Kinetics and Mechanism of the Oxidation of Glycolic and Glyoxylic Acids by Thallium(III) in Acidic Perchlorate Solutions

(Mrs.) Pushpa Gupta, Prem Dutt Sharma, and Yugul Kishore Gupta *
Department of Chemistry, University of Rajasthan, Jaipur, India

---

Glycolic and glyoxylic acids react with Tl^{III} in 1 : 1 mol ratio, the products of oxidation depending on the initial concentration ratio of the reactants. Three complexes $[Tl(ga)]^{2+}$, $Tl(ga)\cdot Hga^{2+}$, and $[Tl(ga)_2]^+$ form from Tl^{III} and Hga, the first and third of these being thought to be reactive. The complete rate law determined from the initial rate of oxidation of glycolic acid in the concentration range 0.001—0.2 mol dm^{-3} is complicated, but for large [Hga], limiting rates are obtained and rate law (i) is obeyed where k_2 and K_3 are the rate constant for the decomposition and the stepwise formation

$$-d[Tl^{III}]/dt = k_2K_3[Tl^{III}]/([H^+] + K_3) \qquad \text{(i)}$$

constant, respectively, of the complex $[Tl(ga)_2]^+$ which were found to be $(6.9 \pm 0.6) \times 10^{-5}\ s^{-1}$ and 1.1 ± 0.1 mol dm^{-3} respectively at 70 °C. The rate law, again from the initial rates, for the oxidation of glyoxylic acid (Hgox) in the concentration range 0.002—0.06 mol dm^{-3} is given by equation (ii) where

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK_HK[Tl^{III}][Hgox]}{[H^+] + K_H + KK_H[Hgox]} \qquad \text{(ii)}$$

K_H, K, and k are the hydrolysis constant of Tl^{3+} and the stability and rate constants for the complex $[Tl(gox)]^{2+}$; K and k were found to be $625 \pm 50\ dm^3\ mol^{-1}$ and $(1.1 \pm 0.1) \times 10^{-4}\ s^{-1}$ respectively at 70 °C. The stability constants of the complexes have also been determined spectrophotometrically.

Organic compounds of thallium(III) have long been known,[1] but the first report on kinetics and mechanism was made by Halvorson and Halpern[2] for the oxidation of formic acid. Subsequently, several papers have appeared on the oxidations of cyclohexanone,[3] cyclohexanol,[4] olefins,[5,6] oxalic acid,[7] hydroxybenzene,[8] pyridine,[9] benzoin,[10] and alcohols.[11] Nevertheless, a systematic kinetics study of the oxidation of organic compounds by thallium(III) has not been made. It is with this aim that we undertook studies on the oxidation of glycolic acid and its substituted derivatives (hydroxycarboxylic acids). A systematic study of these acids with cerium(IV)[12] has already been made, and the oxidations with thallium(III) have also been reported[13] but the work appears to be incomplete in many respects.

Another object of this work was to obtain kinetic evidence for the often reported co-ordination compounds of thallium(III) with organic compounds; such evidence has been reported only in a few cases,[2,7,9] and the paper on the α-hydroxy-acids[13] also does not report such intermediate complexes. The third reason for making this study was to learn whether one or more kinetically important intermediate complexes are formed in such systems since in the oxidation[14] of nitrous acid three complexes have been reported, only one of which was found to be reactive.

We report in this paper the results of kinetic studies of the oxidation of glycolic acid (Hga) and glyoxylic acid (Hgox). Extensive studies of the oxidation of Hga have been made with several oxidants, and in general formaldehyde and carbon dioxide were the products. Recently a paper[15] on the thallium(III) oxidation has also appeared. Oxidation studies of Hgox are few, *e.g.* with vanadium(V),[16] cerium(IV),[17] chromium(VI),[18] manganese(III),[19] and periodate[20] in acidic solutions, and with hexacyanoferrate(III)[21] in alkaline solutions.

Experimental

Materials.—Thallium(III) perchlorate solution was prepared by dissolving BDH (AnalaR) thallium(III) oxide in 70% (AnalaR) Riedel perchloric acid and diluting to the desired strength, but not below 0.3 mol dm^{-3} so as to avoid precipitation of $Tl(OH)_3$. These solutions were standardized iodometrically.[22] The acid concentration was determined by titration against a standard NaOH solution in the presence of an excess of KBr to check the precipitation of $Tl(OH)_3$.

Glycolic acid was from Riedel and glyoxylic acid from Fluka. Their solutions were prepared by dissolving weighed quantities in doubly distilled water and were standardized against a solution of NaOH. Lithium perchlorate solution was prepared by neutralizing 70% $HClO_4$ with lithium carbonate (E. Merck) to pH 6.8. Thallium(I) perchlorate solution was prepared by reducing thallium(III) perchlorate solution with a few drops of H_2O_2 and boiling off the excess of H_2O_2. All solutions were prepared in twice distilled water, the second distillation being from $KMnO_4$.

Kinetic Procedure.—Experiments were carried out in stoppered glass vessels in a thermostatted (±0.1 °C) water-bath. Reaction was initiated by adding thallium(III) perchlorate solution to a mixture containing Hga or Hgox, perchloric acid, *etc.*, both solutions being equilibrated at 70 °C unless stated otherwise. After suitable intervals aliquot portions (5 cm^3) were analyzed iodometrically for thallium(III). The reaction of Hga was slow even at 70 °C and it became slower still on account of the product (formaldehyde) and hence 20—30% of the reaction was followed. In the case of Hgox *ca.* 50% of the reaction was followed. Since the reaction becomes complicated on account of the intermediate complexes, initial rates were determined by the plane-mirror method[23] and the rates of duplicate runs were reproducible to ±10%.

Spectrophotometry.—Spectrophotometric measurements were made on a Toshniwal spectrophotometer with 1-cm cells. The absorbances of thallium(III) perchlorate (5×10^{-5} mol dm^{-3}) and its mixtures with Hga (2×10^{-4}—0.1 mol dm^{-3}) or Hgox (5×10^{-5}—2.5×10^{-2} mol dm^{-3}) were measured at 240 nm. These results indicate the formation of two complexes

Table 1. Initial rates v_0 of the reaction of Tl^{III} with glyoxylic acid: variation of [Hgox] at $[HClO_4] = 0.5$ mol dm^{-3}

(*a*) $[Tl^{III}] = 5.6 \times 10^{-3}$ mol dm^{-3}

10^3[Hgox]/mol dm^{-3}	2.0	4.0	5.0	8.0	10.0	20.0	30.0	40.0	60.0
$10^7 v_0$/mol dm^{-3} s^{-1} (74 °C)	1.7		2.6		4.4	5.7		7.5	8.0
(70 °C)	1.2	1.6	1.9	2.5	3.0	4.1	4.8	5.1	5.4
(65 °C)	0.5		1.15		1.8	2.7		3.3	3.5

(*b*) $[Tl^{III}] = 3.4 \times 10^{-3}$ mol dm^{-3}, 70 °C

10^3[Hgox]/mol dm^{-3}	1.0	5.0	10.0	20.0	40.0	50.0
$10^7 v_0$/mol dm^{-3} s^{-1}	0.67	1.55	2.4	3.1	3.6	3.7

(1 : 1 and 1 : 2) in case of glycolic acid (by Yatsimirskii's method of calculation [24]) and the formation constants were found to be (2 500 ± 100) and 40 ± 15 dm^3 mol^{-1} at 30 °C and $I = 0.55$ mol dm^{-3}. Glyoxylic acid formed only one complex and its formation constant was 850 ± 50 dm^3 mol^{-1} at 30 °C from a plot of (absorbance)$^{-1}$ *versus* [Hgox]$^{-1}$ for [Hgox] > 20[Tl^{III}].

Potentiometry.—An attempt to determine the formation constants of these complexes potentiometrically by Ahrland's [25] method was also made. There was definite evidence for complex formation of Tl^{III} for both organic acids, but no worthwhile quantitative results were obtained.

Results

Stoicheiometry and Products.—The stoicheiometry was determined with an excess of Hga and 0.003 mol dm^{-3} Tl^{III}. Glyoxylic acid as the product was determined colorimetrically.[26] No CO_2 was formed and no formaldehyde was detected [negative test with chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid) [27]]. The reaction occurred as in equation (1). With an excess of Tl^{III}, formaldehyde and CO_2 were the products [equation (2)]. Small amounts of glyoxylic acid were also formed.

$$CH_2OHCO_2H + Tl^{III} \longrightarrow CHOCO_2H + 2H^+ + Tl^I \quad (1)$$

$$CH_2OHCO_2H + Tl^{III} \longrightarrow HCHO + CO_2 + 2H^+ + Tl^I \quad (2)$$

In the case of an excess of Tl^{III} and glyoxylic acid no definite stoicheiometry could be established. The products of oxidation were formic acid (positive test with chromotropic acid) and CO_2. However, with an excess of Hgox (>0.003 mol dm^{-3} Tl^{III}) determined colorimetrically [26] the reaction occurred as in equation (3).

$$CHOCO_2H + Tl^{III} + H_2O \longrightarrow HCO_2H + 2H^+ + CO_2 + Tl^I \quad (3)$$

Thallium(III) *Dependence.*—It will be seen later that both organic acids form reactive intermediate complexes in concentrations comparable to that of thallium(III) and hence the order with respect to thallium(III) could be determined only in the presence of large concentrations of the organic acid. Thallium(III) was varied in the concentration range of (0.77—6.4) $\times 10^{-3}$ mol dm^{-3} at fixed [Hga] = 0.21 mol dm^{-3}. A plot of initial rates *versus* [Tl^{III}] gave a straight line passing through the origin, indicating a first-order dependence on [Tl^{III}]. The pseudo-first-order rate constant at $[H^+] = 0.5$ mol dm^{-3} was found to be 4.7×10^{-5} s^{-1} at 70 °C. In the case of Hgox, Tl^{III} was varied in the range (1.4—7.0) $\times 10^{-3}$ mol dm^{-3} at fixed [Hgox] = 0.02 mol dm^{-3} and the order with respect to [Tl^{III}] was again found to be one. The pseudo-first-order rate constant was 6.1×10^{-5} s^{-1} at $[H^+] = 0.5$ mol dm^{-3} at 70 °C.

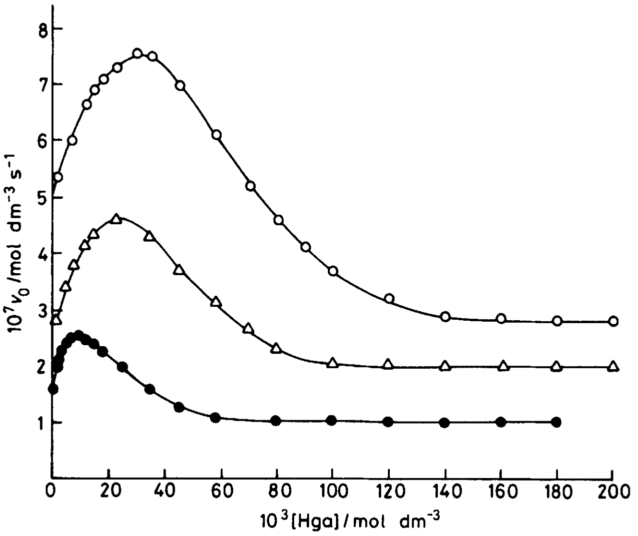


Figure. Plot of initial rate v_0 *versus* [Hga] in the oxidation of glycolic acid with Tl^{III} at $[HClO_4] = 0.3$ mol dm^{-3} and 70 °C. $[Tl^{III}] = 6.07 \times 10^{-3}$ (○), 4.36×10^{-3} (△), and 2.18×10^{-3} mol dm^{-3} (●)

Glycolic and Glyoxylic Acid Dependences.—The concentration of glycolic acid was varied from 0.001 to 0.20 mol dm^{-3} at three different concentrations of Tl^{III} and the results are given in the Figure. The limiting rates (mol dm^{-3} s^{-1}) are 1.0×10^{-7}, 2.0×10^{-7}, and 2.9×10^{-7} for 2.18×10^{-3}, 4.36×10^{-3}, and 6.07×10^{-3} mol dm^{-3} Tl^{III} respectively. Thus, the limiting rate has a first-order dependence on [Tl^{III}]. The concentration of glyoxylic acid was varied at three temperatures and two different concentrations of Tl^{III}. These results are shown in Table 1. The rate increases and tends to a limiting value with increasing [Hgox]. The limiting rates at the two thallium(III) concentrations have a first-order dependence on [Tl^{III}]. The pseudo-first-order rate constants for the limiting range of [Hgox] are 1.5×10^{-4}, 1.0×10^{-4}, and 0.60×10^{-4} s^{-1} at 75, 70, and 65 °C respectively.

Hydrogen-ion Dependence.—The hydrogen-ion concentration was varied with perchloric acid at constant ionic strength adjusted with lithium perchlorate. The results of the oxidation of glycolic acid at three different temperatures and three different concentrations of glycolic acid are given in Table 2. The rate decreases with increasing $[H^+]$. Plots of (rate)$^{-1}$ *versus* $[H^+]$ were linear with different intercepts and slopes for different ranges of [Hga]. The results of the oxid-

Table 2. Initial rates of the reaction of Tl^{III} with glycolic acid: variation of $[H^+]$ at fixed $I = 2.0$ mol dm^{-3}

(*a*) $[Tl^{III}] = 0.012$, $[Hga] = 0.21$ mol dm^{-3}

$[HClO_4]$/mol dm^{-3}	0.5	0.75	1.00	1.25	1.50	1.75
10^7v_0/mol dm^{-3} s^{-1} (65 °C)	5.0	4.35	3.8	3.45	3.2	
(70 °C)	5.4	4.65	4.3	3.8	3.4	3.1
(75 °C)	6.0	5.25	4.5	3.9	3.65	

(*b*) $[Tl^{III}] = 0.006$, $[Hga] = 0.01$ mol dm^{-3}, 70 °C

$[HClO_4]$/mol dm^{-3}	0.5	1.0	1.5	2.0
10^7v_0/mol dm^{-3} s^{-1}	6.3	5.4	4.7	4.2

(*c*) $[Tl^{III}] = 0.006$, $[Hga] = 0.05$ mol dm^{-3}, 70 °C

$[HClO_4]$/mol dm^{-3}	0.5	1.0	1.5	2.0
10^7v_0/mol dm^{-3} s^{-1}	6.7	6.4	6.2	6.0

Table 3. Initial rates of the oxidation of glyoxylic acid with Tl^{III}: variation of $[HClO_4]$ at 70 °C

(*a*) $[Tl^{III}] = 5.4 \times 10^{-3}$, $[Hgox] = 2.0 \times 10^{-2}$, $I = 3.0$ mol dm^{-3}

$[HClO_4]$/mol dm^{-3}	0.5	1.0	1.5	2.0	2.5
10^7v_0/mol dm^{-3} s^{-1}	3.3	3.0	2.3	2.0	1.7

(*b*) $[Tl^{III}] = 2.25 \times 10^{-3}$, $[Hgox] = 1.0 \times 10^{-1}$, $I = 2.0$ mol dm^{-3}

$[HClO_4]$/mol dm^{-3}	0.5	1.0	1.5	2.0
10^7v_0/mol dm^{-3} s^{-1}	2.5	2.4	2.6	2.5

ation of glyoxylic acid are given in Table 3. The rate is independent of $[H^+]$ for large concentrations of Hgox (limiting rates) and decreases with increasing $[H^+]$ in the lower range of [Hgox].

Effect of Ionic Strength.—The ionic strength was varied with lithium perchlorate in the range 0.1—1.0 mol dm^{-3} but there was no change in the rate.

Discussion

In aqueous perchloric acid solutions two species of Tl^{III}, *i.e.* Tl^{3+} and $[Tl(OH)]^{2+}$, exist in equilibrium (4). There has been

$$Tl^{3+} + H_2O \overset{K_H}{\rightleftharpoons} [Tl(OH)]^{2+} + H^+ \qquad (4)$$

some controversy over the value of K_H, but the generally accepted value [28] is 0.073 mol dm^{-3} at 25 °C and $I = 3.0$ mol dm^{-3}. From its values of 0.086 and 0.068 mol dm^{-3} at 25 and 0 °C,[29] an enthalpy change of 6 220 J was calculated, and from this and from the generally accepted value the equilibrium constant at 70 °C was found to be 0.119 mol dm^{-3}. Glycolic and glyoxylic acids would exist as the undissociated molecules since their dissociation constants are small [30,31] and $[H^+]$ is large. However, glyoxylic acid would mainly be hydrated [equation (5)] with a hydration constant [32] of *ca.* 10^3.

$$CHOCO_2H + H_2O \rightleftharpoons HC(OH)_2CO_2H \qquad (5)$$

The Figure shows that the rate varies in a complex manner with [Hga]. Although the actual number of different complexes formed between Tl^{III} and Hga is not known from the kinetics results, the number of reactive complexes appears to be two. Complexing with Hga has been reported for other metal ions like cerium(IV),[33] chromium(VI),[34] cerium(III) [30a,35] and copper(II).[36] In view of these complexes in the present case the complexes formed can be assigned 1 : 1 and 1 : 2 stoicheiometries.

The limiting rate corresponding to complete complexing of Tl^{III} with Hga decreases with increasing $[H^+]$. Since the $[H^+]$ dependence under such conditions cannot be connected with the hydrolysis of Tl^{3+} or the acid dissociation of glycolic acid, it must be involved with deprotonation of the second complex (1 : 2), the deprotonated complex being the reactive species. Thus, a third deprotonated complex (1 : 2) may also be formed. However, the second protonated complex (1 : 2) is not reactive. For the limiting rates in the presence of an excess of Hga, a plot of (rate)$^{-1}$ *versus* $[H^+]$ gives a straight line with a non-zero intercept.

The Figure indicates that a plot of (rate)$^{-1}$ *versus* [Hga]$^{-1}$ would be appropriate and on doing so a more or less straight line is obtained with a non-zero intercept (a rigorous plot was made later). Thus, the empirical rate law for the portion of the curve in the Figure before the maximum is given by equation (6), where *A* and *B* are constants. This is in conformity with the orders in $[Tl^{III}]$ and [Hga] and the inverse fractional order in $[H^+]$ as found experimentally. On the basis of the above results and the information about the intermediate complexes, the mechanism in equations (4) and (7)—(11) may be proposed; Hga has been used for hydrated Hga. Rate law (12) can thus be deduced.

$$-d[Tl^{III}]/dt = A[Tl^{III}][Hga]/([H^+] + B[Hga]) \qquad (6)$$

$$Tl^{3+} + H_2O \overset{K_H}{\rightleftharpoons} [Tl(OH)]^{2+} + H^+ \qquad (4)$$

$$[Tl(OH)]^{2+} + Hga \overset{K_1}{\rightleftharpoons} [Tl(ga)]^{2+} + H_2O \qquad (7)$$

$$[Tl(ga)]^{2+} + Hga \overset{K_2}{\rightleftharpoons} Tl(ga)\cdot Hga^{2+} \qquad (8)$$

$$Tl(ga)\cdot Hga^{2+} \overset{K_3}{\rightleftharpoons} [Tl(ga)_2]^{+} + H^+ \qquad (9)$$

$$[Tl(ga)]^{2+} \xrightarrow{k_1} \text{products} \qquad (10)$$

$$[Tl(ga)_2]^{+} \xrightarrow{k_2} \text{products} \qquad (11)$$

For the range of lower concentrations of Hga corresponding to those to the left of the maximum in the Figure, $[Tl(ga)]^{2+}$ would be present predominantly, and the rate law (13) would

$$\frac{-d[Tl^{III}]}{dt} = \frac{[Tl^{III}]\,(k_1K_1K_H[Hga] + k_2K_1K_2K_HK_3[Hga]^2/[H^+])}{[H^+] + K_H + K_1K_H[Hga] + K_1K_2K_H[Hga]^2 + (K_1K_2K_HK_3[Hga]^2/[H^+])} \qquad (12)$$

Table 4. Observed and calculated initial rates v_0 at concentrations of Hga more than that corresponding to the maximum in the Figure and less than that corresponding to the limiting rates; $[HClO_4] = 0.5$ mol dm^{-3}, 70 °C, $K_2 = 40$ dm^3 mol^{-1}, $K_3 = 1.1$ mol dm^{-3}, $k_1 = 2.3 \times 10^{-4}$ s^{-1}, and $k_2 = 6.9 \times 10^{-5}$ s^{-1}

$10^3[Tl^{III}]$	10^2[Hga]	$10^7 v_0$/mol dm^{-3} s^{-1}	
mol dm^{-3}		calc.	obs.
2.18	1.8	2.2	2.2
2.18	2.5	2.0	2.0
2.18	3.5	1.7	1.6
2.18	4.5	1.6	1.3
4.36	3.5	3.5	4.0
4.36	4.5	3.2	3.5
4.36	5.8	3.0	3.1
6.07	5.8	4.2	5.7
6.07	7.0	4.0	4.8
6.07	8.0	3.9	4.2
6.07	9.0	3.7	3.7
6.07	10.0	3.6	3.5

$$\frac{-d[Tl^{III}]}{dt} = \frac{k_1K_1K_H[Tl^{III}][Hga]}{[H^+] + K_H + K_1K_H[Hga]} \qquad (13)$$

be obtained. This is similar to equation (6) and the value of K_1 can be obtained if the free concentrations of Hga are known. An approximate method [37] is to extrapolate the rising curves in the Figure to the limiting rates. This would yield the rate constant k_1 for the decomposition of the complex $[Tl(ga)]^{2+}$, and this would have been the situation had there been no further complexing of Tl^{III}. The extrapolated value of k_1 was found to be (2.3 ± 0.3) × 10^{-4} s^{-1} at 70 °C. From the rate at any concentration of Hga less than that corresponding to the maximum in the Figure one can calculate the concentration of the complex $[Tl(ga)]^{2+}$ and free Hga. A plot of (rate)$^{-1}$ *versus* $[Hga]_{free}^{-1}$ gives a straight line with a non-zero intercept, from which K_1 was found to be 2 600 ± 200 dm^3 mol^{-1}. Similarly, a plot of (rate)$^{-1}$ *versus* $[H^+]$ at fixed [Hga] yields a value of K_1 of 2 400 ± 100 dm^3 mol^{-1}. These values are quite similar to the one obtained spectrophotometrically. An alternative mechanism involving complex formation between Tl^{3+} and Hga with proton liberation would lead to the same rate law as (13).

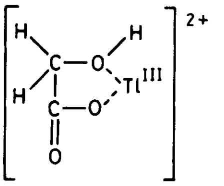
In the situation where limiting rates are obtained, only two complexes $Tl(ga){\cdot}Hga^{2+}$ and $[Tl(ga)_2]^+$ are likely to be present and if only $[Tl(ga)_2]^+$ is reactive, rate law (14) would be obtained. From plots of (rate)$^{-1}$ *versus* $[H^+]$, k_2/s^{-1} and K_3/mol dm^{-3} were found to be (6.0 ± 0.5) × 10^{-5} and 1.2 ± 0.1 at 65 °C, (6.9 ± 0.6) × 10^{-5} and 1.1 ± 0.1 at 70 °C, and (8.0 ± 0.7) × 10^{-5} and 1.0 ± 0.1 at 75 °C respectively. The energy and entropy of activation for the decomposition of the complex $[Tl(ga)_2]^+$ were found to be 30 ± 0.4 kJ mol^{-1} and 2.4 ± 10 J K^{-1} mol^{-1}. It is worth noting that only one complex was reported to be formed in a recent study [15] and its formation constant was 0.85 mol dm^{-3}.

$$\frac{-d[Tl^{III}]}{dt} = \frac{k_2K_3[Tl^{III}]}{[H^+] + K_3} \qquad (14)$$

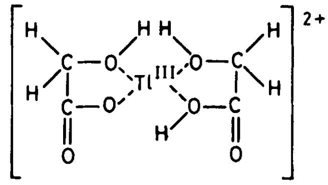
For concentrations of Hga larger than that corresponding to the maximum in the Figure and less than those corresponding to the limiting rates, rate law (12) would reduce to (15). For the verification of rate law (15) in the above concentration range the rate was calculated with the value of 40 dm^3 mol^{-1} for K_2 obtained spectrophotometrically and the values are given in Table 4 alongside the experimental values. In view of the complicated rate law, the agreement between the observed and calculated values is considered satisfactory.

$$\frac{-d[Tl^{III}]}{dt} = \frac{(k_1 + k_2K_2K_3[Hga]/[H^+])[Tl^{III}]}{1 + K_2[Hga] + (K_2K_3[Hga]/[H^+])} \qquad (15)$$

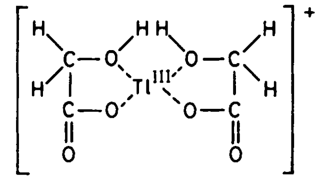
Since different oxidation products are obtained from the reactants in different concentration ratios, the intermediate complexes under the two conditions (excess of Tl^{III} and excess of Hga) are structurally different. In complex (I) a chelate is formed and ultimately C–C bond breaking occurs leading to the products HCHO and CO_2. In complex (III), O–H bond breaking occurs in both molecules of Hga by transfer of one electron from each molecule to Tl^{III}. The product $H_2CO{-}CO_2$ rearranges to $CHOCO_2H$.



(I)



(II)



(III)

For Hgox also the $[H^+]$ dependence should be connected with the hydrolysis of Tl^{3+} and not with the dissociation of Hgox since the dissociation constant of the latter is small.[31] Thus, $[Tl(OH)]^{2+}$ and Hgox should be the reactive species. The mechanism in equations (4), (16), and (17) may be suggested. This would give the rate law (18). The free concentration of Hgox was calculated as described for Hga. The limiting rates at 65, 70, and 74°C are 3.5 × 10^{-7}, 6.2 × 10^{-7}, and 8.5 × 10^{-7} mol dm^{-3} s^{-1} respectively. Thus, the pseudo-first-order rate constant k was found to be 0.62 × 10^{-4}, 1.1 × 10^{-4}, and 1.5 × 10^{-4} s^{-1} at the three temperatures. Plots of (rate)$^{-1}$ *versus* $[Hgox]_{free}^{-1}$ yielded straight lines with non-zero intercepts, from which the values of k/s^{-1} and K/dm^3 mol^{-1} were found to be (0.67 ± 0.05) × 10^{-4} and 750 ± 50 at 65 °C, (1.1 ± 0.1) × 10^{-4} and 625 ± 50 at 70 °C, and (1.5 ± 0.1) × 10^{-4} and 590 ± 50 at 74 °C.

$$Tl^{3+} + H_2O \overset{K_H}{\rightleftharpoons} [Tl(OH)]^{2+} + H^+ \qquad (4)$$

$$[Tl(OH)]^{2+} + Hgox \overset{K}{\rightleftharpoons} [Tl(gox)]^{2+} + H_2O \qquad (16)$$

$$[Tl(gox)]^{2+} \xrightarrow{k} \text{products} \qquad (17)$$

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK_HK[Tl^{III}][Hgox]}{[H^+] + K_H + KK_H[Hgox]} \qquad (18)$$

References

1 A. G. Lee, 'The Chemistry of Thallium,' Elsevier, London, 1971.
2 H. N. Halvorson and J. Halpern, *J. Am. Chem. Soc.*, 1956, **78**,

5562; J. Halpern and S. Taylor, *Discuss. Faraday Soc.*, 1960, **29**, 1741.

3 J. S. Littler, *J. Chem. Soc.*, 1962, 827.

4 J. S. Littler, *J. Chem. Soc.*, 1962, 2170.

5 P. M. Henry, *J. Am. Chem. Soc.*, 1965, **87**, 990, 4423; 1966, **88**, 1597.

6 A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2763; 1974, 1929; 1975, 2465.

7 L. B. Monsted and G. Nord, *Trans. Faraday Soc.*, 1970, **66**, 939.

8 E. Pellizetti, E. Mentesti, and G. Saini, *J. Chem. Soc., Dalton Trans.*, 1974, 721; 1975, 794; *J. Inorg. Nucl. Chem.*, 1975, **37**, 537, 1733.

9 M. D. Johnson and D. Vamplew, *J. Chem. Soc. B*, 1971, 507.

10 S. B. Mohanty, R. C. Acharya, C. N. Nanda, and N. K. Rout, *Indian J. Chem., Sect. A*, 1976, **14**, 42.

11 C. E. Burchill and G. G. Hickling, *Can. J. Chem.*, 1970, **48**, 2466; C. E. Burchill and W. H. Wolodussky, *ibid.*, p. 2955; V. S. Srinivasan and N. Venkatasubramanian, *Indian J. Chem., Sect. A*, 1977, **15**, 791.

12 V. K. Grover and Y. K. Gupta, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2445.

13 S. B. Mohanty, R. C. Acharya, C. N. Nanda, and M. K. Rout, *J. Indian Chem. Soc.*, 1976, **53**, 59.

14 B. M. Thakuria and Y. K. Gupta, *Inorg. Chem.*, 1977, **16**, 1399.

15 M. Ignaczad and G. Andrijewski, *Pol. J. Chem.*, 1980, **54**, 1343.

16 K. K. Sengupta and H. R. Chatterji, *Inorg. Chem.*, 1978, **17**, 2429.

17 K. K. Sengupta, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 298.

18 K. K. Sengupta and S. D. Bhattacharya, *Z. Phys. Chem. (Leipzig)*, 1969, **240**, 279.

19 K. K. Khumriu, D. C. Mukherjee, and K. K. Sengupta, *Indian J. Chem.*, 1975, **13**, 1288.

20 L. Moros, I. Molnar-Perl, and L. Kover, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1337.

21 K. K. Sengupta, T. Sarcar, S. Sengupta, and H. R. Chatterjee, *Indian J. Chem., Sect. A*, 1976, 14, 583; S. Sengupta and H. R. Chatterjee, *ibid.*, p. 586.

22 H. G. S. Senger and Y. K. Gupta, *J. Indian Chem. Soc.*, 1966, **43**, 223; I. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, p. 370.

23 M. Latshaw, *J. Am. Chem. Soc.*, 1925, **47**, 793.

24 K. B. Yatsimirskii, *Zh. Neorg. Khim.*, 1956, **1**, 2306.

25 S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, **264**, 276; S. Ahrland, I. Grenthe, L. Johnson, and B. Noren, *Acta Chem. Scand.*, 1963, **17**, 1567.

26 H. A. SoKol, *Anal. Chim. Acta*, 1977, **89**, 407.

27 F. Fiegl, 'Spot Tests on Organic Analysis,' Elsevier, New York, 1956.

28 G. Biedermann, *Ark. Kemi*, 1964, 6, 527.

29 G. Nord, *Inorg. Chem.*, 1976, **15**, 1921.

30 (*a*) M. Cefols, A. S. Tompa, A. V. Caliano, and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290; (*b*) R. Griessry, B. Prijis, and H. Siegel, *J. Inorg. Nucl. Chem. Lett.*, 1981, **4**, 443.

31 H. Strehlow, *Ber. Bunsenges. Phys. Chem.*, 1966, 66, 392; D. L. Leussing and E. M. Hann, *J. Am. Chem. Soc.*, 1966, **88**, 696.

32 M. L. Ahrens, *Ber. Bunsenges. Phys. Chem.*, 1968, **72**, 691.

33 Z. Ahmad and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1977, 82.

34 F. Hasan and J. Rocek, *J. Am. Chem. Soc.*, 1975, **97**, 1444; 1974, **96**, 6802; G. V. Bakore and A. A. Despande, *Z. Phys. Chem. (Leipzig)*, 1964, **227**, 14; R. N. Singh, L. N. Singh, and H. S. Singh, *Indian J. Chem., Sect..A*, 1977, **15**, 1117.

35 A. Sonesson, *Acta Chem. Scand.*, 1961, **15**, 1.

36 R. P. Martin and R. A. Paris, *Bull. Soc. Chim. Fr.*, 1963, 1600; I. Lundquist, *Acta Chem. Scand.*, 1964, **10**, 858.

37 S. S. Gupta and Y. K. Gupta, *Inorg. Chem.*, 1981, **20**, 1748.

Received 3rd *May* 1983; *Paper* 3/709