

## Kinetics of Tl(III) oxidation of hydroxylamine hydrochloride in aqueous sulphuric acid

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**Abstract.** The kinetics of Tl(III) oxidation of hydroxylamine hydrochloride in 1.0 M H<sub>2</sub>SO<sub>4</sub> at a fixed chloride concentration has been investigated to make a formal comparison of the observed rate with that of hydrazine sulphate. The reaction exhibits total second order kinetics—first order in each reactant. The rate of the reaction depends inversely on the first power of [H<sup>+</sup>] and [Cl<sup>-</sup>] suggesting the possible reactive species as TlOH<sup>2+</sup>. To account for the stoichiometry of the reaction [Tl(III)]: [H<sub>2</sub>NOH.HCl] = 1.5 : 1 and the products of the reaction, HNO<sub>2</sub> and N<sub>2</sub>O, two reaction schemes have been proposed.

**Keywords.** Tl(III)-H<sub>2</sub>NOH.HCl reaction ; TlOH<sup>2+</sup>-active species ;  
 $K_h = 3.3 \times 10^{-5} \text{ M}^2$

### 1. Introduction

Though the kinetics of Tl(III) oxidation of hydrazine sulphate has been investigated in aqueous sulphuric acid by Srinivasan and Venkatasubramanian (1970 ; 1977), the kinetics of Tl(III) oxidation of hydroxylamine has not been investigated so far. This paper has, therefore, been undertaken with a view to compare the reactivity towards these two similar reducing agents.

### 2. Results and discussion

#### 2.1. Dependence of rate on Tl(III) and H<sub>2</sub>NOH.HCl concentrations

The kinetics of Tl(III) oxidation of hydroxylamine hydrochloride were studied in 1M H<sub>2</sub>SO<sub>4</sub> at 30° C. From the rate dependence on the concentration of Tl(III) and H<sub>2</sub>NOH.HCl (table 1) it has been found that the reaction exhibits total second order kinetics—first order with respect to [Tl(III)] and first order with respect to [H<sub>2</sub>N.OH.HCl]. As Tl(III) is known to complex with Cl<sup>-</sup> (Halverson *et al* 1956) total concentration of Cl<sup>-</sup> has been adjusted to be 0.025 M by adding necessary amount of NaCl.

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Table 1.\* Dependence of rate on [Ti(III)] and [H<sub>2</sub>NOH.HCl].  
[KHSO<sub>4</sub>] = 0.10 M; [H<sub>2</sub>SO<sub>4</sub>] = 1.0 M; Temp.: 30° C

| [Ti(III)] M × 10 <sup>3</sup> | [H <sub>2</sub> NOH.HCl] M × 10 <sup>2</sup> | k <sub>2</sub> × 10 <sup>4</sup> litres<br>mole <sup>-1</sup> sec <sup>-1</sup> |
|-------------------------------|--|---|
| 2.1                           | 0.50   | 4.2   |
| 2.0                           | 1.00   | 4.1   |
| 2.0                           | 1.50   | 3.9   |
| 2.0                           | 2.00   | 4.1   |
| 3.0                           | 2.00   | 4.0   |
| 4.0                           | 2.00   | 4.1   |

\* Total chloride ion concentration is kept at 0.025 M by adding required amount of NaCl in each case.

### 2.2. Dependence on acid concentration

The reaction rate is decreased by increasing sulphuric acid concentration from 0.50 M to 2.0 M only (table 2). The plot of log k<sub>2</sub> versus log [acid] is linear with a slope equal to -1 and this is similar to what was observed in the Ti(III) oxidation of hydrazine sulphate (Srinivasan and Venkatasubramanian 1970).

### 2.3. Effect of added chloride ions

With increasing concentration of chloride ions rate decreases (table 3) and a plot of log k<sub>2</sub> versus log [Cl<sup>-</sup>] is linear with a slope very nearly equal to -1.

### 2.4. Temperature influence

The effect of temperature on the reaction rate was studied between 30° and 50° C (table 4) and from the plot of log k<sub>2</sub> versus 1/T, energy of activation has been calculated. The thermodynamic parameters derived therefrom are summarised in table 4.

2.5. A comparative rate picture of hydrazine and hydroxylamine k<sub>2</sub> × 10<sup>2</sup> (N<sub>2</sub>H<sub>4</sub>) = 52 litre mole<sup>-1</sup> sec<sup>-1</sup> and k<sub>2</sub> × 10<sup>2</sup> (NH<sub>2</sub>OH.HCl) = 0.158 l mole<sup>-1</sup> sec<sup>-1</sup> at 30° C under identical conditions) clearly indicates that hydroxylamine gets oxidised about 3.5 × 10<sup>2</sup> times slower than hydrazine sulphate. This is probably due to the lower reducing property of hydroxylamine wherein the removal of hydrogen from nitrogen may be difficult due to the -I effect of the -OH group attached to the nitrogen.

## 3. Mechanism of the oxidation of hydroxylamine by Ti(III)

### 3.1. Nature of active Ti(III) species

In the presence of added chloride ion, Ti(III) forms a complex, TiCl<sup>2+</sup>, which may get hydrolysed under the reaction conditions, according to the equilibrium

Table 2.\* Dependence of rate on acid concentration.

$[\text{H}_2\text{NOH}\cdot\text{HCl}] = 5.0 \times 10^{-3} \text{ M}$ ;  $[\text{Tl(III)}] = 2.0 \times 10^{-3} \text{ M}$ ; Temp.:  $30^\circ \text{C}$

| $[\text{H}_2\text{SO}_4] \text{ M}$ | $k_2 \times 10^3 \text{ litres mole}^{-1} \text{ sec}^{-1}$ |
|-------------------------------------|---|
| 0.50                                | 7.1   |
| 1.00                                | 4.2   |
| 1.50                                | 3.2   |
| 2.00                                | 1.86  |

\* Total ionic strength is maintained at 2.0 by adding suitable amount of  $\text{KHSO}_4$ .

Table 3. Effect of added chloride ion on the rate of oxidation.

$[\text{H}_2\text{NOH}\cdot\text{HCl}] = 5.0 \times 10^{-3} \text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ ;

$[\text{Tl(III)}] = 2.0 \times 10^{-3} \text{ M}$ ;  $[\text{Na}_2\text{SO}_4] = 0.20 \text{ M}$ ; Temp.:  $30^\circ \text{C}$

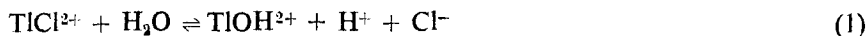
| $10^3 \times [\text{Cl}^-] \text{ M}$ | $k_2 \times 10^4 \text{ litres mole}^{-1} \text{ sec}^{-1}$ |
|---------------------------------------|---|
| 5.0                                   | 15.8  |
| 10.0                                  | 6.7   |
| 20                                    | 4.0   |
| 25                                    | 2.0   |

Table 4. Temperature dependence and thermodynamic parameters.

$[\text{H}_2\text{NOH}\cdot\text{HCl}] = 5.0 \times 10^{-3} \text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ ;  $[\text{Tl(III)}] = 2.0 \times 10^{-3} \text{ M}$ ;

$[\text{Na}_2\text{SO}_4] = 0.20 \text{ M}$

| $k_2 \times 10^3 \text{ litres mole}^{-1} \text{ sec}^{-1}$ | $30^\circ \text{C}$ | $40^\circ \text{C}$ | $50^\circ \text{C}$ |
|---|---------------------|---------------------|---------------------|
|   | 1.60                | 5.1                 | 36                  |
| $E_a \text{ kcal/mole}$                                     | 30                  |                     |                     |
| $\Delta H^\ddagger \text{ kcals/mole}$                      | 29                  |                     |                     |
| $\Delta S^\ddagger \text{ cal/mole/deg}$                    | +25                 |                     |                     |



The hydrolytic constant,

$$K_h = \frac{[\text{TlOH}^{2+}] [\text{H}^+] [\text{Cl}^-]}{[\text{TlCl}^{2+}]} \quad (2)$$

Therefore,

$$[\text{TlOH}^{2+}] = \frac{K_h [\text{TlCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]} \quad (3)$$

Under the reaction conditions, the observed inverse first order dependence on  $[\text{H}^+]$  and  $[\text{Cl}^-]$ , suggests the probable reactive species as  $\text{TlOH}^{2+}$ .

From the rate expression,

$$-\frac{d[\text{Tl(III)}]}{dt} = k_{\text{obs}} [\text{Tl(III)}] [\text{H}_2\text{NOH.HCl}] \quad (4)$$

it follows that

$$-\frac{d[\text{Tl(III)}]}{dt} = k_2 \frac{K_h [\text{TlCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]} [\text{Hydroxylamine hydrochloride}] \quad (5)$$

whence

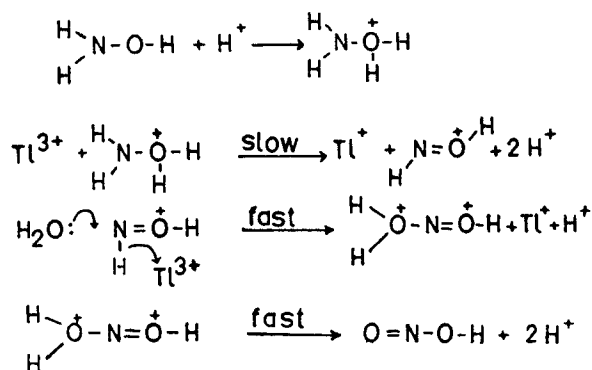
$$k_{\text{obs}} = \frac{k_2 K_h [\text{TlCl}^{2+}]}{[\text{H}^+] [\text{Cl}^-]} \quad (6)$$

It follows from (6) that a plot of  $k_{\text{obs}}$  versus  $1/[\text{Cl}^-]$  should be linear, at a given  $[\text{H}^+]$ , passing through the origin, with the slope equal to  $k_2 K_h/[\text{H}^+]$  where  $k_2$  is the specific rate, in the absence of  $\text{Cl}^-$ , obtained by extrapolation method. From the slope,  $K_h$ , evaluated comes to  $3.3 \times 10^{-5} \text{ M}^2$  which is very close to the hydrolytic constant reported for  $\text{TlCl}^{2+}$  (Basolo and Pearson 1967).

3.2. The oxidation products, in the hydroxylamine—Ti(III) reaction, are  $\text{N}_2\text{O}$  and  $\text{HNO}_2$  (Wiberg 1965) and the reaction has stoichiometry of  $[\text{Tl(III)}] : [\text{H}_2\text{NOH.HCl}] = 1.5 : 1$ . A mechanism consistent with the experimentally observed rate-law

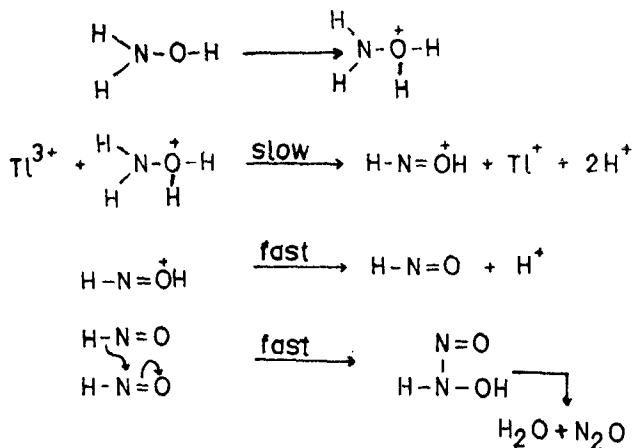
$$-\frac{d[\text{Tl(III)}]}{dt} = k_2 [\text{Tl(III)}] [\text{H}_2\text{NOH.HCl}]$$

could be the following :



SCHEME I

According to scheme 1,  $[Tl(III)] : [Hydroxylamine] = 2 : 1$ . The formation of  $N_2O$  on the other hand may be picturised as follows :



#### SCHEME II

The stoichiometry according to scheme 2 is 1 : 1. As the experimentally observed stoichiometry is  $[Tl(III)] : [H_2NOH \cdot HCl] = 1.5 : 1$ , it will be consistent with both the above schemes. Since the products of the reaction are also reducing agents, there may be more uptake of oxidant during stoichiometric studies and hence stoichiometry tended to vary with time and acidity of the medium.

#### 4. Experimental

Thallic oxide (BDH) was used as such and this had 99% purity as evidenced by iodometric estimation of its solution in sulphuric acid. Sulphuric acid was standardised after suitable dilution using standard carbonate free, NaOH solution. Hydroxylamine hydrochloride (BDH) was used after two recrystallisations. The course of the reaction was followed by pipetting out 5 ml aliquots of the reaction mixture at various intervals and quenching in iodate free KI solution and estimating the iodine liberated using standard thiosulphate to a starch end point. The specific rate ( $k_2$ ) has been evaluated using the integrated rate equation and velocity constants are reproducible within  $\pm 5\%$ .

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