-
10.00	2.62	0.03	-	-	-	-	-	-

Variation of cerium(IV) sulphate: [Benzyl alcohol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [Acetic acid] = 0.10 M, [IrCl$_3$] = 0.67 x 10^{-6} M.
Variation of benzyl alcohol: [Ce(SO$_4$)$_2$] = 2.50×10^{-4} M, [H$_2$SO$_4$] = 1.0 M, [Acetic acid] = 0.10 M, [IrCl$_3$] = 0.67 x 10^{-6} M.
Variation of iridium(III) chloride: [Ce(SO$_4$)$_2$] = 2.50×10^{-4} M, [Benzyl alcohol] = 5.0×10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [Acetic acid] = 0.10 M.

chloride concentrations.–dc/dt values decrease with increasing concentrations of sulphuric acid and externally added $Ce_2(SO_4)_3$ (Table **2**) in the reaction mixture, indicating that these ions have retarding effect on the reaction velocity and are eliminated before the rate determining slow step. Large volumes of potassium chloride required to maintain ionic strength of the medium constant, restricted the study to be conducted at constant ionic strength of the medium. However, effect of change in ionic strength of the medium on the rate was studied with the help of a standard KCl solution. It was observed that the rate values go on decreasing with increasing concentration of externally added potassium chloride in the reaction mixture (Table **2**).
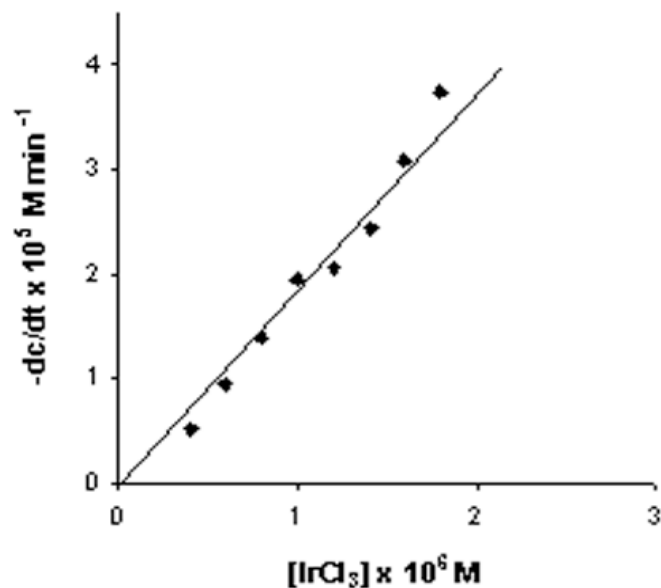

Fig. (2). Effect of variation of [IrCl$_3$] on the rate at 35 ^{0}C.

[Ce(SO$_4$)$_2$] = 2.5 × 10^{-4} M, [Benzyl alcohol] = 5.0 × 10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [CH$_3$COOH] = 0.10 M.

Arrhenius equation was found to be applicable and from the slopes of the Arrhenius plots and by using Eyring equation en-
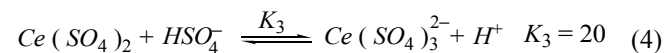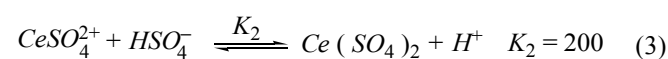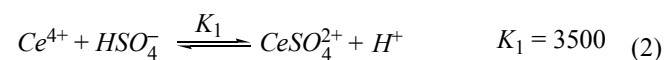
ergy of activation, entropy of activation and free energy of activation values were calculated, which were found to be 15.75 (K cal.), -30.90 (e.u.), 25.27 (K.cal. g^{-1}mole^{-1}) for benzyl alcohol.

It is known that $IrCl_3$ in hydrochloric acid gives $IrCl_6^{3-}$ species [12]. It has also been reported that iridium (III) and iridium (I) ions are the stable species of iridium [13]. Further, the aquation of $[IrCl_6^{3-}]$ gives $[IrCl_5(H_2O)^{2-}]$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_3(H_2O)_3]$ species [14-16]. This equilibrium may be shown by the general equation (1)

$$IrClH^{3-} + nH_2O \rightleftharpoons \left[IrCl_{6-n}(H_2O)_n\right]^{3-n} + Cl^- \qquad (1)$$
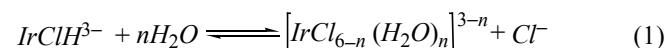
Considering our experimental results and positive effect of chloride ions on the rate, [2,3] $IrCl_5(H_2O)^{2-}$ has been considered to be the reactive species of iridium (III) chloride in the present study.

Cerium(IV) forms a number of complexes in sulphuric acid solution. Hardwick and Robertson [17] have reported the following equilibrium between various complexes in sulphuric acid solutions of 2 M ionic strength at 25 $^{\circ}$C.

$$Ce^{4+} + HSO_4^- \xrightleftharpoons{K_1} CeSO_4^{2+} + H^+ \qquad K_1 = 3500 \qquad (2)$$

$$CeSO_4^{2+} + HSO_4^- \xrightleftharpoons{K_2} Ce(SO_4)_2 + H^+ \qquad K_2 = 200 \qquad (3)$$

$$Ce(SO_4)_2 + HSO_4^- \xrightleftharpoons{K_3} Ce(SO_4)_3^{2-} + H^+ \qquad K_3 = 20 \qquad (4)$$

Under our experimental conditions, probably [cerium(IV)]$_{Total}$ is mainly present as $Ce(SO_4)_2$. Concentration of Ce^{4+} species in a solution having [cerium(IV)] = 0.00025 M, and [H$_2$SO$_4$] = 1.0 M may be calculated from (5), which has been derived from equations (2) and (3). The value is found to be 1.0 x 10^{-10} M.

$$\left[Cerium\,(IV)\right]_{Total} = \left[Ce^{4+}\right]\left[1 + \frac{K_1[HSO_4^-]}{[H^+]} + \frac{K_1K_2[HSO_4^-]^2}{[H^+]^2}\right] \qquad (5)$$

Table 2.   Effect of Variation of [H$^+$], [Ce$_2$(SO$_4$)$_3$] and [Cl$^-$] on the Rate at 35°C

[H$^+$] M	-dc/dt × 10^5 M min^{-1}	[Ce$_2$(SO$_4$)$_3$] × 10^4 M	-dc/dt × 10^5 M min^{-1}	[Cl$^-$] M	-dc/dt × 10^5 M min^{-1}
0.30	-	1.00	-	0.10	1.13
0.40	6.00	1.43	1.95	0.30	1.07
0.50	4.95	1.66	1.73	0.40	1.05
0.60	3.32	2.00	1.67	0.50	1.02
0.70	2.25	2.22	1.67	0.60	0.83
0.80	-	2.25	1.50	-	-
1.00	1.95	2.86	1.39	-	-
1.10	1.83	3.00	-	-	-
1.20	-	3.33	1.31	-	-
1.30	1.20	4.00	-	-	-
1.40	1.31	5.00	-	-	-

Variation of sulphuric acid: [Benzyl alcohol] = 5.0 × 10^{-3} M, [Ce(SO$_4$)$_2$] = 2.50 × 10^{-4} M, [Acetic acid] = 0.10 M, [IrCl$_3$] = 1.00 × 10^{-6} M.
Variation of cerium(III) sulphate: [Benzyl alcohol] = 5.0 × 10^{-3} M, [Ce(SO$_4$)$_2$] = 2.50 × 10^{-4} M, [H$_2$SO$_4$] = 1.0 M, [Acetic acid] = 0.10 M, [IrCl$_3$] = 1.00 × 10^{-6} M.
Variation of potassium chloride: [Benzyl alcohol] = 5.0 × 10^{-3} M, [Ce(SO$_4$)$_2$] = 2.50 × 10^{-4} M, [H$_2$SO$_4$] = 1.0 M, [Acetic acid] = 0.10 M, [IrCl$_3$] = 1.00 × 10^{-6} M.

Range of concentration of acid in which the present study was performed and the steep fall in rate of the reaction with increasing concentration of sulphuric acid indicates that the other species would be present in insignificantly small concentrations and may be considered negligible. Thus, $Ce(SO_4)_2$ has been taken as the reactive species of cerium(IV) in aqueous sulphuric acid medium, which has been considered by other workers also [18,19]. Based on these results the probable scheme for the oxidation of benzyl alcohol may be given as in Scheme 1.

Cerium(IV) forms 1:1 complexes of the type $[ROH.Ce(IV)]^{4+}$ with alcohols [20] and ketones [21] with the elimination of cerium(III) and H^+ ions. Michaelis-Menten type of kinetics [22] and similar results in case of ketones [4-6, 23,24] and cyclic alcohols [25,26] is also very well documented. Strong retarding effect of Ce^{III} and H^+ ions on the rate clearly suggests their elimination before the rate-determining step. Changing orders from one to zero, constancy in k and k' values only in the beginning when complex formation is small and pronounced deviations at higher concentrations of cerium(IV) or organic substrate, supports the formation of complex between cerium(IV) and the organic substrate in our case.

Considering the equilibrium concentrations in steps (I), (II) and (III) of the Scheme 1 and putting the concentrations of $IrCl_6^{3-}$ and $IrCl_5(H_2O)^{2-}$ from steps (I) and (III) of the mechanism, total concentration of catalyst ($[Ir^{III}]_T$) may be given as

$$[Ir^{III}]_T = \frac{[C_2][Ce^{III}][H^+][Cl^-]}{K_1K_3[C_1]} + \frac{[C_2][Ce^{III}][H^+]}{K_3[C_1]} + C_2 \quad (6)$$

Thus, the rate in terms of decreasing concentration of cerium (IV) from step (III) of the mechanism may be given as

$$-\frac{d[Ce^{IV}]}{dt} = \frac{2kK_1K_2K_3[Ce^{IV}][S][Ir^{III}]_T}{[Ce^{III}][H^+][Cl^-] + K_1[Ce^{III}][H^+] + K_1K_2K_3[Ce^{IV}][S]} \quad (7)$$

This equation explains all experimental findings. Equation (7) under the condition when $[Cl^-] \gg K_1$ may also be written in the form of equation (8) as

$$-\frac{d[Ce^{IV}]}{dt} = \frac{2kK_1K_2K_3[Ce^{IV}][S][Ir^{III}]_T}{[Ce^{III}][H^+][Cl^-] + K_1K_2K_3[Ce^{IV}][S]} \quad (8)$$

This equation explains all experimental findings. At low concentrations of oxidant and organic substrate the inequality $[Ce^{III}][H^+][Cl^-] \gg K_1 K_2 [Ce^{IV}][S]$ may hold and the equation (8) reduces to (9) which, explains the nature shown by various reactants at low concentrations.

$$-\frac{d[Ce^{IV}]}{dt} = \frac{2kK_1K_2K_3[Ce^{IV}][S][Ir^{III}]_T}{[Ce^{III}][H^+][Cl^-]} \quad (9)$$

At higher concentrations of oxidant and substrate the reverse inequality $[Ce^{III}][H^+][Cl^-] \ll K_1K_2K_3[Ce^{IV}][S]$ holds good and the equation (8) becomes

$$-\frac{d[Ce^{IV}]}{dt} = 2k[Ir^{III}]_T \quad (10)$$

Further verification of the rate law may be given by re-writing the equation (7) as

$$\frac{1}{-dc/dt} = \frac{[Ce^{III}][H^+][Cl^-]}{2kK_1K_2K_3[Ce^{IV}][S][Ir^{III}]_T}$$
$$+ \frac{[Ce^{III}][H^+]}{2kK_2K_3[Ce^{IV}][S][Ir^{III}]_T} + \frac{1}{2k[Ir^{III}]_T} \quad (11)$$

$kK_1K_2K_3$ values calculated from the slopes of graphs between 1/rate versus $1/[Ce^{IV}]$, 1/[substrate] and $[H^+]$, come out to be 2.0 (x 10^7), 6.0 (x 10^6) and 0.80 (x 10^7). Fair constancy in the $kK_1K_2K_3$ values calculated from three different graphs further indicates the validity of the scheme 1 and the rate law (8). While calculating the rate values concentration of cerium(III) sulphate was neglected because cerium(III) produced in the reaction mixture in the range where –dc/dt values were calculated, will be quite small and it can be neglected for the sake of simplicity. Absence of any reaction between the organic substrate and iridium^{III} rules out the possibility of interaction between these two giving rise to the complex C_2 in second step of Scheme-1. Negative effects of cerium(III), hydrogen ions and chloride ions on the rate shows the possibility of their release before the rate-determining step. Thus we can safely assume the validity of the final rate law and at least formation of the complexes before the rate-determining step.

SYNTHETIC STUDY

It was observed that increase in the amount of iridium(III) chloride in the reaction mixture increases the yield in the beginning but after reaching to a maximum further increase in the amount of catalyst does not affect the yield (entries 1-4, Table **3**). Effect of change of the amount of cerium(IV) sulphate on the yield becomes clear from the entries 5-9 in Table **3**. It is observed that initially the yield increases with increasing amount of the oxidant in the reaction mixture but after a certain point yield starts decreasing. Increase in the temperature of the reaction mixture continuously increases the yield (entries 10-13, Table **3**). However, the effect of temperature on yield was not studied above 100 ℃ considering economy of the system. Increasing duration of the experiment initially increases the yield but after reaching to a maximum further increase in the duration of experiment does not affects the yield.

In the synthetic study contrary to the kinetic results it was observed that higher concentrations of cerium(IV) start decreasing the yield. Reason of this behaviour may be due to the fact that in the kinetic study, while studying the effect of variation of oxidant concentration on the rate, concentration of sulphuric acid was kept constant. As cerium(IV) sulphate was prepared in sulphuric acid, increase in the [oxidant] also increases $[H^+]$ in the reaction mixture which strongly retards the reaction velocity. Increase in the amount of iridium(III) chloride in the reaction mixture initially increases the yield but after reaching to a maximum the yield becomes constant. Probable reason for the different behaviour at higher catalyst concentrations may be due to the fact that in the synthetic study concentration of catalyst was much higher compared to that in the kinetic study. At such a higher concentration catalyst also may form complex with the organic substrate or the

Table 3.   Effect of Various Factors on the Yield of Benzaldehyde

Entry No.	[IrCl$_3$] x 10^4 (mmol)	[Ce(SO$_4$)$_2$] (mmol)	Temperature (^{0}C)	Time (min)	% Yield
1	1.67	2.0	100	120	12.68
2	3.34	2.0	100	120	16.30
3	5.01	2.0	100	120	16.30
4	6.68	2.0	100	120	16.30
5	3.34	1.0	100	120	10.86
6	3.34	2.0	100	120	16.30
7	3.34	2.5	100	120	16.30
8	3.34	3.0	100	120	18.11
9	3.34	4.0	100	120	12.68
10	3.34	3.0	50	120	7.24
11	3.34	3.0	60	120	9.0
12	3.34	3.0	80	120	10.86
13	3.34	3.0	100	120	18.11
14	3.34	3.0	100	60	10.86
15	3.34	3.0	100	120	18.11
16	**3.34**[*]	**3.0**[*]	**100**[*]	**180**[*]	**21.73**[*]
17	3.34	3.0	100	240	21.73

[Benzyl alcohol] = 1.0 mmol, [Acetic acid] = 170 mmol.
[*]Optimum conditions for maximum yield.

oxidant. Constancy of the yield after an optimum duration of experiment may be due to the reason that higher temperature (100 $^\circ$C) may start some side reactions or part of the product may be further oxidized to acid.

REFERENCES

[1]   Ho, T.L. In *Organic Synthesis by Oxidation With Metal Compounds,* Mijs, W.J.; de Jonge, C.R.H. Eds.; Plenum: New York, **1986**, pp. 569-631.
[2]   Manibala; Singh, H.S.; Krishna, B.; Tandon, P.K. *J. Indian Chem. Soc.,* **1985**, *62*, 434.
[3]   Singh, M.P.; Tandon, P.K.; Singh, R.M.; Mehrotra, A. *J. Indian Chem. Soc.,* **1990**, *67*, 458.
[4]   Tandon, P.K.; Sahgal, S.; Singh, A.K.; Gayatri; Purwar, M. *J. Mol. Catal. A: Chem.*, **2005**, *232*, 83.
[5]   Tandon, P.K.; Sahgal, S.; Gayatri; Purwar, M.; Dhusia, M. *J. Mol. Catal. A*: *Chem.*, **2006**, *250*, 203.
[6]   Tandon, P.K.; Sahgal, S.; Singh, A.K.; Kumar, S.; Dhusia, M. *J. Mol. Catal. A*: *Chem.*, **2006**, *258*, 320.
[7]   Tandon, P.K.; Srivastava, M.; Singh, S.B.; Singh, S. *Synth. Commun.,* **2008**, *38*, 1.
[8]   Tandon, P.K.; Srivastava, M.; Singh, S.B.; Srivastava, N. *Synth. Commun.,* **2008**, *38*, 2125.
[9]   Shriner, R.L.; Hermann, C.K.F.; Morrill, T.C.; Curtin, D.Y.; Fuson, R.C. *The Systematic Identification of Organic Compounds*, Wiley & Sons: New York, **1998**, pp. 321-2.
[10]   Feigl, F. *Spot tests in organic chemistry*, Elsevier, New York, **1960**, p. 369.
[11]   Mikes, O. *Laboratory handbook of chromatographic methods*, Chap. 2, D. Van Nostrand Co. Ltd., London, **1966**, p. 96.
[12]   Chang, J.C.; Garner, C.S. *Inorg. Chem.,* **1965**, *4*, 209.
[13]   Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. *Advanced inorganic chemistry*, Wiley- Interscience, **1999**, p.1039.
[14]   Kravtsov, V.I.; Petrova, G.M. *Russ. J. Inorg. Chem.,* **1964**, *9*, 552.
[15]   Poulsen, I.A.; Garner, C.S.; *J. Am. Chem. Soc.,* **1962**, *84*, 2032.
[16]   Domingos, A.P.J.; Domingos, A.M.T.S.; Gabral, J.M.P. *J. Inorg. Nucl. Chem.,* **1969**, *31*, 2568.
[17]   Hardwick, T.J.; Robertson, E. *Can. J. Chem.,* 1951, *29*, 828.
[18]   Sankhla, P.S.; Mehrotra, R.N. *J. Inorg. Nucl. Chem.,* **1972**, *34*, 3781.
[19]   Sankhla, P.S.; Mehrotra, R.N. *J. Inorg. Nucl. Chem.,* **1973**, *35*, 891.
[20]   Young, L.B.; Trahanovsky, W.S. *J. Am. Chem. Soc.,* **1969**, *91*, 5060.
[21]   Littler, J.S. *J. Chem. Soc.,* **1962**, 832.
[22]   Muhammad, S.S.; Rao, K.V. *Bull. Chem. Soc. Jp.,* 1963, 36, 943.
[23]   Shorter, J. *J. Chem. Soc.,* **1950**, 3425.
[24]   Shorter, J.; Hinshelwood, S.C. *J. Chem. Soc.,* **1950**, 3276.
[25]   Hintz, H.L.; Johnson, D.C. *J. Org. Chem.,* **1967**, *32*, 556.
[26]   Tandon, P.K.; Singh, A.K.; Sahgal, S.; Kumar, S. *J. Mol. Catal. A*: *Chem.*, **2008**, *282*,136.