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Reactivity of alkanols and aryl alcohols towards tetrachloroaurate(III) in sodium acetate–acetic acid buffer medium

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ABSTRACT: The oxidative behaviour and relative reactivities of three alkanols and 11 aryl alcohols towards gold(III) in sodium acetate–acetic acid buffer were studied. The reactions are first order with respect to [Au(III)] and in each [R^1R^2CHOH]. Both H^+ and Cl^- ions retard the rate of reactions. The reactions obey the following rate expression:

$$-\mathrm{d}[\mathrm{Au(III)}]/\mathrm{d}t = \left\{k_1 + \frac{(k_2 - k_1)K_2}{[\mathrm{Cl}^-]} + \frac{(k_3 - k_1)K_2K_3}{[\mathrm{H}^+][\mathrm{Cl}^-]}\right\}[\mathrm{R}^1\mathrm{R}^2\mathrm{CHOH}][\mathrm{Au(III)}]$$

$AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ are the reactive species of gold(III) and the reactivity follows the order $AuCl_3(OH)^- > AuCl_3(OH_2) > AuCl_4^-$. The activation parameters of the reactions were calculated. Alkanols react with gold(III) in the order ethanol > methanol > 2-propanol. The unsubstituted benzyl alcohol reacts with gold(III) at a faster rate than benzhydrol. The pseudo-first-order rate constants in the oxidations of aryl alcohols follow the order $NO_2 > H > Cl > OMe$. The reactions occur via C—H bond cleavage and through the intermediate formation of free radicals. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: tetrachloroaurate(III); oxidation; alkanols; aryl alcohols; kinetics

INTRODUCTION

Gold(III) compounds, which are toxic in nature were used earlier[1] in the treatment of tuberculosis. The hydrolysis of $AuCl_4^-$ has been studied by several investigators and the existence of different gold(III) species has been suggested.[2–6] Studies involving the substitution reactions of gold(III) with ethylenediamine[7a,8] and other polyamines[7a,b] have been reported. The mechanism of the oxidation of some inorganic and organic compounds by gold(III) have been studied.[9–15] There are no literature data to date involving the oxidation of alcohols by gold(III), although the kinetics of oxidations of some alkanols and aryl alcohols by copper(III) and silver(III)[16,17] have been studied.

The redox potentials only of $HCHO–CH_3OH$ and $CH_3CHO–CH_3CH_2OH$ couples are known.[18] The values are 0.190 and 0.192 V, respectively, whereas that of the Au(III)–Au(I) couple is 1.401 V.[19] Hence the possibility of the oxidation of the alcohols by gold(III) seems plausible. Since alkanols are soluble in water, the oxidations have been studied in aqueous medium. The substituted benzyl alcohols are partially soluble in water but soluble in different solvents such as acetonitrile, dioxane, dimethylformamide and *tert*-butyl alcohol. Since gold(III) chloride is unreactive towards *tert*-butyl alcohol, the oxidations of aryl alcohols by gold(III) were studied in tert-butyl alcohol (15%, v/v). Again, gold(III) chloride is partially hydrolysed[2,4,5] at lower acidities $(1.1–12.6)\times10^{-7}$ mol dm^{-3}, and the reactions are too slow to be monitored in a highly acidic medium ($>10^{-3}$ mol dm^{-3}), but take place at measurable rates in sodium acetate–acetic acid buffer medium. The oxidations of alkanols and aryl alcohols by Cu(III) and Ag(III) occur by a free radical mechanism. Au(III) may also be reduced to give Au(II) in the rate-determining step followed by disproportionation of Au(II) to give Au(III) and Au(I). Alternatively, a one-step two-electron transfer mechanism may also be operative in the oxidation of these substrates by Au(III). The purpose of this investigation was to elucidate the electron transfer behaviour of the redox reactions involving gold(III) and the substrates. An attempt was also made to compare the present results with those for Cu(III) and Ag(III).

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Table 1. Values of pseudo-first-order rate constants for the oxidations of different alcohols by gold(III) at 298 K with $[Au(III)] = (0.8–3.0) \times 10^{-3}$ mol dm^{-3}, [substrate] = 2.5×10^{-2} mol dm^{-3}, $[Cl^-] = 1.0 \times 10^{-2}$ mol dm^{-3} and pH = 4.05

No.	Alcohol	$k_{obs}(10^{-3}s^{-1})$
1	Methanol	0.645 ± 0.02
2	Ethanol	0.839 ± 0.01
3	2-Propanol	0.462 ± 0.01
4	Benzyl alcohol	7.60 ± 0.06
5	Benzhydrol	2.39 ± 0.2
6	*o*-Nitrobenzyl alcohol	9.18 ± 0.04
7	*m*-Nitrobenzyl alcohol	10.7 ± 0.08
8	*p*- Nitrobenzyl alcohol	12.3 ± 0.2
9	*o*-Chlorobenzyl alcohol	3.19 ± 0.2
10	*m*-Chlorobenzyl alcohol	4.27 ± 0.05
11	*p*-Chlorobenzyl alcohol	6.45 ± 0.1
12	*o*-Methoxybenzyl alcohol	2.73 ± 0.2
13	*m*-Methoxybenzyl alcohol	3.71 ± 0.05
14	*p*-Methoxybenzyl alcohol	5.53 ± 0.07

RESULTS AND DISCUSSION

Effect of reactant concentrations

The reactions were investigated at different concentrations of Au(III) but at constant [substrate], pH, $[Cl^-]$ and temperature. The pseudo-first-order rate constants remain unaltered in the [Au(III)] range $(0.8–3.0)\times10^{-3}$ mol dm^{-3} (Table 1). These results indicate that the rate is first order with respect to [Au(III)]. At constant [Au(III)], $[Cl^-]$, pH and temperature, the rate increases with increase in [substrate]. The results plotted in Fig. 1 indicate that each reaction is first order with respect to [substrate].

Effect of $[H^+]$

The rate of the reaction was studied at 298 K at different pH values (3.72–4.80) using sodium acetate–acetic acid buffer while keeping [Au(III)], [substrate] and $[Cl^-]$ constant at 8.0×10^{-4}, 1.5×10^{-2} and 1.0×10^{-2} mol dm^{-3}, respectively. No attempt was made to keep the ionic strength constant since the values of k_{obs} remains unchanged at different ionic strengths, 0.05–0.15 mol dm^{-3}, varied by the addition of sodium perchlorate. The value of k_{obs} increases with increase in pH. The plot of k ($k = k_{obs}$/[substrate]) vs $[H^+]^{-1}$ gave a straight line with a positive slope and a positive intercept on the ordinate (Fig. 2).

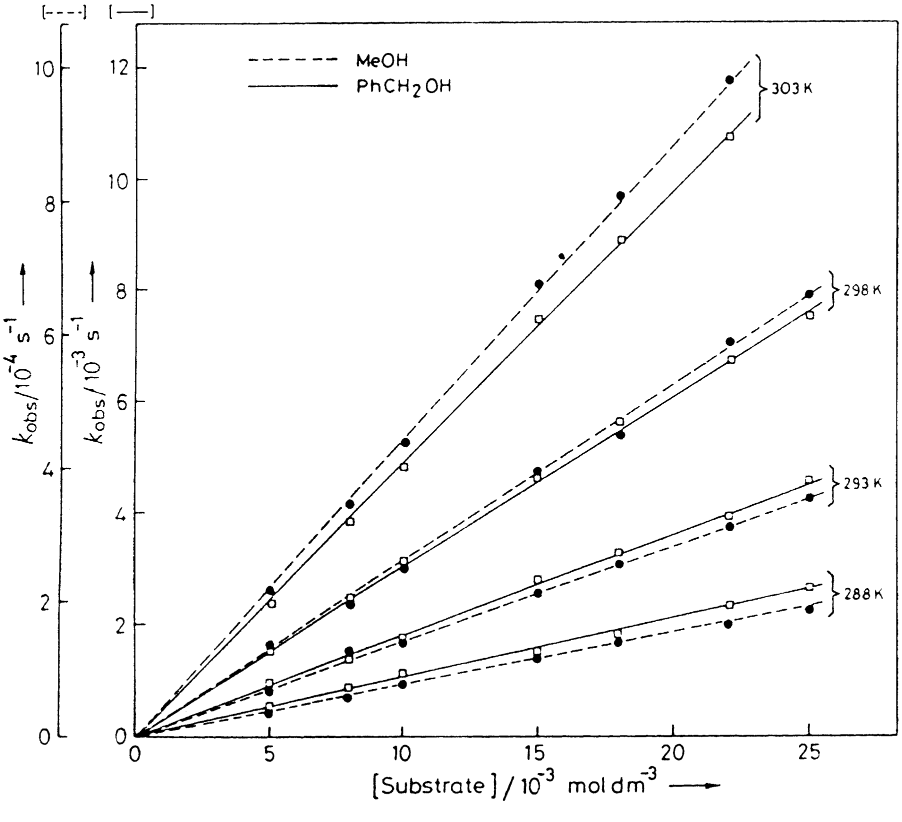

Figure 1. Variation of pseudo-first-order rate constant with substrate concentrations. Oxidation of methanol was studied in aqueous medium unlike benzyl alcohol in 15% *tert*-butyl alcohol. Plots of k_{obs} versus [substrate] at different temperatures. $[Au(III)] = 8 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 8.91 \times 10^{-5}$ mol dm^{-3} and $[Cl^-] = 1.0 \times 10^{-2}$ mol dm^{-3}

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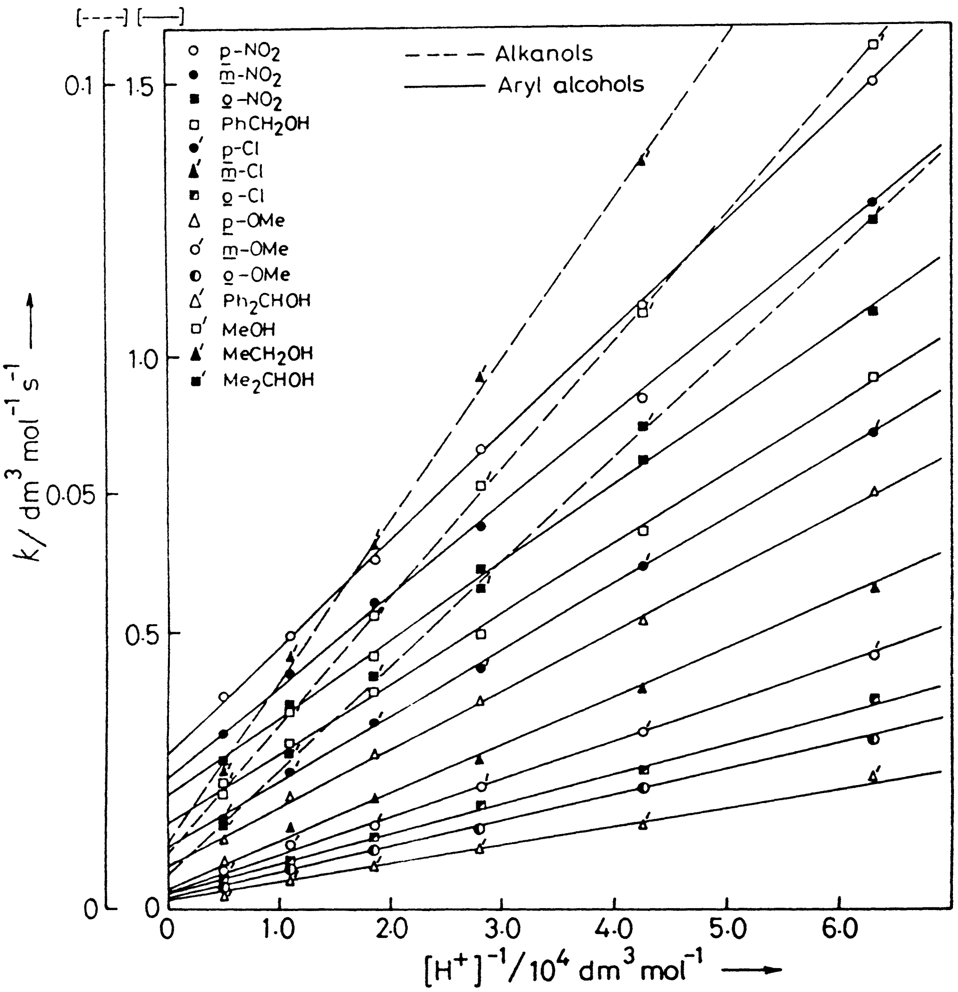

Figure 2. Variation of second-order rate constant with acid concentration. Plots of k vs $[H^+]^{-1}$ for different substrates at 298 K. $[Au(III)] = 8 \times 10^{-4}$ mol dm^{-3}, [substrate] $= 1.5 \times 10^{-2}$ mol dm^{-3} and $[Cl^-] = 1.0 \times 10^{-2}$ mol dm^{-3}

Effect of [Cl$^-$]

The reaction was studied at 298 K at different [Cl$^-$] [(8–35)$\times 10^{-3}$ mol dm^{-3}] varied by the addition of NaCl but at constant [Au(III)], [substrate] and [H$^+$] of 8.0×10^{-4}, 1.5×10^{-2} and 8.91×10^{-5} mol dm^{-3}, respectively. Chloride ion inhibits the rate of the reaction. The plot of k against $[Cl^-]^{-1}$ is linear with a positive slope and positive intercept on the ordinate (Fig. 3).

Table 2. Effect of solvent composition on the pseudo-first-order rate constant for benzyl alcohol with $[Au(III)] = 8.0 \times 10^{-4}$ mol dm^{-3}, [benzyl alcohol] $= 8.0 \times 10^{-3}$ mol dm^{-3}, $[Cl^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, pH = 4.05 and temperature = 303 K

tert-Butyl alcohol (%, v/v)	k_{obs} ($10^{-3}s^{-1}$)
0	4.95
10	4.03
15	3.90
20	2.92
30	2.05
40	1.45

Effect of solvent

The effect of variation of the solvent such as *tert*-butyl alcohol on the pseudo-first-order rate constant was also

Table 3. Values of pseudo-first-order rate constants for the oxidation of alkanols and deuterated alkanols by gold(III) at 298 K with $[Au(III)] = 8.0 \times 10^{-4}$ mol dm^{-3}, [alkanol] $= 2.0 \times 10^{-2}$ mol dm^{-3}, $[Cl^-] = 1.0 \times 10^{-2}$ mol dm^{-3} and pH = 4.05

Alkanol	k_{obs} (10^{-4} s^{-1})	k_H/k_D
CH_3OH	5.21	—
CH_3OD	5.19	1.00
CD_3OD	2.76	1.89
C_2H_5OH	6.69	—
C_2H_5OD	6.72	0.99
C_2D_5OD	3.87	1.73

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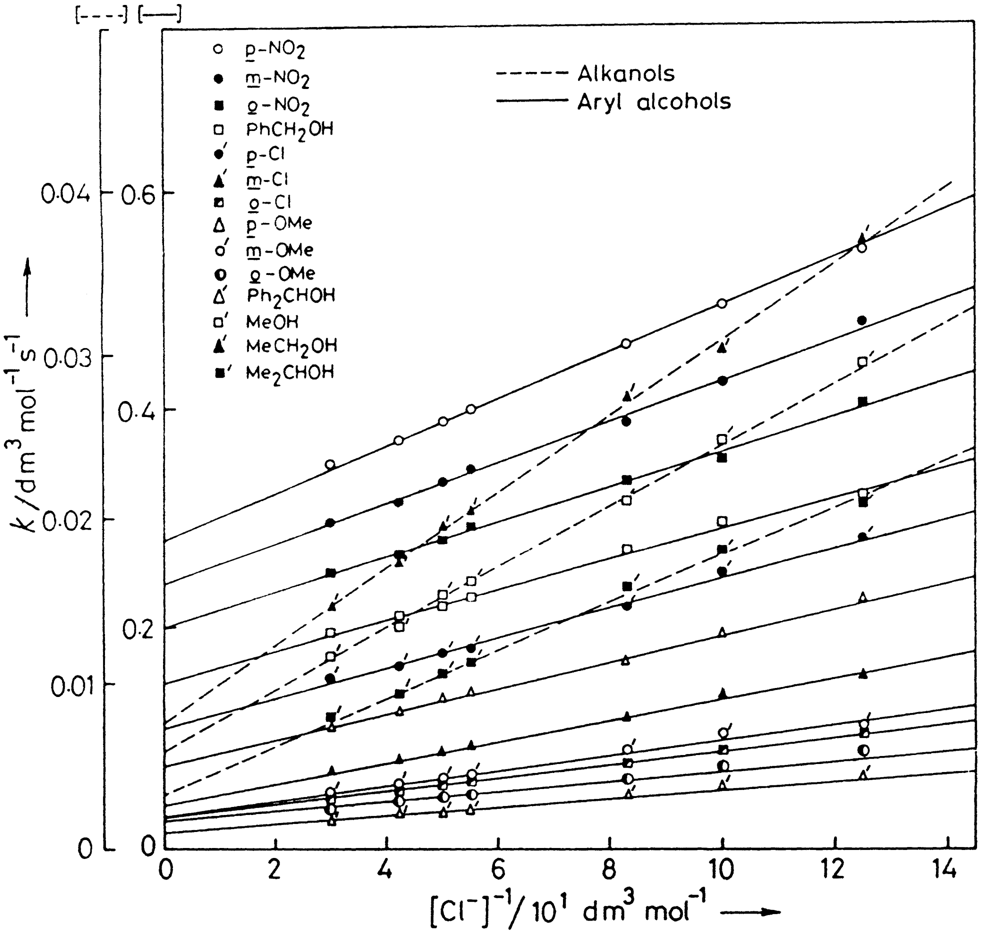

Figure 3. Variation of second-order rate constant with chloride ion concentration. Plots of k vs $[Cl^-]^{-1}$ for different substrates at 298 K. $[Au(III)] = 8 \times 10^{-4}$ mol dm^{-3}, [substrate] $= 1.5 \times 10^{-2}$ mol dm^{-3} and $[H^+] = 8.91 \times 10^{-5}$ mol dm^{-3}

studied for the oxidation of benzyl alcohol by gold(III) at constant reactant concentrations and temperature. The rate increases with increase in dielectric constant (Table 2).

Effect of substituents

The reactivities of alkanols towards gold(III) was studied in aqueous medium and follow the order ethanol > methanol > 2-propanol. This order is in agreement with those reported by Hoare and Waters[20] for the cobalt(III) oxidations of the same alcohols. The rate of oxidation increases in the presence of electron - withdrawing groups and decreases in the presence of electron-donating groups. When the substituent is chlorine, the rate was found to be between those for the nitro and methoxy derivatives. The pseudo-first-order rate constants follow the order $NO_2 > H > Cl > OMe$. The plots of log k_{obs} against σ give a good linear relationship ($r = 0.9847$) and the value of ρ was calculated to be 0.323. This low value of ρ is not unexpected and has also been reported by other workers.[21] 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 alcoholic carbon makes the reaction less favourable[22] than benzyl alcohol with gold(III), thereby decreasing the rate in benzhydrol.

Kinetic isotope effect

The kinetic isotope effects of CH_3OH, CH_3OD, C_2H_5OH and C_2H_5OD were studied (Table 3). The k_H/k_D values were 1.00 and 0.99, respectively. On the other hand, CD_3OD and C_2D_5OD are oxidised at slower rates than the respective parent alcohols. The results are given in Table 3. The values of k_H/k_D are 1.89 and 1.73, respectively. Smaller values k_H/k_D of 1.2–2.0 have also been observed[23,24] in the oxidations of some organic compounds by manganese(III), vanadium(V), cerium(IV) and cobalt(III) in acidic medium where the oxidations have been shown to occur via C—H bond fission. All these results indicate that oxidations of the alcohols by gold(III) do not occur via O—H bond fission but rather via C—H bond cleavage[25,26].

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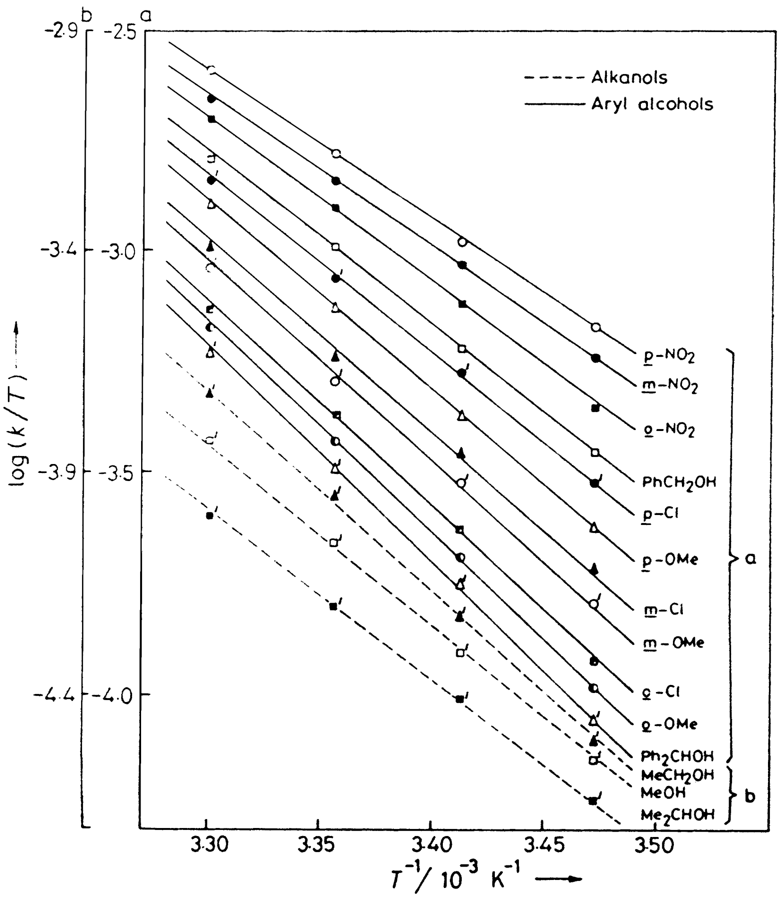

Figure 4. Influence of temperature on second-order rate constant. Plots of log (k/T) vs T^{-1} for the oxidations of alkanols and aryl alcohols

Activation parameters

The second-order rate constants (k) were determined at different temperatures (288–303 K). The activation enthalpies ($\Delta H^{\neq}$) were calculated from the plots of log(k/T) vs T^{-1} (Fig. 4) followed by entropies of activation ($\Delta S^{\neq}$) using the equation

$$\log(k/T) = [\log(k_B/h) + \Delta S^{\neq}/2.303R] - \Delta H^{\neq}/2.303RT \qquad (1)$$

where k_B and h have their usual significance.

The activation parameters are given in Table 4. The enthalpy of activation is linearly related to the entropy of activation, as shown in Fig. 5. The isokinetic temperature was calculated to be 280 K for alkanols and 350 K for aryl alcohols. The isokinetic behaviour is also supported by the linear plot of log k' versus log k, where k' and k are the second-order rate constants at temperatures 293 K (T_1) and 298 K (T_2), respectively (Fig. 5). All these results indicate that a similar mechanism may be operative in all these reactions. The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1-f)/(T_1-T_2 f)$, where f is the slope of the Exner plot.[27] The value of β was found to be 266 K for alkanols and 359 K for aryl alcohols. The value of β for alkanols is lower than the experimental temperature of 295 K whereas β for aryl alcohols is higher than 295 K. Hence the reactions of

Table 4. Values of activation parameters for the oxidation of different alcohols by gold(III)

No	Alcohol	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
1	Methanol	77 ± 2	-17 ± 7
2	Ethanol	85 ± 2	11 ± 7
3	2-Propanol	72 ± 4	-36 ± 14
4	Benzyl alcohol	73 ± 2	-10 ± 7
5	Benzhydrol	92 ± 4	44 ± 14
6	*o*-Nitrobenzyl alcohol	70 ± 4	-18 ± 14
7	*m*-Nitrobenzyl alcohol	66 ± 6	-30 ± 7
8	*p*-Nitrobenzyl alcohol	64 ± 2	-36 ± 7
9	*o*-Chlorobenzyl alcohol	88 ± 2	33 ± 7
10	*m*-Chlorobenzyl alcohol	83 ± 8	19 ± 27
11	*p*-Chlorobenzyl alcohol	74 ± 4	-8 ± 14
12	*o*-Methoxybenzyl alcohol	91 ± 2	42 ± 7
13	*m*-Methoxybenzyl alcohol	86 ± 2	28 ± 7
14	*p*-Methoxybenzyl alcohol	81 ± 2	14 ± 7

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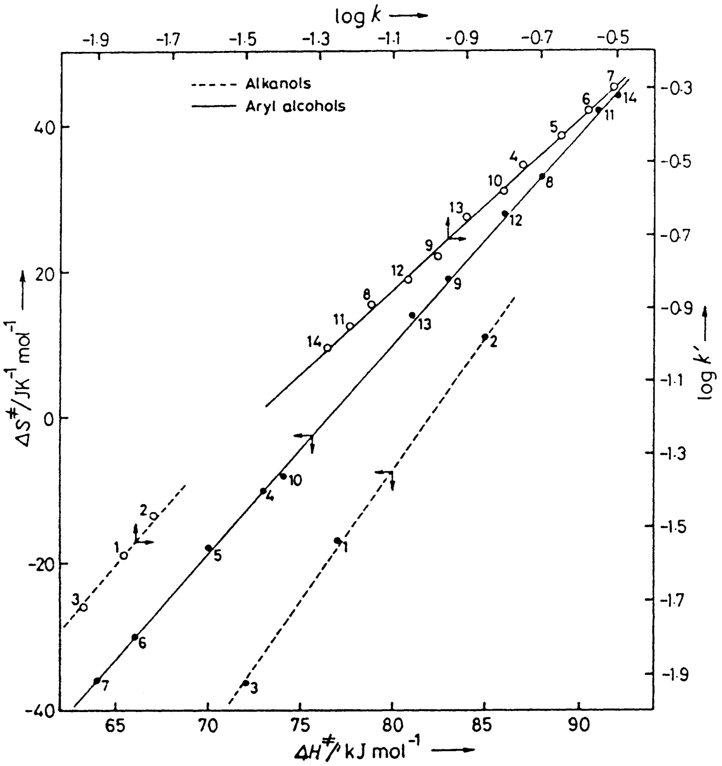

Figure 5. Isokinetic plots of the oxidations of alcohols by gold(III). Plots of (i) $\Delta S^{\neq}$ vs $\Delta H^{\neq}$ and (ii) log k' vs log k. (1) MeOH; (2) $MeCH_2OH$; (3) Me_2CHOH; (4) $PhCH_2OH$; (5) *o*-NO_2; (6) *m*-NO_2; (7) *p*-NO_2; (8) *o*-Cl; (9) *m*-Cl; (10) *p*-Cl; (11) *o*-OMe; (12) *m*-OMe; (13) *p*-OMe; (14) Ph_2CHOH

alkanols are entropy controlled[28] whereas those involving aryl alcohols are believed to be enthalpy controlled.[29] It may be mentioned that the oxidation of alkanols has been studied in aqueous medium, unlike aryl alcohols, studied in *tert*-butyl alcohol (15%, v/v).

The following equilibria are known[6,9,30] to exist in a dilute solution of tetrachloroauric(III) acid:

$$HAuCl_4 \overset{K_1}{\rightleftharpoons} H^+ + AuCl_4^- \tag{2}$$

$$AuCl_4^- + H_2O \overset{K_2}{\rightleftharpoons} AuCl_3(OH_2) + Cl^- \tag{3}$$

$$AuCl_3(OH_2) \overset{K_3}{\rightleftharpoons} AuCl_3(OH)^- + H^+ \tag{4}$$

where $K_1 = 1.0$, $K_2 = 9.5 \times 10^{-6}$ and $K_3 = 0.25$ at 298 K. Consequently, four different species, viz. $HAuCl_4$, $AuCl_4^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$, may act as oxidants under the present experimental conditions. However, in a solution of $[H^+] \approx 10^{-4}$ mol dm^{-3}, [$HAuCl_4$] is insignificant compared with [$AuCl_4^-$]. Alcohols are known to be weak proton acceptors and are converted to alkoxonium ions only in the presence of high concentrations of mineral acids. Since the present reactions were studied at low acidities ($\sim 10^{-4}$ mol dm^{-3}), it is highly unlikely that an appreciable amount of each alcohol remains as alkoxonium ion, $R^1R^2CHOH_2^+$ or $XC_6H_4CH_2OH_2^+$. Hence the molecular forms of the alcohols and not their anions or protonated forms react with the oxidant.

Gold(III) is known[9] to behave as a one- or two-electron transfer oxidant. In the present investigation, the reaction mixture gave a polymeric suspension in the presence of acrylonitrile. This suggests that free-radical intermediates are formed during the reactions, when gold(III) is reduced to gold(II) in the rate-determining step. The formation of unstable gold(II) as an intermediate has been predicted by a number of workers.[2,31–33] Consequently, reduction of gold(III) to gold(I) in a one-step, two-electron process may be ignored. A free-radical intermediate may also be produced by the reaction between R^1R^2CHOH with gold(I). However such a possibility has been discounted since neither colloidal gold nor any precipitate of gold(0) was detected under the kinetic conditions.

The reactions were carried out in alcohol–water mixtures and it is believed that radical intermediates are formed during the reactions [Eqns ((7)–(9))]. Spin trapping studies during the oxidation of benzyl alcohol by hexachlorometallate ions (M = Pt, Pd and Ir) have shown[34] the formation of $PhCH_2O^{\cdot}$ in pure alcoholic medium whereas in alcohol–water mixtures the radical $Ph\dot{C}HOH$ is formed either directly or via secondary

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reactions of $PhCH_2O^{\cdot}$ by H atom transfer reaction [Eqn. (5)] or an isomerization reaction [Eqn. (6)]:[35]

$$PhCH_2O^{\cdot} + PhCH_2OH \rightarrow Ph\dot{C}HOH + PhCH_2OH \qquad (5)$$

$$PhCH_2O^{\cdot} + H_2O \rightarrow Ph\dot{C}HOH + H_2O \qquad (6)$$

However, the observed kinetic isotope effect rules out the involvement of Eqns (5) and (6). The free radical further reacts with another Au(III) to give R^1R^2CO and Au(II) as shown in steps (10)–(12). The following steps may be proposed to explain the reaction. The addition of alcohol to the mixture containing gold(III) and buffer solution failed to increase the absorbance, indicating the absence of intermediate complex formation between the reactants. $AuCl_4{}^-$, $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ react with the substrates R^1R^2CHOH or $XC_6H_4CH_2OH$ according to the steps (7)–(9):

$$AuCl_4^- + R^1R^2CHOH \xrightarrow[slow]{k_1} R^1R^2\dot{C}OH + AuCl_4^2 - +H^+ \qquad (7)$$

$$AuCl_3(OH_2) + R^1R^2CHOH \xrightarrow[slow]{k_2} R^1R^2\dot{C}OH + AuCl_3(OH_2)^- + H^+ \qquad (8)$$

$$AuCl_3(OH)^- + R^1R^2CHOH \xrightarrow[slow]{k_3} R^1R^2\dot{C}OH + AuCl_3(OH)^{2-} + H^+ \qquad (9)$$

The free radicals react further with the respective gold(III) species to give the carbonyl compound and gold(II) as shown in steps (10)–(12):

$$AuCl_4^- + R^1R^2\dot{C}OH \xrightarrow{fast} R^1R^2CO + AuCl_4^{2-} + H^+ \qquad (10)$$

$$AuCl_3(OH_2) + R^1R^2\dot{C}OH \xrightarrow{fast} R^1R^2CO + AuCl_3(OH_2)^- + H^+ \qquad (11)$$

$$AuCl_3(OH)^- + R^1R^2\dot{C}OH \xrightarrow{fast} R^1R^2CO + AuCl_3(OH)^{2-} + H^+ \qquad (12)$$

Au(II) undergoes fast disproportionation into Au(I) and Au(III):

$$2AuCl_4^{2-} \xrightarrow{fast} AuCl_2^- + AuCl_4^- + 2Cl^- \qquad (13)$$

$$2AuCl_3(OH_2)^- \xrightarrow{fast} AuCl_2^- + AuCl_4^- + 2H_2O \qquad (14)$$

$$2AuCl_3(OH)^{2-} + 2H^+ \xrightarrow{fast} AuCl_2^- + AuCl_4^- + 2H_2O \qquad (15)$$

According to the suggested mechanism, the rate of disappearance of [Au(III)] may be expressed as

$$\frac{-d[Au(III)]}{dt} = \{k_1[AuCl_4^-] + k_2[AuCl_3(OH_2)] + k_3[AuCl_3(OH)^-]\}[R^1R^2CHOH] \qquad (16)$$

If C_0 = [Au(III)], x = $[AuCl_3(OH)_2)]$ and y = $[AuCl_3(OH)^-]$ Eqn. (16) may be written as

$$\frac{-d[Au(III)]}{dt} = \{k_1(C_0 - x - y) + k_2x + k_3y\}[R^1R^2CHOH] \qquad (17)$$

Again, the value of K_2 indicate that $C_0 \gg x, y$, so that

$$K_2 = \frac{x[Cl^-]}{C_0 - x - y} \cong \frac{x[Cl^-]}{C_0}$$

Therefore,

$$x = \frac{K_2C_o}{[Cl^-]}$$

and

$$K_3 = \frac{y[H^+]}{x} = \frac{y[H^+][Cl^-]}{K_2C_0}$$

or

$$y = \frac{K_2K_3C_0}{[H^+][Cl^-]}$$

Substitution of x and y in Eqn. (17) gives

$$\frac{-d[Au(III)]}{dt} = \left\{k_1\left(C_0 - \frac{K_2C_0}{[Cl^-]} - \frac{K_2K_3C_0}{[H^+][Cl^-]}\right) + k_2\frac{K_2C_0}{[Cl^-]} + k_3\frac{K_2K_3C_0}{[H^+][Cl^-]}\right\}[R^1R^2CHOH] \qquad (18)$$

Now,

$$\frac{-1}{[Au(III)]}\frac{d[Au(III)]}{dt} = k_{obs}$$

Therefore,

$$k_{obs} = \left\{k_1 + \frac{(k_2 - k_1)K_2}{[Cl^-]} + \frac{(k_3 - k_1)K_2K_3}{[H^+][Cl^-]}\right\} \times [R^1R^2CHOH] \qquad (19)$$

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Table 5. Rate-determining steps for the oxidations of the alcohols by different gold(III) species at 298 K with [substrate] = 1.5×10^{-2} mol dm^{-3}, [Cl$^-$] = 1.0×10^{-2} mol dm^{-3} [Au(III)] = 8.0×10^{-4} mol dm^{-3} and pH = 4.05

No.	Alcohol	k_1 (10^{-2} dm^3 mol^{-1}s^{-1})	k_2 (10^{-2} dm^3 mol^{-1}s^{-1})	k_3 (10^{-2} dm^3 mol^{-1}s^{-1})
1	Methanol	0.600	0.916	1.25
2	Ethanol	0.732	1.05	1.56
3	2-Propanol	0.334	0.544	0.869
4	Benzyl alcohol	15.0	18.2	20.3
5	Benzhydrol	2.10	2.32	3.20
6	*o*-Nitrobenzyl alcohol	20.0	23.2	25.8
7	*m*-Nitrobenzyl alcohol	24.0	27.2	31.0
8	*p*- Nitrobenzyl alcohol	28.0	31.2	36.1
9	*o*-Chlorobenzyl alcohol	3.00	3.53	5.29
10	*m*-Chlorobenzyl alcohol	4.00	6.11	7.65
11	*p*-Chlorobenzyl alcohol	11.0	13.1	16.0
12	*o*-Methoxybenzyl alcohol	2.50	2.82	4.44
13	*m*-Methoxybenzyl alcohol	3.10	4.05	5.81
14	*p*-Methoxybenzyl alcohol	8.00	10.1	12.5

and

$$k = \left\{ k_1 + \frac{(k_2 - k_1)K_2}{[\mathrm{Cl}^-]} + \frac{(k_3 - k_1)K_2K_3}{[\mathrm{H}^+][\mathrm{Cl}^-]} \right\} \qquad (20)$$

where $k = k_{obs}/[R^1R^2CHOH]$.

Equation (19) predicts a linear plot of k_{obs} against $[R^1R^2CHOH]$, passing through the origin at constant [Au(III)], $[H^+]$, $[Cl^-]$ and temperature. This has been verified experimentally (Fig. 1).

Equation (3) further indicates that the addition of Cl^- decreases the concentrations of $AuCl_3(OH_2)$ and $AuCl_3(OH)^-$ thereby increasing the concentration of the less reactive species $AuCl_4{}^-$ and hence the retarding effect of the Cl^- ion on the reaction rate. From the intercept of the linear plot of k against $[Cl^-]^{-1}$ (Fig. 3) at constant temperature the value of k_1 was evaluated at 298 K for different substrates (Table 5).

The reactions are inhibited by H^+ ions at constant $[Cl^-]$, indicating that $AuCl_3(OH)^-$ is the most reactive amongst different Au(III) species. The linear plot of k vs $[H^+]^{-1}$ at 298 K (Fig. 2) conforms to Eqn. (20). From the intercept and slope of the straight line and using the value of k_1 obtained earlier, the values of k_2 and k_3 were evaluated at 298 K for different substrates (Table 5). Thus the reactivity of three Au(III) species follow the order $AuCl_3(OH)^- > AuCl_3(OH_2) > AuCl_4{}^-$ and this is in keeping with the observations made earlier.[14] The fact that $AuCl_3(OH)^-$ and $AuCl_3(OH_2)$ are more reactive than $AuCl_4{}^-$ is due to the easier displacement of an OH^-/OH_2 group than a Cl^{-1} ion.[14] Substituting the values of k_1, k_2 and k_3 into Eqn. (19), the values of k_{obs} were calculated under different experimental conditions. The calculated and experimental values are shown in Table 6. The two values are not widely different, which confirms that three different gold(III) species participate in the reactions.

The rate of the copper(III) and silver(III) oxidation of the alkanols and aryl alcohols increases with the first power of each of [M(III)] and [substrate] but the rate is independent of $[OH^-]$. The gold(III) oxidation of the substrates studied in sodium acetate–acetic acid buffer medium is kinetically dissimilar. Three different species of gold(III) are involved in the buffer medium, unlike in alkaline medium where a single species of each of copper(III) and silver(III) oxidize the substrates. Consequently, the rate constants of the present reactions cannot be compared with those reported earlier for the oxidation of respective substrates with copper(III) and silver(III). However, irrespective of whether the oxidations were carried out in alkaline or buffer medium, one common piece of information was obtained, namely that both alkanols and aryl alcohols are oxidized to give carbonyl

Table 6. Measured and calculated pseudo-first-order rate constants of the oxidations of different alcohols by gold(III) at 298 K with [Au(III)] = 8.0×10^{-4} mol dm^{-3}, [substrate] = 1.5×10^{-2} mol dm^{-3}, [Cl$^-$] = 1.0×10^{-2} mol dm^{-3} and pH = 4.05

No.	Alcohol	k_{obs} (10^{-3} s^{-1})	k_{cal} (10^{-3} s^{-1})
1	Methanol	0.376	0.352
2	Ethanol	0.489	0.439
3	2-Propanol	0.282	0.294
4	Benzyl alcohol	4.53	4.39
5	Benzhydrol	0.96	0.785
6	*o*-Nitrobenzyl alcohol	5.46	5.33
7	*m*-Nitrobenzyl alcohol	6.41	6.40
8	*p*- Nitrobenzyl alcohol	7.46	7.43
9	*o*-Chlorobenzyl alcohol	1.60	1.37
10	*m*-Chlorobenzyl alcohol	2.42	2.11
11	*p*-Chlorobenzyl alcohol	3.82	3.67
12	*o*-Methoxybenzyl alcohol	1.32	1.17
13	*m*-Methoxybenzyl alcohol	1.80	1.58
14	*p*-Methoxybenzyl alcohol	3.25	2.98

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Table 7. Identification of products of the reactions[a]

No.	Alcohol	Yield (%) (2,4-DNP derivative)	M.p. (°C)	Lit. m.p.[44] (°C)
1	Methanol	43	166	166–167
2	Ethanol	47	147	148
3	2-Propanol	51	127	126–128
4	Benzyl alcohol	61	238	237
5	Benzhydrol	64	239	238
6	*o*-Nitrobenzyl alcohol	56	265	265
7	*m*-Nitrobenzyl alcohol	58	291	292
8	*p*- Nitrobenzyl alcohol	59	321	320
9	*o*-Chlorobenzyl alcohol	63	208	209
10	*m*-Chlorobenzyl alcohol	65	248	248
11	*p*-Chlorobenzyl alcohol	68	265	265
12	*o*-Methoxybenzyl alcohol	69	252	253
13	*m*-Methoxybenzyl alcohol	72	233	232
14	*p*-Methoxybenzyl alcohol	78	255	254

[a] The oxidation products except Nos 1–3 were identified in 15% *tert*-butyl alcohol.

compounds through the intermediate formation of free radicals.

EXPERIMENTAL

Reagents. The alcohols (BDH, Merck or Sigma) were used as supplied. CH_3OD, CD_3OD, C_2H_5OD, C_2D_5OD and D_2O (by 99 atom% D) were obtained from Aldrich. A stock solution of gold(III) was prepared by dissolving $HAuCl_4$ (Johnson Matthey) in 0.01 mol dm^{-3} HCl. The strength of the solution was estimated gravimetrically.[36] To a known volume (5 ml) of the standard gold solution in a 150 ml beaker was added dropwise with stirring, a 1 M solution of KOH until the yellow color was just discharged. A further 2 ml of KOH solution were added, followed by dilution to ca. 75 ml with distilled water. Then 5–6 ml of 1 N oxalic acid were added dropwise with stirring and the contents were kept on a boiling water-bath. The solution turned purple with a violet tinge when gold separated out. The beaker was kept on the water-bath for about 1 h with occasional stirring. The solution was filtered through a whatman No. 42 (7 cm) filter-paper. The precipitate was washed with distilled water, dried, ignited in a silica crucible and weighed as metal. The gold(III) solution after estimation was stored in the dark and used under subdued lighting and was diluted to the desired concentrations before kinetic experiments.

Inorganic materials were of the highest available purity. All solutions were made in doubly distilled water. The oxidation studies were carried out in a sodium acetate–acetic acid buffer. Buffer solutions were prepared[37] from standard solutions of sodium acetate and acetic acid.

Instrumentation. Spectral measurements were recorded in the UV–Vis region using a Systronics (India) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz). The pH of the solution was measured at room temperature (~25 °C) using an Elico (LI 120) pH meter (India), calibrated against standard pH solutions. Melting-point determinations were carried out using a Gallenkamp apparatus.

Absorption spectra of gold(III) and carbonyl compounds. The spectrum of $AuCl_4^-$ has been reported to have two intense absorption maxima at 226 nm ($\epsilon = 25\,600$ mol dm^{-3} cm^{-1}) and 315 nm ($\varepsilon = 4800$ mol dm^{-3} cm^{-1}) in 1 mol dm^{-3} HCl,[38] Spectra of $AuCl_4^-$ were also recorded for different $[Cl^-]$ at the various acidities. The spectrum for gold(III)[14] at $[Cl^-]$ of 1.0 mol dm^{-3} and pH 2.0 is identical with that obtained for 1.0 mol dm^{-3} HCl. However, as $AuCl_4^-$ is hydrolysed a blue shift in the spectrum is observed.[4] There is an isosbestic point at 295 nm ($\varepsilon = 3.02 \times 10^3$ mol $dm^{-3}cm^{-1}$) and under conditions in which the absorbance at the isosbestic point does not change, $AuCl_4^-$ and $AuCl_3(OH^-)$ are the main species present, the latter obviously being generated by the rapid dissociation of $AuCl_3(H_2O)$.

Saturated carbonyl compounds exhibit three bands in the UV region: a weak band at 280 nm, a more intense band around 190 nm and a still more intense band around 150 nm, which are assigned to $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions respectively.[39] The $n \rightarrow \pi^*$ transition of a large number of carbonyl derivatives have been reported in the literature.[40(a)] The position of the $n \rightarrow \pi^*$ band of carbonyl group varies with the substituents on the molecule of aliphatic compounds and are formed in the region 277–291 nm. The aromatic carbonyl compounds absorb at higher wavelength (>325 nm) than acetone (277 nm). The absorption maxima for benzophenone and benzaldehyde are at 348 and 328 nm, respectively, owing to conjugation[39] of these molecules. Since carbonyl compounds were obtained as the products of oxidation, the kinetic studies were carried out in the visible region at

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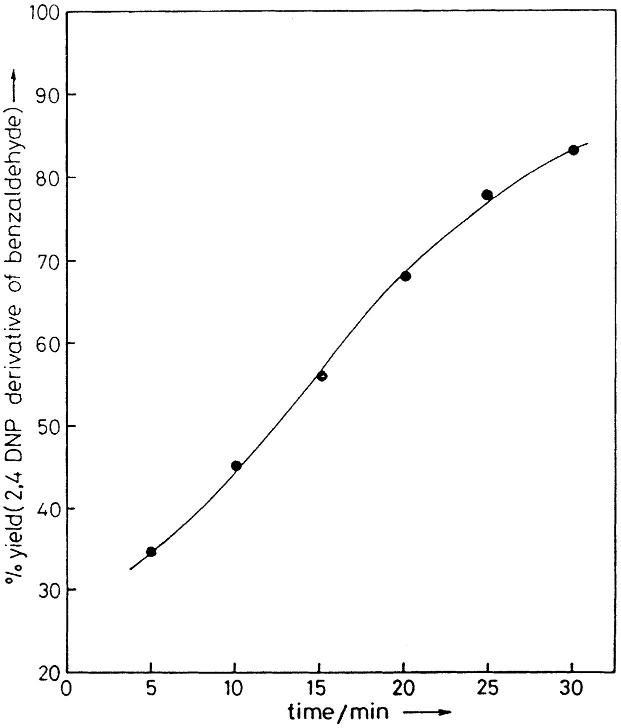

Figure 6. Plots of% yield (2,4-DNP derivative of benzaldehyde) vs time for the oxidations of benzyl alcohol by gold(III)

400 nm in order to eliminate the absorptions due to carbonyl compounds. Alkanols and aryl alcohols are transparent at this wavelength.

Product analyses. After the kinetic experiments, each mixture was allowed to stand for 3 h and then filtered to remove suspended particles, if any. In one part of the filtrate the oxidation products in the oxidations of alkanols were tested by colour tests as described.[41–43] The other part of the filtrate was acidified with dilute H_2SO_4, then added to 2,4-dinitrophenylhydrazine hydrochloride solution, heated on a steam-bath for 15 min and left at room temperature for 1 h, giving yellow crystals of 2,4-dinitrophenylhydrazone derivatives of the respective carbonyl compounds. The derivatives were filtered, washed and dried, followed by determination of the melting-points[44] and yields (Table 7).

In another experiment, the amount of benzaldehyde formed in the absence of *tert*-butyl alcohol was determined by the preparation of 2,4-dinitrophenylhydrazone derivatives at different time intervals at 303 K. The results shown in Fig. 6 indicate that the amount of benzaldehyde formed increased with time (yields calculated based on total parent compound concentration at $t = 0$). The lower percentage yields of 2,4-DNP derivative obtained (Table 7) as compared with those in Fig. 6 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 oxidation product of benzyl alcohol was extracted with diethyl ether, washed thoroughly with $NaHCO_3$ and water, dried over anhydrous Na_2SO_4 and the ether was then evaporated. ^1H and ^{13}C NMR spectra of the oxidation product of benzyl alcohol in $CDCl_3$ showed the —CHO proton peak at 10.05 and 192.4 ppm, respectively. These values are close to the literature values[40b] of 9.98 ppm and 192 ppm reported for the —CHO proton of benzaldehyde. The oxidations occur according to the following reactions:

$$R^1R^2CHOH + Au(III) \rightarrow R^1R^2CO + Au(I) + 2H^+ \qquad (21)$$

where $R^1 = R^2 = H$ for methanol, $R^1 = H$, $R^2 = Me$ for ethanol and $R^1 = R^2 = Me$ for 2-propanol, and

$$XC_6H_4CH_2OH + Au(III) \rightarrow XC_6H_4CHO + Au(I) + 2H^+ \qquad (22)$$

where, X = NO_2, Cl and OMe.

The oxidation of methanol and ethanol by gold(III) leads to the formation of formaldehyde and acetaldehyde, respectively, and further oxidation of the aldehydes does not take place at lower acidities.[45] Again, aldehyde oxidation proceeds via the aldehyde hydrate as shown in the following sequence:

$$RCH_2OH \rightarrow RCHO \xrightarrow{H_2O\ H^+} RCH(OH)_2 \rightarrow RCOOH \qquad (23)$$

Since the hydration reaction is acid catalyzed, it is likely that the reaction might be sufficiently retarded at low acidities to make formic acid and acetic acid formation negligible. A few runs with the respective oxidation products, formaldehyde, acetaldehyde and acetone, with gold(III) were made at pH 4.05 and it was found that oxidation is too slow compared with the oxidation of the alcohols. Aromatic aldehydes are not hydrated to any appreciable extent owing to the extra resonance stabilization. The results in Fig. 6 indicate that further oxidation of benzaldehyde to give benzoic acid is also insignificant during kinetic investigations. The comparatively lower yields obtained in the oxidations of alkanols compared with the oxidations of aryl alcohols may be due to volatilization of the oxidation products.

Test for free radicals. Acrylonitrile [50% (v/v)] was added to the reaction mixture during the course of the reactions. An immediate haziness appeared during the oxidation of alcohol by gold(III). The appearance of a white precipitate of polyacrylonitrile shows the presence of free-radical intermediates in the oxidation process. Blank experiments in which either gold(III) or alcohols were excluded gave no detectable polymers.

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Kinetic measurements. The reaction rate was determined spectrophotometrically at 400 nm using a sodium acetate–acetic acid buffer solution under conditions where [alcohols] $\gg$ [Au(III)]. After the requisite volumes of the reactants at the appropriate temperature had been mixed, the mixture was immediately transferred to a cell having a pathlength of 1 cm. The cell compartment of the spectrophotometer was kept at constant temperature. The rate of decrease of gold(III) was followed for at least two half-lives. Pseudo-first-order rate constants were calculated from log$A$ (A = absorbance) against time plots. The maximum error in the measurement of the rate constant was ±5%, depending upon the experimental conditions. However, for most experiments, duplicate measurements were reproducible to within ±3%.

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