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KINETICS AND MECHANISM OF THE REDUCTION OF Tl(III) BY ACETAMIDE FORMAMIDE AND N-METHYL FORMAMIDE IN AQUEOUS ACID PERCHLORATE MEDIA

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Abstract—The kinetics of reduction of Tl(III) by acetamide, formamide and N-methyl formamide have been studied at 70°C in acid perchlorate media. The reaction requires one mole of Tl(III) for one mole of amide. All rates were first order in each reactant and were independent of [Tl(I)] and [$NaClO_4$]. A free radical mechanism consistent with these results has been proposed for these reactions. Activation energies and entropies are calculated for each reaction.

INTRODUCTION

Oxidation reduction studies involving Tl(III) reveal that Tl(III) may be reduced either by one electron change steps, or by conforming with Schaffer's principle[1] of equivalent change. The noncomplimentary oxidation of Fe(II)[2, 3] and U(IV)[4] occurs in two steps involving an intermediate formation of Tl(II) and the oxidation of Formic acid[5] and Hg^{2+}[6, 7] appears to be accomplished in a single step in accordance with Schaffer's principle. Baker *et al.*[8] found that both mechanisms occur in the oxidation of V(II). Although the amide are one kind of biologically and industrially important compounds but the kinetics of the oxidation of Dimethyl formamide[9] by Tl(III) have been reported and we have extended this study to homologous amides, in order to obtain additional information on such redox reactions. This paper presents the study of oxidation of acetamide formamide and N, methyl formamide by Tl(III) in aquous perchloric acid medium.

EXPERIMENTAL

Stock solutions of thallic perchlorate was prepared by oxidizing AnalaR. thallous nitrate with bromine. Thallic oxide was precipitated by treating the resulting solution with sodium hydroxide solution. The oxide was thoroughly washed till bromide was beyond detection, and dissolved in perchloric acid. The oxide was reprecipitated and redissolved in perchloric acid to ensure removal of foreign ions. The final solution, standardized iodometrically[10] was 0.38 M-Tl(III) in 4.56 M-$HClO_4$. A known volume of Tl(III) in perchloric acid solution was diluted to yield less than 0.25 M solution in $HClO_4$ and added to a 2% solution of KI. The liberated iodine was titrated against thiosulfate. The end point was marked by the change from dirty blue to clear yellow of the precipitate of thallous iodide. The dilution of the reaction mixture was necessary as concentrated solutions of $HClO_4$ liberate iodine from a solution.

Perchloric acid was 60% (Riedel), sodium perchlorate (Koch light, England) was used to maintain the ionic strength. Formamide (Koch light, England), Acetamide (BDH) and N-Methyl formamide (BDH) was used as such because the Tlc of these amides show no organic impurity. All solutions were prepared in double distilled water, the second distillation being from permanganate solution.

Kinetic experiments were carried out in a temperature controlled (±0.1°C) oil bath. The order of mixing was without any effect. 5 ml aliquot portions after suitable intervals were analysed for Tl(III) iodometrically with thiosulphate of about half the concentration of Tl(III) in the reaction mixture. In most cases 70–80% reaction was followed. The maximum error in the analysis of portions was ±0.02 ml of $Na_2S_2O_3$. This introduced an error of ±1–6% in the rate constant depending on the volume of the titrant. In most cases duplicate rate measurements were reproducible to ±4%.

All the rate measurements described here were made at 70°C unless otherwise stated. Pseudo first order rate constants reported here are the slopes of the log [Tl(III)] against time plots.

Oxidation products. With acetamide, acetic acid is the final product and did not undergo oxidation under the condition employed. The presence of CO_2 was confirmed in the case of formamide and methyl formamide and was measured gasometrically by passing the total gas through three wolf bottles—half filled with 40% KOH. The presence of methylamime[11] in the case of methyl formamide was confirmed and it was not oxidised in our experimental conditions. The gasometric results were in agreement with the proposed stoichiometry (Table 1).

RESULTS

Amide and thallic perchlorate in suitable perchloric acid solution and of different concentration were kept at 70°C for sufficient time to complete the reaction. Excess of [Tl(III)] was determined iodometrically. It was found that one mole of amide required one mole of Tl(III).

Order with respect to Tl(III) *and amide*

The order with respect to [Tl(III)] is unity. The plots of log [Tl(III)] against time were straight line at different fixed concentration of amide.

The order with respect to [amide] (where present in excess) was found to be one in each case from plots of k_{obs} against [amide]. Thus the kinetic results were in accordance with eqn (1). The values of k_{obs} at different [amide] are given in Table 2.

Effect of [H^+]

The effect of varying [H^+] was noted by varying the concentration of perchloric acid at constant $\mu = 3.0$ M, adjusted with sodium perchlorate. The oxidation rate increase on increasing [H^+] in case of acetamide reaction but increase in the [H^+] had slight effect on the k_{obs} of formamide and no effect in case of methyl formamide (Table 3).

Effect of Tl(I) *and sodium perchlorate*

Reactions were carried out in the presence of 0.2 M–0.6 M Tl(I) perchlorate but there was no change in the

Table 1. Gasometric results for the reaction at 20°C. [Tl(III)] = 0.002 M; 0.0038 M for acetamide, formamide and methyl formamide respectively; [Amide] = 0.06 M; [HClO$_4$] = 1.00 M for all reactions

Amide	V_{tol} (ml)	V_{KOH} (ml)	V_{Pyrag} (Ml)
Acetamide	1.8	1.8	1.8
Formamide	3.5	0.7	3.4
Methyl formamide	3.2	0.2	3.1

V_{tol} = Total gas evolved;

V_{KOH} = gas over 40% KOH

V_{pyrag} = gas over 30% pyragallol.

Table 2. Dependence of oxidation rate on [amide] and [NH$_4$ClO$_4$] at 70°C. [HClO$_4$] = 1.0 M, [Tl(III)] = 0.003 M for formamide, 0.0036 M for NMF and 0.004 M for acetamide and ammonium perchlorate; *u* = 1.1 M

[Amide] or [NH$_4$ClO$_4$] M×10^2	CH_3CONH_2 k_{obs} (sec^{-1}) ×10^5	$KCONH_2$ k_{obs} (sec^{-1}) ×10^5	HCONHMe k_{obs} (sec^{-1}) ×10^5	NH_4ClO_4 k_{obs} (sec^{-1}) ×10^5
6.0	2.1	2.9	2.3	2.0
7.0	-	3.3	-	-
7.5	-	-	2.7	-
8.0	2.5	3.8	-	-
9.0	2.9	4.3	3.2	2.9
10.0	-	4.9	-	-
10.5	-	-	3.8	-
11.0	3.3	-	-	-
12.0	3.6	-	4.9	3.8

Table 3. Dependence of oxidation rate on [H$^+$] at 70°C; [Tl(III)] = 0.004 M, 0.003 M, 0.0036 M for acetamide, formamide and methylformamide; [Amide] = 0.06 M, 0.07 M, 0.12 M for acetamide, formamide and methyl formamide formamide

[H$^+$] M	CH_3CONH_2 k_{obs}(sec^{-1}) ×10^5	$HCONH_2$ k_{obs}(sec^{-1}) ×10^5	HCONHMe k_{obs}(sec^{-1}) ×10^5
1.0	2.1	3.3	4.8
1.5	2.4	3.35	4.8
2.0	2.7	3.4	4.8
2.5	3.0	3.5	5.1
3..0	3.5	3.65	4.9

rate of reaction. Similarly the change in rate was not observed when varying the concentration of $NaClO_4$ in the range 2.0–6.0 M.

Effect of temperature

Effect of temperature on the oxidation rate was studied in the temperature range 70–80°C. The plots of log k_{obs} against $1/T$ are linear and various activation parameters are evaluated using Arrhenius and Eyring equations with linear least squares treatment. Results are given in Table 4.

DISCUSSION

Our study shows that the oxidation of amides is extremely slow below 60°C. This suggests that the oxidation of amides by Tl(III) follows the hydrolysis of amides

$$RCONHR + H_2O \rightleftharpoons RCOOH + NH_2R. \qquad (1)$$

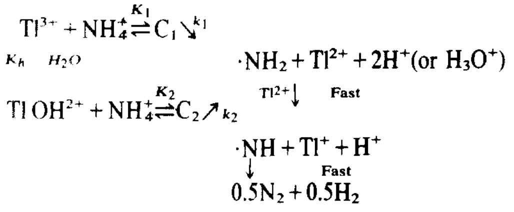
Reaction (1) has been reported by large number of workers[12–15] and it has been demonstrated that at high temperatures and in acidic medium amides are completely hydrolysed[9, 12].

Our results show that the oxidation of acetamide is following a different mechanism as compared to formamides. In the case of acetamide gasometric results indicate that the evolved gas is neither carbon-dioxide nor oxygen where as in the case of formamide more than 80% of the total gas is carbon dioxide and in the case of Methylformamide it is only carbon dioxide. In the oxidation of all the amides, it is found that for one mole of gas one mole of Tl(III) is consumed.

Secondly, the effect of $[H^+]$ is also quite interesting. In the oxidation of acetamide, the observed rate constant shows a marked increase with increasing $[H^+]$. The rate constants in the oxidation of formamide show only a slight increase where as the oxidation rate constant for N-methyl formamide does not show any effect.

We understand that the oxidation of these amides may be explained as the oxidation of ammonia and formic acid which are formed by the hydrolysis. The following mechanisms satisfy our results

Mechanism A:



$$Tl^{3+} + NH_4^+ \overset{K_1}{\rightleftharpoons} C_1 \searrow^{k_1}$$

$$K_h \quad H_2O \qquad \cdot NH_2 + Tl^{2+} + 2H^+ (\text{or } H_3O^+)$$

$$TlOH^{2+} + NH_4^+ \overset{K_2}{\rightleftharpoons} C_2 \nearrow_{k_2} \qquad Tl^{2+}\downarrow \quad \textbf{Fast}$$

$$\cdot NH + Tl^+ + H^+$$

$$\downarrow \quad \textbf{Fast}$$

$$0.5N_2 + 0.5H_2$$

Table 4. Activation parameters for the oxidation of amides

Amide	$\Delta E^{\neq}$	$\Delta S^{\neq}$
Acetamide	21.4 ± 0.2	-29.0 ± 7.0
N-methyl formamide	19.1 ± 0.1	-35.5 ± 0.4
Formamide	18.6 ± 0.9	-35.9 ± 2.5

rate of reaction is given by

$$\begin{aligned} r.r. &= k_1C_1 + k_2C_2 \\ &= \left\{\frac{k_1 + k_2/[H^+]}{1 + K_h/[H^+]}\right\} \cdot [Tl(III)]_T \cdot [NH_4^+] \end{aligned}$$

if $k_1 \gg k_2/[H^+]$

$$\text{therefore } r.r. = \left\{\frac{k_1}{1 + K_h/[H^+]}\right\}[Tl(III)]_T[NH_4^+] \qquad (2)$$

Mechanism B:

$$HCOOH \overset{K_a}{\rightleftharpoons} HCOO^- + H^+$$

$$HCOOH + Tl^{3+} \overset{K_c}{\rightleftharpoons} TlHCOOH^{3+} \text{ Ref.[5]}$$

$$TlHCOOH^{3+} \overset{k_3}{\rightarrow} CO_2 + 2H^+ + Tl^+$$

rate of reaction is given by

$$\begin{aligned} r.r. &= k_3[TLHCOOH^{3+}] \\ &= k_ck_3[HCOOH][Tl(III)] \\ &= k_3k_c \frac{1}{1 + \frac{K_h}{[H^+]}} \; \frac{1}{1 + \frac{K_a}{[H^+]}} \, |[Tl(III)]_T[Amide]_T \qquad (3) \end{aligned}$$

The oxidation of acetamide

The mechanism A represents the oxidation of acetamide by Tl(III). It satisfies the requirements that the reaction is first order with respect to [Tl(III)] and with respect to [Acetamide]. It also satisfies the stoichiometric requirements, (a) that one mole of acetamide should consume one mole of Tl(III) and (b) that one mole of Tl(III) should produce one mole of gas. The oxidation of NH_4ClO_4 by Tl(III) gives rate constant comparable to the observed rate constant for the oxidation of acetamide under similar condition Table 5. Oxidation of ammonium per chlorate gives the same gasometric results. The rate expression for the oxidation of acetamide is given by eqn (2).

The oxidation of formamide

It appears that the mechanism A as well as mechanism B are involved in the oxidation of formamides. However, it is evident on the basis of gasometric results that mechanism A represents only a minor reaction path. This suggests that most of Tl(III) is complexed by HCOOH as shown in mechanism B. If we assume K_h and K_a to be less than 1 (K_h is 0.073 at 25°C[16] K_a is 0.00018 at 25°C[17]) this may give the expression,

$$\left\{\frac{1}{1 + (K_h/[H^+])}\right\}\left\{\frac{1}{1 + (K_a/[H^+])}\right\}$$

a constant value at different $[H^+]$, thus making the rate constant for the oxidation of formic acid to be independent of $[H^+]$. Therefore a slight increase in the k_{obs} for the oxidation of formamide is probably due to the effect of $[H^+]$ in mechanism A. The rate expression for the oxidation of formamide is given by eqns (2) and (3).

The oxidation of NMF

The oxidation of NMF is exclusively proceeding by way of the oxidation of formic acid as only carbon-dioxide is produced and the k_{obs} is independent of $[H^+]$.

Also the rate constant for the oxidation of NMF compares well with the k^s (rate constants). for the oxidation of formic acid and also DMF[9] as Saxena and Gupta has been reported for the oxidation of DMF which proceeds by way of oxidation of formic acid under similar conditions. The rate expression for the oxidation of NMF is given by eqn (3).

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