

## Kinetics & Mechanism of Oxidation of Benzoin & Its Derivatives by Tl(III) in Aqueous Acetic Acid

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The kinetics of oxidation of benzoin and its derivatives by Tl(III) in aqueous acetic acid have been investigated. The reactions obey second order kinetics. The observed rate decreases with increasing [Tl(III) acetate].  $Tl(OAc)_2^+$  is found to be the most electrophilic species in aq. acetic acid. Activation parameters have been calculated and the structure reactivity relationships discussed. A mechanism involving oxythallation-dethallation is suggested.

THE kinetics of Tl(III) oxidation of a number of organic substrates, viz. olefins<sup>1,2</sup>, acetylenes<sup>3</sup>, arylcyclopropanes<sup>4</sup>, alcohols<sup>5</sup>, ketones<sup>6</sup> and arenes<sup>7</sup> have been studied by several workers. It appears that Tl(III) oxidation of aromatic ketones has not been investigated. Hence, for the present study we have chosen benzoin and its derivatives.

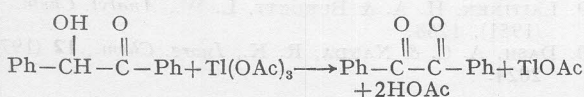
### Materials and Methods

Thallic oxide (BDH) dissolved in hot acetic acid (GR) and the solution filtered to give a stock solution of thallic acetate which was standardized iodometrically. Benzoin and its derivatives were prepared in the laboratory. Demineralized distilled water was used for preparing the solvent mixtures. All other chemicals used were of either analar or reagent grade.

The reaction was initiated by mixing equal volumes of the equilibrated reactant solutions in definite acetic acid-water mixtures. The experiments were conducted at constant ionic strength and acidity. The reaction was followed by estimating the rate of disappearance of Tl(III) by iodometry<sup>1</sup> at different time intervals. The ketone was always taken in sufficient excess over Tl(III) so that the observed kinetics were pseudo-first order and a particular run gave a linear plot for about 70% of the reaction. The duplicate rate measurements were reproducible to  $\pm 3\%$ .

### Results and Discussion

**Stoichiometry** — The results for Tl(III) oxidation of benzoin conform to 1:1 stoichiometry. The product of oxidation, benzil, has been identified by mixed m.p. and IR spectra. The reaction can be represented as



Tl(III) oxidation of benzoin has been studied in greater detail and the results of the kinetic experiments at fixed compositions of acetic acid-water mixtures (*v/v*) at constant acidity and ionic strength are recorded in Table 1.

The order with respect to Tl(III) and benzoin has been found to be one each. The first order rate constant for the disappearance of Tl(III) at a given acidity and [aromatic ketone] has been found to decrease with increasing [Tl(III)]. Similar observations have also been made in the case of Tl(III) oxidation of benzoic acid and  $\alpha$ -phenylethyl alcohol<sup>5</sup>. However, this type of behaviour has not been observed in the case of aliphatic ketones (unpublished work). Second order rate constant has been found to be  $9.1 \times 10^{-4} \text{ mole}^{-1} \text{ sec}^{-1}$  from the slope of the linear plot of  $k_{\text{obs}}$  versus [benzoin]. The empirical rate law conforming to these orders may be written as:

$$-\frac{d[\text{Tl}(\text{III})]}{dt} = \frac{-d[\text{ketone}]}{dt} = k[\text{Tl}(\text{III})][\text{ketone}]$$

**Acid dependence** — The data given in Table 2 show that the rate is first order with respect to [perchloric acid]. A similar rate dependence on [acid]

TABLE 1 — DEPENDENCE OF REACTION RATE ON [Tl(III)] AND [BENZOIN]

{[HClO<sub>4</sub>] = 1.071M; solvent: 90% HOAc-H<sub>2</sub>O (*v/v*);  $\mu = 1.124M$ ; temp. = 30°C}

[Tl(III)] $\times 10^3 M$	[BENZOIN] $\times 10^3 M$	$k \times 10^5$ sec <sup>-1</sup>
6.23	2.0	23.0
6.23	2.4	26.8
6.23	3.0	32.6
6.23	3.4	36.3
6.23	4.0	41.7
6.85	2.0	17.6
7.08	2.0	14.2
8.31	2.0	11.6
8.54	2.0	8.3
8.76	2.0	5.2

has been observed in the case of Tl(III) oxidation of  $\alpha$ -hydroxy acid.

*Effect of solvent composition* — The reaction rate increases with the increase in acetic acid content in the solvent mixture. The values of rate constant ( $k \times 10^5 \text{ sec}^{-1}$ ) in the benzoin oxidation are found to be 10.7, 13.5, 16.8, 20.7 and 23.0 for 70, 75, 80, 85 and 90% acetic acid.

The plot of  $\log k$  versus reciprocal of dielectric constant has been found to be linear with a positive slope indicating a positive ion-dipole reaction<sup>8</sup>. Considering a monopositive thallium species as the active oxidant, the value of  $r$ , the minimum distance of approach between the ion and the dipole, has been calculated from the slope of the above plot and found to be 0.96 Å. This value is of expected magnitude.

*Effect of added salt* — Addition of either sodium sulphate or sodium perchlorate seems to have negligible effect on the reaction rate. However, the rate has been found to decrease significantly on adding sodium chloride or sodium acetate (Table 3). This may be due to the formation of less electrophilic

and more covalent species of Tl(III), viz.  $\text{Tl}(\text{OAc})_2$ ,  $\text{Tl}(\text{OAc})_2\text{Cl}$  or  $\text{Tl}^+\text{Cl}_2$  (refs 9-11).

*Nature of Tl(III) species* — Since the oxidation has been carried out in aq. acetic acid, the following species of Tl(III) are expected to be involved in the oxidation:  $\text{Tl}(\text{OAc})_3$ ,  $\text{Tl}(\text{OAc})_2^+$ ,  $\text{Tl}(\text{OAc})_2^-$ ,  $\text{Tl}(\text{OAc})_2^+$ ,  $\text{OAc}^-$  and  $\text{Tl}_2(\text{OAc})_4$ . The ion pair  $\text{Tl}(\text{OAc})_2^+\text{OAc}^-$  and the double salt  $\text{Tl}_2(\text{OAc})_4$  have been shown to play insignificant role in redox reactions in acetic acid medium<sup>4</sup>. The possibility of  $\text{Tl}(\text{OAc})_2^-$  participating in the reaction can be ruled out since it is less reactive and a negative ion is not warranted in this reaction. Although  $\text{Tl}(\text{OAc})_3$  has been suggested<sup>4</sup> to be the active species in redox reactions, the rate dependence on dielectric constant of the medium suggests a positive thallic ion species as an active oxidant in the present study.  $\text{Tl}(\text{OAc})_2^+$  seems to be the most active electrophilic species in the oxidation of benzoin by Tl(III) in aq. acetic acid medium. This has also been shown to be the important reactive species in the oxidation of olefins<sup>1</sup>.

*Structure-reactivity relation* — The reaction rates for all the benzoin derivatives have been measured at four different temperatures ranging from 30 to 45°. Arrhenius equation has been found to be valid within the temperature range studied. The rate data for the substituted benzoin derivatives are recorded in Table 4 and the reactivity conforms to the following order:  $p\text{-OCH}_3 > p\text{-CH}_3 > p\text{-Cl} > \text{H} > p\text{-p}'\text{-dinitro}$ .

Nitro substituent retards the reaction in consonance with electronic effect<sup>12</sup>.  $p$ -Chloro-substituted compound, however, exhibits an anomalous behaviour as its reactivity is higher than that of unsubstituted compound. This may be due to the predominance of electromeric effect at the instant of the reaction. The entropy of activation values have been calculated by the use of Eyring's equation and these indicate rigid transition states. The logarithm of the rate constants at 30° correlates well with Brown's  $\sigma^+$  values. The value of  $\rho^+$  was calculated to be  $-1.00$  which indicates an electron deficient carbon centre in the transition state of the reaction.

*Mechanism* — In oxidation reaction, a ketone may react directly or through its enol form. Direct oxidations<sup>13-15</sup> by cobaltic, manganic and ceric salts have been shown to involve one electron transfer and seem to have a free radical mechanism. Oxidations proceeding through enol intermediates<sup>16-18</sup> have been reported for Tl(III) and its isoelectronic salts like Pb(IV) and Hg(II). Since the enol form of

TABLE 2 — ACID DEPENDENCE ON REACTION RATE

{[Tl(III)] =  $6.23 \times 10^{-3} M$ ; [benzoin] =  $2 \times 10^{-1} M$ ; solvent: 90% HOAc-H<sub>2</sub>O (*v/v*); temp. = 30°C}

[HClO <sub>4</sub> ] <i>M</i>	$k \times 10^5$ sec <sup>-1</sup>	$\frac{k \times 10^3}{[\text{HClO}_4]}$ mole <sup>-1</sup> sec <sup>-1</sup>
0.65	14.9	0.23
1.07	23.0	0.22
1.61	36.3	0.23
1.86	42.7	0.23
2.14	49.2	0.23
2.45	55.7	0.23

TABLE 3 — DEPENDENCE OF RATE ON ADDED SALT

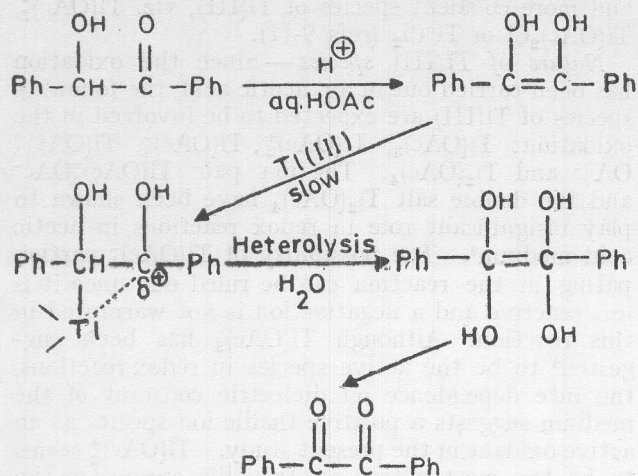
{[Tl(III)] =  $6.23 \times 10^{-3} M$ ; [benzoin] =  $2 \times 10^{-1} M$ ; [HClO<sub>4</sub>] =  $1.071 M$ ; solvent: 90% HOAc-H<sub>2</sub>O (*v/v*); temp. = 30°C}

Added salt	[Salt] $\times 10^2 M$	$k \times 10^5$ sec <sup>-1</sup>
—	—	23.2
NaClO <sub>4</sub>	1.6	23.1
Na <sub>2</sub> SO <sub>4</sub>	2.0	22.8
NaCl	0.2	9.4
NaOAc	2.0	11.3

TABLE 4 — EFFECT OF VARIOUS SUBSTITUENTS ON REACTION RATE

{[Tl(III)] =  $6.23 \times 10^{-3} M$ ; [Benzoin] =  $2 \times 10^{-1} M$ ; [HClO<sub>4</sub>] =  $1.071 M$ ; Solvent: 90% HOAc-H<sub>2</sub>O (*v/v*),  $\mu = 1.124 M$ }

Substituent	$k \times 10^5 \text{ sec}^{-1}$				<i>E</i> kcal mole <sup>-1</sup>	- $\Delta S^\ddagger$ cal deg. <sup>-1</sup> mole <sup>-1</sup>	$\Delta F^\ddagger$ (30°) kcal mole <sup>-1</sup>
	30°	35°	40°	45°			
4-OCH <sub>3</sub>	64.7	86.9	112.8	160.3	10.0	41.6	22.0
4-CH <sub>3</sub>	64.7	67.9	88.6	118.7	10.2	41.5	22.2
4-Cl	38.3	49.6	64.9	81.6	10.3	42.2	22.5
H	23.0	30.1	40.2	51.1	11.1	40.7	22.8
2,2'-Dinitro	4.8	8.8	14.5	22.4	19.1	17.0	23.6



Scheme 1

the ketone contains a double bond, Tl(III) salt is expected to undergo facile reaction with olefins and acetylenes<sup>1-3</sup>. The oxidation of benzoin to benzil via enediol finds further support from the study of the electrolytic oxidation of phenyl acetylenes<sup>19</sup> where it has been concluded that stilbenediol diacetate is the precursor to benzil. Formation of enol is, however, not a rate determining step as the observed rate is not independent of [Tl(III)].

Tl(III) acetate essentially behaves as a two-electron oxidant and the experimental results show that each  $\alpha$ -C-H bond ruptures by a two-electron transfer. Therefore, the oxidation of benzoin to benzil in aq. acetic acid medium in the presence of perchloric acid may be interpreted by invoking oxythallation of the enol form of the ketone followed by dethallation (Scheme 1).

The above mechanism finds support from the fact that the stable oxythallation adducts of the type  $\text{H}-\text{O}-\text{C}(\text{OH})-\text{C}(\text{OH})-\text{Ti}(\text{OAc})_2$  have actually been isolated in the oxidation of olefins<sup>20,21</sup> in aq. acetic acid. Tl(III) oxidation of alkenols in aq.  $\text{HClO}_4$  also shows

the formation of oxythallation adduct<sup>3</sup>. These facts reveal that the oxidation of ketomethylene compounds through enol form would involve carbon thallium bond formation and this is supported by the  $\rho^+ = -1.00$  which indicates an electron deficient carbon centre in the transition state. Organothallium derivatives of the type  $\text{R}-\text{Ti}(\text{OAc})_2$  are known to be highly unstable to solvolysis<sup>22</sup> and decompose easily to give a diketone. A similar mechanism has also been envisaged for the Tl(III) oxidation of cyclic and aliphatic ketones studied by us.

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