Oxidative Behaviours and Relative Reactivities of Some Alkanols and Aryl Alcohols Towards Bis(dihydrogentellurato)-cuprate(III) and -argentate(III) in Alkaline Medium

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The oxidative behaviours and relative reactivities of some alkanols and aryl alcohols towards bis(dihydrogentellurato)metallate(III) ion (where M = Cu^{III} and Ag^{III}) in alkaline medium have been investigated. The reactions are first-order in each [R^1R^2CHOH] and [$M^{III}(H_2TeO_6)_2$]$^{5-}$ but the rate is independent of [OH^-]. The activation parameters of the reactions have been computed. The unsubstituted benzyl alcohol reacts at a faster rate than benzhydrol. The influence of *o, m* and *p* substituents on the rate for benzyl alcohol have been examined. The mechanism of the reactions is discussed.

A considerable amount of work has been done on the mechanistic studies involving the oxidations of some alcohols by transition metal ion oxidants like chromium(VI),[1a] vanadium(V),[1b] cobalt(III),[1c] manganese(VII),[1d] cerium(IV)[1e] in an acid medium and with copper(II)[2a] and ruthenium tetroxide[2b] in an alkaline medium. Thus not much information is available in the literature concerning the oxidations of different alcohols in alkaline medium. Amongst the different oxidation states, compounds of trivalent copper[3] and silver[4] are powerful oxidizing agents and stable complexes can be obtained by oxidations[5,6] of copper (II) and silver(I) in the presence of complexing agents. The present report describes the reactions of some alkanols and aryl alcohols with bis(dihydrogentellurato)-cuprate(III) and -argentate(III) in alkaline medium.

Experimental

Reagents.—The alcohols (BDH, E Merck or Sigma) were used as supplied. Deuteriated alkanols and D_2O (99.9 atom % D) were of Sigma grade. All other chemicals including acrylamide were of reagent grade and used as received. The oxidation studies were carried out in alkaline medium varied 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 using a Gouy magnetic balance. EPR spectra were recorded with a Varian EPR spectrometer at varying stages of the reactions. Melting point determinations were carried out on a Gallenkamp melting point apparatus.

Preparation and Estimation of Bis(dihydrogentellurato)-cuprate(III) *and -argentate*(III).—The same procedures as described earlier[6] were used to prepare the copper(III) and silver(III) complexes which were preserved in a refrigerator.

The copper(III) complex was estimated as follows. An aliquot (5 cm^3) was taken from the stock solution and to it was added 10 cm^3 arsenite solution (2 × 10^{-2} mol dm^{-3}). The mixture was allowed to stand for 3–4 min and then acidified with 0.5 mol dm^{-3} sulfuric acid until the green suspension disappeared. A solution of 0.5 mol dm^{-3} sodium hydrogencarbonate (5 cm^3) was added and the unused arsenite was back titrated against standard iodine solution using starch as indicator to a blue end point. Ditelluratocuprate(III) shows two bands at 406 ± 3 nm and 274 ± 2 nm.

The silver(III) complex was standardised by treating 5 cm^3 of the solution with 10 cm^3 of 2 × 10^{-2} mol dm^{-3} sodium arsenite solution letting it stand for 1 min and then acidifying with dilute 0.5 mol dm^{-3} H_2SO_4 until the solution became colourless. The 5 cm^3 of 0.5 mol dm^{-3} $NaHCO_3$ solution and 1 cm^3 of 10% KI solution were added followed by back titration of the unconsumed arsenite with standard iodine solution. Ditelluratoargentate(III) shows maxima at 355 ± 2 nm and 264 ± 2 nm respectively.

Product Analyses.—After the kinetic experiments the reaction mixtures were filtered to remove solid particles which were found to be green and black for the oxidations by copper(III) and silver(III) complexes respectively. Magnetic susceptibility studies of the green product showed the compounds to be paramagnetic. The green precipitates obtained were dissolved in dilute perchloric acid and then made ammoniacal when a deep blue colour due to the formation of cuproammonium complex appeared. This indicated that the copper(III) complex was reduced to copper(II). However, for the other reaction, the black product was dissolved in dilute nitric acid and the solution gave a yellow precipitate of silver iodide with potassium iodide. The filtrates were divided in two. In one part of the filtrate the oxidation products were tested by the formation of colours with different reagents.[7–9] The other part of the filtrate was acidified with dilute H_2SO_4 and added to 2,4-dinitrophenylhydrazine hydrochloride whereupon, 2,4-dinitrophenylhydrazone derivatives were obtained. The precipitates were filtered, washed, dried and the melting points were checked against the literature values. The yields of the derivatives were also determined. The results recorded in Table 1 indicate that formaldehyde,[7,10a] acetaldehyde,[8,10b] acetone,[9,10c] benzaldehyde[10d] and benzophenone[10d] are formed in the oxidations of methanol, ethanol, isopropanol, benzyl alcohol and benzhydrol respectively according to eqns. (1) and (2).

$$R^1R^2CHOH + 2Cu^{III} + 2OH^- \longrightarrow R^1R^2CO + 2Cu^{II} + 2H_2O \quad (1)$$

$$R^1R^2CHOH + Ag^{III} + 2OH^- \longrightarrow R^1R^2CO + Ag^{I} + 2H_2O \quad (2)$$

Test for Free Radicals.—Acrylamide (40%, w/v) was added during the course of the reactions. The appearance of white polyacrylamide is consistent with the presence of free radical intermediates in the oxidations by both copper(III) and silver(III)

Table 1 Identification of products of the reactions

Alcohol	Product	Test	Colour	% Yield (2,4 DNP derivative)[10,a]
Methanol	CH_2O	Chromotropic acid and conc. H_2SO_4	Pinkish[7] violet	45 (45)
Ethanol	MeCHO	Equal volumes of 20% piperidine and 5% sodium nitroprusside	Blue[8]	60 (60)
Isopropanol	Me_2CO	Equal volumes of 5% sodium nitroprusside and 30% NaOH	Red[9]	60 (60)
Benzylalcohol	PhCHO	—	—	94 (90)
Benzhydrol	Ph_2CO	—	—	90 (88)

[a] Figures in parentheses represent the values with Ag^{III} complex.

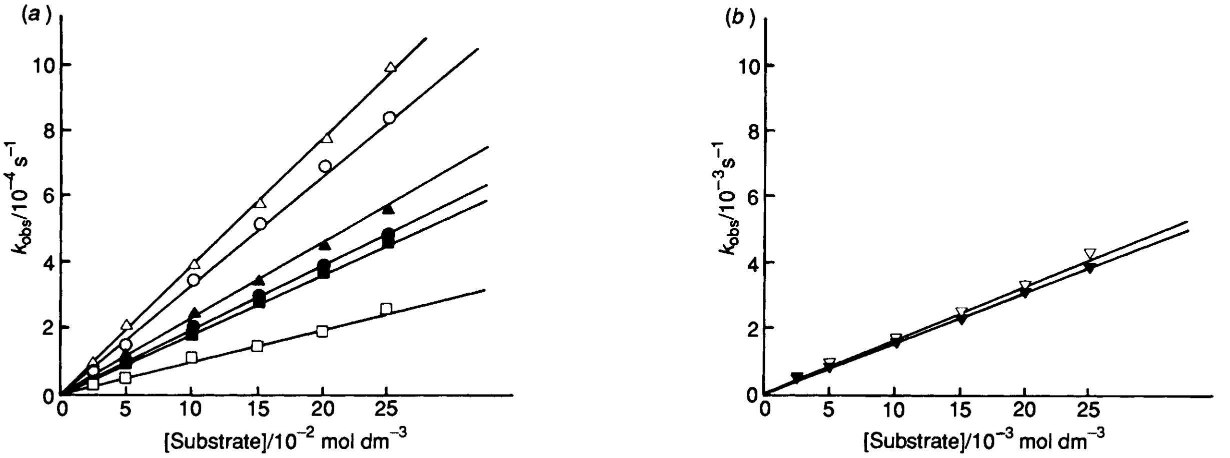

Fig. 1 Variation of pseudo-first-order rate constant with substrate concentrations. Plots of k_{obs} *vs.* [substrate] for the oxidations by ditelluratocuprate(III) ($[Cu^{III}] = 1.17 \times 10^{-3}$ mol dm^{-3}, $[OH^-] = 2.3 \times 10^{-1}$ mol dm^{-3} and $T = 298$ K) and ditelluratoargentate(III) ($[Ag^{III}] = 2.22 \times 10^{-3}$ mol dm^{-3}, $[OH^-] = 3.75 \times 10^{-1}$ mol dm^{-3} and $T = 313$ K.). (*a*) Cu^{III}: △, ethanol; ○, methanol; □, isopropanol. Ag^{III}: ▲, ethanol; ●, methanol; ■, isopropanol. (*b*) Cu^{III}: ▽, benzyl alcohol. Ag^{III}: ▼, benzyl alcohol.

complexes. Blank experiments in which copper(III) or silver(III) was excluded gave no polymeric suspensions.

Kinetic Measurements.—The rate of decrease of ditelluratometallate(III) in the alkaline medium was followed titrimetrically. The reactions were studied under the conditions at which $[R^1R^2CHOH] \gg [M^{III}(H_2TeO_6)_2]^{5-}$. Solutions of the $[M^{III}(H_2TeO_6)_2]^{5-}$ and the mixture containing $[R^1R^2CHOH]$ and $[OH^-]$ were thermostatted separately (± 0.1 °C) for nearly 1 h. The reaction was started by adding the oxidant to the reaction mixture. 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 8–10 readings were taken in each run and the pseudo-first-order rate constants (k_{obs}) 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 $[R^1R^2CHOH]$, $[OH^-]$ and temperature. The values of k_{obs} in the oxidation of methanol by ditelluratocuprate(III) is $7.93 \pm 0.2 \times 10^{-4}\ s^{-1}$ at $[Cu^{III}(H_2TeO_6)_2]^{5-}$, [Methanol], $[OH^-]$ and temperature of $(5.0\text{–}20) \times 10^{-4}$ mol dm^{-3}, 1.5×10^{-1} mol dm^{-3}, 2.3×10^{-1} mol dm^{-3} and 303 K respectively whereas for the other oxidant it is $(4.9 \pm 0.15) \times 10^{-4}\ s^{-1}$ at $[Ag^{III}(H_2TeO_6)_2]^{5-}$, [Methanol], $[OH^-]$ and temperature of $(3\text{–}24) \times 10^{-4}$ mol dm^{-3}, 2.5×10^{-1} mol dm^{-3}, 2.12×10^{-1} mol dm^{-3} and 313 K respectively. Similar observations have also been made with other alkanols and benzyl alcohol. The pseudo-first-order rate constants are independent of initial $[M^{III}(H_2TeO_6)_2]^{5-}$. The rate of each reaction was found to increase with the increase in $[R^1R^2CHOH]$. The plots of k_{obs} against $[R^1R^2CHOH]$ are linear passing through the origin (Fig. 1) indicating that the order with respect to each $[R^1R^2CHOH]$ is unity. The effect of added $[OH^-]$ on pseudo-first-order rate constants was studied over a wide range of $[OH^-]$ in the region $(0.5\text{–}3.5) \times 10^{-1}$ mol dm^{-3} but at a constant $[R^1R^2CHOH]$, $[M^{III}(H_2TeO_6)_2]^{5-}$ and temperature as mentioned above. The rate of each reaction was found to be independent of the initial $[OH^-]$.

The influence of substituents on the rates has been studied under comparable experimental conditions. All the substituted benzyl alcohols are insoluble in water but soluble in acetonitrile, dimethylformamide, dioxane and *tert*-butyl alcohol. However, both copper(III) and silver(III) complexes are highly reactive towards the solvents, except *tert*-butyl alcohol and hence the rate measurements were made in *tert*-butyl alcohol (25% v/v). The values of rate constants along with the relative rates are recorded in Table 2. The unsubstituted benzyl alcohol reacts at a faster rate than benzhydrol. In benzhydrol probably the steric hindrance due to the second phenyl group on the alcohol carbon makes the reactions with the oxidants less favourable than benzyl alcohol,[11] thereby decreasing the rate in benzhydrol. The results further indicate that the rate of oxidation increases with the electron withdrawing groups and decreases with the presence of electron donating groups. When the substituent is chlorine, the rate has been found to be in between those for the nitro and methoxy derivatives. The oxidation rates follow the order: nitro > chloro > methoxy. However, the values of ρ have been calculated to be 0.76 and 0.63 from the least square plots of log k_{obs} *vs.* σ ($r = 0.7959$ and 0.8870 respectively) for the respective oxidants.

The second-order rate constants (k_2) were determined at different temperatures in the region (298–313) K and (313–328)

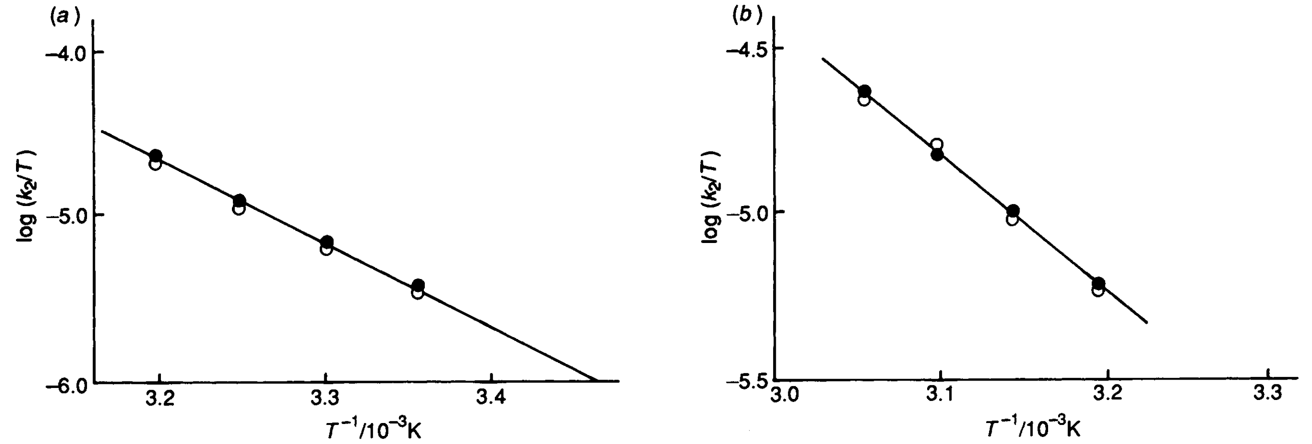

Fig. 2 Influence of temperature on second-order-rate constant of the oxidation of methanol. Plots of log k_2/T *vs.* $1/T$. (*a*) Cu^{III} (in methanol): ●, theoretical; ○, experimental. (*b*) Ag^{III} (in methanol): ●, theoretical; ○, experimental.

Table 2 Influence of substituents on the rates of the reactions

Alcohols	$k_{obs}{}^a/10^{-4}$ s^{-1}	$k_{obs}{}^b/10^{-4}$ s^{-1}	$k_{rel}{}^a$	$k_{rel}{}^b$
Benzyl alcohol	3.2	1.63	1	1
Benzhydrol	1.53	0.64	0.47	0.39
o-Nitrobenzyl alcohol	3.84	1.83	1.2	1.1
m-Nitrobenzyl alcohol	6.4	2.10	2.0	1.28
p-Nitrobenzyl alcohol	7.72	2.80	2.4	1.71
o-Chlorobenzyl alcohol	2.04	0.895	0.63	0.54
m-Chlorobenzyl alcohol	2.43	1.18	0.75	0.72
p-Chlorobenzyl alcohol	2.92	1.23	0.91	0.75
o-Methoxybenzyl alcohol	1.91	0.81	0.59	0.49
m-Methoxybenzyl alcohol	2.30	0.89	0.71	0.54
p-Methoxybenzyl alcohol	2.78	1.05	0.86	0.64

[a] $[Cu^{III}] = 9.75 \times 10^{-4}$ mol dm^{-3}, [alcohol] $= 2.5 \times 10^{-2}$ mol dm^{-3}, $[OH^-] = 2.5 \times 10^{-1}$ mol dm^{-3}, $T = 288$ K. [b] $[Ag^{III}] = 2.35 \times 10^{-3}$ mol dm^{-3}, [alcohol] $= 2.5 \times 10^{-2}$ mol dm^{-3}, $[OH^-] = 3.75 \times 10^{-1}$ mol dm^{-3}, $T = 318$ K.

K in the oxidations by copper(III) and silver(III) complexes respectively. The values of $\Delta H^‡$ (enthalpy of activation) followed by $\Delta S^‡$ (entropy of activation) were evaluated using eqn. (3) where k and h have their usual significances. Typical

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

plots of log k_2/T against $1/T$ in the oxidation of methanol by these oxidants are shown in Fig. 2. The values of activation parameters are recorded in Table 3 and the plot of $\Delta S^‡$ against $\Delta H^‡$ is linear (Fig. 3).

The salient features concerning the oxidations of the alcohols by both ditelluratocuprate(III) and ditelluratoargentate(III) are as follows. The rate of the reactions is directly proportional to $[R^1R^2CHOH]$ and $[M^{III}(H_2TeO_6)_2]^{5-}$ but independent of $[OH^-]$. Little is known about the effect of pH on the structure of $[M^{III}(H_2TeO_6)_2]^{5-}$ which is not altered by changes in $[OH^-]$ in the range used. Again loss of proton from the ligand followed by its reaction with the alkoxide may be discounted. Consequently the lack of variation of rate with $[OH^-]$ could be taken to suggest the involvement of alcohol rather than alkoxide. The alcohols are oxidized to give carbonyl compounds as major products. Moreover, irrespective of whether the substrates are alkanols or aryl alcohols, ditelluratocuprate(III) reacts at faster rates than the corresponding reactions with ditelluratoargentate(III) (Tables 2 and 4). The results are to be expected since the third ionisation potential[12] for silver is less than that of copper. Moreover, in cases where Ag^{III}/Ag^{II}[13] couples can be compared with Cu^{III}/Cu^{II}[14] couples, results indicate that the redox potential for silver is less than that for copper. The infrared, analytical and conductometric measurements used for the study of copper(III) and silver(III) complexes suggest[6] the presence of protons in these complexes which are bonded to the tellurate ligand and the charge on the anion was found to be −5.

Spin trapping studies[15] showed that many of the photo-oxidations of alcohols by hexachlorometallate(IV) ions (M = Pt, Pd or Ir) lead to the initial formation of $RCH_2\dot{O}$ in pure alcoholic media whereas in alcohol–water mixtures the radical $R\dot{C}HOH$ is formed either directly or *via* secondary reactions of $RCH_2\dot{O}$ such as the well known H atom transfer eqn. (4) or the isomerisation reaction eqn. (5).

$$RCH_2\dot{O} + RCH_2OH \longrightarrow R\dot{C}HOH + RCH_2OH \quad (4)$$

$$RCH_2\dot{O} + H_2O \longrightarrow R\dot{C}HOH + H_2O \quad (5)$$

The increase in rates from secondary alkanols to primary alkanols (3.8 and 1.5 fold respectively) with the respective oxidants under comparable conditions of experiment may indicate the involvement of $R^1R^2CH\dot{O}$ in the present investigation. However, the oxidations of [O-^{2}H]methanol and [O-^{2}H]ethanol by these oxidants were carried out and the rates of oxidation of alkanol and [O-^{2}H]alkanol were found to be practically the same under identical conditions (Table 4). These results indicate that breaking of the O–H bond is not significant in the rate limiting step and since the present reactions have been carried out in alcohol–water mixtures it is not unreasonable to propose a radical intermediate $R^1R^2\dot{C}OH$ which is formed either *via* C–H rupture or by the transformation of $R^1R^2CH\dot{O}$ to give $R^1R^2\dot{C}OH$ as shown in eqns. (4) and (5). The EPR spectra of the reaction mixtures involving the alcohols and the copper(III) complex at different time intervals indicate that the peak intensity initially increases with the increase in time. Some results during the oxidation of benzyl alcohol by copper(III) complex as shown in Fig. 4 indicate that the peak intensity increases and then decreases after 15 min. This is possibly because of the formation of solid copper(II) thereby decreasing the effective concentration of copper(II) in the reaction mixture with progress of the reaction. The intermediate formation of free radicals is further evidenced by the formation of polymerised products when the vinyl compound was added to the reaction mixtures. Thus ditelluratometallate(III) is reduced by the alcohols to give free radicals and ditelluratometallate(II).[16] Two alternative mechanistic paths may be proposed. Of these, oxidations by both the copper(III) and the silver(III) complex occur by eqns. (6) and (7) of Scheme 1,

Table 3 Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the oxidation of different alcohols by copper(III) and silver(III) complexes

	Cu$^{\mathrm{III}}$		Ag$^{\mathrm{III}}$	
Alcohols	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
Methanol	86 ± 8	−3 ± 27	75 ± 4	−58 ± 13
Ethanol	96 ± 10	31 ± 35	105 ± 8	38 ± 28
Isopropanol	65 ± 6	−81 ± 19	46 ± 4	−150 ± 14
Benzyl alcohol	80 ± 8	7 ± 29	76 ± 8	−38 ± 26

Table 4 Values of pseudo-first-order rate constants for the oxidations of alkanol and [O-^{2}H]alkanol by the oxidants

Alcohol	$k_{\mathrm{obs}}{}^a/10^{-4}$ s^{-1}	$k_{\mathrm{obs}}{}^b/10^{-4}$ s^{-1}
Methanol	6.9	3.95
[O-^{2}H] Methanol	7.0	3.8
Ethanol	7.7	4.6
[O-^{2}H] Ethanol	7.8	4.5

[a] [Cu$^{\mathrm{III}}$] = 1.17×10^{-3} mol dm^{-3}, [alcohol] = 2.0×10^{-1} mol dm^{-3}, [OH$^-$] = 2.3×10^{-1} mol dm^{-3}, T = 298 K. [b] [Ag$^{\mathrm{III}}$] = 2.025×10^{-3} mol dm^{-3}, [alcohol] = 2.0×10^{-1} mol dm^{-3}, [OH$^-$] = 3.75×10^{-1} mol dm^{-3}, T = 313 K.

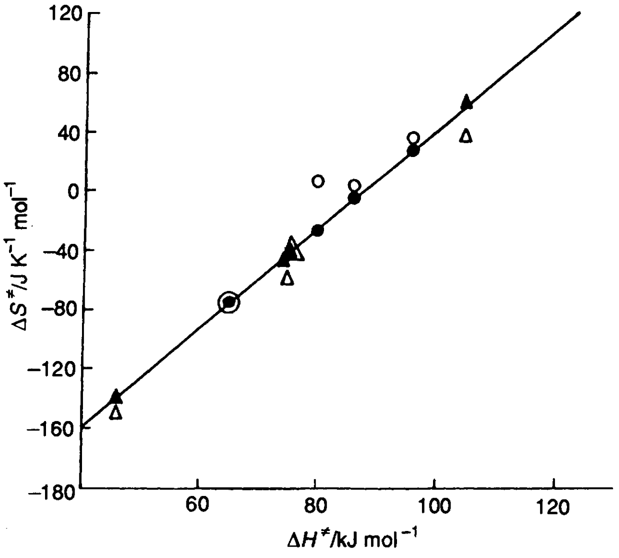

Fig. 3 Plot of $\Delta S^\ddagger$ *vs.* $\Delta H^\ddagger$ for the oxidations of alkanols and benzyl alcohol by ditelluratocuprate(III) and ditelluratoargentate(III). Cu$^{\mathrm{III}}$: ●, theoretical; ○, experimental. Ag$^{\mathrm{III}}$: ▲, theoretical; △, experimental.

whereas the one-step two-electron path shown in Scheme 2 may be discounted. However, in the oxidations by the silver(III) complex, silver(II) which is generated in the slow step disproportionates to give silver(I) and silver(III) as shown in eqn. (8).

$$\mathrm{R^1R^2CHOH + [M^{III}(H_2TeO_6)_2]^{5-} \xrightarrow{slow} R^1R^2\dot{C}OH + [M^{II}(H_2TeO_6)_2]^{6-} + H^+} \quad (6)$$

$$\mathrm{R^1R^2\dot{C}OH + [M^{III}(H_2TeO_6)_2]^{5-} \xrightarrow{fast} R^1R^2CO + [M^{II}(H_2TeO_6)_2]^{6-} + H^+} \quad (7)$$

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

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

Scheme 1

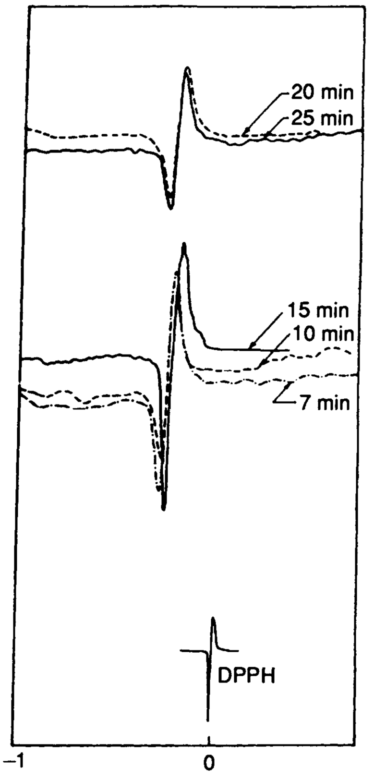

Fig. 4 The EPR spectra of the reaction mixture involving ditelluratocuprate(III) and benzyl alcohol at different time intervals and at 9.45 GHz

$$\mathrm{R^1R^2CHOH + [M^{III}(H_2TeO_6)_2]^{5-} \xrightarrow{slow} R^1R^2CO + [M^{I}(H_2TeO_6)_2]^{7-} + 2H^+} \quad (10)$$

[followed by eqn. (9).]

Scheme 2

The alcohols are thus oxidised to either aldehyde or ketone. The formation of anions of the type RCH(OH)O$^-$ has been observed[17,18] with increasing pH for strongly hydrated carbonyl compounds and has been confirmed by equilibrium and kinetic studies based on measurements of polarographic currents. Moreover, benzaldehyde which does not exist in hydrated form at lower pH values has been found to add OH$^-$ in a rapidly established reversible acid–base reaction in alkaline medium to give PhCH(OH)O$^-$ which absorbs at a maximum of 250 nm.[19,20] The UV spectrum of the reaction mixture in the oxidation of benzyl alcohol showed an absorption maximum at 250 nm thus indicating the formation of PhCH(OH)O$^-$ in the present reaction. The formation of higher yields of 2,4-DNP derivatives (>90%) suggests that internal oxidation and reduction of benzaldehyde leading to the formation of benzyl alcohol and benzoate ion do not occur. On the other hand, the comparatively lower yields of 2,4-DNP derivatives as obtained with formaldehyde, acetaldehyde and acetone might be due to the partial oxidation, as well as volatalisation, of aliphatic carbonyl compounds.

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