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A Comparative Study of the Oxidation of Benzoin by Thallium(III) Salts in Methanol Medium: A Kinetic and Mechanistic Approach

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A comparative study of the oxidation of benzoin by different thallium(III) salts in methanol medium is studied. The reaction is first order each in thallium(III), benzoin and acid concentrations. The effect of substituents is studied and the value of reaction constant (σ) is obtained. Activation parameters for the oxidation of benzoin by different thallium(III) salts were evaluated and discussed. The proposed mechanism is consistent with the observed results.

Key Words: Thallium(III), Benzoin, Kinetics, Oxidation.

INTRODUCTION

A literature survey shows that the work on the thallium(III) oxidation of organic compounds is scanty. Thallium(III) derivatives should be examined more closely as oxidizing agents in organic chemistry because of their rapid rate of reaction. Ouellette *et al.*[1] showed that the selectivity of thallium(III) is higher than that of mercury(II) and lead(IV). One of the mechanistic advantages of the study of thallium(III) oxidation is that intermediate organothallium derivatives can be isolated if desirable[2].

The oxidation of olefins[3], cyclopropanes[4], acetylenes[5] and carbonyl compounds[6] has been carried out using thallium(III) acetate (TTA). Although thallium(III) acetate has been the most frequently used oxidant in such work, McKillop and co-workers[7] have shown the utility of thallium(III) nitrate (TTN) in methanol because of its much higher reactivity in a number of oxidations. Thallium(III) nitrate in methanol reacts with olefins about 10^5 times faster than thallium(III) acetate in acetic acid[7]. Detailed kinetic studies of thallium(III) nitrate oxidation of olefin compounds in methanol are available[8], but those pertaining to the oxidation of carbonyl compounds by thallium(III) nitrate in methanol have not been attempted. In view of the work of McKillop and coworkers[9] on the thallium(III) nitrate oxidations of carbonyl compounds in methanol, a detailed kinetic study is needed. The data on the oxidation of benzoin by thallium(III) acetate in 90% acetic acid are available[10]. Even though, in view of noticeable differences in the reactivities of thallium(III) salts, the study of the oxidation of benzoin by different thallium(III) salts in methanol medium to see any change in the mechanism is undertaken. A detailed kinetic study of the oxidation of benzoin has been performed by using thallium(III) nitrate as the oxidant.

EXPERIMENTAL

Reagent grade chemicals were used throughout this work. Thallium(III) nitrate (TTN) was prepared[9] by dissolution of thallium(III) oxide (Tl_2O_3, BDH) in 3–4 mL of concentrated nitric acid by warming (70–80°C). Cooling of the pale yellow solution to 0°C yielded colourless crystals of a trihydrate, which was dried *in vacuo* over phosphorus pentoxide and these crystals were used to prepare the solutions. A stock solution of thallium(III) perchlorate (TTP) was prepared by dissolving thallium(III) oxide in 60% perchloric acid (Riedel). Thallium(III) sulfate (TTS) was prepared[12] by dissolving thallium(III) oxide in dilute sulphuric acid. The solution volume reduced, the crystals of thallium(III) sulfate (TTS) settled at the bottom. These crystals were removed and used for the preparation of solutions. Thallium(III) acetate (TTA) was prepared[13] by dissolving thallium(III) oxide in hot acetic acid and filtering the solution to remove any insoluble material. The different thallium(III) salt solutions prepared as above were standardized just before use by EDTA (AnalaR) using xylenol orange as an indicator[14] and in some cases, by an iodometric procedure[15]. While benzoin (BDH) was directly used, the substituted benzoins were synthesized by known methods[16]. Methyl alcohol (E. Merck) and dioxane were purified by standard methods[17]. Thallium(I) solution was obtained by dissolving thallous nitrate (BDH) in methanol. Sulphuric acid and lithium sulfate were used to maintain constant acidity and ionic strength respectively. In case of thallium(III) perchlorate oxidations lithium perchlorate was used to maintain the ionic strength.

Kinetics were followed at 30 ± 0.1°C and $I = 1.81$ mol dm^{-3}. The reaction was initiated by mixing previously thermostated reactant solutions of thalium(III) nitrate and benzoin which also contained the required amounts of sulphuric acid and lithium sulfate. The kinetics were followed under psuedo first-order conditions by taking benzoin concentration in excess. The progress of the reaction was followed by withdrawing the aliquots from the reaction mixture at regular time intervals and determining the unreacted oxidant, thallium(III) nitrate, by titrating with EDTA using xylenol orange as indicator[14]. Kinetic runs were followed up to about 90% completion of the reaction and good first order kinetics were observed. In the oxidation of benzoin by TTN, it was found that the TTN also oxidized the solvent methanol. Hence, a correction for the solvent oxidation was applied in the case of each run by studying a parallel blank run under similar conditions in the absence of the substrate. The first order rate constants, k_1, were obtained from the plots of log $a/(a - Tx)$ *vs.* time. The rate constants were reproducible within ± 5%.

RESULTS AND DISCUSSION

Different reactant concentration in 0.50 mol dm^{-3} sulphuric acid at constant ionic strength of 1.81 mol dm^{-3} were kept at 30°C for over 6 h and then analyzed for thallium(III) and thallium(I) respectively by titrating with EDTA[14] and with potassium bromate[16]. Another product benzil was identified with spot test[18]. The results showed that the stoichiometry is 1 : 1, *i.e.*, one mole of thallium(III) was required to oxidize one mole of benzoin.

Reaction Order

At constant acidity and ionic strength, the order with respect to thallium(III) in the 5.0×10^{-4}–5.0×10^{-3} mol dm^{-3} concentration range was unity. First order plots under these conditions were linear to over 85% of reaction for different initial thallium(III) concentrations and the absence of any variation in the rate constants with different thallium(III) concentrations confirms the unit order in [thallium(III)]. The apparent order in benzoin for concentrations between 0.01 and 0.12 mol dm^{-3} was found to be unity (Table-1).

TABLE- 1

EFFECT OF VARIATION OF THALLIUM(III) NITRATE (TTN) AND BENZOIN ON THE OXIDATION OF BENZOIN BY THALLIUM(III) NITRATE IN ETHANOL AT 30°C

$[H_2SO_4] = 0.50$; I = 1.81 dm^{-3}/mol

[TTN] × 10^3 (mol dm^{-3})	Benzoin × 10^2 (mol dm^{-3})	$k_1 \times 10^5$ (mol dm^{-3})	$k_2 \times 10^3 = k_1$/Benzoin (dm^3 mol^{-1} s^{-1})
0.5	5.0	8.31	—
1.0	5.0	8.96	—
2.0	5.0	8.84	—
3.0	5.0	8.23	—
4.0	5.0	8.77	—
5.0	5.0	8.89	—
2.0	1.0	1.85	1.85
2.0	2.0	3.95	1.95
2.0	4.0	5.89	1.47
2.0	5.0	8.84	1.77
2.0	6.0	9.98	1.66
2.0	7.5	11.7	1.56
2.0	8.0	12.4	1.55
2.0	10.0	14.7	1.47
2.0	12.0	18.1	1.51

Effect of acid: At fixed ionic strength and with other conditions remaining constant, the rate was found to increase with increasing acidity (Table-2). The order in acid was unity as found from a plot of log k_1 *vs.* log $[H_2SO_4]$.

Effect of initially added products: The effect of initially added products, thallium(I) and benzil, was studied in the 1.0×10^{-4}–1.0×10^{-3} mol dm^{-1} concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. No significant effect on the reaction was observed in either case.

Effect of dielectric constant and ionic strength: At constant acidity and other constant conditions, as the dioxane content increases in the reaction mixture the rate constants increase. Since the dielectric constants of the mixtures of methanol and dioxane are not available in the literature, they were computed from the pure liquid values[19]. The plot of log k_1 *vs.* 1/D is linear with a positive slope.

Variation of ionic strength between 1.5 and 2.5 mol dm^{-3}, using lithium sulfate, did not have any significant effect on the reaction rate.

TABLE-2
EFFECT OF VARIATION OF $[H_2SO_4]$ ON THE OXIDATION OF BENZOIN BY THALLIUM(III) NITRATE (TTN) IN METHANOL AT 30°C

$[TTN] = 2.0 \times 10^{-3}$; $[Benzoin] = 5.0 \times 10^{-2}$; $I = 3.41/ dm^3 mol^{-1}$

H_2SO_4 (mol dm^{-3})	$k_1 \times 10^5$ (s^{-1})	$k_2 \times 10^4 = k_1/[H_2SO_4]$ (dm^3 mol^{-1} s^{-1})
0.10	1.62	1.62
0.30	5.44	1.81
0.50	8.84	1.77
0.75	12.60	1.68
1.00	17.10	1.71

Effect of added salts: Salt effect was studied by keeping the ionic strength reactant concentrations and other conditions constant. The added $NaClO_4$ and $NaNO_3$ did not have any significant effect on the reaction rate. While added NaCl and NaCN decrease the reaction rate.

Substituents effects: The effects of substituents were studied under pseudo first-order conditions at constant acidity and ionic strength. The substituents used were *p*-methoxy, *p*- methyl and *p*-chloro. The plot of log k_1 *vs.* substituent constants was obtained (Fig. 1). It has a slope of –0.35. The substituent constants were taken from literature[20].

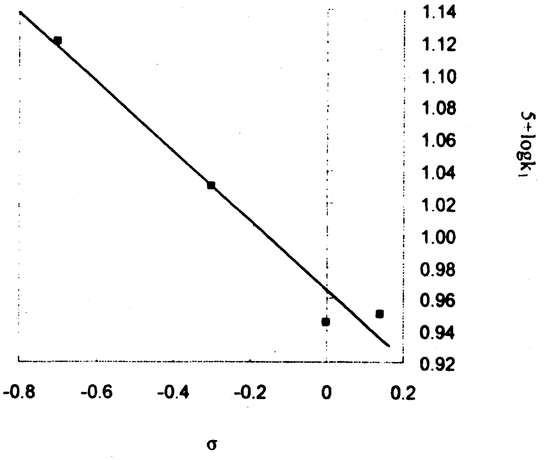


Fig. 1. Plot of log k_1 *vs.* substituent constants

Effect of temperature: At constant acidity and ionic strength the reaction was studied at four different temperatures with different thallium(III) salts. The activation parameters from the plots of log k_1 *vs.* 1/T in each case were calculated and compared (Table-3).

TABLE-3
ACTIVATION PARAMETERS OF OXIDATION OF BENZOIN WITH THALLIUM(III) SALTS

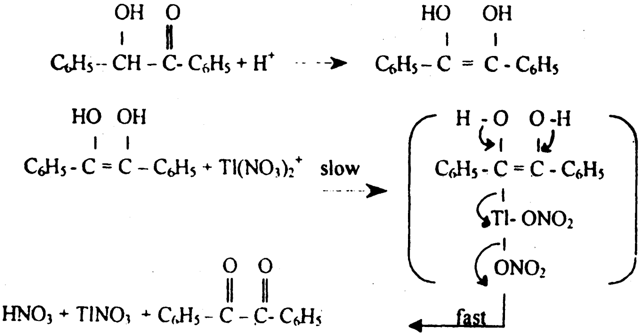
$[Tl(III)] = 2.0 \times 10^{-3}$; $[Benzoin] = 5.0 \times 10^{-2}$; $H_2SO_4 = 0.50$; $I = 1.81/dm^3 mol^{-1}$

Oxidant	$k_1 \times 10^5 s^{-1}$				E_a (kJ mol^{-1})	s (J K^{-1} mol^{-1})
	Temperature (°C)					
	25	30	35	40		
Thallium(III) nitrate	5.62	8.84	13.30	20.30	76 ± 3	–84 ± 4
Thallium(III) perchlorate	6.72	11.10	21.10	36.50	87 ± 3	–42 ± 2
Thallium(III) sulfate	1.66	5.04	10.60	21.10	112 ± 5	–34 ± 2
Thallium(III) acetate	2.29	4.45	7.52	11.20	82 ± 3	–67 ± 3

The oxidation of benzoin by thallium(III) takes place quantitatively yielding around 95% benzil. A stoichiometry of 1 : 1 is involved in the reaction. The reaction, carried out with thallium(III) nitrate (TTN) in methanol, has been found to be first order in oxidant, substrate and acid concentrations. Although the TTN consumption followed a first order rate law under constant acidity and constant ionic strength conditions, the rate nevertheless decreased as the TTN concentration increased. Such results have also been observed in the case of oxidation with thallium(III) acetate[10]. As in the case of aqueous solutions[21] of TTN, species such as $Tl(NO_3)_3$, $Tl(NO_3)_2^+$ and $Tl(NO_3)^{2+}$ can also be expected in methanol solutions of TTN and presumably the proportion of the active species decreases as the concentration of TTN increases, which is because the enol form of the substrate reacts. The added products did not have any significant effect on the reaction rate. The added anions such as ClO_4^- and NO_3^- do not affect the rate appreciably but the added Cl^- and CN^- lower the rate. This may be due to the formation of the less reactive species such as Tl^+, $TlCl_2^+$ and $Tl(CN)_2^+$ which decrease the concentration of the active species[22]. During the study of the effect of dielectric constant, it is found that the rate of oxidation increases with lowering the dielectric constant of the reaction medium. This result may be expected in case of a reaction between ion and a dipole[23]. The ionic strength does not affect the reaction appreciably, indicating the reaction between ion and neutral molecule. If the substituents affect, the reaction rate decreases along the series of p-OCH_3 > p-CH_3 > p-Cl > H, the p-chloro substituent behaves anomalously which may be due to the electromeric effect predominating at the moment of the reaction. The value of the reaction constant, σ, is obtained as –0.35 showing a small amount of carbonium ion character of the reactive carbon in the activated state. This is substantially different from –1.0 observed for the reaction in the case of the TTA oxidation in 90% acetic acid[10]. The above experimental results can be accommodated in terms of **Scheme-1.**

In presence of acid, benzoin forms an enol form. In the rate determining step this enol form reacts with the mono positive species, $Tl(NO_3)_2^+$, being an active oxidant to give oxythallation adducts such as the one shown in this mechanism which have also been postulated in other cases involving the oxidant TTN in methanol[9].

The activation parameters of the oxidation of benzoin with different thallium(III) salts in methanol, except TTN which is in 90% acetic acid, are shown in Table-3. The comparison of the oxidizing ability of all the thallium(III) salts was made, especially of the ionic characters displayed by different thallium(III) salts[7]. A comparison of the activation energies shows that the E_a in the case of TTS oxidation is the highest probably due to electrostatic effects. The positive entropy of activation in the latter case might very well be due to the participation of species such as $Tl(SO_4)_2^-$ as the active oxidant. The equilibrium constant of formation of $Tl(SO_4)_2^-$ in aqueous solution is particularly high[22] (log K = 3.74) and in other solutions containing high sulfate concentrations it may form with facility. The activation energies in the other three cases are not much different, but the entropies of activation are all negative. In particular that of the TTN oxidation in methanol is more negative than others and rigid transition states can be expected of all the three cases, an expectation which is in agreement with the mechanism of **Scheme-1.**



Scheme-1

Conclusion

The expectation that the oxidation of benzoin by TTN in methanol might be dramatically different in reaction rates and other details is not realized. Kinetically at least the mechanisms of TTA oxidation of benzoin in aqueous acetic acid and of the TTA oxidation in methanol appear to be broadly similar. The mechanism of oxythallation followed by dethallation is similar to the case of the thallium(III) oxidation of olefins and yet it is not clear why there should be large rate differences between TTN and TTA cases as regards the oxidation of olefins and not with regard to ketones such as benzoin. The differences in oxidizing abilities of the different degrees of ionic character do not seem to matter much when the reactions are carried out under similar conditions. The one exception is TTS for which the entropy of activation is very favorable while E_a is somewhat unfavourable.

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