

## Oxidation of benzaldehyde semicarbazone by Tl(III) acetate—a structure reactivity correlation

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**Abstract.** The kinetics of Tl(III) acetate oxidation of semicarbazones of benzaldehyde and substituted benzaldehydes have been investigated in aqueous (90%) acetic acid. Electron-releasing substituents in the phenyl ring enhance the rate of the reaction, whereas electron-withdrawing substituents retard the rate. The rho value of  $-1$  favours electron-deficient transition state. To account for the major product of the reaction, *viz* respective benzaldehyde, a suitable scheme involving N-thallated intermediate has been proposed.

**Keywords.** Tl(III) acetate; oxidation of aryl semicarbazones; carbonyl product; N-thallated intermediate.

### 1. Introduction

The present work has been undertaken to study the structure-activity relationship in the Tl(III) acetate oxidation of benzaldehyde semicarbazone and for this purpose a large number of substituted semicarbazones of benzaldehyde have been prepared following the procedure available in literature (Vogel 1978).

### 2. Results and discussion

The kinetics of Tl(III) acetate oxidation of semicarbazones of benzaldehyde have been studied in binary solvent mixtures of acetic acid–water in the temperature range 40 to 60°C.

#### 2.1. Dependence of rate on the concentration of reactants

The reaction exhibits total second order kinetics—first order with respect to oxidant and reductant used. The rate expression for the reaction is,

$$\frac{-d[\text{Tl(III)}]}{dt} = k_2[\text{Tl(III)}][\text{semicarbazone}] \quad (1)$$

#### 2.2. Dependence of rate on ionic strength

Table 1 summarises the influence of added neutral salt,  $\text{Na}_2\text{SO}_4$ , on the oxidation rate in the range 0.1–0.5 M. The small but positive salt effect may be attributed to the ionic strength effect on dipole–dipole reaction.

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### 2.3 Influence of added $\text{OAc}^-$ and $\text{Cl}^-$ ions on the oxidation rate

The oxidation rate has been retarded to a larger extent by the initial addition of NaCl in small quantities (table 2) which cannot, therefore, be attributed entirely to the ionic strength effect alone. This can be traced to the formation of species like  $[\text{Tl}(\text{OAc})_2\text{Cl}]$  or  $[\text{Tl}(\text{OAc})_3\text{Cl}]^-$  which are less powerful oxidant compared to the reactive species like  $\text{Tl}(\text{OAc})_3$  or the ion-pair  $[\text{Tl}(\text{OAc})_2^+ \text{OAc}^-]$ . A similar behaviour has also been observed with  $\text{OAc}^-$  (table 2) and the retardation observed in this case may be due to the formation of  $[\text{Tl}(\text{OAc})_4]^-$ .

### 2.4 Effect of initially added $\text{Tl}(\text{OAc})$

There is approximately 8% reduction in rate due to the addition of  $\text{Tl}(\text{OAc})$  of concentration  $2 \times 10^{-2}$  M but in any kinetic run, a second order kinetics has been observed over three half-lives.

### 2.5 Structural influence

Introduction of a strongly electron withdrawing substituent such as *m*-nitro produces a five-fold decrease in rate while an electron-releasing substituent like *p*-methoxy increases the rate. Figure 1 gives the Hammett plots for this reaction at different temperatures and the respective rho values.

**Table 1.** Rate dependence on ionic strength\*.

{[semicarbazone] =  $2 \times 10^{-3}$  M;  $[\text{Tl}(\text{III})]$  =  $2 \times 10^{-3}$  M; Solvent = 90% aq. HOAc; Temp. = 50°C}

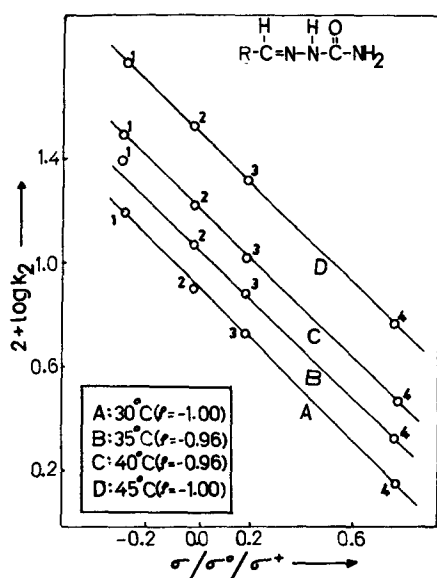
$[\text{Na}_2\text{SO}_4]$ M	$k_2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
—	0.89
0.1	0.99
0.2	1.2
0.4	1.7
0.5	1.9

\*at 0.02 M NaCl

**Table 2.** Effect of added  $\text{Cl}^-$  and  $\text{OAc}^-$  on the rate of oxidation.

{[Semicarbazone] =  $2 \times 10^{-3}$  M;  $[\text{Tl}(\text{III})]$  =  $2 \times 10^{-3}$  M; solvent = 90% aq. HOAc; Temp. = 60°C}

	$10^2 [\text{Salt}]$ M	$k_2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
(a) NaCl	—	68
	1	4.5
	2	2.0
	4	0.94
(b) NaOAc	10	18
	30	5.2
	50	3.0
	60	2.2



**Figure 1.** Hammett plot for Tl(III) acetate oxidation of aryl semicarbazones. R = (i) *p*-OCH<sub>3</sub>; (ii) -H; (iii) *o*-Cl (iv) *m*-NO<sub>2</sub>.

### 2.6 Dependence of rate on solvent dielectric constant

The specific rates for the Tl(III) acetate oxidation of semicarbazone increases with increasing water content in the system (table 3). The experimental data give linear plots of  $\log k_2$  versus  $(D-1)/(2D+1)$ , indicating that the reaction is dipole-dipole. Also  $\log k_D$  versus  $1/D$  graph is linear in keeping with Amis equation,

$$\ln k_D = \ln k_\infty - \frac{2\mu_1\mu_2}{kTDr^3} \quad (2)$$

**Table 3.** Influence of solvent dielectric constant on rate  
 {[Semicarbazone] =  $2 \times 10^{-3}$  M; [Tl(III)] =  $2 \times 10^{-5}$  M; Temp. = 35°C}

Substituent	Solvent composition		$k_2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
	%HOAc	%H <sub>2</sub> O	
H	90	10	1.2
	80	20	4.0
	70	30	6.4
<i>o</i> -Chloro	90	10	0.79
	80	20	2.4
	70	30	3.9
<i>m</i> -Nitro	90	10	0.22
	80	20	0.81
	70	30	1.3
<i>p</i> -methoxy	90	10	2.4
	80	20	7.9
	70	30	13

for a dipole-dipole reaction. Due to the non-availability of dipole moment for these compounds, the evaluation of  $r$  values from the slopes was hampered.

### 2.7 Temperature influence

The reaction exhibits Arrhenius dependence and from the plots of  $\log k_2$  versus  $1/T$ , activation energies have been evaluated. From these values, enthalpies, entropies and free energies of activation have been derived and summarised in table 4. These are in the right order of magnitude observed for a bimolecular reaction.

### 3. Mechanism of Tl(III) acetate oxidation of aryl semicarbazones

The reduction of Tl(III) to Tl(I) can occur by two one-electron processes, producing an organic radical which can reduce mercuric chloride to mercurous chloride. Hence the mechanism proposed for the Tl(III) acetate oxidation of benzaldehyde semicarbazones involves a radical intermediate which in subsequent step can form the product, benzaldehyde, according to scheme 1:

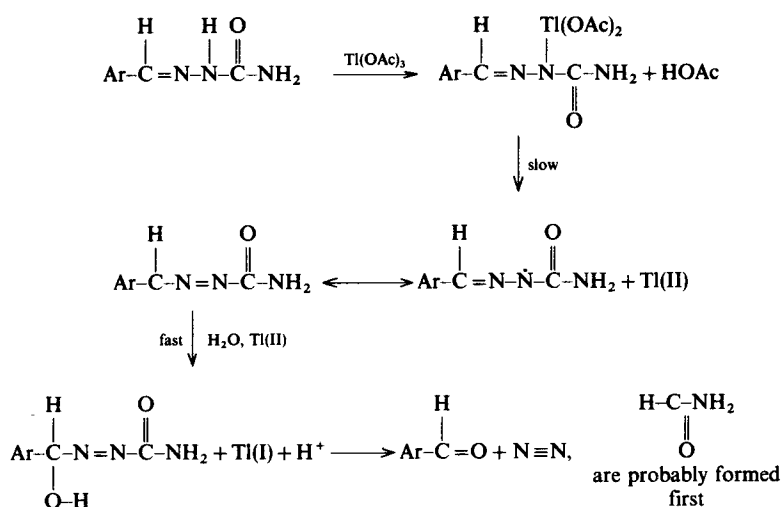


Table 4. Arrhenius parameters

Substituents	$E_a$ (i)	$\Delta H^*$ (ii)	$\Delta S^*$ (iii)	$\Delta G^*$ (iv)
H	13.1	12.5	-22	19.5
<i>o</i> -Chloro	13.0	12.5	-23	19.7
<i>m</i> -Nitro	13.2	12.6	-24	20
<i>p</i> -Methoxy	13.5	12.9	-20	19.1

(i), (ii), and (iv) K.cal/mole; (iii) cal/mol/deg.

This scheme is similar to the one proposed for the Ce(IV) oxidation of semicarbazones (Anand Rao *et al* 1981).

According to the above scheme the N-thallated intermediate formed decomposes in a slow step to form a nitrogen radical which in subsequent steps form benzaldehyde as one of the products. The decomposition of N-thallated intermediate is aided by electron-releasing substituents like *p*-methoxy group and the observed Hammett correlation for the substituent influences seems to agree with the above mechanism. The intermediate may then get decomposed to yield benzaldehyde.

By analogy with Pb(OAc)<sub>4</sub> (Gladstone *et al* 1969; Butler and King 1977) and Hg(OAc)<sub>2</sub> (Butler *et al* 1981), Tl(OAc)<sub>3</sub> reactions probably involve an N-metallo intermediate. In all cases a carbonyl product is regenerated.

It is interesting to note that specific rates of Tl(III) acetate oxidation of benzaldehyde semicarbazone is comparable to the rate of benzophenone semicarbazone (table 5) which does not possess a C-H bond adjacent to the phenyl ring. This favours the C-H bond remaining in tact in the Tl(III) acetate oxidation of benzaldehyde semicarbazone. Probably in the case of the former, the C-thallation is sterically hindered and N-thallation predominates. The comparable rate of Tl(OAc)<sub>3</sub> oxidation of benzophenone semicarbazone and benzaldehyde semicarbazone, therefore, seems to favour scheme 1.

#### 4. Materials and methods

The aromatic aldehydes used for preparing semicarbazones were of extra pure variety (Fluka AG/Koch light/K and K/Aldrich) and the physical constants of semicarbazones agreed with literature values. Tl(III) acetate was prepared from thallic oxide (BDH) by dissolving a known quantity of it in 100% acetic acid at 60°C in 4 hr. The resultant solution is filtered off and standardised by an iodometric procedure to a starch end point (Henry 1966, 1967). Thallous acetate was prepared by dissolving calculated quantity of thalious carbonate (BDH) in acetic acid. The other compounds such as sodium acetate, sodium chloride, potassium nitrate, sodium sulphate etc (BDH) were used as such. The velocity of the reaction has been measured by estimating the concentration of unreacted Tl(III) iodometrically (Henry 1966, 1967). The specific rates are reproducible to within  $\pm 7\%$  and these are the average of atleast two runs. The specific rates, calculated either by using integrated rate equations or from the plot of

**Table 5.** Specific rates of Tl(III) acetate oxidation of aryl semicarbazones

Compound	$k_2(\text{M}^{-1}\text{s}^{-1})$
$\begin{array}{c} \text{H}_5\text{C}_6-\text{C}=\text{N}-\text{N}-\text{C}-\text{NH}_2 \\   \quad   \quad    \\ \text{H} \quad \text{H} \quad \text{O} \end{array}$	0.16
$\begin{array}{c} \text{H}_5\text{C}_6-\text{C}=\text{N}-\text{N}-\text{C}-\text{NH}_2^* \\   \quad   \quad    \\ \text{C}_6\text{H}_5 \quad \text{H} \quad \text{O} \end{array}$	0.18

\* Product of the reaction is benzophenone

**Table 6.** Stoichiometry.

[Tl(III)] initial mM	[Semicarbazone] mM	[Oxidant] consumed mM	[Reductant] taken mM
6.2	3	2.9	3
6.2	2	1.8	2

$x/a-x$  or  $\log(b-x/a-x)$  versus time, closely agree with each other. The velocity for all these substrates was measured over a temperature range of 40 to 60°C and the activation energies were obtained graphically by plotting  $\log k_2$  against  $1/T$ .

#### 4.1 Product analysis

The semicarbazone (10 mmol) was dissolved in acetic acid–water mixture 90% HOAc–10% H<sub>2</sub>O (V/V). The oxidant, Tl(III) acetate, dissolved in the same solvent mixture, was then added to the semicarbazone solution (30 mmol, in excess) and maintained at 30°C for 4 hr. The mixture was then diluted with equal volume of ice water and extracted with CHCl<sub>3</sub> in three portions. Extracts were dried over anhydrous MgSO<sub>4</sub>, filtered and the acetic acid was neutralised by adding saturated NaHCO<sub>3</sub> solution. The organic product is then extracted with ether and from the UV and IR spectra, it has been identified as the corresponding aldehyde. The inorganic product has not been identified.

#### 4.2 Stoichiometry

Table 6 summarises the stoichiometric results obtained in the Tl(III) acetate oxidation of aryl semicarbazones and it has been found that for nearly 1 mole of Tl(III) acetate consumed 1 mole of semicarbazone is oxidised.

#### 4.3 Mercuric chloride test

The product solution gives a white precipitate with mercuric chloride solution whereas the blank solutions containing either Tl(III) or semicarbazone do not give any precipitate with HgCl<sub>2</sub>.

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