

# Kinetics of hexachloroiridate(IV) reduction by some aryl alcohols in sodium acetate–acetic acid buffer medium

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**ABSTRACT:** The kinetics of the reduction of hexachloroiridate(IV) by benzyl alcohol (PhCH<sub>2</sub>OH), some substituted benzyl alcohols (XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH, where X = NO<sub>2</sub>, Cl and OMe), and benzhydrol (Ph<sub>2</sub>CHOH) to give benzaldehyde, the corresponding substituted benzaldehydes and benzophenone, respectively, were investigated in sodium acetate–acetic acid buffer medium. A mechanism is proposed involving the formation of an intermediate 1:1 complex between iridium(IV) and the alcohol, followed by the decomposition of the complex to give products through the formation of free radicals. Thermodynamic parameters associated with the equilibrium step and activation parameters associated with the rate-determining step were also evaluated. Copyright © 2000 John Wiley & Sons, Ltd.

**KEYWORDS:** hexachloroiridate (IV); reduction; aryl alcohols; kinetics

## INTRODUCTION

The reactivities of some aliphatic alcohols towards hexachloroiridate(IV) have been reported,<sup>1</sup> but no attempt has been made to study the reactivities of aryl alcohols towards this oxidant. This paper describes an investigation of the kinetics and mechanism of the reduction of hexachloroiridate(IV) by benzyl alcohol and its substituted derivatives in sodium acetate–acetic acid buffer in the pH range 3.42–4.45. Since the substituted alcohols are insoluble in water, the reactions were carried out in 15% *tert*-butyl alcohol under comparable experimental conditions.

## RESULTS AND DISCUSSION

The kinetics of the reactions were followed spectrophotometrically at 488 nm, where IrCl<sub>6</sub><sup>2-</sup> absorbs to a considerably greater extent than any of the other reactants or products.<sup>2</sup> The effect of oxidant concentration on the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) was studied by varying the initial [Ir(IV)] in the range (0.5–5.0) × 10<sup>-4</sup> mol dm<sup>-3</sup>, keeping [aryl alcohol], pH and temperature constant at 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, 4.45 and 318 K, respectively. The values of  $k_{\text{obs}}$  were found to be independent of [Ir(IV)], as shown in Table 1. The fact that the  $k_{\text{obs}}$  values do not differ widely from each other indicates that the reactions probably take place by a common mechanism.

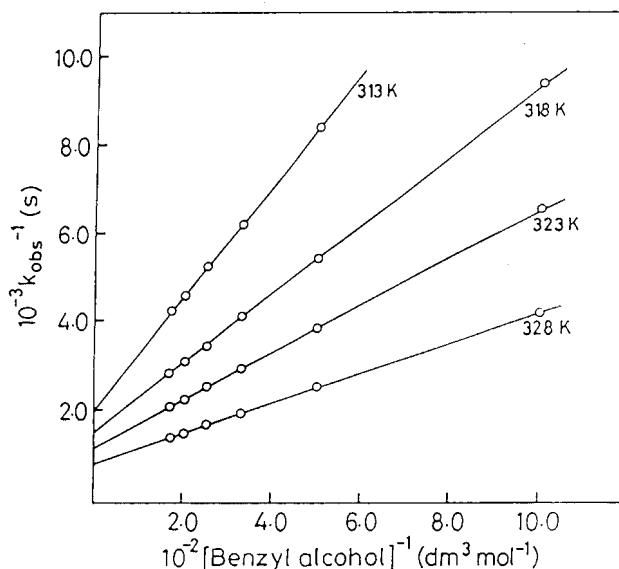
The effect of variation of alcohol concentration on the

pseudo-first-order rate constant was also studied at constant [Ir(IV)] and pH of 1.12 × 10<sup>-4</sup> mol dm<sup>-3</sup> and 4.45, respectively, but at different temperatures. The values of  $k_{\text{obs}}$  increases with increase in the substrate concentration. A double reciprocal plot was obtained when 1/ $k_{\text{obs}}$  was plotted versus 1/[XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH] for each reaction. Typical plots are shown in Fig. 1. This indicates that the reaction proceeds via a 1:1 intermediate complex. In addition to this kinetic evidence for complex formation, the abrupt increase in absorbance at 488 nm on addition of the substrates to Ir(IV) in buffer medium is also suggestive of the formation of a complex between the reactants. From the slope and intercept of each plot of 1/ $k_{\text{obs}}$  versus 1/[XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH], the value of  $K_{\text{e}}$  (the equilibrium constant for complex formation) and  $k_{\text{d}}$  (the constant for the rate-limiting step) were calculated at the four different temperatures.

**Table 1.** Values of pseudo-first-order rate constants of the oxidations of aryl alcohols in 15% *tert*-butyl alcohol at 318 K with [IrCl<sub>6</sub><sup>2-</sup>] = (0.5–5.0) × 10<sup>-4</sup> mol dm<sup>-3</sup>, [aryl alcohol] = 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> and pH = 4.45

| Substrate                       | $k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$ |
|---------------------------------|--|
| Benzyl alcohol                  | 1.84 ± 0.05  |
| <i>o</i> -Methoxybenzyl alcohol | 2.59 ± 0.08  |
| <i>m</i> -Methoxybenzyl alcohol | 1.69 ± 0.03  |
| <i>p</i> -Methoxybenzyl alcohol | 2.44 ± 0.07  |
| <i>o</i> -Nitrobenzyl alcohol   | 1.94 ± 0.05  |
| <i>m</i> -Nitrobenzyl alcohol   | 1.82 ± 0.04  |
| <i>p</i> -Nitrobenzyl alcohol   | 1.98 ± 0.05  |
| <i>o</i> -Chlorobenzyl alcohol  | 1.63 ± 0.04  |
| <i>m</i> -Chlorobenzyl alcohol  | 1.65 ± 0.04  |
| <i>p</i> -Chlorobenzyl alcohol  | 1.72 ± 0.05  |
| Benzhydrol                      | 2.25 ± 0.06  |

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**Figure 1.** Variation of pseudo-first-order rate constant with [benzyl alcohol]. Plots of  $k_{\text{obs}}^{-1}$  versus  $[\text{benzyl alcohol}]^{-1}$  at different temperatures.  $[\text{Ir}^{\text{IV}}] = 1.12 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $\text{pH} = 4.45$

The influence of pH on the rate of the reaction was studied at  $[\text{PhCH}_2\text{OH}]$ ,  $[\text{Ir}(\text{IV})]$  and temperature of  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $1.12 \times 10^{-4} \text{ mol dm}^{-3}$  and 318 K, respectively, in 15% *tert*-butyl alcohol. The ionic strength of each run was adjusted to  $0.1 \text{ mol dm}^{-3}$  by the addition of sodium perchlorate. The change of pseudo-first-order rate constants with pH is insignificant in the range 3.42–4.45.

The effect of variation of solvent polarity on the pseudo-first-order rate constant was also studied for the oxidation of benzyl alcohol by iridium(IV). The value of  $k_{\text{obs}}$  increases with increase in the dielectric constant of the solvent. For compositions of *tert*-butyl alcohol in water of 0, 15, 20, 25 and 30% (v/v), the values of  $k_{\text{obs}}$  were found to be  $3.69 \times 10^{-4}$ ,  $1.84 \times 10^{-4}$ ,  $1.39 \times 10^{-4}$ ,  $0.96 \times 10^{-4}$  and  $0.73 \times 10^{-4} \text{ s}^{-1}$ , respectively. The concentrations of reactants, pH and temperature were the same as in Table 1.

The enthalpy change ( $\Delta H^\circ$ ) associated with the equilibrium step was calculated from the slope of the plot of  $\log K_e$  versus  $1/T$ . The corresponding change of entropy ( $\Delta S^\circ$ ) was calculated from the relation

$$\log K_e = [\Delta S^\circ - (\Delta H^\circ/T)]/2.303R \quad (1)$$

The enthalpy of activation  $\Delta H^\ddagger$ , was obtained from the plot of  $\log(k_d/T)$  versus  $1/T$  followed by the evaluation of the entropy of activation  $\Delta S^\ddagger$ , using the theory of absolute reaction rate, the equation being

$$k_d = RT(e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R})/Nh \quad (2)$$

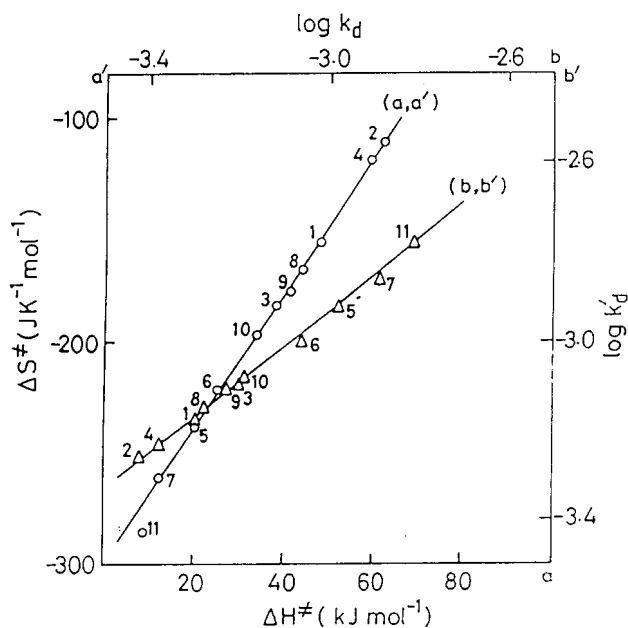
where  $R$ ,  $N$  and  $h$  have their usual meanings. The  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values for the different reactions are recorded in Table 2. The enthalpy of activation is linearly related to the entropy of activation ( $r = 0.9973$ ). This indicates that all the aryl alcohols follow the same mechanistic pathway. The isokinetic behaviour is also supported by the linear plot of  $\log k_d$  versus  $\log k_d'$  ( $r = 0.9988$ ), where  $k_d$  and  $k_d'$  are constants for the rate-limiting step at 313 K ( $T_1$ ) and 318 K ( $T_2$ ), respectively. (Fig. 2). The isokinetic temperature  $\beta$  was found to be 339 K using the relation  $\beta = T_1 T_2 (1-f)/(T_1 - T_2 f)$ , where  $f$  is the slope of the Exner plot.<sup>3</sup> The value of  $\beta$  which is higher than  $T$ , the mid-point of the experimentally used range of temperatures, indicates that the reactions are enthalpy controlled.<sup>4</sup>

Alcohols are known to be weak proton acceptors and since the present reactions were studied at lower acidity ( $10^{-4} \text{ mol dm}^{-3}$ ), the possibility of the formation of  $\text{XC}_6\text{H}_4\text{CH}_2\text{OH}_2^+$  can be discounted. Consequently, the molecular forms of the alcohols react with hexachloroiridate(IV), which is kinetically fairly inert.<sup>5</sup>

The reaction may take place through the intermediate formation of a transition state in which an electron is transferred to give  $[\text{RCHOH}_2^+ \cdots \text{IrCl}_6^{3-}]$  followed by the deprotonation of the intermediate species to give  $\text{PhCHOH}$  and  $\text{IrCl}_6^{3-}$ . However, the deprotonation of the intermediate transition state is likely to be very fast. The

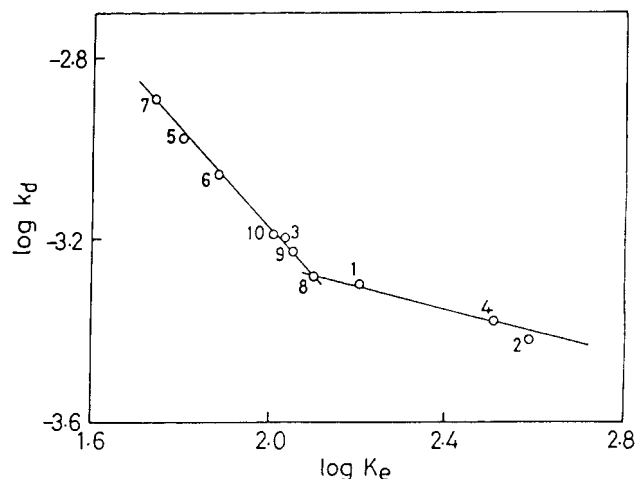
**Table 2.** Thermodynamic data associated with the 1:1 complex formation and activation parameters associated with the slowest step of the oxidations of aryl alcohols by iridium(IV)

| Substrate                       | $\Delta H^\circ$ (kJ mol <sup>-1</sup> ) | $\Delta S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> ) | $\Delta H^\ddagger$ (kJ mol <sup>-1</sup> ) | $\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|---------------------------------|--|---|---|--|
| Benzyl alcohol                  | 27 ± 4                                   | 43 ± 13   | 48 ± 2                                      | -156 ± 7   |
| <i>o</i> -Methoxybenzyl alcohol | 11 ± 4                                   | -15 ± 13  | 63 ± 2                                      | -112 ± 7   |
| <i>m</i> -Methoxybenzyl alcohol | 38 ± 2                                   | 84 ± 7  | 38 ± 2                                      | -184 ± 7   |
| <i>p</i> -Methoxybenzyl alcohol | 17 ± 2                                   | 5 ± 7   | 60 ± 2                                      | -120 ± 7   |
| <i>o</i> -Nitrobenzyl alcohol   | 67 ± 2                                   | 180 ± 7   | 20 ± 2                                      | -239 ± 7   |
| <i>m</i> -Nitrobenzyl alcohol   | 56 ± 4                                   | 143 ± 13  | 25 ± 2                                      | -223 ± 7   |
| <i>p</i> -Nitrobenzyl alcohol   | 72 ± 2                                   | 197 ± 7   | 12 ± 4                                      | -261 ± 13  |
| <i>o</i> -Chlorobenzyl alcohol  | 32 ± 4                                   | 62 ± 13   | 44 ± 4                                      | -168 ± 13  |
| <i>m</i> -Chlorobenzyl alcohol  | 35 ± 2                                   | 73 ± 7  | 41 ± 2                                      | -177 ± 7   |
| <i>p</i> -Chlorobenzyl alcohol  | 41 ± 4                                   | 92 ± 13   | 34 ± 4                                      | -197 ± 13  |
| Benzhydrol                      | 77 ± 4                                   | 212 ± 13  | 9 ± 4                                       | -286 ± 13  |



**Figure 2.** Isokinetic plots of the oxidations of aryl alcohols by hexachloroiridate(IV) in buffer medium. (a, a') Plot of  $\Delta S^\ddagger$  versus  $\Delta H^\ddagger$ ; (b, b') plot of  $\log k_d$  versus  $\log k_d$ . 1, Benzyl alcohol; 2, *o*-methoxybenzyl alcohol; 3, *m*-methoxybenzyl alcohol; 4, *p*-methoxybenzyl alcohol; 5, *o*-nitrobenzyl alcohol; 6, *m*-nitrobenzyl alcohol; 7, *p*-nitrobenzyl alcohol; 8, *o*-chlorobenzyl alcohol; 9, *m*-chlorobenzyl alcohol; 10, *p*-chlorobenzyl alcohol; 11, benzhydrol

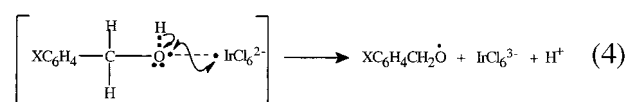
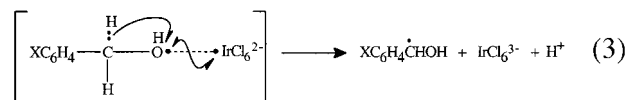
reaction therefore takes place by the alternative path where the oxidation takes place via an intermediate 1:1 complex. The complex is most probably an unstable seven-coordinated species in which the alcohol moiety occupies the seventh coordination site,<sup>6</sup> through the lone pair of electrons on oxygen. There is also published evidence<sup>7,8</sup> of the rapid reversible formation of metal-alcohol complexes with some transition metal ions. The 1:1 complex then decomposes to give the free radical in the rate-determining step. The free radical further reacts



**Figure 3.** First Hammett plot of  $\log k_d$  versus  $\log K_e$  for the oxidations of substituted benzyl alcohols. 1–11 as in Fig. 2

with another Ir(IV) to give the product carbonyl compound and Ir(III). The formation of free radicals in the present study is evidenced by the formation of polymerized products when vinyl compounds are added to the reaction mixtures. The kinetic pattern remained unaltered when the reaction was studied in the presence of oxygen and aldehyde was found to be the reaction product. Hence the possibility that free radicals react with  $O_2$  may be discounted.

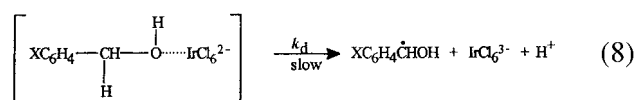
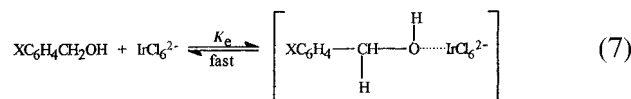
The free radical may be obtained by either of the two steps (3) or (4):



Spin trapping studies<sup>9</sup> during the oxidation of benzyl alcohol by hexachlorometallate ions ( $\text{MCl}_6^{2-}$ , where M = Ir, Pd and Pt) have shown the formation of  $\text{PhCH}_2\text{O}^\cdot$  in pure alcoholic medium, whereas in alcohol-water mixtures the radical  $\text{Ph}\dot{\text{C}}\text{HOH}$  is formed either directly or by secondary reactions of  $\text{PhCH}_2\text{O}^\cdot$ , i.e. the H-atom transfer reaction [step (5)] or the water-promoted isomerization reaction<sup>10</sup> [step (6)]:



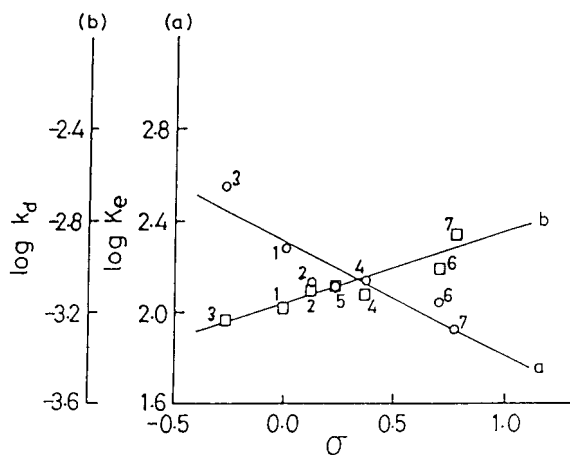
Since the present reactions were studied in alcohol-water mixture, it is suggested that  $\text{XC}_6\text{H}_4\dot{\text{C}}\text{HOH}$  reacts with the oxidant as shown in step (9). The steps of the reaction are as follows:



The reactions obey the following rate expression:

$$-\frac{d[\text{IrCl}_6^{2-}]}{dt} = \frac{k_d K_e [\text{IrCl}_6^{2-}] [\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]}{1 + K_e [\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]} \quad (10)$$

$$k_{\text{obs}} = \frac{k_d K_e [\text{IrCl}_6^{2-}] [\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]}{1 + K_e [\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]} \quad (11)$$



**Figure 4.** Plots of  $\log k_d$  and  $\log K_e$  versus Hammett  $\sigma$  values. 1–11 as in Fig. 2

where

$$k_{\text{obs}} = \frac{1}{[\text{IrCl}_6^{2-}]} \frac{-d[\text{IrCl}_6^{2-}]}{dt} \quad (12)$$

Therefore,

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_d} + \frac{1}{k_d K_e [\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]} \quad (13)$$

The plot of  $1/k_{\text{obs}}$  against  $1/[\text{XC}_6\text{H}_4\text{CH}_2\text{OH}]$  would give a straight line with a positive intercept and positive slope. This was found to be true experimentally.

The effects of substituents on the rate were studied under comparable experimental conditions. The  $k_d$  values for the slow step are found to follow the order  $\text{NO}_2 > \text{Cl} > \text{H} > \text{OMe}$  for the substituted benzyl alcohols. An attempt was also made to correlate the values of  $k_d$  and  $K_e$  of the different substituted alcohols. The first Hammett plot<sup>11</sup> of  $\log k_d$  against  $\log K_e$  is shown in Fig. 3. The plots of  $\log K_e$  and  $\log k_d$  versus  $\sigma^2$  (the Hammett substituent constants) are linear ( $\rho$  values  $-0.429$  and  $0.313$  for the *m*- and *p*-substituted benzyl alcohols, respectively) (Fig. 4).

According to the mechanistic scheme, the electron-donating or electron-withdrawing character of the substituent X should have a marked effect on the rate of the reaction.<sup>13,14</sup> When X is the electron-donating methoxy group, formation of the intermediate complex is favoured owing to greater availability of the lone pair of electrons on the oxygen of the alcohol's OH group. This is supported by the high  $K_e$  and low  $k_d$  values for the *o*- and *p*-methoxy alcohols. The *m*-methoxy alcohol shows higher  $k_d$  and lower  $K_e$  values than its *o*- and *p*-isomers because the *m*-methoxy group does not have an electron-donating mesomeric effect.<sup>11</sup> On the other hand, the electron-withdrawing nitro group lowers the  $K_e$  values for the nitro-substituted benzyl alcohols. The radical intermediate  $\text{XC}_6\text{H}_4\dot{\text{C}}\text{HOH}$  formed in the slow step is highly stabilized by the electron-withdrawing  $\text{NO}_2$  group. Consequently, the rate of decomposition of the complexes with electron-withdrawing substituents is likely to be higher. This explains the relatively higher  $k_d$  values for the  $\text{NO}_2$  derivatives. The effect of substituents on the values of  $k_d$  and  $K_e$  is also reflected in the V-shaped plot obtained when  $\log k_d$  is plotted against  $\log K_e$  for the oxidations of aryl alcohols by this oxidant (Fig. 3). The formation of the highly stabilized radical  $\text{Ph}_2\dot{\text{C}}\text{OH}$  in the slow step of benzhydrol oxidation provides the driving force for the reaction and accounts for its high reactivity.

## EXPERIMENTAL

$\text{Na}_2\text{IrCl}_6$  (Aldrich) and the aryl alcohols (Aldrich or Lancaster) were used. Inorganic materials were of the highest available purity. Hexachloroiridate(IV) solutions were standardized spectrophotometrically at the absorption maximum for  $\text{IrCl}_6^{2-}$ .<sup>15</sup> All solutions were made with doubly distilled water. The absorbances were measured on a Systronics (India) spectrophotometer, the cell compartment of which was kept at constant temperature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 300 spectrometer. Melting-point determina-

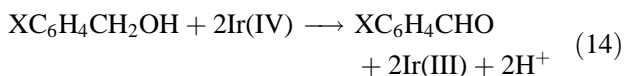
**Table 3.** Yields and observed and literature melting-points of the 2,4-DNP derivatives of the oxidation products in *tert*-butyl alcohol

| Substrate                       | Yield (%) | M.P. of derivative (°C) | Literature m.p. (°C) |
|---------------------------------|-----------|-------------------------|----------------------|
| Benzyl alcohol                  | 76        | 235                     | 237                  |
| <i>o</i> -Methoxybenzyl alcohol | 56        | 251                     | 253                  |
| <i>m</i> -Methoxybenzyl alcohol | 58        | 230                     | 232                  |
| <i>p</i> -Methoxybenzyl alcohol | 51        | 252–253                 | 253                  |
| <i>o</i> -Nitrobenzyl alcohol   | 74        | 263–264                 | 265                  |
| <i>m</i> -Nitrobenzyl alcohol   | 68        | 291                     | 292                  |
| <i>p</i> -Nitrobenzyl alcohol   | 62        | 318–319                 | 320                  |
| <i>o</i> -Chlorobenzyl alcohol  | 66        | 207                     | 209                  |
| <i>m</i> -Chlorobenzyl alcohol  | 77        | 247–248                 | 248                  |
| <i>p</i> -Chlorobenzyl alcohol  | 72        | 264                     | 265                  |
| Benzhydrol                      | 73        | 236–237                 | 238                  |

tions were carried out on a Gallenkamp melting-point apparatus.

*Kinetic runs.* The kinetic studies were carried out at 488 nm under pseudo-first-order conditions with the concentration of the aryl alcohols in large excess over that of Ir(IV). Requisite volumes of the reactants were mixed and the mixture was immediately transferred to a cell of path length 1 cm. Pseudo-first-order rate constants were calculated from  $\log A$  ( $A$  = absorbance) versus time plots. Duplicate measurements were reproducible to  $\pm 3\%$ . Runs were made in a room illuminated partly by fluorescent lights and diffuse daylight; the results did not seem to be affected appreciably by such lighting.<sup>2</sup>

*Product studies.* Identification of carbonyl compounds as the reaction products when  $\text{IrCl}_6^{2-}$  is present in excess over substrates requires the following stoichiometry:



where  $X = \text{H, OMe, NO}_2$  and  $\text{Cl}$ .  $^1\text{H}$  and  $^{13}\text{C}$ NMR of the oxidation product of benzyl alcohol in  $\text{CDCl}_3$  showed the CHO peak at 9.95 and 192.4 ppm, respectively. These values are close to the literature values<sup>16</sup> of 9.98 and 192 ppm reported for the CHO proton of benzaldehyde and confirm the presence of a CHO group in the oxidation product.

The reaction products were characterized as their 2,4-dinitrophenylhydrazone derivatives. The yields and melting points<sup>17</sup> of the derivatives are recorded in Table 3. The methoxybenzaldehydes being more susceptible to oxidation,<sup>14</sup> the yields of their 2,4-DNP derivatives were lower than those of the chloro and nitro derivatives. In another set of experiments, a fixed aliquot of the reaction mixture containing benzyl alcohol (in water) and Ir(IV) at pH 4.45 was taken at different time intervals, treated with an excess of 2,4-DNP solution and the yields of the derivatives formed were plotted against time. It was found that the amount of benzaldehyde formed increased with time. This indicates that the oxidation of benzalde-

hyde to benzoic acid is insignificant during the kinetic studies.<sup>18</sup>

*Test for free radicals.* Acrylamide [40% (v/v)] was added during the course of the reactions. The appearance of a white polymeric suspension on addition of an excess of dioxane to the reaction mixture containing acrylamide indicates that free radicals are generated in the solution. A blank experiment from which either the substrate or Ir(IV) was excluded gave no polymeric suspension.

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### REFERENCES

1. Sen Gupta KK, Chatterjee U. *J. Inorg. Nucl. Chem.* 1981; **43**: 2491–2497.
2. Poulson IA, Garner CS. *J. Am. Chem. Soc.* 1962; **84**: 2032–2037.
3. Exner O. *Nature (London)* 1964; **201**: 488–490.
4. Leffler JE. *J. Org. Chem.* 1955; **20**: 1202–1231.
5. Cotton FA, Wilkinson G. *Advanced Inorganic Chemistry*. Interscience: New York, 1962; 524.
6. Martell AE, Calvin M. *Chemistry of the Metal Chelates*. Prentice Hall: Englewood Cliffs, NJ, 1962; 212.
7. Littler JS, Waters WA. *J. Chem. Soc.* 1959; 4046–4052.
8. Littler JS. *J. Chem. Soc.* 1959; 4135–4136.
9. Fadnis AG, Kemp TJ. *J. Chem. Soc., Dalton Trans.* 1989; 1237–1240.
10. Gilbert BC, Holmes RGG, Laue HAH, Norman ROC. *J. Chem. Soc., Perkin Trans. 2* 1976; 1047–1052.
11. Sykes P. A. *Guidebook to Mechanism in Organic Chemistry* (6th edn). Orient Longman, New Delhi, 1988; 359.
12. March J. *Advanced Organic Chemistry* (3rd edn). Wiley Eastern: New Delhi, 1986; 244.
13. Sen Gupta KK, Kumar SC, Sen PK, Banerjee A. *Tetrahedron* 1988; **44**: 2225–2231.
14. Sen PK, Sanyal A, Sen Gupta KK. *Int. J. Chem. Kinet.* 1995; **27**: 379–389.
15. Payne S. *Analyst* 1960; **85**: 698.
16. Silverstein RM, Bassler GC, Morill TL. *Spectrometric Identification of Organic Compounds* (5th edn). Wiley: New York, 1991; **219**: 246.
17. Vogel AI. *Textbook of Quantitative Inorganic Analysis* (4th edn). Longman: London, 1986; **1192**: 1196.
18. Sen Gupta KK, Nandy BK, Sen Gupta S. *J. Org. Chem.* 1994; **59**: 858–863.