THALLIMETRIC OXIDATIONS – A REVIEW*

Sanni Prasada Rao Muvvala
Inorganic Chemistry Laboratories, Andhra University,
Visakhapatnam - 530 003, India

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[*] This article is dedicated to my teacher and mentor, Prof. S.R. Sagi, Department of Inorganic and Analytical Chemistry, Andhra University.

SUMMARY

Thallium(III) is a stable and powerful two electron oxidant capable of oxidising many organic and inorganic substrates. The kinetics and mechanisms of the reactions involving thallium(III), as oxidant, have been widely studied and some of these reactions led to the development of analytical methods for the determination of thallium as well as the substrates. All these reactions are summarised and the probable mechanistic patterns are discussed. The thermal and photochemical thallimetric oxidations in the presence and absence of catalysts and their analytical applications for the determination of organic and inorganic substrates are summarised. The application of these reactions under controlled conditions, in the presence of suitable catalysts and inhibitors, for the estimation of various combinations of the binary and ternary mixtures of these substances is discussed. Basing on the salient features of these reports a probable mechanism and the role of chloride and bromide in the thallimetric oxidations are discussed.

INTRODUCTION

Thallium mainly exists in two oxidation states. The importance of the +3 state, and the special stability of the +1 state and the thallium(I)-thallium(III) relationship is a dominant feature of the chemistry of thallium. Nowadays thallium compounds are increasingly used as reaction intermediates in a variety of syntheses wherein both the oxidising power of thallium(III) and the special stability of thallium(I) derivatives are used to advantage /1/.

The standard redox potentials for the Tl(III)/(Tl(I) and Tl(I)/Tl systems in aqueous solution have been measured /2-4/ in different acid media. These values indicate that thallium(I) salts can be oxidised only by very powerful oxidising agents in high hydrochloric acid medium and that thallium(III) is a good oxidising agent in acid media other than hydrochloric acid. On the other hand thallium(I) is a powerful reducing agent in alkaline medium.

In the case of thallium there is a slight reluctance to exhibit the highest possible oxidation state just as in the case of other heavy post-transition metals. In group III, the (+1) oxidation state becomes more stable as the group is descended, while the trivalent state is important for the four elements /5/. The occurrence of an oxidation state, two below the group valency, is sometimes attributed to the so-called inert pair effect which first makes itself evident in group III, though it made its presence felt in II B through the low reactivity of mercury. This term refers to the resistance of a pair of 's' electrons to be lost or to participate in covalent bond formation /5/.

The intermediate oxidation state thallium(II) is unstable, although its formation has been proposed in several kinetic studies. In non-complementary reactions involving thallium(III), the formation of thallium(II) always has to be invoked. In complementary reactions also there is a possibility of formation of thallium(II), provided the transfer of the two electrons takes place in two successive steps. Gurnee and Magee /6/ stated that although the probability of simultaneous two-electron transfer calculated from perturbation theory is less than that of a single electron, the difference is not very large. Further there are many reports giving evidence for the formation of thallium(II) as an unstable species. It has been reported that γ-irradiation of thallous sulphate in sulphuric acid glasses at 77°K produces an absorption spectrum suggestive of thallium(II) /7/. The presence of thallium(II) has been confirmed in γ-irradiated glasses by e.s.r. spectroscopy /8/. The absorption spectra of aqueous solutions of thallous sulphate after pulse radiolysis also gave evidence of formation of thallium(II) /9,10/. Further, divalent thallium has been postulated to be formed in the rate determining step in the electrolysis of thallium(III) perchlorate /11/. Also electrolytic reduction of (2,2'-bipyridyl)thallium(III) cation at a dropping mercury electrode has been shown to proceed via thallium(II) species /12/.

Recently the existence of thallium(II) as an intermediate in the bromide catalysed photochemical thallimetric oxidations has been suggested /13/.

2. KINETICS OF THALLIUM(III) OXIDATIONS

The investigations on the redox reactions of thallium(III) with both inorganic and organic substrates have been extensively investigated. Most of the reactions were carried out in perchloric acid medium, although a few reactions have been studied in acetic or sulphuric acid medium as well. These reactions may be broadly divided into three categories on the basis of their mechanisms.

a. *Reactions which proceed through complex formation, the decomposition of the complex being rate determining.*

Most of the thallium(III) oxidations, involving complexation, proceed through this mechanism. In this category of reactions, the substrate first forms a complex with thallium(III), which decomposes to give the products, the decomposition of the complex being determining. The oxidations of arsenic /14,15/, antimony /16/, hypophosphite /17/, acetophenone and substituted acetophenones /18/, oxalic acid /19/, catechol /20/, hydroxylamine /21/, catecholamines /22/, tris(2,2'-bipyridyl)- and tris-(1,10-phenanthroline)osmium(II) /23/, 2-mercapto succinic acid /24/, formic acid /25/, formamide and N-methylformamide /26/, 1,2-dihydrobenzene /27/, chloroacetamide /28/, iodoacetamide /28/, N-bromoacetamide /28/, *p*-methylphenylhydrazine /29/, quinol /30/ and thiocyanate /31/ have been reported to proceed through this mechanism. However, there is neither kinetic nor spectrophotometric evidence for complexation with any of these substrates except quinol. Evidently, this shows that the stability constants of the complexes formed with these substrates are very small.

A study was carried out to know the medium effects on the oxidation of hypophosphite /32/ with thallium(III). In the oxidation of phosphite /33/, nitrous acid /34/, hydrogen peroxide /35,36/ dimethylformamide /37/, formamide /38/, N-methylformamide /39/ and 4-methylquinoline-2-hydrazine /40/ the kinetic evidence indicates that the formation constants of the complexes formed between thallium(III) and these substrates have significant values compared to the substrates mentioned earlier. Kinetic and spectrophotometric evidence for complexation has also been obtained in the oxidation of lactic and mandelic acids /41/. In these cases, the formation constants of the complexes formed are so large that, at the higher concentrations of the substrates, limiting rates are obtained and the order in substrate becomes zero.

b. Reactions which proceed through formation of a complex, the formation of the complex itself being rate-determining:

Among the thallium(III) oxidation reactions proceeding through complexation, the oxidations of ethylene /42/, propylene /43/, hydrazine /44/, substituted benzyl alcohols /45/, benzoin and its derivatives /46/, *l*-hydroxy acids such as atrolactic, benzilic and benzyl phenyl glycolic acids /47/ and *l*-sorbose /48/ have been reported to proceed through this mechanism, wherein the formation of complex constitutes the rate determining step.

c. Reactions which proceed directly without complexation:

In the case of complementary reactions, thallium(III) reacts directly with a substrate in a single step to give products. The oxidations of mercury(I) /49/, sulphurous acid /50/, chromium(II) /51/, tellurium(IV) /522/, uranium(IV) /53/, tin(II) /54/, vanadium(II) /55/, *l*-phenyl ethyl alcohol /56/, hydrazine sulphate /57/, pinacol /58/, cyclopentanone /58/, methyl ethyl ketone /58/, aryl hydrazone /59/, hydroxylamine hydrochloride /60/ and cinnamic aldehyde /61/ have been reported to proceed through this mechanism. The oxidation reactions of hyponitrous acid /62/ by thallium(III) in the presence and absence of EDTA are reported.

In the case of non-complementary reactions, thallium(III) reacts with the substrate giving the oxidised form of substrate and thallium(II), which subsequently reacts in a fast step with another substrate species giving thallium(I) and the oxidised form of substrate.

In the case of ruthenium(III) catalysed oxidation of mannitol /63/, the formation of an adduct between the substrate and catalyst is proposed; this adduct subsequently gets oxidised by thallium(III) in a slow step.

The oxidation of iron(II) /64/, vanadium(IV) /65-67/, vanadium(III) /68/, tris-bipyridylosmium(II) /69/, tris-ortho-phenanthrolineruthenium(II) /70/, tris-dipyridylruthenium(II) /70/, bis-terpyridylruthenium(II) /70/ and tris-orthophenanthroline-iron(II) /71/, have been reported to proceed through this mechanism.

Chloride ion exerts considerable inhibitory effect in many thallium(III) oxidations involving both inorganic and organic substrates. A survey of the literature revealed inhibition by chloride ion in the thallium(III) oxidation of arsenic(III) /14,15/, nitrous acid /34/, hydrogen peroxide /35,36/, hydrazine /44/, uranium(IV) /53/, hydrazine sulphate /57/, vanadium(III) /68/, hydroxylamine /21/, formic acid /25/, *p*-methylphenylhydrazine /29/, 4-methylquinoline-2-hydrazine /40/, lactic and mandelic acids /41/, benzoin and its derivatives /46/, *l*-sorbose /48/, *l*-phenyl ethyl alcohol /56/, hydroxylamine hydrochloride /60/, tris-dipyridylosmium(II) /69/, phenyl styryl ketone /72/, cinnamaldehyde /72/, captive oxalates /73/, *d*-glucose /74/, arylhydrazones /59/, aldoses /75/, melibose /76/ and *d*-fructose /77/. All these reactions have been reported to proceed through formation of an intermediate complex between thallium(III) and substrate, in the absence of chloride ions. It has been presumed that the same mechanism operates in the presence of chloride ions too. Chloride ion is known to form various complexes with thallium(III) like $TlCl_2^+$, $TlCl^{2+}$, $TlCl_3$ and $TlCl_4^-$ deending on its concentration /78/. The blocking of the coordination sites on hallium(III) and the resultant inhibition in the formation of an intermediate omplex is presumed to be responsible for the deceleration by chloride ions. he oxidation of tris-dipyridylosmium(II) /69/, vanadium(III) /68/, ydrazine sulphate /57/, hydrazine /44/, *d*-glucose /74/, arylhydrazones /59/, ydroxylamine hydrochloride /60/, aldoses /75/, *d*-fructose /77/ and captive xalate /73/ by thallium(III) has been reported to proceed directly without omplexation. In these cases inhibition by chloride ion has been attributed to he lower reactivity of chlorocomplexes.

On the other hand, the oxidations of iron(II) /64/, antimony(III) /16/, hosphite /33/ and hypophosphite /17,32,79/, as well as the thallium(I)-hallium(III) exchange /80/ are accelerated by chloride ions. This acceleraion has been attributed to the formation of a chloride-bridged intermediate, vhich facilitates electron transfer.

From these reports it is clear that the effect of chloride ion on the kinetic nd mechanistic patterns of thallium(III) reductions with different substrates as been thoroughly investigated. But surprisingly, no attempt seems to have een made to study the effect of bromide ion. Recently Rao /81/ has studied he kinetics and mechanism of reduction of bromothallium(III) species with ydrogen peroxide in perchloric acid medium. The bromide ion is found to ccelerate the reaction in low concentrations and the activity is attributed to he bromobridge formation between thallium(III) and the substrate.

3. ANALYTICAL APPLICATIONS

Determination of thallium

Thallium(III) being a stable and powerful two electron oxidant is widely sed for oxidimetric determinations of inorganic and organic substances. he same property has been conveniently utilised for the determination of hallium itself by using a suitable reductant.

In case thallium is in the lower oxidation state, the redox methods for the determination of thallium involve the oxidation of thallium(I) to thallium(III). The reaction is carried out by direct titration with powerful oxidants such as potassium bromate /82-84/, potassium iodate /85,86/, chloramine-T /87,88/, potassium ferricyanide /89/, potassium permanganate /86,90-93/, lead tetraacetate /94/, potassium dichromate /3,95,96/, cerium(IV) sulphate /86,97,98/ and sodium vanadate /99/. Alternatively an excess of an oxidant such as iodine /100/ in alkaline medium is added and the thallium(III) hydroxide is separated. The excess of iodine in the filtrate is acidified and titrated with thiosulphate. Sometimes the thallium(III) so formed can be estimated by utilising a suitable reductant.

Several direct reductimetric methods are known for the determination of thallium(III). Some of the titrants used for direct reduction are titanium(III) /83/, hydrazine sulphate /101/, thiosulphate /102/, ascorbic acid /103,104/, vanadium(III) /105/, chromium(II) /106/, hydroquinone /107/, tin(II) /108-111/ and iron(II) /112/.

An indirect method was also reported utilising excess of iron(II) as reductant /113/ and back titrating the excess with a suitable oxidant. Dindi and Sharma /114/ utilised mercury reductor for the estimation of thallium(III). The photochemical thallimetric oxidations have been utilised for the determination of thallium(III) by reduction with several reagents /115-123/. The same technique was extended for the analysis of mixtures /81,115,117-119,124,125/ of thallium(III) with thallium(I) and iron(III).

b. Determination of inorganic and organic substrates and their mixtures

Thallimetric oxidations have been utilised for the determination of organic and inorganic substrates. Several mixtures were also analysed under controlled conditions. Sagi *et al.* have estimated formic /116/ and oxalic /126/ acids by employing photochemical thallimetric oxidation methods. Many organic substances can be oxidised to formic acid, but further oxidation to carbon dioxide and water is very difficult, especially in acid medium. These authors were successful in oxidising formic acid to the carbon dioxide and water stage under mild experimental conditions by using bromide catalyst in the photochemical thallimetric oxidations. Glyoxylic acid and binary mixtures of glyoxylic, formic and oxalic acids were estimated /127/ by utilising photochemical thallimetric oxidation methods under controlled conditions and selective catalysts. Cl^-, Br^- and Mn^{2+} were appropriately chosen to control the progress and extent of these reactions.

A convenient thermal thallimetric method was developed /128/ for determination of malonic acid and a mechanism was proposed for the probable route of oxidation of malonic acid. Methods were also proposed for the analysis of tartronic acid /129/ and mesoxalic acid /13/. Based on the principle of selective reactivity of thallium(III) in the presence of light and at higher temperatures in the absence and presence of catalysts, a convenient titrimetric method has been developed for the estimation of oxalic and malonic acids in a mixture /130/.

Rao *et al.* have developed methods for the estimation of hydrogen peroxide /131/, phosphite /118/ and hypophosphite /119. The same technique was utilized for the determination of hydrazine /81/, phenyl hydrazine /81/, fumaric acid /120/, maleic acid /120/, benzoic acid /121/, lactic acid /122/ or glyoxal /123/.

Bromide was found to interfere with the thermal thallimetric oxidations /121/ by getting itself reduced to bromine. This reaction was utilised to propose a titrimetric method for the determination of bromide ion.

Rao and his coworkers have described methods for the determination of binary mixtures of phosphite and oxalate /118/, oxalate and hydrogen peroxide /132/ and ternary mixtures of hydrogen peroxide, oxalate and phosphite /133/ and also hypophosphite, phosphite and hydrogen peroxide /119/ under controlled conditions.

The estimation /81,118,119,126,131-133/ of many of these substances and their mixtures was also carried out in μ mole range by adapting a spectrophotometric method. In this method of determination of th substrates, alone and in mixtures in μ mole range, the absorption o thallium(III) chloro species is followed at 260 nm, where there is n absorption for thallium(I) chloride or other reagents.

Thermal thallimetric oxidation reactions have been reported /134-144/ i solid state for the trisoxalatothallate(III) complexes of NH_4^+, K^+, Rb^+, Cs^+, Tl^+, Tl^{3+}, Na^+, Ca^{++}, Sr^{++}, Ba^{++} and pyridinium salts. In these reaction thallium(III) oxidises oxalate, thereby reducing itself to thallium(I), and th final thermal decomposition product is a mixture of thallium(I) an thallium(III) oxides.

Based on the thermal behaviour and the solubility of barium bis-oxalatothallate(III) complex, a gravimetric method for the estimation o thallium was also described /145/.

4. DISCUSSION

a. Salient features of the thermal and photochemical thallimetric oxidations.

From the data reported so far, the salient features of the thallimetric oxidations can be summarised as follows:

1. Chloride ions are found to catalyse only few of the thermal redox reactions involving thallium, but most of the reactions were found to be inhibited.
2. Bromide interferes in the thermal thallimetric oxidations by becoming oxidised to bromine.
3. The quantitative oxidation of malonic and tartronic acid to the carbon dioxide stage does not take place in less than 3.0 M perchloric acid media.

4. For the oxidation of most of the substrates studied, the time required for quantitative oxidation either remains constant or increases with the increase in perchloric acid concentration.
5. In perchloric acid medium the reactions between thallium(III) and these reducing substances proceed at a negligible rate in the dark at room temperature. However, these reactions are catalysed either photochemically or thermally or both.
6. Chloride ions catalyse the photochemical thallimetric oxidation of oxalate and the first stage of the oxidation of hypophosphite, i.e. up to the phosphite stage.
7. Bromide ions catalyse most of the photochemical thallimetric oxidations.
8. Mn(II) retards most of the photochemical reactions except in the case of oxalic acid.

Bis-oxalato and mono-oxalato complexes of thallium(III) were reported /19,146/ to be present in perchloric acid solutions. Aggarwal and Srivastava /147/ observed that whenever bis-oxalotothallate(III) complex was isolated from lower acid media, some of the thallium(III) was always reduced to thallium(I). The mechanism of oxidation of oxalic acid by thallium(III) in perchloric acid medium was explained by Mønsted *et al.* /19/ by assuming the existence of $[Tl(C_2O_4)]^+$ as the reactive species. Spectral evidence was also provided for the formation of complex between thallium(III) and oxalic acid. Ole Farver studied /148/ the effect of oxalic acid on the rate of thallium(I)-thallium(III) exchange reaction and he could explain the decrease in the exchange quantitatively by considering the formation of $Tl(C_2O_4)^+$ species which did not participate in the exchange reaction. Halvorson and Halpern /149/ have studied the kinetics of the reaction between thallium(III) and formic acid in perchloric acid medium. To explain the observed facts they proposed the thallium(III) formic acid complex as the reaction intermediate which is in rapid equilibrium with the reactants. They could also show spectral evidence for the formation of a complex between thallium(III) and formic acid in 3.0 M perchloric acid medium. Ignaczak and Andrijewski /150/ showed kinetic evidence for the formation of complexes of thallium(III) with glyoxylic and glycolic acids.

Basing himself on the above reports, Rao /13/ argued that the uncatalysed thallimetric oxidation reactions reported so far mainly proceed through the formation of a complex between thallium(III) and the reactant which is in rapid equilibrium with the reactants. This intermediate complex eventually decomposes either photochemically or thermally to give the products.

b. Role of chloride ion

Chloride ions, when present in higher concentrations, retard all the thermal and photochemical reactions reported so far. However, when present in low concentrations, chloride ions do catalyse some thermal reactions as reported in the kinetic investigations and the photochemical oxidation of oxalic acid. The reasons for the retarding effect of chloride ions were explained on the basis of chloride ions blocking the coordination sites on thallium(III) /21,35/, thereby decreasing the possibility of the complex formation between thallium(III) and substrate, thus resulting in negative catalysis.

In the case of oxalic acid /13/ also, chloride ions retarded the thermal reaction, but in low concentrations the chloride ion catalysed the photochemical reaction. The catalytic activity of chloride ion in this case was assumed to be through a chloro-bridge mechanism.

In solutions containing chloride ion equal to or less than thallium(III) all the chloride is present in the form of $TlCl^{2+}$ and when the thallium(III) to chloride ratio is 1:2 in the form of $TlCl_2^+$ /151/. $TlCl_3$ is the principal species only in the narrow range of thallium(III) to chloride ratio of 1:2.5 to 1:3. Further, considerable disproportionation of $TlCl_3$ into $TlCl_2^+$ and $TlCl_4^-$

is reported /151/. When the thallium(III) to chloride ratio is between 1:4.5 and 1:10, the stability constants show that most of the thallium(III) exists in the form of $TlCl_4^-$. Therefore, in solutions containing thallium(III) and chloride under the conditions where the chloride catalysis was observed, the principal thallium(III) chloride species present are $TlCl^{2+}$ and $TlCl_2^+$.

At a concentration ratio where a minimum in the rate of exchange between thallium(III) and thallium(I) in the presence of chloride ions /152/ was observed, the catalysis of the photochemical reaction between thallium(III) and oxalic acid was observed to be maximum. This indicates the presence of two competing reactions: 1) electron exchange between thallium(I) and thallium(III) and 2) electron transfer from oxalate to thallium(III).

$$Tl(III) + 2e \longleftrightarrow Tl(I)$$

$$Tl(III) + C_2O_4^= \longleftrightarrow 2CO_2 + Tl(I)$$

The electron exchange between thallium(I) and thallium(III) in the presence of chloride ion was explained through the formation of chloro-bridges and the catalytic activity was observed to be maximum in high chloride ion concentrations /152/.

But the rate of electron exchange between thallium(I) and thallium(III) was found to be minimum when the thallium(III) to chloride ratio is 1:2. Under these conditions the lower chlorothallium(III) species is likely to be present in the solution. No spectral evidence was available for the formation of complex between chlorothallium(III) species and oxalate. On the base of these facts Rao /13/ suggested that the chloride ion will be slightly depleted of electron density when it is attached to a tripositive metal ion /79/ and the oxalate ion attacks the halide ion attached to the highly positive metal centre, resulting in a chloride bridge between the metal and substrate. After the bridge formation, photochemically aided transfer of electron density from the substrate to the metal is facilitated, thus resulting in the reduction of thallium(III) to thallium(I). A similar mechanism was proposed by Gupta and Gupta /32,33/ in explaining the chloride catalysis in the reduction of thallium(III) by hypophosphite and phosphite. Here the active form of the substrate was believed to attack the electron depleted chloride ion attached to the tripositive metal ion, thereby facilitating the electron transfer.

Such a type of electron transfer and subsequent reduction of thallium(III) was not observed in solutions containing high chloride ion concentrations. This paradox was attributed /13/ to two reasons: 1) The thallium(I) and thallium(III) exchange rate is facilitated in high chloride medium; 2) In higher chlorothallium(III) species the electrophilic nature decreases, thereby making the attack by the nucleophilic substrate less favourable.

Rao /13/ assumed a similar type of chloride bridge in the case of other substrates also, but the absence of catalytic activity in these cases was attributed to the incapability of the chloride bridge to facilitate such an electron transfer as it does in the case of oxalate ion. However, the catalysis by bromide was related to its better bridging and electron transferring capabilities.

c. *Role of bromide ion*

In spite of the differences in the nature of the reducing substances, the photochemical thallimetric oxidations catalysed by bromide have many similarities.

1. Considerable catalysis is observed in the oxidation of substrates with thallium(III) where the thallium(III) to bromide ratio is in the range of 10:1 to 1:1.
2. Considerable decrease in catalytic activity is observed in reaction mixtures containing thallium(III) and bromide in ratios between 1:2 and 1:3.
3. When the ratio of thallium(III) to bromide is 1:4 and above, drastic reduction in the rate of oxidation of the substrate is observed.

This is apparently due to the fact that thallic ion forms various bromocomplexes which differ greatly in their reactivities, and that the overall reaction is determined by the properties of the individual species and by their concentrations in the system. Rao /13/ has investigated the mechanism of bromide catalysis in thallimetric photochemical oxidations; from the observations recorded in these studies it appears that the thallimetric photochemical oxidations proceed via two different mechanisms.

Basing himself on the stability constants data of bromothallium(III) species /153/, Rao /81/ has calculated the percentage populations of various bromothallium(III) species in different bromide ion concentrations. This data confirms that under the conditions where catalytic activity was observed, the main bromothallium(III) species existing in the reaction mixture are $TlBr^{2+}$ and $TlBr_2^+$.

Hence, the bridge mechanism proposed in the case of chloride ion was invoked /138,81/ to explain the reaction between thallium(III) and the substrates in the presence of bromide ions. Here also the thallium(I)-thallium(III) exchange reaction in the presence of bromide was observed to be the slowest /153/ under the conditions when the photochemical reactions are the fastest. Hence, the bromide ion attached to thallium(III) in the lower bromothallium(III) species was supposed to be attacked by the nucleophilic substrate, thus forming a bridged complex, and subsequent transfer of electron density was believed to be facilitated in the presence of light. The higher bromothallium(III) species were ineffective in bringing out the reactions.

However in the presence of bromide ion these reaction mixtures, under light from a mercury vapour lamp, were able to initiate polymerization in acrylonitrile, indicating the formation of free radicals /13/. But such free radical formation was not observed in the case of chloride ion. Schäefer /155/ has observed that in the presence of UV light, $TlBr_2^+$ and $TlBr_3$ species reversibly decomposes to give thallium(II) and bromine radical whereas $TlBr^{2+}$ remains as a stable species. Equations of reversible equilibrium similar to decomposition were assumed /13/ to be present under the light from a mercury vapour lamp as well. The bromide radicals formed in this manner were obviously thought to be responsible for the initiation of the polymerization reaction. Hence, the highly reactive thallium(II) species and the bromine radicals were suggested /13/ to be responsible for bringing out the oxidations of the substrates studied by thallium(III).

Rao felt that proof of the existence of such reactive species can also be obtained from the study of the role of manganese(II) on the present reactions as thallium(II) is known to oxidise /154/ Mn(II) to Mn(III). In concurrence with the reports of Schäefer /155/, the experiments conducted /13/ in the presence of manganese(II) ions also showed that $TlBr_2^+$ and $TlBr_3$ species, when exposed to light from mercury vapour lamps, readily decomposed to form thallium(II) and bromine radicals, which was indicated by the formation of Mn(III) in the reaction mixture. The absence of retarding effect of Mn(II) on the photochemical oxidation of oxalic acid was attributed to the formation of Mn(III)-oxalato complex which readily undergoes redox decomposition. In cases where the Mn(III)-substrate complex cannot undergo redox decomposition, retardation of the reaction was observed.

In light of the above discussion it appears that Rao /13/ was quite justified in his conclusion that the bromide catalysis in these photochemical reactions is taking place through bridge mechanism as proposed in the case of chloride, when the thallium(III) to bromide ratio is equal to or less than 1:1. In higher bromide ion concentrations the free radical mechanism also appears to be operating and dominating over the bridge mechanism. This assumption was based on the fact that the electrophilic nature of thallium(III) is less in higher bromothallium(III) species.

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