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KINETICS AND MECHANISM OF ELECTRON-TRANSFER REACTION OF AQUOTHALLIUM(III) AND COORDINATED THALLIUM(III). OXIDATION OF METOL WITH THALLIUM(III) IN ACID PERCHLORATE MEDIUM

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The kinetics of oxidation of metol (*N*-methyl-*p*-aminophenol) by thallium(III) have been studied in a perchloric acid medium. This organic compound is employed extensively in photographic work. The stoichiometry of the reaction is represented by:

$$C_6H_4(OH)NHCH_3 + Tl^{III} \rightarrow C_6H_4(O)NCH_3 + Tl^{I} + 2H^+$$

The kinetics indicate the rate law:

$$k' = \frac{Kk\,[\text{metal}]}{1 + K\,[\text{metol}]}$$

where k' is the pseudo-first-order rate constant. The rate constants and thermodynamic parameters for the rate-limiting step have been evaluated.

INTRODUCTION

Despite extensive studies[1] of thallium(III) as an oxidant, much work is still required to reveal the reactivity pattern of this species in solution. This is all the more important in view of the extensive applications of the oxidant in synthetic organic chemistry.[2] The intermediate thallium(II) species is reportedly generated in solutions through radiolytic processes;[3] evidence for this more powerful oxidant has yet to be produced in non-radiolytic processes.

Thallium(III) is known[4,5] to be a cumulative poison and is excreted from the body owing to the soft tissue turnover, Thallotoxicosis is a subject of medical importance and deals with studies of thallium-containing rodenticides and insecticides.[6] These observations prompted us to undertake studies on the redox chemistry of thallium(III), from two main viewpoints.

The first aim was to determine whether *N*-methyl-*p*-aminophenol (metol) – an organic compound employed extensively in photographic work – undergoes oxidation via an intramolecular electron transfer to an intermediate complex, and whether the complex ruptures to an organic free-radical species generating a thallium(II) species.

Second, preventive measures are always required to protect archival photographic materials, from environmental deterioration. An understanding of the interaction of inert metal ions with metol is therefore required to rationalize its reactivity pattern in solution.[7] Thus the effect of both cations and anions on the rate of oxidation should provide useful information in understanding the mechanistic chemistry of this photographically useful reagent.

EXPERIMENTAL

Materials. Solutions of phallic perchlorate were prepared by dissolving phallic oxide (BDH) in 70% perchloric acid (E. Merck); the solution was standardized iodometrically.[7,8] Hydrogen ion concentration in solution was determined by titrating a known aliquot of thallic perchlorate solution against sodium hydroxide in the presence of pre-added KBr, employing phenolphthalein as an indicator. The addition of KBr checked precipitation of thallic hydroxide at the equivalence point. Metaol (Glaxo AR) was recrystallized from

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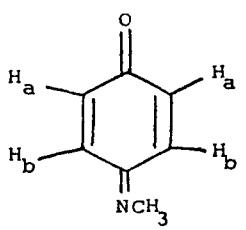
alcohol and the white solid material was kept in bottles painted black on the outside to prevent photodeterioration. However fresh solutions of metol were always prepared when required. Lithium perchlorate was prepared by neutralizing perchloric acid with lithium carbonate (BDH AR) to pH ≈ 6·8. All other reagents were either of AnalaR or G.R. Merck quality and were used as received.

Doubly distilled water was employed throughout the study; the second distillation was from alkaline permanganate solution in an all-glass still.

Reactions were carried out in stoppered Erlenmeyer flasks blackened on the outside. The flasks containing all reagents except thallium(III) were immersed in a thermostatted water bath maintained at 45 ± 0·1 °C, unless stated otherwise. Reactions were initiated by adding a known aliquot sample of pre-equilibrated thallium(III) solution into the reaction mixture, and the time at which the pipette was half empty was recorded. The kinetics were monitored by measuring thallium(III) iodometrically in an aliquot sample (5 cm^3) which was withdrawn periodically.

Initial rates were computed[9] employing the plane mirror method. Pseudo-first-order plots were also made wherever reaction conditions permitted. Triplicate rate measurements were reproducible to within ±4%.

Stoichiometry and product analysis. The stoichiometry of the reaction was determined by identifying the oxidation product of metol spectrally. Reactions with an excess of [metol] over [Tl^{III}] were allowed to occur in a thermostatted water bath and the product extracted with diethyl ether. NMR spectral analysis of the product was carried out on a Jeol FX90Q spectrometer. The NMR spectrum exhibits two signals: one doublet for 'a' type protons at δ = 7·72 and 7·66 ppm and another doublet for 'b' type protons at δ = 8·45 and 8·85 ppm in a ratio of 1 : 1. Two types of methyne (−CH−) are due to the vicinity of >C=O and −C=N*f*CH_3 groups, and are designated by H_a and H_b. Two H_a protons are more deshielded as compared to H_b protons, which are flanked by a central =C=NCH_3 group.



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The IR spectrum of the product exhibits a >C=O absorption band in the region 1600–1620 cm^{-1}, which can be ascribed to a cross conjugated >C=O group. These spectral observations clearly assign the product to be *N*-methyl quinone. Thus the stoichiometry of the reaction on the basis of the quinone as a product corresponds to the reaction represented by:

$$C_6H_4(OH)NHCH_3 + Tl^{III} \rightarrow C_6H_4(O)NCH_3 + Tl^{I} + 2H^{+} \quad (1)$$

RESULTS

Thallium(III) dependence

The concentration of thallium(III) was varied in the range $(1·0–5·0) \times 10^{-3}$ mol dm^{-3} at different metol concentrations, namely 2×10^{-2}, 3×10^{-2} and 5×10^{-2} mol dm^{-3}, respectively, and $[H^+] = 0·5$ mol dm^{-3}. Initial rates (k_i) were calculated and the plot of initial rate against $[Tl^{III}]$ yielded a straight line passing through the origin, indicating unit order with respect to the oxidant. Pseudo-first-order plots were also made (Figure 1) wherever reaction conditions permitted. Also, pseudo-first-order rate constants were found to be independent of the initial thallium(III) concentrations. (Table 1).

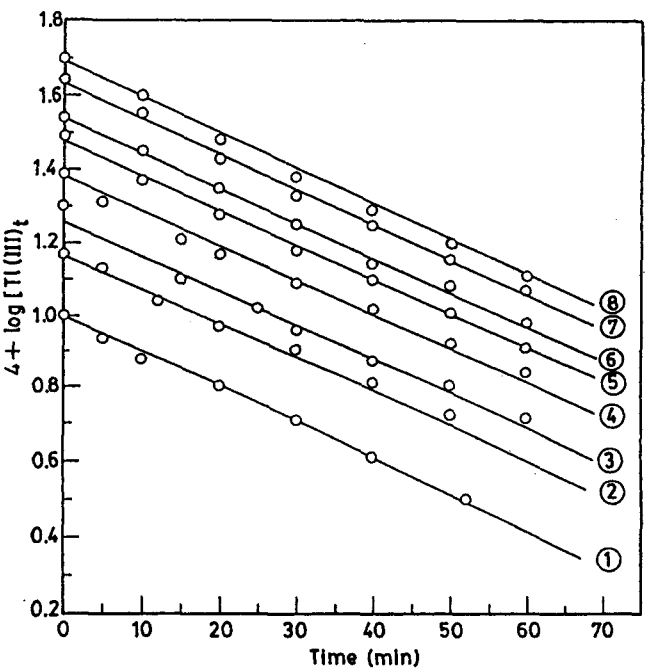


Figure 1. Pseudo-first-order plots. [metol] = 5×10^{-2} mol dm^{-3}; $[H^+] = 0·5$ mol dm^{-3}; temperature = 45 °C; $[Tl^{III}]$ (mol dm^{-3}) = ① $1·0 \times 10^{-3}$; ② $1·5 \times 10^{-3}$; ③ $2·0 \times 10^{-3}$; ④ $2·5 \times 10^{-3}$; ⑤ $3·0 \times 10^{-3}$; ⑥ $3·5 \times 10^{-3}$; ⑦ $4·5 \times 10^{-3}$; ⑧ $5·0 \times 10^{-3}$

Table 1. Pseudo-first-order rate constants. $[H^+] = 0{\cdot}5$ mol dm^{-3}; temperature = 45 °C

10^3 $[Tl^{III}]$ (mol dm^{-3})	10^2 [metol] (mol dm^{-3})	$10^4(k')$ (s^{-1})
1·0	2·0	1·8
1·5	2·0	1·8
2·0	2·0	1·7
1·0	3·0	2·4
2·0	3·0	2·5
3·0	3·0	2·5
1·0	5·0	3·7
1·5	5·0	3·7
2·0	5·0	3·7
2·5	5·0	3·8
3·0	5·0	3·7
3·5	5·0	3·7
4·5	5·0	3·8
5·0	5·0	

Metol dependence

Metol concentration was varied from $3{\cdot}0 \times 10^{-3}$ to 8×10^{-2} mol dm^{-3} at $[Tl^{III}] = 4{\cdot}0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 0{\cdot}5$ mol dm^{-3} and temperatures of 40, 45 and 50 °C, respectively. There is a proportional increase in the rate with increasing metol concentration in the lower ranges; however, a limiting rate tends to be attained at higher concentrations of metol. Such rate behaviour can be attributed to a weak intermediate complex of thallium(III) and metol.

Hydrogen ion dependence

Hydrogen ion concentration was varied, by means of $HClO_4$, from 0·5 to 2·0 mol dm^{-3} at $[Tl^{III}] = 2{\cdot}0 \times 10^{-3}$ mol dm^{-3}, $[metol] = 2 \times 10^{-2}$ mol dm^{-3} and ionic strength (I) = 2·0 mol dm^{-3} (I was adjusted employing lithium perchlorate). The rate is not affected by hydrogen ion concentration.

Ionic strength dependence

Ionic strength in the reaction mixture was varied from 0·25 to 2·0 mol dm^{-3} at $[Tl^{III}] = 2{\cdot}0 \times 10^{-3}$ mol dm^{-3}, $[metol] = 2{\cdot}0 \times 10^{-2}$ mol dm^{-3} and $[H^+] = 0{\cdot}5$ mol dm^{-3}. The rate decreases with increasing ionic strength (Table 2).

Table 2. Ionic strength effect. $[Tl^{III}] = 2 \times 10^{-3}$ mol dm^{-3}; $[metol] = 2 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 0{\cdot}5$ mol dm^{-3}; temperature = 45 °C

$[LiCl_4]$ (mol dm^{-3})	0·25	0·5	0·75	1·0	1·25	1·5	1·75	2·0
$10^4(k')(s^{-1})$	1·6	1·4	1·3	1·1	1·0	0·9	0·8	0·7

Effect of chloride ion

Chloride ions are known[10] to coordinate thallium(III). However, the chloride ion concentration was varied from 1×10^{-3} to 1×10^{-2} mol dm^{-3} at $[Tl^{III}] = 2{\cdot}0 \times 10^{-3}$ mol dm^{-3}, $[metol] = 2{\cdot}0 \times 10^{-2}$ mol dm^{-3} and $[H^+] = 0{\cdot}5$ mol dm^{-3}. The rate of the reaction is independent in the lower range of chloride ion concentration, $[Cl^-] < 5{\cdot}0 \times 10^{-3}$ mol dm^{-3}, and then decreases slightly. This corroborates our earlier results for the variation of metol concentration. Had the complex between the oxidant and substrate been strong, the rate of the reaction would have decreased in lower chloride ion concentrations in view of the known strong chlorothallium(III) complexes. It appears that the rates of aquothallium(III) and chlorothallium(III) complexes in lower $[Cl^-]$ are comparable. The slight decrease in the rate at higher $[Cl^-]$ can be attributed to the fact that the chloride ion blocking of coordination sites of thallium(III) resists incorporation of metol in the coordination shell of the oxidant.

DISCUSSION

Thallium(III) in perchloric acid undergoes hydrolysis as represented by:

$$Tl^{3+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} TlOH^{2+} + H^+ \qquad (2)$$

various values of K_h have been reported;[11] however, the most widely employed value[12] is $K_h = 0{\cdot}073$ mol dm^{-3} in 3·0 mol dm^{-3} $NaClO_4$ at 25 °C. If $TlOH^{2+}$ is calculated employing this value, it decreases by about 20% for $[H^+]$ variation from 0·5 to 2·0 mol dm^{-3}. Since the rate is not affected by hydrogen ion concentraton, Tl^{3+} appears to be a more reactive species of thallium(III). This also appears to be the predominant factor that brings about the rate independence of hydrogen ion concentration. Further, the limiting rate attained at higher concentrations of metol is ascribed to a weak complexation between the oxidant and the substrate. In view of these observations, the most appropriate model of the reaction events can be envisaged by the following proposed mechanism:

$$Tl^{3+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} TlOH^{2+} + H^+ \qquad (2)$$

$$Tl^{2+} + \text{metol} \underset{}{\overset{K}{\rightleftharpoons}} (Tl\cdot\text{metol})^{3+} \qquad (3)$$

$$(Tl\cdot\text{metol})^{3+} \xrightarrow{k} \text{products} \qquad (4)$$

The loss of thallium(III) leads to rate law (5) or (6):

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK[Tl^{III}]_T[\text{metol}][H^+]}{[H^+] + K_h + K[H^+][\text{metol}]} \qquad (5)$$

$$k' = \frac{kK[\text{metol}][H^+]}{[H^+] + K_h + K[H^+][\text{metol}]} \qquad (6)$$

Since $K_h < ([H^+] + K[H^+][metol])$, rate law (6) reduces to (7) or (8):

$$k' = \frac{kK[metol][H^+]}{[H^+](1 + K[metol])} \quad (7)$$

$$k' = \frac{kK[metol]}{1 + K[metol]} \quad (8)$$

where k' is a pseudo-first-order rate constant and [metol] is an equilibrium concentration of metol.

A plot of $1/k'$ *versus* $[metol]^{-1}$ was made from equation (8) at higher concentrations of metol ($[metol] > 10[Tl^{III}]$) and a straight line with non-zero intercept was obtained (Figure 2). The values of k and K were calculated from the intercept and the ratio of slope and intercept to be $1{\cdot}25 \times 10^{-4}$ s^{-1} and 6·27 dm^3 mol^{-1} at 40 °C, 1·66 s^{-1} and 6·0 dm^3 mol^{-1} at 45 °C, and 2·22 s^{-1} and 5·72 dm^3 mol^{-1} at 50 °C, respectively. These significantly lower values of K indicate weak complexation of the metol by the oxidant. The energy and entropy of activation for the rate limiting step were calculated to be 49 ± 5 kJ mol^{-1} and -163 ± 20 J K^{-1} mol^{-1}, respectively. The negative value of activation entropy signifies a more organized transition state in the reaction. Thallium(III) is also known[13] for complexation by oxygen donors, and the complexation, in general, is weak except for acetates. Also, complex formation preceded by intramolecular electron transfer is an established mechanism in the oxidation of most organic compounds by thallium(III) in solutions. So far as the mode of electron transfer from metol to thallium(III) is concerned, the reaction shown in Scheme 1 adequately accounts for all the observed results.

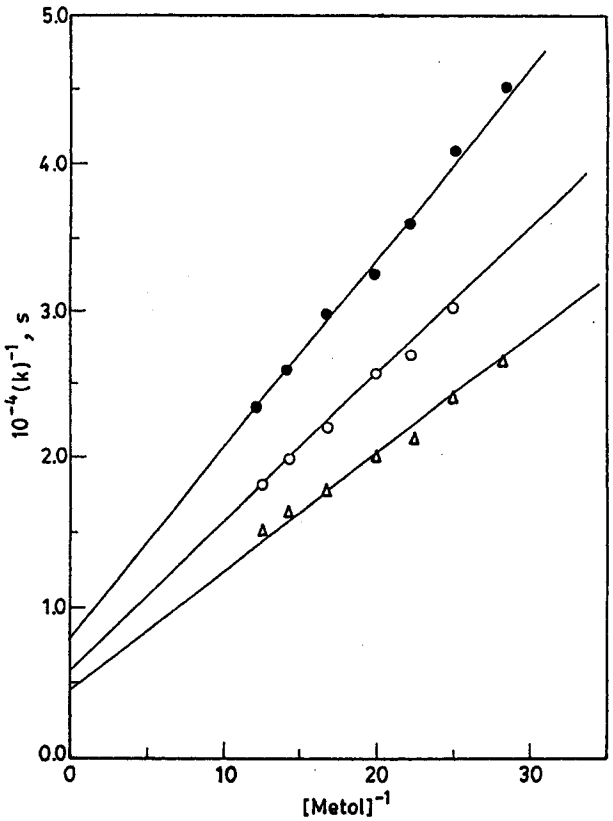


Figure 2. Metol concentration dependence. $[Tl^{III}] = 4 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 0{\cdot}5$ mol dm^{-3}; •, 40 °C; ○, 45 °C; △, 50 °C

An alternative proposal for the reaction events is also possible via an interaction of $TlOH^{2+}$ species with the protonated metol for. Since the protonation of metol is known to occur, the following reaction mechanism can account for such a proposal:

$$Tl^{3+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} TlOH^{2+} + H^+ \quad (2)$$

$$metol + H^+ \overset{K_p}{\rightleftharpoons} metol \cdot H^+ \quad (9)$$

$$TlOH^{2+} + metol \cdot H^+ \overset{K_i}{\rightleftharpoons} complex \quad (10)$$

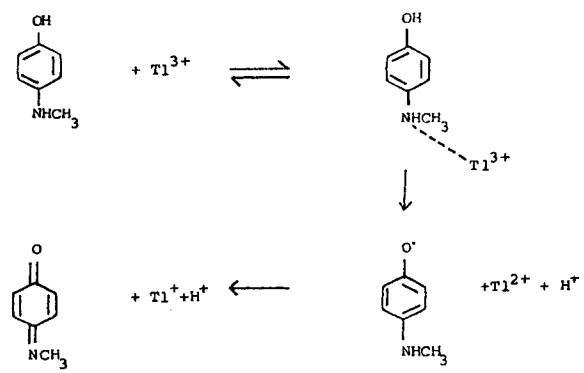
$$complex \xrightarrow{k_i} products \quad (11)$$

The loss of thallium(III) leads to rate law (12) or (13):

$$-\frac{d[Tl^{III}]}{dt} = \frac{k_i K_i K_p K_h [Tl^{III}][metol][H^+]}{K_h + [H^+] + K_i K_h K_p [metol][H^+]} \quad (12)$$

$$k'' = \frac{k_i K_i K_p K_h [metol][H^+]}{K_h + [H^+] + K_i K_h K_p [metol][H^+]} = \frac{k_i K''[metol][H^+]}{K_h + [H^+] + K''[metol][H^+]} \quad (13)$$

where $K'' = K_i K_p K_h$.



Scheme 1

Since $K_h < ([H^+] + K''[\text{metol}][H^+])$, rate law (13) reduces to:

$$k'' = \frac{k_1 K''[\text{metol}]}{1 + K''[\text{metol}]} \quad (14)$$

The rate law (14) is similar to the earlier derived rate law (8), the only difference being that $k_1 k''$ is substituted for kK. However, this proposal was abandoned only on the premise that the rate of the reaction decreases with increasing ionic strength, thus the probability of the interaction of the likely charged species is not consistent with this observation.

Since the rate for ligand substitution in aquothallium(III) (10^8 dm^3 mol^{-1} s^{-1}) ascribes to the probability of inner-sphere electron transfer, the complexation of the metal ion by metol, as indicated in the reaction mechanism, eliminates this substitutionally controlled electron transfer. The electron transfer within the precursor complex to successor complex is rate limiting, thus the title reaction can be assigned to be a redox-controlled reaction.

The pre-added acrylic acid in the reaction mixture is not polymerized, therefore the generation of metol-free radicals in the reaction can be ruled out. However, the possibility of formation of a Tl^{2+} intermediate cannot be completely ruled out on this observation alone. There is every possibility of the formation of Tl^{2+} intermediate as one-equivalent change is the most desired pathway in the electron transfer reactions of thallium(III). Since no evidence of free radicals is obtained, the possibility of Tl^{2+} reaction with the substrate in the solvent cage before diffusing out of the cage cannot be eliminated. Such a proposition is also strengthened by thermodynamic considerations, more particularly in view of the fact that the redox potential[14] of Tl^{2+}/Tl^+ couple (1·5 V) is more than that of the Tl^{3+}/Tl^+ couple (1·25 V). These values of the redox potentials adequately confirm the fact that Tl^{2+} is a stronger oxidant than Tl^{3+} in solutions.

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