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Kinetics and Mechanism of the Oxidation of Formic Acid by Thallium(III). Reinvestigation of Hydrogen Ion Dependence

Von

S. D. Saxena* and **K. S. Gupta**

Department of Chemistry, University of Rajasthan, Jaipur, India

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The rate of the oxidation of formic acid by thallium(III) in (Li, H)ClO_4 solutions is not affected by variation in hydrogen ion concentration and the experimental rate law,

$$\frac{-\mathrm{d}\,[\mathrm{Tl(III)}]}{\mathrm{d}\,t} = \frac{k_1 K\,[\mathrm{Tl(III)}]\,[\mathrm{HCOOH}]}{1 + K\,[\mathrm{HCOOH}]}$$

is consistent with the mechanism which requires the formation of intermediate complex $[HCOOHTl]^{3+}$ in a rapid preequilibrium followed by its slow decomposition to yield the final products. At 75°, k_1 and K have the values of $16 \pm 1 \times 10^{-5}\,\mathrm{sec}^{-1}$ and $7.3 \pm 0.5 M^{-1}$ resp.

Introduction

The oxidation of formic was first investigated by *Halvorson* and *Halpern*[1]. Later the dependence of the rate on hydrogen ion concentration in (Na, H)ClO_4 solutions was investigated by *Halpern* and *Taylor*[2], who reported that the rate has an inverse hydrogen ion dependence when $[HCOOH] < 0.5M$ and no dependence when $[HCOOH] > 0.5M$. They proposed a mechanism[2] which included the formation of the intermediate complex $[HCOOTl]^{2+}$, the decomposition of which was rate-determining. If formic acid is in excess, this would lead to the rate law

$$\frac{-\mathrm{d}\,[\mathrm{Tl(III)}]}{\mathrm{d}\,t} = \frac{k_1 K\,[\mathrm{Tl(III)}]\,[\mathrm{HCOOH}]}{[\mathrm{H}^+] + K\,[\mathrm{HCOOH}]} \tag{1}$$

where K is the equilibrium constant for the formation of $[HCOOTl]^{2+}$ and k_1 is the rate constant for the decomposition of this complex giving products. It seems that the reported[2] hydrogen ion dependence

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* Permanent address: Chemistry Department, D.A.V. College, Kanpur, India.

which changes with change in formic acid concentration is probably due to the medium effects[3, 4] introduced by the use of sodium perchlorate[2] for keeping the total perchlorate ion concentration constant. Since it is now well established that the use of sodium perchlorate rather than lithium perchlorate is likely to have a significant effect on hydrogen ion dependencies of rates of redox reactions[3, 4], it was considered worthwhile to investigate the kinetics of this reaction in (Li, H)ClO_4 solutions in order to establish whether the hydrogen ion dependence observed earlier is real or a case of medium effect[3, 4].

Experimental

Formic acid was B.D.H., L.R. quality which was distilled twice before use. $HClO_4$ was 60 per cent Riedel, R.G., quality. Thallic and lithium perchlorate solutions were prepared as described[3, 5]. The experiments were conducted in stoppered conical flasks immersed in a thermostated water-bath at desired temperature ± 0.1°. The order of mixing of reagents was without any effect. The kinetics was followed by analysing the aliquots for Tl(III) iodometrically[3, 5]. The duplicate rate measurements were reproducible within ± 5 per cent.

Results

In all the kinetic runs formic acid was at least fifteen times the concentration of Tl(III). Under these conditions the overall kinetics was characterised by a pseudo-first order behaviour and order with respect to Tl(III) consumption was one.

The concentration of perchloric acid was varied from 0.55 to 1.1M at fixed $[ClO_4^-] = 1.1M$ adjusted by $LiClO_4$.

The results of such variations at 0.0593—0.47M formic acid and at different temperatures (Table 1) clearly show that the rate of the reaction does not depend on hydrogen ion concentration. The results of the variation of formic acid (Table 1) are consistent with the experimental rate law (2).

$$\frac{\text{Rate}}{[\text{Tl(III)}]} = k_{\text{obs.}} = \frac{k_1 K\,[\text{HCOOH}]}{1 + K\,[\text{HCOOH}]} \qquad (2)$$

The plots of $1/k_{\text{obs.}}$ and 1/[HCOOH] were linear. These yielded k_1 values of $4.9 \pm 0.4 \times 10^{-5}$, $6.8 \pm 0.5 \times 10^{-5}$, and $16.0 \pm 1 \times 10^{-5} M^{-1}\,\text{sec}^{-1}$ and K values of 20 ± 2, 14 ± 1 and $7.3 \pm 0.5 M^{-1}$ at 65, 70, and 75° resp. The values of ΔH^{+} and ΔS^{+} associated with K are -29 ± 2 kcal/mole and -80 ± 6 e.u. and associated with k_1 are 28 ± 2 kcal/mole and 8 ± 6 e.u. resp.

Discussion

The results of this study clearly show that the rate of the oxidation of formic acid by thallium(III) does not have any hydrogen ion dependence and that the results obtained previously[4] with regard to hydrogen ion effect should be ascribed to medium effects obtaining in (Na, H)ClO_4 solutions[4]. Incidentally in the oxidation of H_3PO_2

too where a rate law similar to (2) is obeyed, a pseudo hydrogen ion dependence in (Na, H)ClO$_4$ solutions was found. This disappeared when LiClO$_4$ was used instead of NaClO$_4$[3].

Table 1. $k_{\text{obs.}}$ *for Thallium(III)/Formic Acid Reaction at Different Perchloric Acid, and Thallium(III) Concentrations*[a]

$10^3 \cdot$ [Tl(III)] *M*	[HCOOH] *M*	[HClO$_4$] *M*	$10^5\, k_{\text{obs.}}$ sec^{-1}	$10^5\, k_1$ (Eq. 2) M^{-1} sec^{-1}	$10^5\, k_1 \cdot$ K
	$t = 70°$				95 ± 7
4.04	0.1185	0.550	4.22	6.8	
4.90	0.1185	0.550	4.30	6.9	
6.06	0.1185	0.550	4.22	6.8	
2.02	0.1185	0.550	4.20	6.8	
4.04	0.1185	0.750	4.22	6.8	
4.04	0.1185	1.100	4.30	6.9	
4.04	0.1185	0.665	4.20	6.8	
4.04	0.2370	0.665	5.03	6.6	
4.04	0.4740	0.665	5.75	6.6	
	$t = 75°$				126 ± 8
3.96	0.0593	0.665	5.00	16	
3.96	0.0593	0.805	5.00	16	
3.96	0.0593	1.100	5.00	16	
3.96	0.1778	0.665	9.00	16	
3.96	0.2963	0.665	11.3	16	
3.96	0.4740	0.665	12.0	15	
	$t = 65°$				98 ± 10
4.04	0.1185	0.550	3.45	4.9	
4.04	0.1185	0.750	3.50	5.0	
4.04	0.1185	1.100	3.50	5.0	
4.04	0.1185	0.668	3.45	4.9	
4.04	0.2963	0.665	4.20	4.9	
4.04	0.4740	0.665	4.40	4.9	
4.04	0.4740	0.750	4.40	4.9	
4.04	0.4740	1.100	4.50	5.0	

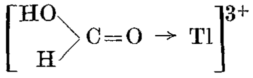
[a] Ionic Strength = 1.1*M*, adjusted with LiClO$_4$.

The kinetic results of this investigation are in conformity with the following mechanism.

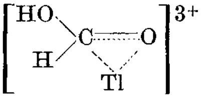
$$\mathrm{Tl^{3+} + HCOOH \overset{K}{\rightleftarrows} [HCOOHTl]^{3+}} \text{ (rapid)} \tag{3}$$

$$\mathrm{[HCOOHTl]^{3+} \xrightarrow{k_1} Tl^{+} + CO_2 + 2\, H^{+}} \text{ (slow)} \tag{4}$$

The proposed formation of the intermediate complex between neutral HCOOH molecule and Tl^{3+} is not a pecularity of this system alone, rather in all oxidations of this acid with metal ions such as Mn^{3+}[6], Co^{3+}[7], and Ce^{4+}[8], there is at least one path which involves the formation of the intermediate complex of the type $[HCOOHM]^{n+}$ prior to the redox step. Similarly thallic ion too in many of its redox reactions[3, 4, 9] forms intermediate complexes with neutral substrates before being reduced. Similar to those proposed for olefin[10] and H_3PO_2[11] oxidations, the complex $[HCOOHTl]^{3+}$ may have the following structures



or



and may decompose analogously[10, 11] to give final products.

A significant point which merits attention is the reported[1] thermoneutrality of the equilibrium constant, K. In contrast, the analysis of our data shows that it is the product, k_1K which is nearly independent of temperature (Table 1) and K decreases with increase in temperature. Similar trends in the K values for intermediate complexes $[HCOOHMn]^{3+}$ and $[C_2O_4Tl]^+$ have been noted elsewhere[6, 12].

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Correspondence and reprints:
Dr. K. S. Gupta
Department of Chemistry
University of Rajasthan
302004 Jaipur
India