

Kinetics and mechanism of oxidation of aromatic secondary alcohols by Tl(III) acetate

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Abstract. The kinetics of oxidation of ortho, meta and para substituted α -phenyl ethyl alcohols by Tl(III) shows that these reactions are susceptible to electronic influences. The negative ρ (-2.11) points to the formation of electron deficient carbon atom. The oxidation of benzhydrol exhibits a kinetic isotope effect 6.4. The Tl(III) oxidation of 1-phenyl propyl alcohol, 4-chloro benzhydrol, 1-naphthyl methyl carbinol, 2-naphthyl methyl carbinol and fluorenol has been studied. A mechanism involving the loss of hydrogen atom as a hydride ion is proposed. The thermodynamic parameters of the reaction are also presented.

Keywords. Tl(III) oxidation of secondary alcohols; mechanism; kinetic isotope effect.

1. Introduction

The oxidation of a variety of substrates by Pb(IV) and Hg(II) salts has been extensively studied. The reaction potential of Tl(III) lies between those of Hg(II) and Pb(IV) and one would expect this oxidant to be more selective than Pb(IV). Yet it is surprising that oxidation of alcohols by Tl(III) salts have not been investigated so far. Tartaric acid induces the oxidation of U(IV) by Tl(III) in aqueous HClO₄ (Love *et al* 1965) and thallium (III) acetate in acetic acid oxidises olefines to 1, 1 and 1, 2 diacetates (Kabbe 1962; Henry 1962). Literature survey indicates that the kinetic and mechanistic aspect of oxidation of aromatic secondary alcohols by Tl(III) has not been investigated. We report here the kinetics of the Tl(III) oxidation of α -phenyl ethyl alcohol and a number of substituted α -phenyl ethyl alcohols. These systems have been selected to throw light on the substituent effects in the reaction with a view to propose a suitable mechanism for the oxidation.

The Tl(III) oxidation of α -phenyl ethyl alcohol was investigated as a standard reaction to study the effect of changing various parameters on the rate law and mechanism. The standard conditions employed were 50% HOAc-50% H₂O as solvent in the presence of 0.9 M sulphuric acid at constant ionic strength.

2. Results

2.1. Dependence on Tl(III) concentration

The dependence on the rate of oxidation by Tl(III) has been determined at [Tl(III)] = 0.0015 M to 0.0125 M. At any particular concentration the reaction exhibits first

order dependance over 80% of the reaction. For instance the value of $k_1 \times 10^4$, calculated from the integrated first order equation was $2.09 \pm 0.08 \text{ sec}^{-1}$ at 55°C with $(\alpha\text{-phenyl ethyl alcohol}) = 0.06566 \text{ M}$ and $[\text{Tl(III)}] = 0.002027 \text{ M}$. However, when Tl(III) was varied at constant alcohol, the reaction was first order in Tl(III) but k_1 values gradually varied with concentration. For example at 55°C with $[\alpha\text{-phenyl ethyl alcohol}] = 0.0617 \text{ M}$, variation of $[\text{Tl(III)}]$ from 0.001674 M to 0.02158 M altered the value of $k_1 \times 10^5$ from 16.6 to 0.829 sec^{-1} . This is traceable to the presence of several reactive species of Tl(III) which depend on the Tl(III) concentration. In view of this complication, the initial Tl(III) was fixed in all experiments so that rate data with these systems could be compared with one another.

2.2. Dependence on α -phenyl ethyl alcohol concentration

The variation in the value of the first order rate constant, as the concentration of alcohol is changed from 0.02629 M to 0.06302 M , shows that this reaction exhibits first order dependence on the alcohol concentration. Hence the reaction between α -phenyl ethyl alcohol and Tl(III) under the aforesaid conditions is governed by the rate expression,

$$-d[\text{Tl(III)}]/dt = k_2[\text{Tl(III)}]_{\text{aq}} [\text{alcohol}]. \quad (1)$$

2.3. Effect of acidity on the reaction rate

The reaction rate increases with increasing acidity. A plot of $\log k_1$ vs (H^+) is linear with a slope equal to three.

2.4. Dependence on ionic strength

Since one of the reactants in ionic and the reaction medium is polar, the effect of change in ionic strength has been studied (table 1) by varying the concentration of an added salt K_2SO_4 over the range 0.1 M to 1.0 M . The small negative salt effect is indicative of an ion dipole reaction.

Table 1. Influence of ionic strength over the Tl(III) oxidation of α -phenyl ethyl alcohol

$[\alpha\text{-phenyl ethyl alcohol}] = 0.04528 \text{ M}$
 $(\text{H}_2\text{SO}_4) = 0.9 \text{ M}$

$[\text{Tl(III)}] = 0.001985 \text{ M}$
 Temp. = 55°C
 Solvent = $50\% \text{ HOAc}$

$[\text{K}_2\text{SO}_4] \text{ M}$	$k_2 \times 10^3 \text{ lit. mole}^{-1} \text{ sec}^{-1}$
...	1.80
0.1	1.92
0.2	1.75
0.3	1.68
0.4	1.07

2.9. Primary kinetic isotope effect

Benzyhydrol- α -D is oxidised 6.4 times slower than the protio compound.

2.10. Substituent effect

The effect of suitably positioned substituents in the phenyl ring of α -phenyl ethyl alcohol on the rate of oxidation was studied for the following compounds *p*-chloro, *m*-chloro, *o*-chloro, *p*-bromo, *p*-fluoro, *p*-methyl alpha *p*-phenyl alpha phenyl ethyl alcohols. The oxidations were carried out in 50% HOAc—50% H₂O between 40–60° at constant ionic concentrations. The compounds are smoothly oxidised to the corresponding ketones. The reaction exhibits actual second order dependence—first order with respect to Tl(III) and alcohol. The rate constants are presented in table 4. It is evident from the magnitude of the changes in the rate constants that the reaction is susceptible to polar effects considerably. Table 4 gives the rate constants for the oxidation of alcohols at 55° C and figure 1 gives the Hammett plot. There exists a fair linear relationship between reaction constants and log k_2 . The magnitude of ρ obtained is -2.11 (correlation coefficient = 0.995) and the negative ρ points to an electron deficient carbon centre in the transition state of the reaction.

Table 4. Substituent effects in Tl(III) oxidation of ortho, meta and para substituted α -phenyl ethyl alcohols

[ROH] = 0.061 M [H₂SO₄] = 0.9 M Solvent = 50% HOAc
[Tl(III)] = 0.002119 M

R-C ₆ H ₄ -CHOH-CH ₃ (R =)	$k_2 \times 10^4$ lit. mole ⁻¹ sec ⁻¹				
	40°C	45°C	50°C	55°C	60°C
H	—	9.09	10.5	17.5	34.7
<i>p</i> -CH ₃	10.0	18.1	38.1	78.9	—
<i>p</i> -C ₆ H ₅	—	12.1	22.1	42.4	56.4
+ <i>p</i> -F	—	—	—	12.8	—
<i>p</i> -Cl	—	1.97	2.62	4.32	6.67
<i>p</i> -Br	—	4.58	8.95	15.1	20.8
<i>m</i> -Cl	—	1.23	1.78	2.21	6.14
<i>o</i> -Cl	—	3.21	4.60	13.6	18.9
+ + <i>p</i> -NO ₂	—	—	—	0.515	1.02

[ROH] = 0.007565 M + + at 65°C $k_2 \times 10^4 = 2.41$

Table 5. Tl(III) oxidation of aromatic secondary alcohols

[alcohol] = 0.0432 M [Tl(III)] = 0.002119 M
[H₂SO₄] = 0.9 M Temp.: 55°C Solvent = 70% HOAc

Alcohol	$k_2 \times 10^4$ lit. mole ⁻¹ sec ⁻¹
1-phenyl propyl alcohol	22.9
Benzyhydrol	45.1
4-chloro benzhydrol	23.7
Fluoren-9-ol	32.4
1-naphthyl methyl carbinol	234
2-naphthyl methyl carbinol	167

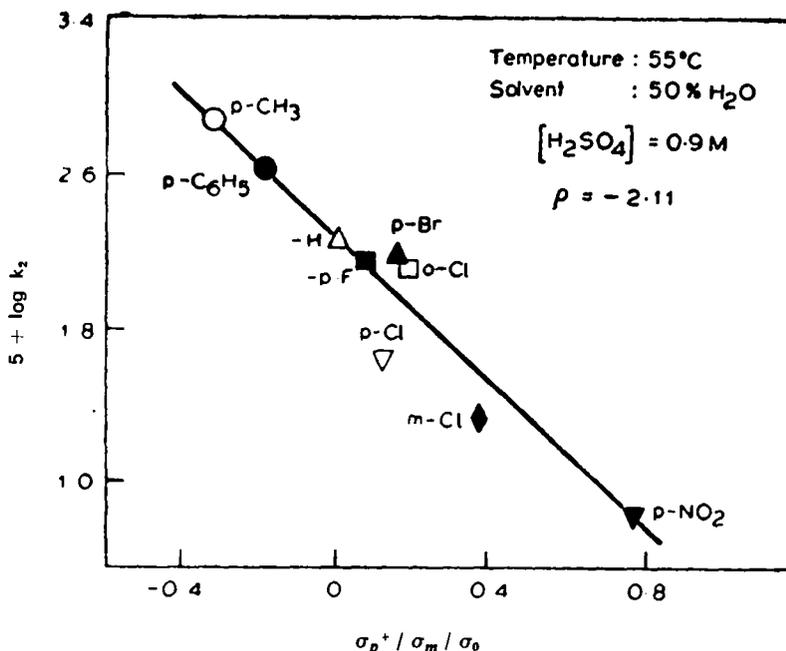


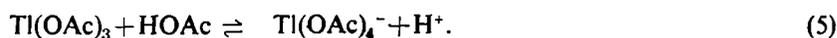
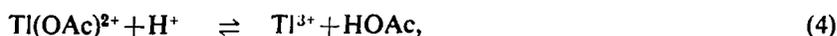
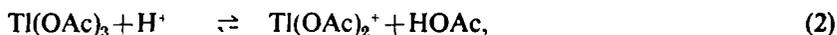
Figure 1. Hammett plot for substituted α -phenyl ethyl alcohols
 Temp.: 55 °C Solvent: 50% H_2O [H_2SO_4] = 0.9M 1. -H 2. $p\text{-C}_6\text{H}_5$ 3. $p\text{-CH}_3$
 4. $p\text{-F}$ 5. $p\text{-Br}$ 6. $o\text{-Cl}$ 7. $p\text{-Cl}$ 8. $m\text{-Cl}$ 9. $p\text{-NO}_2$

2.11. Oxidation of aromatic secondary alcohols

The Tl(III) oxidation of 1-phenyl propyl alcohol, benzhydrol, 4-chlorobenzhydrol, fluorene-9-ol, 1-naphthyl methyl carbinol and 2-naphthyl methyl carbinol in 50% HOAc—50% H_2O in presence of 0.9 M H_2SO_4 at constant ionic strength, also follows an identical rate law. The second order rate constants for these reactions are collected in table 5.

3. Discussion

3.1. The nature of Tl(III) species in aqueous acetic acid depends on the concentration of acetic acid and $[\text{H}^+]$. The following equilibria are possible



The present investigations have been carried out in aqueous acetic acid in the presence of 0.9M H_2SO_4 . The observed third order dependence on $[\text{H}^+]$ in these oxidations

would be mostly due to aquated Tl(III) ion whose concentration will be given by the equation

$$[\text{Tl}^{3+}]_{\text{aquated}} = \frac{K_1 K_2 K_3 [\text{Tl}(\text{OAc})_3] [\text{H}^+]^3}{[\text{HOAc}]^3}$$

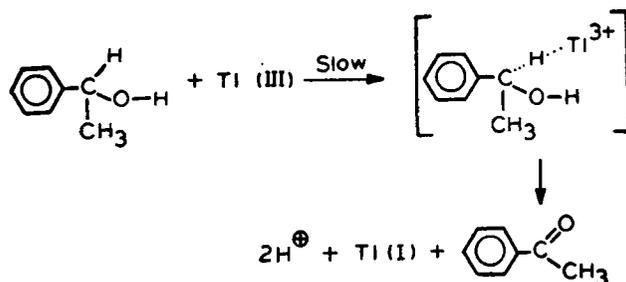
In the presence of added Cl^- ion, inactive species like TlCl^{2+} , TlCl_2^+ may be formed and this would account for reduction in the rate oxidation.

3.2. The mechanism of Tl(III) oxidation of secondary alcohols

The experimental observation that the reaction rates are not affected by oxygen and the actions do not induce polymerisation of acrylonitrile, is a clear evidence against radical mechanism for the reaction.

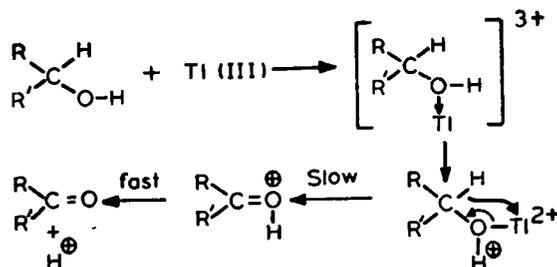
While it is true that Tl(III) could be reduced to Tl(I) via an intermediate Tl(II) species, this route seems to be normally not available to organic reductants. That the reaction under investigation is essentially a two-electron process is well brought out by the structure reactivity results in the present studies.

The following mechanism is, therefore, proposed for the oxidation of aromatic secondary alcohols by Tl(III) in aqueous acetic acid solutions.



Scheme 1

The above scheme envisages Tl(III) acting as a two-electron oxidant with the removal of the α -hydrogen on the C—H bond as a hydride ion in the rate determining step. The alternative possibility of an alcohol-Tl(III) complex which unimolecularly decomposes in a slow step cannot be entirely ruled out.



Scheme 2

Although no kinetic proof can be adduced on the formation of an alcohol-Tl(III) complex, other transition metal ions like Ce(IV) and V(V) are known to react via a

performed complex (Wiberg 1965). The involvement of C—H bond on the secondary carbon atom in the rate determining step is shown by the isotope effect studies ($k_H/k_D = 6.4$). A comparison of the isotope effect for the oxidation of similar substrates with one electron and two electron oxidants is given in table 6. There is a consistent change in the value of k_H/k_D with the nature of the oxidant—two electron oxidant Cr(VI) affords values for k_H/k_D which closely approximate the theoretical value as predicted by the Bigeleisen theory (Bigeleisen 1949) while this ideality is not evident for any typical one-electron oxidants that involve hydrogen atom abstraction. The value of 6.4 for Tl(III) oxidation of benzhydrol thus shows that Tl(III) is behaving essentially as a two-electron oxidant. The above formulation involving a hydride ion transfer with the consequent production of electron deficient centre (viz.) carbonium ion would demand a pronounced rate enhancing effect with electron releasing substituents and vice versa with electron attracting substituents. The Hammett plots in the case of α -phenyl ethyl alcohols as also the benzyl alcohols give satisfactory fits with $\sigma_p^+/\sigma_m/\sigma_o$. The former system has ρ of -2.11 and the latter has -1.33 . The simplest explanation for such a negative ρ can be the production of an electron deficient centre produced by the loss of a hydride ion from the α -carbon atom. It is pertinent to mention here that the Tl(III) oxidation of phenyl cyclopropanes and substituted styrenes have the ρ values of -4.2 and -2.2 respectively (South and Ouellette 1968; Ouellette *et al* 1969). The ρ value obtained with α -phenyl ethyl alcohols in our studies is almost identical with the value for Tl(III)-styrene reaction justifiably because the intermediates in both cases are almost identical. The ρ values for the addition of bromine to substituted styrenes -2.23 (Yates and Wright 1965) and for the N-bromosuccinimide oxidation of α -phenyl ethyl alcohols -2.1 (Srinivasan and Venkatasubramanian 1970) are also of the same order. The latter reaction is of particular relevance, because it has been shown to involve a hydride ion abstraction in the slow step of oxidation. The magnitude of the aforesaid ρ values are consistent with the stability of the intermediate carbonium ion systems. The benzyl alcohols form generally the least stable carbonium ion and exhibit the lowest ρ value. The ρ value of -2.53 calculated from the oxidation rates of benzyhydrol and 4-chlorobenzhydrol by Tl(III) is also in accord with the above picture.

Table 6. Kinetic isotopic effect in the oxidation of secondary alcohols by different metal ions

Oxidant	Substrate	k_H/k_D	Temp. (°C)	Ref.
Chromium (VI)	propan-2-ol	6.0	40	1
	Cyclohexanol	5.9	25	2
Thallium (III)	Benzhydrol	6.4	50	3
Vanadium (V)	Cyclohexanol	4.5	50	4
Manganese (III)	Cyclohexanol	1.6	50	5
Cerium (IV)	Cyclohexanol	1.9	50	6
Cobalt (III)	Cyclohexanol	1.7	10	7
	Propan-2-ol	1.4	15	7

References: 1. Westheimer *et al* 1949. 2. Richer and Hoa 1969. 3. Present studies 4. Littler and Waters 1969. 5. Littler 1962. 6. Littler 1959. 7. Hoare and Waters 1962.

3.3. Structural effects

The observed reactivity with regard to the other aryl phenyl alcohols such as 1-phenyl propyl alcohol, benzhydrol, 4-chlorobenzhydrol and fluoren-9-ol falls well within the orbit of the above proposal.

3.4. Thermodynamic parameters for the oxidation reaction

The thermodynamic parameters of the above alcohols show that the reactions are not isoentropic. There are large variations in the enthalpy values. The observed relationship between $\log k_2$ and $\sigma_p^+/\sigma_m/\sigma_0$ should be reflected in a linear relationship between ΔS^\ddagger and ΔH^\ddagger (Leffler 1955; Wells 1963; Schalegan and Long 1963). The plots of ΔH^\ddagger and ΔS^\ddagger are linear with least square slopes of these lines being 365° K .

4. Experimental

4.1. Thallic oxide was dissolved in a mixture of acetic acid and sulphuric acid and used as such after determining the concentration of Tl(III) by an iodometric titration (Henry 1962). All other chemicals are reagent grade and purified by conventional methods. Kinetic experiments were started by mixing equal volumes of the two reactants kept in a thermostat for about three hours. The reaction was followed by estimating the amount of unreacted Tl(III) at various intervals by an iodometric procedure. The rate constants were evaluated using integrated rate equations or by least square plots of related quantities. The values reported were the average of at least two runs and are generally reproducible within $\pm 3\%$. The activation parameters were also evaluated by least square plots of $\log k_2$ vs $1/T$.

4.2. Preparation of benzhydrol- α -D

Benzhydrol- α -D was prepared by the reduction of benzophenone (10 g) with sodium (10 g) in a mixture of pure dry ether (100 ml) and D_2O (30 g); yield is 65%; m.p. 65°C . Mass spectrometry and NMR studies confirmed that the isotopic purity of the sample is 90%.

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