Kinetics of Oxidation of Some Aryl Alcohols by Bis(dihydridotellurato)cuprate(III) and -argentate(III) in Alkaline Medium

Kalyan Kali Sen Gupta,* Bijay Kumar Nandy, and Shipra Sen Gupta

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

The oxidative behaviors and relative reactivities of benzyl alcohol and some substituted benzyl alcohols ($XC_6H_4CH_2OH$, where X = $-NO_2$, $-Cl$, and $-OMe$) toward bis(dihydridotellurato)-metallate(III) ions (where M = Cu^{III} and Ag^{III}) in alkaline medium have been investigated. The reactions are first order with respect to $[XC_6H_4CH_2OH]$ and $[M^{III}(H_2TeO_6)_2]^{5-}$. The rate is independent of $[OH^-]$. The activation parameters of the reactions have been computed. The mechanism of the reactions is discussed.

Introduction

The kinetics of oxidations of some aryl alcohols by chromic acid,[1] permanganate,[2a] lead tetraacetate,[2b] bromate,[3] and ruthenium tetraoxide[4] have been studied. There is no detailed investigation involving the oxidations of the aryl alcohols toward metal ion oxidants in alkaline medium. The present report deals with the reactions of some aryl alcohols with bis(dihydridotellurate)metallate(III) ions represented as $[M^{III}(H_2TeO_6)_2]^{5-}$ [5,6] in alkaline medium. The substituted benzyl alcohols are insoluble in water but soluble in different solvents like acetonitrile, dioxane, dimethyl formamide, and *tert*-butyl alcohol. However, all the solvents except *tert*-butyl alcohol are unstable toward copper(III) and silver(III) complexes. Hence, the experiments involving the oxidations of aryl alchols by these oxidants were carried out in 15% *tert*-butyl alcohol medium unless otherwise mentioned. The kinetic behavior and relative reactivities of the substrates toward these complexes are reported in this paper.

Experimental Section

Materials. Benzyl alcohol (BDH) was purified by distillation just before use. The aryl alcohols (BDH, E Merck, or Sigma) were used. All other chemicals were of reagent grade and used as received. The oxidation studies were carried out in alkaline medium adjusted by the addition of potassium hydroxide. All solutions were made in doubly distilled water.

Instrumentation. Absorbances were measured on a Cary 17D Model UV–vis spectrophotometer. Magnetic measurements were carried out in a Gouy magnetic balance. EPR spectra were recorded with a varian EPR spectrometer. The melting point determinations were carried out on a Gallenkamp melting point apparatus. Preparation of bis(dihydridotellurato)cuprate(III) and -argentate(III) was carried out by slightly modifying earlier methods[6] and their estimations.

Ditelluratocuprate(III) solution was prepared as follows. Copper sulfate (1.56 g) was added to a mixture of potassium

tellurite (3.17 g), potassium persulfate (4.22 g), and potassium hydroxide (8.0 g) in water (80 mL). The mixture was heated until the solution was an intense red. The boiling was continued for another 15 min to ensure complete removal of persulfate. The mixture was cooled and filtered (sintered glass crucible, porosity 4). The filtrate was diluted to 100 mL. Ditellurato-cuprate(III) shows two bands at 406 ± 3 nm and 274 ± 2 nm. The copper(III) complex was estimated as follows. An aliquot from the stock solution was taken, and then arsenite solution of 2 × 10^{-2} mol dm^{-3} was added. The mixture was allowed to stand for 3–4 min and acidified with 0.5 mol dm^{-3} of sulfuric acid until the green suspension disappeared. Five mL of 0.5 mol dm^{-3} sodium bicarbonate was then added, and the unusued arsenite was back-titrated against standard iodine solution using starch as indicator.

The silver(III) complex was synthesized as follows. To a 150-mL mixture containing silver nitrate (1.36 g), potassium tellurite (3.8 g), and potassium persulfate (6.5 g) was very slowly added potassium hydroxide solution (9 g in 50 mL) with constant stirring. The mixture was then heated to boiling on a hot plate, with constant agitation (~1 h), until the last trace of excess persulfate was removed by decomposition. The light red solution was filtered as mentioned before. The filtrate containing ditellurato-argentate(III) was diluted to 250 mL. Ditelluratoargentate(III) showed maximums at 355 ± 2 and 264 ± 2 nm. The silver(III) complex was standardized by treating 5 mL of the solution with 10 mL of 2 × 10^{-2} mol dm^{-3} sodium arsenite solution, letting it stand for 1 min, and then acidifying it with dilute 0.5 mL dm^{-3} H_2SO_4 until the solution became colorless. Then 5 mL of 0.5 mol dm^{-3} $NaHCO_3$ solution and 1 mL of 10% KI solution were added followed by back-titration of the unconsumed arsenite with standard iodine solution.

Product Studies. After the kinetic experiments, each reaction mixture was allowed to stand for 2 h and then filtered to remove the solid residues. The filtrate was acidified with dilute H_2SO_4, and 2,4-dinitrophenylhydrazine hydrochloride was added when 2,4-dinitrophenylhydrazone derivatives were obtained. The derivatives were filtered, washed, and dried followed by the determination of the melting points and yields in 15% *tert*-butyl alcohol (Table 1). In another experiment the amount of benzaldehyde formed in the absence of *tert*-butyl alcohol was determined by the preparation of 2,4-dinitrophenyl hydrazone derivatives at different time intervals at 308 K. The results as shown in Figure 1 indicate that the amount of benzaldehyde formed increased with an increase in time. The lower percent yields of 2:4 DNP derivative obtained with benzaldehyde (Table 1) as compared to those in Figure 1 are to be expected since the values were determined in 15% *tert*-butyl alcohol. This is due to the solubility problems associated with *tert*-butyl alcohol that make it difficult to isolate all the aldehyde. The solid residues were found to be green and black for the oxidations by copper(III) and silver(III), respectively. Magnetic susceptibility studies of the green product showed the compounds to be paramagnetic. The green precipitates were then dissolved in dilute perchloric acid and made ammoniacal when a deep blue color due to the

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* To whom correspondence should be addressed.

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(1) Sen Gupta, K. K.; Samanta, T.; Basu, S. N. *Tetrahedron* **1986**, *42*, 681.

(2) (a) Wiberg, K. B. *Oxidation in Organic Chemistry*; Part A, Academic Press: New York, 1965; Part A, p 48; (b) p 284.

(3) Sen Gupta, K. K.; Kumar, S. C.; Sen, P. K.; Banerjee, A. *Tetrahedron* **1988**, *44*, 2225–2231.

(4) Trahanovsky, W. S. *Oxidation in Organic Chemistry*; Academic Press: New York, 1973; Part B, p 198.

(5) Levason, W.; Spicer, M. D. *Coord. Chem. Rev.* **1987**, *76*, 45.

(6) Balikungeri, A.; Pelletier, M.; Monnier, D. *Inorg. Chim. Acta* **1977**, *22*, 7.

Table 1. Identification of Products of the Reactions. Yields and mps of the 2,4-DNP Derivatives of the Oxidation Products in 15% *tert*-Butyl Alcohol
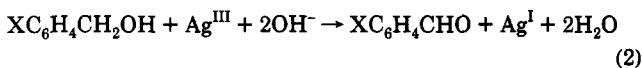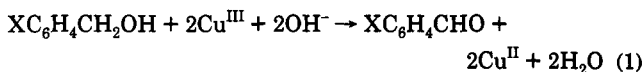
alcohols	% yield 2,4 DNP derivatives[c]	mp[a] (°C)	lit. mp (°C)
benzyl alcohol	60 (58)	235 (235)	237[b]
o-nitrobenzyl alcohol	48 (36)	264 (263)	265[b]
m-nitrobenzyl alcohol	52 (51)	291 (290)	292[b]
p-nitrobenzyl alcohol	55 (52)	318 (317)	320[b]
o-chlorobenzyl alcohol	56 (54)	207 (207)	209[b]
m-chlorobenzyl alcohol	58 (57)	246 (246)	248[b]
p-chlorobenzyl alcohol	61 (59)	264 (263)	265[b]
o-methoxybenzyl alcohol	62 (60)	251 (251)	253[b]
m-methoxybenzyl alcohol	66 (64)	231 (230)	232[c]
p-methoxybenzyl alcohol	74 (71)	253 (253)	254[c]

[a] Numbers in parentheses represent the values with Ag[III] complexes. [b] Vogel, A. I. *Text book of Practical Organic Chemistry*, 4th ed. Longman: England, 1980; pp 1192–1193. [c] Determined in the laboratory from an authentic sample.
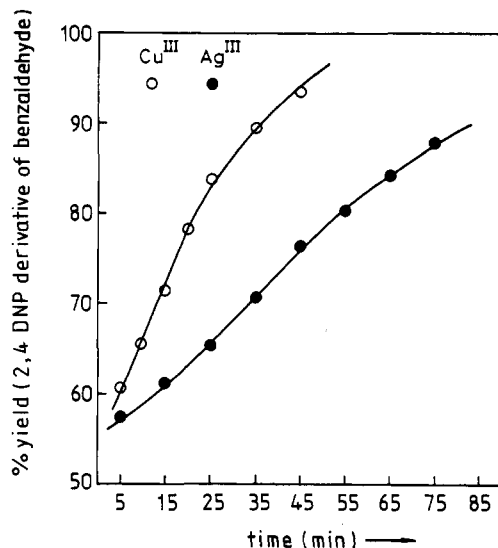

Figure 1. Plots of percent yield (2,4 DNP derivative of benzaldehyde) vs time (min) for the oxidations of benzyl alcohol by ditelluratocuprate(III) and ditelluratoargentate(III).

formation of cuproammonium complex appeared. This indicated that the copper(III) complex was reduced to copper(II). However, the black product was dissolved in dilute nitric acid, and the solution gave a yellow precipitate of silver iodide with potassium iodide. The absence of silver(0) precipitation at a very high excess of substrate concentration may be attributed to the increased stability of silver(I) toward unreacted substrates. The results indicated that aryl alcohols are oxidized according to eqs 1 and 2.

$$XC_6H_4CH_2OH + 2Cu^{III} + 2OH^- \rightarrow XC_6H_4CHO +$$
$$2Cu^{II} + 2H_2O \quad (1)$$

$$XC_6H_4CH_2OH + Ag^{III} + 2OH^- \rightarrow XC_6H_4CHO + Ag^I + 2H_2O \quad (2)$$

Test for Free Radicals. Acrylamide (40% w/v) was added during the course of the reactions. The appearance of white precipitate shows the presence of free-radical intermediates in the oxidations by both these oxidants. The blank experiment in the absence of substrate or oxidants did not show appreciable formation of any such polymer.

Kinetic Studies. The rate of decrease of ditelluratometallate-(III) in alkaline medium was followed titrimetrically. The reactions were studied under the conditions at which $[XC_6H_4-CH_2OH] \gg [M^{III}(H_2TeO_6)_2]^{5-}$. Solutions of the $[M^{III}(H_2TeO_6)_2]^{5-}$ and the mixture containing aryl alcohols and OH⁻ were ther-
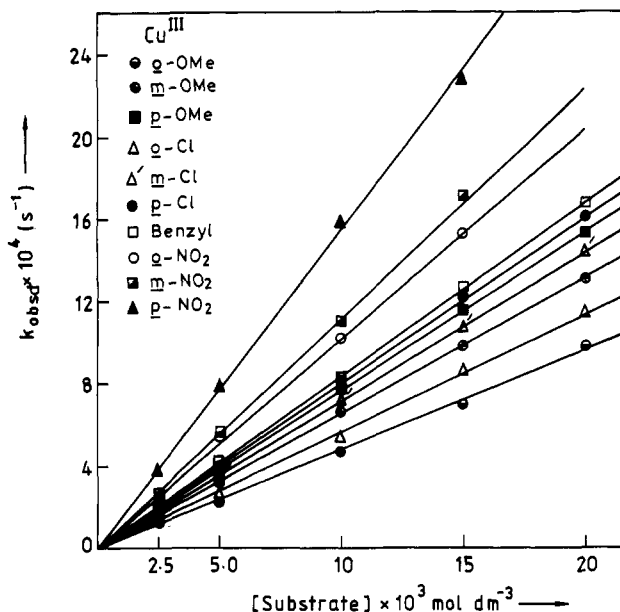
Figure 2. Variation of pseudo-first-order rate constant with aryl alcohol concentrations for the oxidation by Cu(III) complex. Plots of k_{obsd} against [aryl alcohol]: $[Cu(III)] = 1.4 \times 10^{-3}$ mol dm⁻³, $T = 298$ K; $[OH^-] = 3.2 \times 10^{-1}$ mol dm⁻³.

Table 2. Values of Pseudo-First-Order Rate Constants of the Oxidations of Aryl Alcohols in 15% *tert*-Butyl Alcohol

(a) $[Cu(III)] = [0.7–7.0] \times 10^{-3}$ mol dm⁻³, [aryl alcohol] = 1.5 × 10^{-2} mol dm⁻³, $[OH^-] = 3.2 \times 10^{-1}$ mol dm⁻³, and $T = 298$ K

(b) $[Ag(III)] = [0.67–2.24] \times 10^{-3}$ mol dm⁻³, [aryl alcohol] = 1.5 × 10^{-2} mol dm⁻³, $[OH^-] = 4.0 \times 10^{-1}$ mol dm⁻³, and $T = 318$ K

substrate	$k_{obsd}^{a} \times 10^{-4}$ (s⁻¹)	$k_{obsd}^{b} \times 10^4$ (s⁻¹)
benzyl alcohol	12.8 ± 0.3	4.79 ● 0.2
o-nitrobenzyl alcohol	15.35 ± 0.5	4.98 ± 0.15
m-nitrobenzyl alcohol	19.2 ± 0.4	5.75 ± 0.2
p-nitrobenzyl alcohol	24.9 + 0.4	6.14 ± 0.3
o-chlorobenzyl alcohol	8.77 ± 0.2	3.1 ± 0.15
m-chlorobenzyl alcohol	10.7 ± 0.3	3.45 ± 0.1
p-chlorobenzyl alcohol	12.3 ± 0.3	4.47 ± 0.15
o-methoxybenzyl alcohol	6.9 ± 0.2	2.68 ± 0.1
m-methoxybenzyl alcohol	9.9 ± 0.2	3.26 ± 0.15
p-methoxybenzyl alcohol	11.5 ± 0.35	3.8 ± 0.1

mostated separately for nearly 1 h. Each reaction was started by adding the oxidant to other reactants. An aliquot from the reaction mixture was withdrawn and added to a known excess of sodium arsenite solution. The unconsumed arsenite after acidification by dilute H_2SO_4 was titrated against standard iodine using starch as an indicator. Generally eight to 10 readings are taken in each run, and the pseudo-first-order rate constants (k_{obsd}) were reproducible to within ±5%.

Results and Discussion

The pseudo-first-order rate constants were determined at different $[M^{III}(H_2TeO_6)_2]^{5-}$ but at constant $[XC_6H_4-CH_2OH]$, $[OH^-]$, and temperature. The rate was found to be independent of $[M^{III}(H_2TeO_6)_2]^{5-}$ as shown in Table 2. The reactions were also studied at different [substrate] but at constant $[M^{III}(H_2TeO_6)_2]^{5-}$ and temperature. The plots of k_{obsd} against [substrate] give straight lines passing through the origin as shown in Figures 2 and 3. The reactions are first order with respect to [substrate].

The effect of added $[OH^-]$ on the pseudo-first-order rate constant was studied over a wide range of $[OH^-]$ in the region $(0.7–4.2) \times 10^{-1}$ mol dm⁻³ but at constant
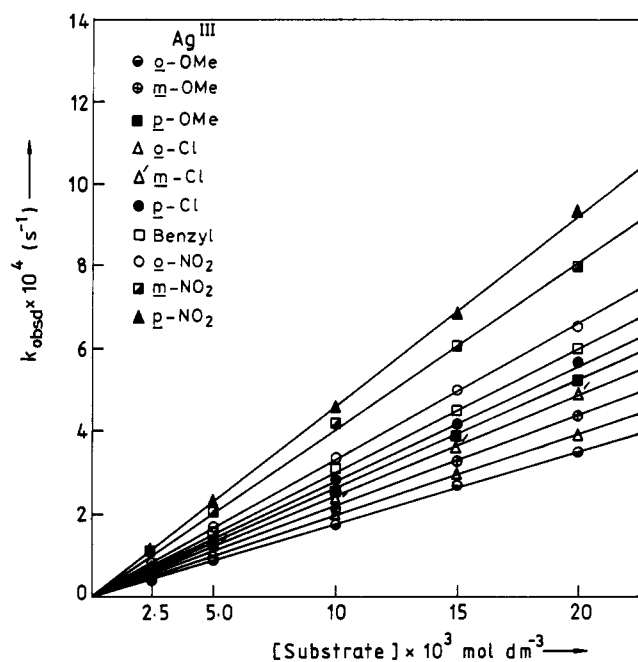
Figure 3. Variation of pseudo-first-order rate constants with aryl alcohol concentrations for the oxidation by Ag(III) complex. Plots of k_{obsd} against [aryl alcohol]: [Ag(III)] = 1.34 × 10⁻³ mol dm⁻³, T = 318 K; [OH⁻] = 4.0 × 10⁻¹ mol dm⁻³.

Table 3. Values of Pseudo-First-Order Rate Constant of the Oxidation of Benzyl Alcohol at Different Solvent Compositions

(a) [Cu(III)] = 1.4 × 10⁻³ mol dm⁻³, [benzyl alcohol] = 1.5 ×

    10⁻² mol dm⁻³, [OH⁻] = 3.2 × 10⁻¹ mol dm⁻³, and T = 288 K

(b) [Ag(III)] = 1.34 × 10⁻³ mol dm⁻³, [benzyl alcohol] = 1.5 ×

    10⁻² mol dm⁻³, [OH⁻] = 4.0 × 10⁻¹ mol dm⁻³, and T = 318 K

tert-butyl alcohol (% v/v)	k_{obsd}^{a} × 10⁴ (s⁻¹)	k_{obsd}^{b} × 10⁴ (s⁻¹)
0	9.88	5.76
15	5.79	4.79
20	3.07	2.30
25	1.91	1.02
30	1.15	0.76

concentration of [XC₆H₄CH₂OH], [Mᴵᴵᴵ(H₂TeO₆)₂]⁵⁻, and temperature. The rate of each reaction was found to be independent of the initial [OH⁻].

The effect of variation of solvent like *tert*-butyl alcohol on the pseudo-first-order rate constant was also studied for the oxidation of benzyl alcohol by these oxidants at constant reactant concentrations and temperature. The rate increases with an increase in dielectric constant (Table 3).

The second-order rate constants were determined at constant reactant and hydroxide ion concentration but at different temperatures in the regions 283–298 and 303–318 K for the oxidation of the substrates by copper(III) and silver(III) complexes, respectively. The activation enthalpies (ΔH^{*}) were calculated from the least-squares plots of log (k_2/T) vs $1/T$ (Figures 4 and 5) followed by entropies of activation (ΔS^{*}) using eq 3 where k and h

$$\log k_2/T = \log k/h + \Delta S^{*}/2.303R - \Delta H^{*}/2.303RT \quad (3)$$

have their usual significance. The values of activation

parameters are recorded in Table 4. The plots of ΔH^{*} vs ΔS^{*} are found to be linear (Figure 6). The linear correlations between ΔH^{*} and ΔS^{*} indicate that the aryl alcohols are oxidized by each oxidant by the same mechanism, and the changes in rates are governed by changes in both ΔH^{*} and ΔS^{*}.

The important features concerning the oxidations of the aryl alcohols by both these oxidants are as follows. The rate of the reactions is directly proportional to [XC₆H₄-CH₂OH] and [Mᴵᴵᴵ(H₂TeO₆)₂]⁵⁻ but independent of [OH⁻]. The alcohols are oxidized to the respective substituted aldehydes, and [Mᴵᴵᴵ(H₂TeO₆)₂]⁵⁻ is reduced by an inner-sphere mechanistic path. Moreover, irrespective of whether the substrate is an ortho-, meta-, or para-substituted alcohol, [Cuᴵᴵᴵ(H₂TeO₆)₂]⁵⁻ reacts at faster rates than the corresponding reactions with [Agᴵᴵᴵ(H₂TeO₆)₂]⁵⁻. Again, of the different nuclear-substituted benzyl alcohols, nitro compounds react at much faster rates than the corresponding chloro- and methoxy-substituted derivatives. The pseudo-first-order rate constants follow the order −NO₂ > −H > −Cl > −OMe. The plots of the log k_{obsd} against σ failed to give good linear relationships (r = 0.7822 and 0.7900 for copper(III) and silver(III) respectively).

The oxidants may react with the XC₆H₄CH₂OH and XC₆H₄CH₂O⁻ to give products. Since nitro compounds react at much faster rates than the chloro and methoxy derivatives, the possibility that the alkoxide ions are also involved in the reaction cannot be totally ruled out. On the other hand, since the rate is independent of [OH⁻], it is believed that the major reaction path is taking place between the molecular alcohol and the oxidant. Again the possibility of hydride transfer during the reaction may be ruled out although the hydrogen atom abstraction process may be operative. However, regardless of whether hydrogen atom abstraction or one-electron transfer process occurs, one piece of information is obtained with certainty; the reactions occur through the intermediate formation of free radicals.

It is suggested that ditelluratometallate(III) is reduced by the alcohols to give free radicals and ditellurato-metallate(II). A radical intermediate was proposed[7,8] in the decomposition of copper(III) tetraamine complexes which produced Cu(II) complexes containing imine donors. In the oxidation of methyl ethyl ketone and cyclohexanone by Cu(III) it has been shown[9] that Cu(III) undergoes a one-electron transfer rather than a two-electron transfer. The kinetic studies of the oxidation of pinacol and cyclic 1:2 diols by S₂O₈²⁻ catalyzed by Ag(I) involved the intermediate formation of Ag((II).[10,11] Kirschenbaum et al.[12–18] have studied the redox reactions involving some reductants like hydrogen peroxide,[12] hypophosphite,[13] arsenite,[14] sulfite,[15] thiosulfate,[16] azide,[17] and polypeptide[18] by silver(III). They have shown that silver(III) reductions

(7) Barefield, E. K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.

(8) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1971**, *10*, 463.

(9) Panigrahi, G. P.; Pathy, A. C. *Inorg. Chem.* **1984**, *23*, 2133.

(10) Huyser, E. S.; Rose, L. G. *J. Org. Chem.* **1972**, *37*, 649.

(11) Huyser, E. S.; Rose, L. G. *J. Org. Chem.* **1972**, *37*, 851.

(12) Borish, E. T.; Kirschenbaum, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 749.

(13) Mehrotra, R. N.; Kirschenbaum, L. J. *Inorg. Chem.* **1989**, *28*, 4327.

(14) Kirschenbaum, L. J.; Rush, J. D. *Inorg. Chem.* **1983**, *22*, 3304.

(15) Kirschenbaum, L. J.; Kouadio, I.; Mentasti, E. *Polyhedron.* **1989**, *10*, 1299–1305.

(16) Rush, J. D.; Kirschenbaum, L. J. *Inorg. Chem.* **1985**, *24*, 744.

(17) Borish, E. T.; Kirschenbaum, L. J. *Inorg. Chem.* **1984**, *23*, 2355.

(18) Kirschenbaum, L. J.; Rush, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 1003.
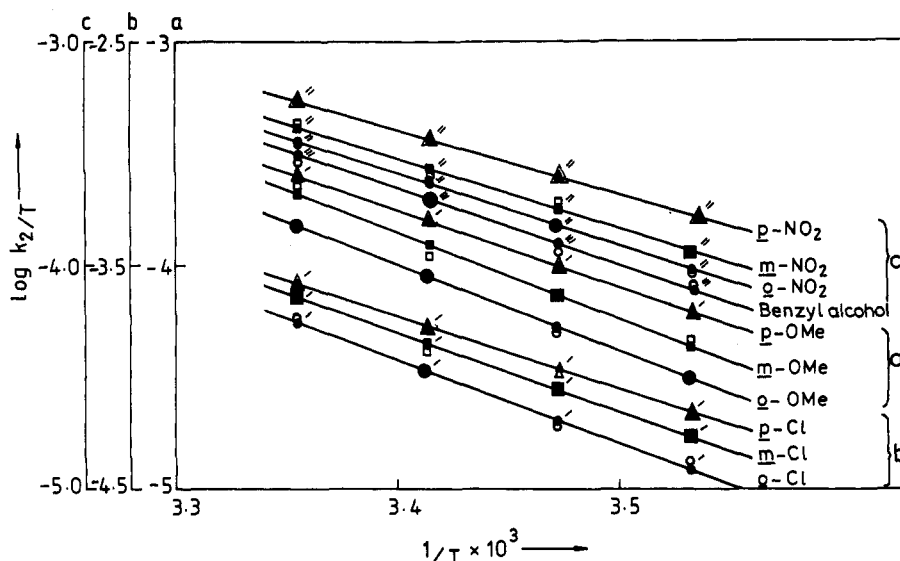
Figure 4. Influence of temperature on second-order rate constants of the oxidations of aryl alcohols by Cu(III). Plots of log k_2/T against $1/T$.
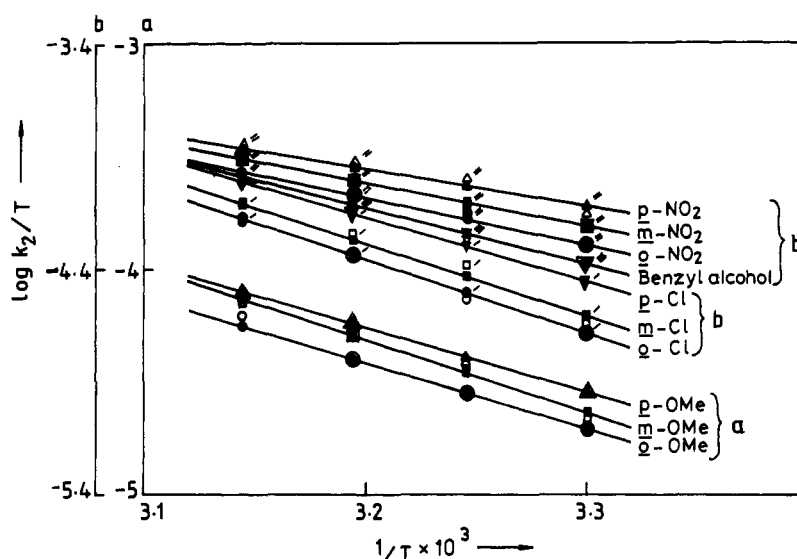

Figure 5. Influence of temperature on second-order rate constants of the oxidations of aryl alcohols by Ag(III). Plots of log k_2/T against $1/T$.

Table 4. Values of Activation Parameters for the Oxidation of Different Aryl Alcohols by Copper(III) and Silver(III) Complexes in 15% *tert*-Butyl Alcohol

alcohols	Cu^{III}		Ag^{III}	
	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})
benzyl alcohol	65 ± 4	−46 ± 13	47 ± 2	−125 ± 7
o-nitrobenzyl alcohol	62 ± 4	−55 ± 13	40 ± 2	−147 ± 7
m-nitrobenzyl alcohol	59 ± 3	−64 ± 10	36 ± 2	−160 ± 7
p-nitrobenzyl alcohol	56 ± 3	−70 ± 10	32 ± 2	−172 ± 7
o-chlorobenzyl alcohol	71 ± 6	−30 ± 21	63 ± 4	−79 ± 14
m-chlorobenzyl alcohol	69 ± 6	−36 ± 20	61 ● 4	−83 ± 13
p-chlorobenzyl alcohol	62 ± 4	−57 ± 13	54 ± 3	−104 ± 10
o-methoxybenzyl alcohol	74 ± 4	−21 ± 13	64 ● 4	−77 ± 13
m-methoxybenzyl alcohol	72 ± 4	−25 ± 13	62 ± 4	−80 ± 13
p-methoxybenzyl alcohol	65 ± 4	−48 ± 13	55 ± 3	−103 ± 10

can involve either one- or two-electron changes. The formation and stabilities of Ag(II) complexes of macrocyclic amines have been examined[19-21] which are exceptionally stable in the solid state but in solution they are

powerful oxidants. The existence of several organic complexes of Ag(II) have been confirmed by magnetic measurement as well as by electron paramagnetic resonance spectra of the complexes.

The intermediate formation of free radicals in the present study is evidenced by the formation of polymerized products when a vinyl compound was added to the reaction
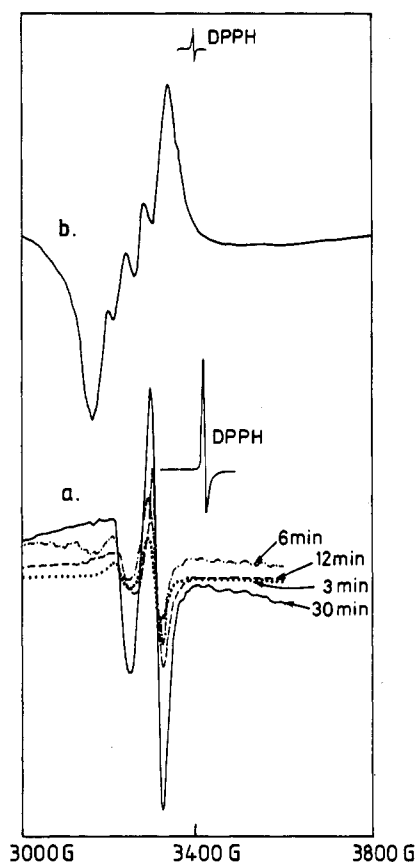
(19) Kestner, M. O.; Allred, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 7189.
(20) McMillan, J. A. *Chem. Rev.* **1962**, *62*, 65.
(21) Barefield, E. K.; Mocella, M. T. *Inorg. Chem.* **1973**, *12*, 2829.
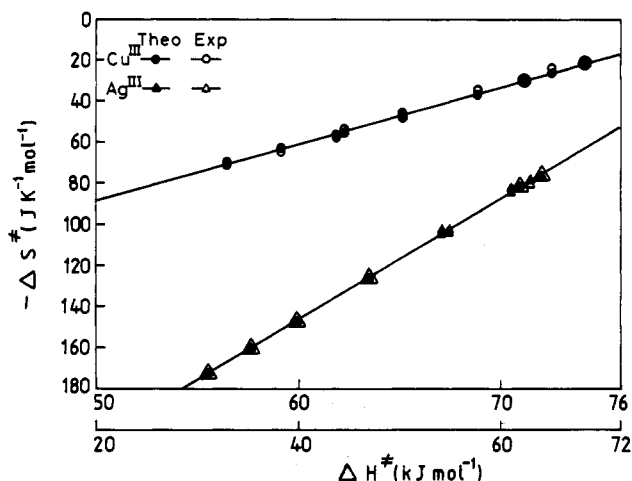
Figure 6. Plots of $\Delta S^{\ddagger}$ vs $\Delta H^{\ddagger}$ for the oxidations of aryl alcohols by ditelluratocuprate(III) and ditelluratoargentate(III).

Figure 7. EPR spectra of the reaction mixture at 298 K involving (a) ditelluratocuprate(III) and p-nitrobenzyl alcohol in 15% *tert*-butyl alcohol at different time intervals and (b) blue cupro-ammonium complex both at microwave frequency and receiver gain of 9.45 GHz and 5 × 10^3, respectively.
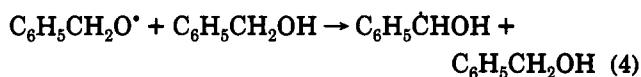
mixtures. Spin trapping studies during the oxidation of benzyl alcohol by hexachlorometallate ions (M = Pt, Pd, and Ir) have shown[22] the formation of $C_6H_5CH_2O^\bullet$ in pure alcoholic medium whereas in alcohol water mixtures the radical $C_6H_5\dot{C}HOH$ is formed either directly or via secondary reactions of $C_6H_5CH_2O^\bullet$ by the H atom transfer

(22) Fadnis, A. G.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1237.

Table 5. Influence of Substituents on the Rates of Oxidation of Benzaldehyde and Para-Substituted Benzaldehyde in 15% *tert*-Butyl Alcohol

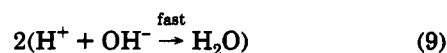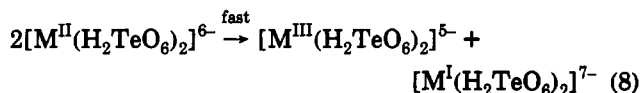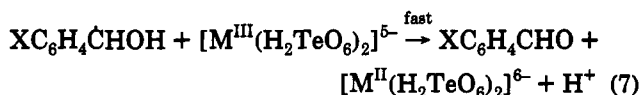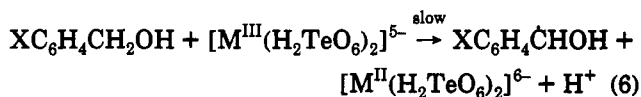(a) [Cu(III)] = 2.0 × 10^{-3} mol dm^{-3}, [aldehyde] = 3.0 ×

$\qquad$ 10^{-2} mol dm^{-3}, [OH$^-$] = 3.0 × 10^{-1} mol dm^{-3}, and T = 298 K

(b) [Ag(III)] = 1.67 × 10^{-3} mol dm^{-3}, [aldehyde] = 3.0 ×

$\qquad$ 10^{-2} mol dm^{-3}, [OH$^-$] = 3.3 × 10^{-1} mol dm^{-3}, and T = 313 K

aldehyde	k_{obsd}^a × 10^4 (s^{-1})	k_{obsd}^b × 10^4 (s^{-1})
benzaldehyde	5.74	2.82
p-nitrobenzaldehyde	26.7	10.2
p-chlorobenzaldehyde	5.02	1.29
p-methoxybenzaldehyde	3.87	1.22

reaction (eq 4) or the isomerization reaction (eq 5).[23] Since

$$C_6H_5CH_2O^\bullet + C_6H_5CH_2OH \rightarrow C_6H_5\dot{C}HOH + C_6H_5CH_2OH \quad (4)$$

$$C_6H_5CH_2O^\bullet + H_2O \rightarrow C_6H_5\dot{C}HOH + H_2O \quad (5)$$

the reactions have been carried out in alcohol–water mixtures, it is believed that radical intermediates XC_6H_4-$\dot{C}HOH$ are formed during the reactions (eq 6). The free radical further reacts with another $[M^{III}(H_2TeO_6)_2]^{5-}$ to give XC_6H_4CHO and $[M^{III}(H_2TeO_6)_2]^{6-}$ as shown in (eq 7). The EPR spectrum of reaction mixtures involving copper(III) was recorded at different time intervals, and some typical results are shown in Figure 7. The results indicate that the peak intensity increases with the increase in time indicating that copper(II) is involved during the reaction. This is further supported by the EPR spectrum of the blue cuproammonium complex as shown in Figure 7. Again in the oxidations by silver(III) complex, silver(II) which is generated in the slow step disproportionates to give silver(I) and silver(III) as shown in (eq 8). The steps of the reaction are

$$XC_6H_4CH_2OH + [M^{III}(H_2TeO_6)_2]^{5-} \xrightarrow{slow} XC_6H_4\dot{C}HOH + [M^{II}(H_2TeO_6)_2]^{6-} + H^+ \quad (6)$$

$$XC_6H_4\dot{C}HOH + [M^{III}(H_2TeO_6)_2]^{5-} \xrightarrow{fast} XC_6H_4CHO + [M^{II}(H_2TeO_6)_2]^{6-} + H^+ \quad (7)$$

$$2[M^{II}(H_2TeO_6)_2]^{6-} \xrightarrow{fast} [M^{III}(H_2TeO_6)_2]^{5-} + [M^{I}(H_2TeO_6)_2]^{7-} \quad (8)$$

$$2(H^+ + OH^- \xrightarrow{fast} H_2O) \quad (9)$$

Though aliphatic aldehydes and some aliphatic ketones undergo a reversible hydration[24,25] in neutral aqueous solution to form *gem* diols, aromatic aldehydes are not hydrated to any appreciable amount owing to the extra resonance stabilization. Since benzaldehyde and most of its derivatives substituted on the aromatic ring are known

(23) Gilbert, B. C.; Holmes, R. G. G.; Laue, H. A. H.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1047.
(24) Hine, J.; Koser, G. F. *J. Org. Chem.* **1971**, *36*, 1348.
(25) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1.

to give ionized *gem* diol[26,27] in basic solutions, it is believed that the oxidation products in the present investigation will exist mainly as $XC_6H_4CH(OH)O^-$. The reactions have been studied in dilute aqueous alkali, and hence the internal oxidation and reduction of benzaldehyde to give carboxylate ion and aromatic alcohols can be discounted. Moreover, the results as recorded in Figure 1 indicate that further oxidation of benzaldehyde to give benzoic acid is insignificant during kinetic studies. The oxidation of the aromatic aldehydes, however, takes place at an appreciable rate at higher aldehyde concentrations. Some preliminary experiments on the oxidations of benzaldehyde and some para-substituted benzaldehydes have been studied. The pseudo-first-order rate constants as recorded in Table 5 follow the order p-NO_2 > p-H > p-Cl > p-OMe. The rate of oxidation thus increases with the presence of an electron-withdrawing group and decreases with an electron-donating group on the aromatic ring. The experimentally observed percent of 2,4-dinitrophenylhydrazone derivatives which follow the order p-NO_2 < p-H < p-Cl < p-OMe corroborates the experimental findings.

(26) Bover, W. J.; Zuman, P. *J. Chem. Soc., Perkin Trans. 2* 1978, 786.
(27) Greenzaid, P. *J. Org. Chem.* 1973, *38*, 3164.