

Tl(III) acetate oxidation of cyclanols and bicyclo(2,2,1) heptan-2-ols

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Abstract. Tl(III) acetate oxidation of cyclohexanol, cyclopentanol, cycloheptanol, *trans*-2-chlorocyclohexanol, *cis*-4-*t*-butylcyclohexanol, *trans*-4-*t*-butylcyclohexanol, borneol, isoborneol, exo (β) norborneol and endo (α) norborneol has been studied in the presence of 0.90 M H_2SO_4 . The observed reactivity pattern among the cyclanols is cyclopentanol < cyclohexanol > cycloheptanol < cyclooctanol which is the same as the one noted in V(V) oxidation of the substrates under similar conditions—an order contrary to the I-strain concept. In both cases Mn(II) catalysis and acrylonitrile polymerisation have been observed in cyclohexanol oxidation alone. The kinetic isotope effect in the Tl(III) oxidation of cyclohexanol is 2.82 as against a value of 6.4 obtained for Tl(III) oxidation of benzhydrol. The kinetic observations are explained on the basis of a radical mechanism operating in the case of cyclohexanol, as it is a strainless ring system, with the intermediacy of Tl(II). *Trans*-2-chloro and *trans*-2-phenyl groups, due-I effect, retard the rate of the reaction. *Cis*-4-*t*-butylcyclohexanol reacts faster than the *trans* compound due to relief of strain in the transition state. The reactivity pattern among the bicyclo (2,2,1) heptan-2-ols is, isoborneol > borneol > exo (β)-norborneol > cyclopentanol > endo-(α)-norborneol. This is consistent with the relief of strain in the transition state due to the hybridisation change from sp^3 to sp^2 and lessening of torsional interaction. This can also be due to the formation of less-strained products.

Keywords. Tl(III) acetate oxidation ; stereochemical aspects.

1. Introduction

The survey of literature indicates that the kinetic and mechanistic aspects of oxidation of alicyclic alcohol by Tl(III) has not been studied so far. The present work on Tl(III) oxidation of cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, *trans*-2-chlorocyclohexanol, *trans*-2-phenylcyclohexanol, *trans*-4-*t*-butylcyclohexanol and *cis*-4-*t*-butylcyclohexanol, throws light on the effect of ring size on the oxidation rate and stereochemical and electronic effects on these reactions.

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2. Results and discussion

The oxidations were carried out in 50% HOAc-50% H₂O mixture in the presence of 0.9 M H₂SO₄. The individual rate behaviour with reference to cyclohexanol, cyclopentanol, cyclooctanol, *trans*-2-chlorocyclohexanol and borneol was investigated (table 1). The reaction exhibits total second order kinetics—first order with respect to each reactant. The rate law is, therefore,

$$\frac{-d [\text{Ti(III)}]}{dt} = k_2 [\text{Ti(III)}] [\text{alcohol}]$$

2.1. Dependence of rate on sulphuric acid concentration

With increasing concentration of sulphuric acid, the rate of oxidation increases in the range 0.9M—3.0M (table 2). This shows that this reaction is an acid catalysed one.

2.2. Effect of added Mn(II)

While the addition of Mn(II) has negligible influence in the Ti(III) oxidation of α -phenyl ethyl alcohol and cyclopentanol, it is interesting to note, that only in the case of cyclohexanol oxidation, there is a pronounced increase in rate with increasing Mn(II) concentration (table 3). Also this reaction alone initiates acrylonitrile polymerisation. The above facts point to a different type of mechanism operating in the Ti(III) oxidation of cyclohexanol.

2.3. Ring size and reactivity

A perusal of data in table 4 shows the following order of reactivity among cyclanols : cyclopentanol < cyclohexanol > cycloheptanol < cyclooctanol. This result is surprising and unexpected in alicyclic system, which is governed by the I-strain (Gerstein and Brown 1950 ; Fletcher *et al* 1951 ; Brown 1956). One would have expected the following order of reactivity, cyclopentanol > cyclohexanol < cycloheptanol < cyclooctanol as was in the Cr(VI) oxidation of these substrates (Srinivasan and Venkatasubramanian 1967 ; Richer and Hoa 1969). Similar results contrary to I-strain concept is obtained in the V(V) oxidation of cyclanols where the same order of reactivity has been observed (Ganapathisundaram 1970). A plot of $\log k_{2\text{V(V)}}$ versus $\log k_{2\text{Ti(III)}}$ is linear indicating similar transition state in both the cases. It is pertinent to point out here that in the V(V) oxidation of cyclohexanol, Mn(II) catalysis was observed and the reaction also induced acrylonitrile polymerisation. The results contrary to I-strain concept in Ti(III) oxidation of cyclanols is therefore, due to a different type of mechanism operating in this case. The mechanism of V(V) oxidation of cyclohexanol involves the formation of a radical formed by the homolytic cleavage of C-H bond (Littler and Waters 1959). Probably in the Ti(III) oxidation of cyclohexanol, radical path seems to be more preferred as it is a strain free system. This may also be the reason for its close relationship in the reactivity pattern with V(V).

The rates of oxidation of *trans*-2-chlorocyclohexanol and *trans*-2-phenylcyclohexanol are considerably slower than cyclohexanol which can be attributed to -I effect of the 2-chloro and 2-phenyl groups. The stereoisomeric substrates like *cis*- and *trans*-4-*t*-butylcyclohexanols are oxidised by Tl(III)—the *cis* compound getting oxidised faster than the *trans* compound, as the 1, 3 interactions engendered in the ground state is being released in the transition state or the transition state is more product-like.

Table 1. Dependence of rate of Tl(III) oxidation of cyclanols on substrate concentration.

[Tl(III)] = 0.0020 M; [H₂SO₄] = 0.90 M; Temp : 50° C. Solvent : 50% aqueous acetic acid.

	Compound	$k_2 \times 10^3$ litre-mole ⁻¹ sec ⁻¹
(a)	0.029	1.74
	0.051	1.77
	0.111	1.79
	0.153	1.80
	0.22	1.84
(b)	0.0047	66
	0.0094	66
	0.0148	66
	0.022	65
	0.026	68
(c)	0.0109	1.55
	0.043	1.54
(d)	0.0055	31
	0.020	31
(e)	0.033	10.4
	0.056	10.5

a = cyclopentanol ; b = cyclohexanol ; c = *trans*-2-chlorocyclohexanol ; d = cyclooctanol ; e = borneol.

Table 2. Influence of varying acid concentration on Tl(III) oxidation of cyclohexanol [cyclohexanol] = 0.0060 M, [Tl(III)] = 0.0020 M, Temp. 50° C. Solvent : 50% aqueous acetic acid.

[H ₂ SO ₄] M	$k_2 \times 10^3$ litre mole ⁻¹ sec ⁻¹
0.90	4.0
1.50	15.0
2.0	32
2.5	34
3.0	68

Table 3. Effect of added Mn(II) salt on Tl(III) oxidation of secondary alcohols [Tl(III)] = 0.0020 M. Temp : 50°C ; Solvent : 50% aqueous acetic acid.

	[Mn(II)] M	$k_2 \times 10^3$ litre mole ⁻¹ sec ⁻¹
(a)	—	1.80
	0.0080	1.78
	0.020	1.82
(b)	—	68
	0.0055	89
	0.0010	129
	0.0050	147
	0.020	179
(c)	—	2.1
	0.0010	2.1
	0.010	2.1

a = cyclopentanol ; b = cyclohexanol ; c = phenyl ethyl alcohol

Table 4. Ring size and reactivity pattern among the cyclanols in V(V) and Tl(III) oxidations Solvent : 50% aqueous acetic acid.

Compound	$k_2 \times 10^2$ litre mole ⁻¹ sec ⁻¹				
	A		B		
	55°C	40°C	45°C	50°C	55°C
Cyclopentanol	0.0117	0.106	0.166	0.186	0.55
Cyclohexanol	0.155	3.2	4.0	6.8	7.5
Cycloheptanol	0.023	0.28	0.98	1.20	...
Cyclooctanol	0.047	0.45	1.90	3.0	4.0
<i>Trans</i> -2-chlorocyclohexanol	0.109	0.175	0.28
<i>Trans</i> -2-phenylcyclohexanol	0.0057	3.0	5.3
<i>Cis</i> - <i>t</i> -butylcyclohexanol	1.55	...
<i>Trans</i> - <i>t</i> -butylcyclohexanol	0.95	...
Cyclohexanol- α -d	2.4	...

A : V(V) oxidation in 50% HOAc and 1.00 M H₂SO₄.

B : Tl(III) oxidation in 50% HOAc and in 0.90 M H₂SO₄.

2.4. Oxidation of bicyclo(2, 2, 1) heptan-2-ols

The kinetics of Tl(III) oxidation of isonorneol, borneol, endo(β) and exo(α)-norneols have been studied under the same conditions (table 5). The effect of bridging cyclopentane ring with two carbon bridge to form norbornane (bicyclo(2,2,1) heptane) is known to introduce considerable total angle strain (largely centered around C₁C₇C₄ angle). This results from the action of the two carbon

Table 5. Comparative rate of Tl(III) oxidation of borneols and norborneols [Tl(III)] = 0.0020 M, (H₂SO₄) = 0.90 M. Temp. 50°C. Solvent : 50% aqueous acetic acid

Compound	$k_2 \times 10^3$ litre mole ⁻¹ sec ⁻¹			
	45°C	50°C	55°C	60°C
Isoborneol	...	53
borneol	5.5	10.7	22	...
exo- β -norborneol	...	2.6	3.2	8.0
endo- α -norborneol	...	0.74	1.46	...
cyclopentanol	1.66	1.86	5.4	...

bridge in accentuating the puckering effect exercised by the cyclopentane molecule itself in order to reduce its energetically costly torsional interactions (Sargent 1966 ; Eliel 1962). Further, in exo-(β)-norborneol molecule an additional source of instability is the compression of van der Waals radii of the bridgehead (C₇) and the exo-hydroxyl group(C₂). The possible change in hybridisation when alcohol becomes ketone, from sp³ to sp², resulting in a considerably increased rate of oxidation of exo-(β)-norborneol over endo-(α)-norborneol and cyclopentanol (table 5). The increased reactivity of borneol and isoborneol over the norborneols, can be traced to the + I effect of three methyl groups facilitating the removal of secondary hydrogen as hydride ion. This may be transmitted through the series of σ -bonds or directly through space. Although definite answers are sometimes elusive, it is thought likely that through-space interactions predominate in norbornane and bornane systems, featuring carbonium ion centers (Story and Clark 1972). The driving force for the reaction may also be the formation of less strained product, ketone.

2.5. Kinetic isotope effect

The kinetic isotope effect, k_D/k_H , observed in the Tl(III) oxidation of cyclohexanol is 2.82 (table 4) whereas in the oxidation of benzhydrol it is 6.4 (Srinivasan and Venkatasubramanian 1974).

2.6. Temperature influence

The temperature effect on the rate of oxidation of alicyclic alcohols and borneols was determined between 45°C and 60°C (tables 4 and 5).

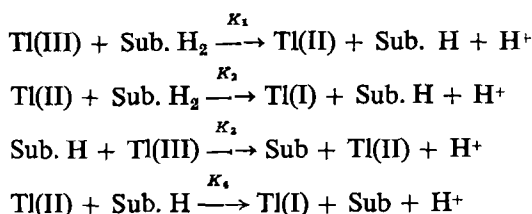
3. Mechanism of oxidation of alicyclic alcohols

On the basis of substituent effect on the Tl(III) oxidation of aromatic primary and secondary alcohols (Srinivasan and Venkatasubramanian 1975, 1970, 1978),

from the large negative rho value and kinetic isotope effect, a mechanism involving $-C-H$ bond cleavage in the rate determining step as a hydride ion, has been proposed. In general, a mechanism including one electron chain process involving bimolecular initiation and a cross termination process which would also lead to a second order equation as

$$\text{rate} = K[\text{Tl(III)}] [\text{sub. H}_2],$$

can also be proposed (Srinivasan and Venkatasubramanian 1979). (Where K is a composite of different rate constants corresponding to chain propagating steps)



In most of the secondary alcohols, such as α -phenyl ethyl alcohol, benzhydrol and cyclopentanol, the chain propagating reactions are too rapid, acrylonitrile and Mn(II) do not intervene. Even in the V(V) oxidation of α -phenyl ethyl alcohol, the reaction mixture does not induce acrylonitrile polymerisation and a mechanism involving an electron deficient transition state, tending more towards carbonium ion character, has been proposed (Ganapathisundaram 1970). This also points to V(V) preferring one electron-transfer route in the case of cyclohexanol but probably not so in the case of α -phenyl ethyl alcohol. Only in the case of cyclohexanol the competition between the chain propagating species with acrylonitrile and Mn(II) are possible. Probably the one electron route $\text{Tl(III)} \rightarrow \text{Tl(II)} \rightarrow \text{Tl(I)}$ is more available for the strain free six membered ring than for the other cyclanols.

4. Experimental

Thallic oxide was dissolved in a mixture of acetic acid and sulphuric acid and was used as such after determining the concentration of Tl(III) by an iodometric procedure (Henry 1965). All other chemicals were of 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 two hr. The reaction was followed by estimating the unreacted Tl(III) at various intervals by an iodometric procedure. The rate constants were evaluated using integrated equations or by least square plots of related quantities. The values reported were the average of at least two runs and were reproducible within $\pm 5\%$. The activation parameters were evaluated by least square plots of $\log k_2$ versus $1/T$. Mass spectrometry and NMR studies confirmed that the isotopic purity of cyclohexanol- α -d was 99%.

In the case of cyclopentanol, cycloheptanol and cyclooctanol, the corresponding ketones were formed as products whereas in the case of cyclohexanol, the cyclohexanone formed gets converted into cyclopentanecarboxylic acid (Wiberg and Evans 1960).

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