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## Kinetics and Mechanism of Electron-Transfer Reactions of Aquothallium(III) and Coordinated Thallium(III). 13. Reduction of Thallium(III) by Nitrous Acid in Perchloric Acid Solution

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The reaction between thallium(III) and nitrous acid has been studied at 25 °C in acid perchlorate media. The stoichiometry of the reaction corresponds to the equation  $\text{Tl(III)} + \text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{Tl(I)} + \text{NO}_3^- + 3\text{H}^+$ . Thallium(III) probably forms three complexes,  $\text{TlNO}_2^{2+}$ ,  $\text{Tl(NO}_2)_2^+$ , and  $\text{Tl(NO}_2)_3$ , and the reduction of  $\text{Tl}^{\text{III}}$  occurs via an internal redox reaction of  $\text{Tl(NO}_2)_2^+$ . The complete rate law for the reaction for  $[\text{HNO}_2] > [\text{Tl}^{\text{III}}]$  is  $-\text{d}[\text{Tl}^{\text{III}}]/\text{d}t = kK_2[\text{HNO}_2][\text{H}^+][\text{Tl}^{\text{III}}]/([\text{H}^+]^2 + K_2[\text{H}^+][\text{HNO}_2] + K_2K_3[\text{HNO}_2]^2)$ , where  $k$  is the rate constant for the rate-determining step and  $K_2$  and  $K_3$  are the second and third successive formation constants for  $\text{Tl}^{\text{III}}\text{-HNO}_2$  complexes.  $k$  was found to be  $(3.9 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$  at 25 °C and  $I \approx 0.3 \text{ M}$ . Kinetic values of  $K_2$  and  $K_3$  were found to be  $653 \pm 24$  and  $6.9 \pm 0.3$ , respectively, at 25 °C and  $I \approx 0.3 \text{ M}$  from the variation of the rate on the concentrations of nitrite and perchloric acid. The energy and entropy of activation for the rate-determining step were found to be  $18.2 \pm 1.0 \text{ kcal mol}^{-1}$  and  $-10.4 \pm 4.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$ , respectively. The rate increases with increasing ionic strength but is strongly inhibited by chloride ions. Added thallium(I) and nitrate have no effect on the rate.

### Introduction

A number of papers have appeared on oxidations by thallium(III) from this laboratory. Among the nitrogen reductants studied are hydroxylamine<sup>1</sup> and hydrazine.<sup>2,3</sup> Interest in the oxidation of nitrite arose because it is one of the products of oxidation of hydroxylamine and it is likely to form complexes with thallium(III). Nitrous acid is known to act as an oxidant as well as reductant. As an oxidant its reactions with  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{HCOO}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{Fe}^{2+}$ ,  $\text{NO}_2^-$ , and  $\text{SO}_3\text{NH}_2^-$  have been reported.<sup>4</sup> Kinetics studies of reactions in which nitrite is a reducing substance seem to be few. Oxidations of nitrite by 1-equiv oxidants like cobalt(III)<sup>5</sup> and manganese(III)<sup>6</sup> are accompanied by the intermediate formation of the  $\text{NO}_2\cdot$  radical. There is evidence for intermediate complex formation in the oxidation by chromium(VI).<sup>7</sup> In oxidations by Caro's acid, peroxyacetic acid, and hydrogen peroxide, nucleophilic displacement of oxygen by nitrite has been proposed.<sup>8</sup> Oxidation by hypochlorite<sup>9</sup> has also been studied. The present study, apart from giving the kinetics behavior, is likely to throw light on the nature of the complexes of thallium(III) with nitrite.

### Experimental Section

Stock solutions of thallic perchlorate and lithium perchlorate were prepared as described.<sup>1</sup> Nitrite was used in the form of its sodium salt (BDH, AnalaR). Solutions of nitrite were prepared daily although no appreciable decomposition occurred even in 2 days as also reported by earlier workers.<sup>10</sup> These solutions were standardized<sup>11</sup> with cerium(IV) and back-titrated with iron(II). Perchloric acid was 60% Riedel AnalaR. All other chemicals were either BDH AnalaR or GR Merck quality. Solutions were prepared in twice-distilled water, the second distillation being from potassium tetraoxomanganate(VII) solution.

Kinetics experiments were carried out in a temperature-controlled ( $\pm 0.1$  °C) water bath. Nitrite was always the last component to be

added. The reaction was followed by measuring thallium(III) iodometrically.<sup>12</sup> When the concentration of thallium(III) used was low, it was determined colorimetrically.<sup>13</sup> The reaction was quenched by mixing the aliquots with a solution of HCl since thallium(III) forms strong complexes<sup>14</sup> with chloride which are not reactive. Since nitrite interferes in the determination of  $\text{Tl}^{\text{III}}$ , it was decomposed by the addition of urea before carrying out the iodometric determination.

In a few experiments, the rate was followed by determining nitrite cerimetrically<sup>11</sup> (back-titration being performed in sulfuric acid medium). The results obtained by this method were within 5% of those obtained iodometrically, and this shows that the decomposition of nitrite, if any, is within experimental error limits. However, in cases where the ratio  $[\text{NO}_2^-]/[\text{Tl}^{\text{III}}]$  was large (5 times or more), 5–20% decomposition occurred in 2 half-lives. A separate study of the rate of decomposition of nitrous acid under similar conditions showed that it is negligible for the initial period of the reaction. The decomposition, therefore, was not taken into consideration.

The treatment of data is based on the initial rates obtained by the plane mirror method.<sup>15</sup> Duplicate rate measurements were reproducible to  $\pm 5\%$ .

Colorimetric measurements were made in a Spectronic 20 spectrophotometer at 380 nm. Absorption studies of nitrite solutions and mixtures of thallium(III) and nitrite were made in a Beckman DU spectrophotometer using 1-cm cells in the range 290–410 nm. Each observation on reaction mixtures was taken immediately after mixing fresh reactant solutions.

### Results

The acid dissociation constant<sup>16</sup> of  $\text{HNO}_2$  at 30 °C is  $6 \times 10^{-4} \text{ M}$ ; hence at the perchloric acid concentrations employed in the present investigation, nitrite is predominantly present as  $\text{HNO}_2$ .

**Stoichiometry.** Thallium(III) and nitrite in suitable acid medium were kept for ca. 24–48 h. Excess thallium(III) was then determined iodometrically.<sup>9</sup> In case of excess nitrite the usual procedure was not followed since free nitrous acid

Table I. Rate Constant  $k$  for the  $Tl^{III}$ - $HNO_2$  Reaction at 25 °C and  $[HClO_4] = 0.30$  M

$10^3 [Tl^{III}]$ , M	$10^3 [HNO_2]_{initial}$ , M	$10^3 [HNO_2]_{max}$ , M	$10^6 (rate)_{max}$ , M s <sup>-1</sup>	$10^3 k$ , s <sup>-1</sup>
1.00	0.50-30.0	6.5	3.5	3.5
2.00	1.00-30.0	8.5	7.2	3.6
3.00	3.00-18.0	12.0	10.6	3.5
5.00	4.00-30.0	15.0	18.3	3.7
8.00	4.00-40.0	22.0	27.2	3.4
10.00	5.00-40.0	24.0	36.5	3.7
19.00	20.00-60.0	41.0	66.3	Av 3.6 ± 0.1

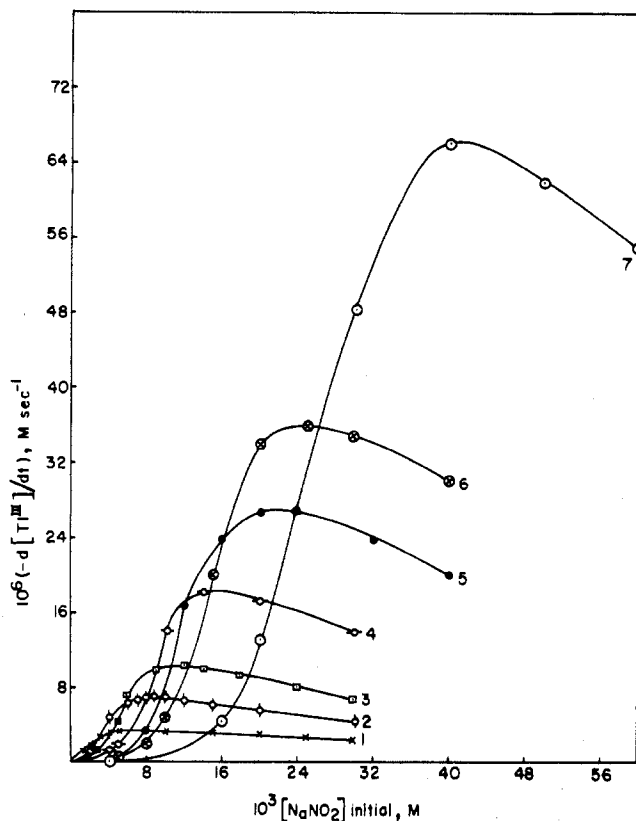


Figure 1. Variation of nitrite in the  $Tl^{III}$ - $NO_2^-$  reaction at different  $Tl^{III}$  concentrations ( $[HClO_4] = 0.3$  M; 25 °C).  $[Tl^{III}] = 1$  (×), 0.001 M; 2 (○), 0.002 M; 3 (□), 0.003 M; 4 (◇), 0.005 M; 5 (●), 0.008 M; 6 (⊕), 0.010 M; 7 (⊙), 0.019 M.

undergoes decomposition. In such cases the stoichiometry was calculated by estimating both thallium(III) and nitrite separately after the same intervals of time from two identical reaction mixtures. With either of the two reactants in excess, 1 mol of thallium(III) reacts with 1 mol of nitrite. A slightly higher (2-5%) consumption of nitrite is obtained in case of excess nitrite, only because of the decomposition of the latter.

**Kinetics. Nitrite Dependence.** The concentration of nitrite was varied from 0.001 to 0.06 M at seven fixed concentrations of thallium(III). These results are shown in Figure 1. Plots of initial rate vs. [nitrite] exhibited maxima. With increasing nitrite concentration, the increase in the rate is initially small until the concentrations of thallium(III) and nitrite are nearly equal. With further increase of nitrite, the rate increases significantly and passes through a maximum. On the basis of these results a clear-cut order with respect to nitrite cannot be obtained. This behavior may be ascribed to the formation of various complexes between  $Tl^{III}$  and nitrous acid at their different relative concentrations, and probably only one of these complexes is redox reactive. There is direct proportionality between the concentrations of thallium(III) and rates at the maxima of the curves of Figure 1 (see eq 1). The values of  $k$  (s<sup>-1</sup>) thus calculated are given in Table I. This result implies

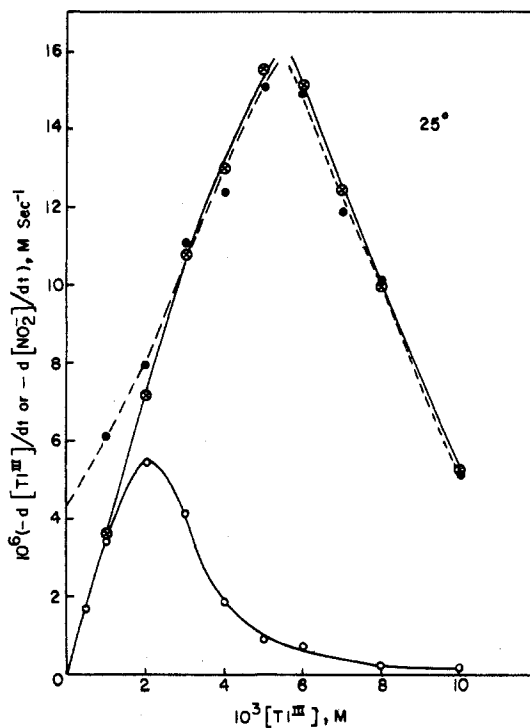


Figure 2. Thallium(III) dependence in the  $Tl^{III}$ - $NO_2^-$  reaction; ( $[HClO_4] = 0.3$  M): ○,  $[NO_2^-] = 4.0 \times 10^{-3}$  M ( $[Tl^{III}]$  estimated); ⊕,  $[NO_2^-] = 10.0 \times 10^{-3}$  M ( $[Tl^{III}]$  estimated); ●,  $[NO_2^-] = 10.0 \times 10^{-3}$  M ( $[NO_2^-]$  estimated).

Table II. Variation of  $[Tl^{III}]$  in the  $Tl^{III}$ - $HNO_2$  Reaction<sup>a</sup>

$10^5 [Tl^{III}]$ , M	3.0	4.0	5.0	6.0	8.0	10.0
$10^7$ (initial rate), M s <sup>-1</sup>	1.07	1.45	1.88	2.23	3.04	3.77
$10^3 k_1$ , s <sup>-1</sup>	3.6	3.6	3.8	3.7	3.8	3.8

<sup>a</sup> Initial rates and pseudo-first-order rate constants,  $k_1$ , at 25 °C;  $[HNO_2] = 2.0 \times 10^{-3}$  M;  $[HClO_4] = 0.30$  M. Reaction monitored spectrophotometrically at 380 nm.

$$-(d[Tl^{III}]/dt)_{max} = k[Tl^{III}] \quad (1)$$

that the reactive form is proportional to total thallium(III) present in  $[Tl^{III}]$  at the maximum of the curve.

**Thallium(III) Dependence.** The concentration of thallium(III) was varied from  $5 \times 10^{-4}$  to  $1 \times 10^{-2}$  M at  $[nitrite] = 4 \times 10^{-3}$  and  $1 \times 10^{-2}$  M (Figure 2) and from  $3 \times 10^{-5}$  to  $1 \times 10^{-4}$  M at  $[nitrite] = 2 \times 10^{-3}$  M. The rates obtained by nitrite estimation are within 5% of those obtained from estimation of thallium(III), except when the nitrite to  $[Tl^{III}]$  ratio is high and the decomposition of free nitrous acid occurs. Plots of initial rate vs.  $[Tl^{III}]$  are typical of the curves shown in Figure 2 with maxima at  $[nitrite]/[Tl^{III}] \approx 2$ . Beyond these maxima, the rate first decreases sharply and then slowly tends toward zero. Thus a simple order in  $[Tl^{III}]$  is not obvious. However, when  $[Tl^{III}] \ll [nitrite]$ , the order with respect to thallium(III) was found to be one from the log-log plot of initial rate vs. concentration and pseudo-first-order plots of

**Table III.** Variation of  $[\text{HClO}_4]$  in the  $\text{Tl}^{\text{III}}\text{-HNO}_2$  Reaction at  $25^\circ\text{C}$  ( $[\text{Tl}^{\text{III}}] = 2.0 \times 10^{-3}\text{ M}$ ;  $I \approx 0.3\text{ M}$ )

$[\text{HClO}_4]$ , M	$10^6$ (initial rate), $\text{M s}^{-1}$					
	$10^3 [\text{Tl}^{\text{III}}] = 1.00\text{ M}$			$10^3 [\text{Tl}^{\text{III}}] = 2.00\text{ M}$		
	$10^3 [\text{HNO}_2], \text{M}$			$10^3 [\text{HNO}_2], \text{M}$		
	2.00	6.50	20.0	4.00	8.50	10.0
1.10	2.55	3.5	1.75	5.75	7.2	5.95
0.15	2.35	3.5	2.2	5.4	7.2	6.45
0.20	2.2	3.5	2.5	5.15	7.2	6.75
0.30	1.9	3.5	2.8	4.75	7.2	7.1

log  $[\text{Tl}^{\text{III}}]$ , vs. time were straight lines. The results are given in Table II. The order of 1 with respect to thallium(III) is also obvious from Table I in the variation of nitrite, by the fact that the maximum rate in each case is proportional to  $[\text{Tl}^{\text{III}}]$ .

**Hydrogen Ion Dependence.** The effect of hydrogen ion concentration was studied by varying the concentration of perchloric acid in the range 0.1–0.3 M at constant ionic strength adjusted with lithium perchlorate. Sodium perchlorate was not employed to avoid medium effects.<sup>17</sup> A limited range of hydrogen ion concentrations could be investigated because at lower concentrations hydrolysis<sup>18</sup> of  $\text{Tl}^{\text{III}}$  occurs, and at larger concentrations decomposition<sup>19</sup> of nitrous acid takes place. The effect of hydrogen ion concentration was of varying nature depending upon the relative concentrations of nitrite and thallium(III). The results are given in Table III. With the increase of hydrogen ion concentration, three situations are obvious: (1) when the ratio  $[\text{nitrite}]/[\text{Tl}^{\text{III}}]$  is less than that corresponding to the maximum rate obtained in the variation of nitrite, the rate decreases; (2) when this ratio is greater than that corresponding to the maximum, the rate increases; (3) when the ratio nearly corresponds to the maximum, there is no effect on the rate.

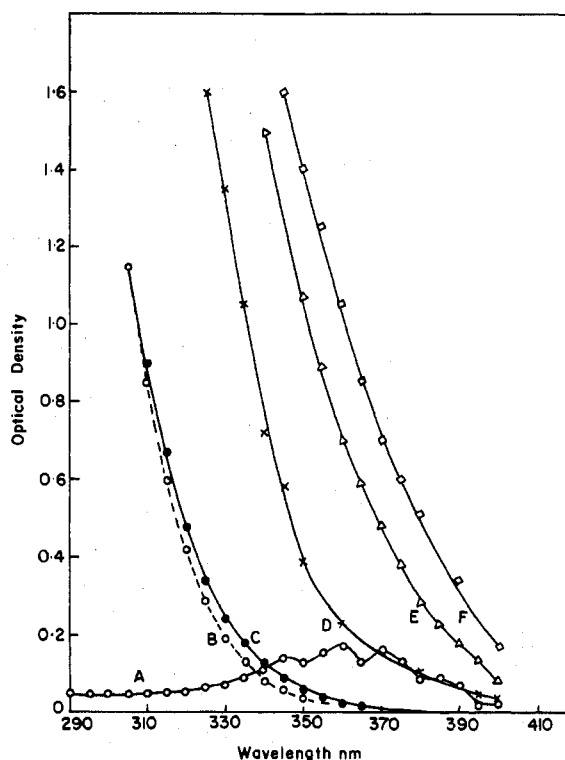
**Effect of Ionic Strength.** Ionic strength was varied with lithium perchlorate in the range 0.3–2.3 M at constant concentrations of the reactions. The rate increases with increasing ionic strength.

**Effect of Chloride Ions.** The rate of reaction significantly decreases with increasing chloride concentration. A similar trend has been reported in the oxidations of hydroxylamine,<sup>1</sup> hydrazine,<sup>2</sup> arsenic(III),<sup>20</sup> hydrogen peroxide,<sup>21</sup> osmium(II),<sup>22</sup> ruthenium(II),<sup>23</sup> vanadium(III),<sup>24</sup> and uranium(IV)<sup>25</sup> with thallium(III) in the presence of chloride. Strong thallium(III) complexes,<sup>14</sup>  $\text{TlCl}_2^+$ ,  $\text{TlCl}_2^+$ ,  $\text{TlCl}_3$ , and  $\text{TlCl}_4^-$ , are formed in the presence of chloride, and the formation of reactive intermediate, a complex of thallium(III) and  $\text{HNO}_2$ , is inhibited. In the present case the reaction almost ceases when  $[\text{Cl}^-]/[\text{NO}_2^-] = 3$ . Since the formation constants<sup>14</sup> of  $\text{TlCl}_2^+$  and  $\text{TlCl}_3$  are large, it appears that the formation of  $\text{TlCl}_2^+$  completely blocks the coordination sites on thallium(III) for nitrite to be incorporated.

Thallium(I) nitrate (0.001–0.01 M) and sodium nitrate (0.01–0.5 M) had no effect on the rate of reaction.

**Energy and Entropy of Activation.** The reaction was studied at four different temperatures by varying nitrite at  $5.0 \times 10^{-5}\text{ M}$  thallium(III). The values of  $k$  ( $\text{s}^{-1}$ ) obtained from the maximum rate (such as those of Figure 1) are  $1.14 \times 10^{-3}$ ,  $1.88 \times 10^{-3}$ ,  $3.18 \times 10^{-3}$ , and  $4.64 \times 10^{-3}$  at 15, 20, 25, and  $28.5^\circ\text{C}$ , respectively. The energy and entropy of activation were found to be  $18.2 \pm 1.0\text{ kcal mol}^{-1}$  and  $-10.4 \pm 4.0\text{ cal deg}^{-1}\text{ mol}^{-1}$ , respectively.

**Spectrophotometric Results.** These are given in Figure 3. Nitrite complexes of  $\text{Tl}^{\text{III}}$  absorb significantly in the range 290–380 nm.  $\text{Tl}^{3+}$  and  $\text{TlOH}^{2+}$  do not absorb and nitrous acid only does so to a small extent in this spectral region. Three important features are obvious from Figure 3. (i) Curves B and C are very similar; hence the complexation must



**Figure 3.** Optical densities of mixtures of  $\text{Tl}^{\text{III}}$  and nitrite ( $[\text{HClO}_4] = 0.3\text{ M}$ ): A,  $4.0 \times 10^{-3}\text{ M}$   $[\text{NO}_2^-]$ ; B,  $4.0 \times 10^{-3}\text{ M}$   $\text{Tl}^{\text{III}}$  and  $4.0 \times 10^3\text{ M}$   $\text{NO}_2^-$ ; C,  $8.0 \times 10^{-3}\text{ M}$   $\text{Tl}^{\text{III}}$  and  $4.0 \times 10^{-3}\text{ M}$   $\text{NO}_2^-$ ; D,  $4.0 \times 10^{-3}\text{ M}$   $\text{Tl}^{\text{III}}$  and  $8.0 \times 10^{-3}\text{ M}$   $\text{NO}_2^-$ ; E,  $4.0 \times 10^{-3}\text{ M}$   $\text{Tl}^{\text{III}}$  and  $16.0 \times 10^{-3}\text{ M}$   $\text{NO}_2^-$ ; F,  $4.0 \times 10^{-3}\text{ M}$   $\text{Tl}^{\text{III}}$  and  $24.0 \times 10^{-3}\text{ M}$   $\text{NO}_2^-$ .

be strong and there is no free  $\text{HNO}_2$ . The fact that there is no absorption beyond 370 nm supports the absence of  $\text{HNO}_2$ . (ii) With the increase of  $\text{HNO}_2$  at fixed  $[\text{Tl}^{\text{III}}]$  the absorption increases. (iii) For  $[\text{HNO}_2]/[\text{Tl}^{\text{III}}] > 1$ , the mixtures have absorptions somewhat similar to that of nitrous acid beyond 370 nm.

### Discussion

The rate dependences on thallium(III) and nitrous acid indicate that the redox reaction occurs via intermediate complex formation between them. From studies of the effect of different anions on the redox potential of the  $\text{Tl}^{\text{III}}/\text{Tl}^{\text{I}}$  system, Abegg and Spencer<sup>26</sup> have found that nitrite forms strong complexes with thallium(III), but no further study appears to have been made on such complexes. Thallium(III) nitrite has been obtained as a pale yellow solid<sup>27</sup> by reaction between thallium(III) sulfate and  $\text{Ba}(\text{NO}_2)_2$  in aqueous solution and is unstable. Thallium(I) nitrite has also been obtained<sup>28</sup> as orange-red crystals. A large number of complexes of  $\text{Tl}^{\text{III}}$  with nitrogen donors are reported in a recent review.<sup>29</sup>

The results of Figure 1 show that at least three types of complexes of  $\text{Tl}^{\text{III}}$  with nitrous acid are being formed in the system of the present investigation. The 1:1 complex  $\text{Tl}(\text{NO}_2)^{2+}$  appears to have a large formation constant and to be unreactive. The 1:2 complex  $\text{Tl}(\text{NO}_2)_2^+$  appears to be reactive and to have a comparable formation constant. The 1:3 complex appears to have a much smaller formation constant and to be unreactive or much less reactive. Higher complexes of chloride<sup>30</sup> and acetate<sup>31</sup> have been reported, but there is no kinetic evidence for higher complexes of nitrite. Kul'ba and co-workers<sup>32</sup> have reported three thallium(III)–nitrate complexes, 1:1, 1:2, and 1:3. It is, therefore, possible that the ratio of the ultimate complex with nitrite is 1:3. Such a situation of one complex being reactive and the

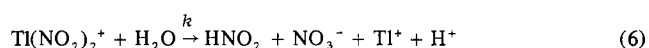
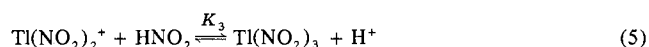
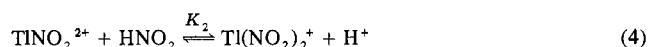
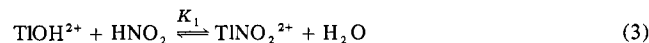
Table IV. Values of  $k$ ,  $K_2$ , and  $K_3$  in the  $Tl^{III}$ - $HNO_2$  Reaction at 25 °C and  $I = 0.3$  M from Plots of Eq 9 and 10

$10^3 [Tl^{III}], M$	$10^3 [HNO_2], M$	$[HClO_4], M$	$10^3 k, s^{-1}$	$K_2$	$K_3$
2.0	4.0-9.0	0.30	4.0	645	
1.0	2.0-5.0	0.30	3.9	625	
0.05	0.40-2.0	0.30	3.8	702	
2.0	4.0	0.10-0.30	4.0	641	
0.05	3.0-15.0	0.30	3.5		7.0
1.0	10.0-30.0	0.30	3.9		7.0
2.0	10.0-30.0	0.30	4.0		7.5
2.0	10.0	0.10-0.30	4.0		6.2
1.0	2.0	0.10-0.30	4.1	654	
1.0	20.0	0.10-0.30	3.9		6.8
Av			$3.9 \pm 0.1$	Av $653 \pm 24$	Av $6.9 \pm 0.3$

other being unreactive is not unique to nitrite. Higher complexes of oxalate in the thallium(III)-oxalate reaction<sup>33</sup> and of thiocyanate in the  $Tl^{III}$ - $SCN^-$  reaction<sup>34</sup> are not reactive. In the  $Tl^{III}$ - $Tl^I$  exchange reaction,<sup>35</sup> in the presence of chloride ions,  $TlCl^{2+}$  is less reactive than  $Tl^{3+}$  and higher complexes of  $Tl^{III}$ . In the same exchange reaction in the presence of cyanide,<sup>36</sup>  $TlCN^{2+}$  and  $Tl(CN)_2^+$  are inert but higher complexes are reactive. The rate of the  $U^{IV}$ - $Tl^{III}$  reaction<sup>37</sup> increases slightly and then decreases with increasing fumaric acid probably because the 1:1 complex of  $Tl^{III}$  with the acid is more reactive and higher complexes are less reactive.

Busev and Tiptsova<sup>38</sup> have reported the oxidation of thallium(I) by nitrite but under our experimental conditions no such reaction was observed since the addition of thallium(I) to the reaction mixture had no effect on the rate.

Considering the first-order dependence of the rate on  $[Tl^{III}]$ , the complex dependence on the nitrite as discussed above, and the hydrogen ion dependence, the mechanism of eq 2-6 may



be suggested. Since  $K_h$  is of the order of 0.06-0.08 M<sup>39</sup> and  $K_1$  appears to be large, as is also obvious from the spectrophotometric results, the concentration of  $Tl^{3+}$  and  $TlOH^{2+}$  species would be negligible, particularly when  $[NO_2^-]/[Tl^{III}] > 1$ . With this assumption eq 7 can be easily deduced from

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK_2[HNO_2][H^+][Tl^{III}]}{[H^+]^2 + K_2[H^+][HNO_2] + K_2K_3[HNO_2]^2} \quad (7)$$

(2)-(6).  $[HNO_2]$  and  $[H^+]$  are equilibrium (free) concentrations and  $[Tl^{III}]$  represents the total concentration of all of the thallium(III) species.

At a concentration of  $HNO_2$  less than that corresponding to the maximum rate and greater than  $[Tl^{III}]$ ,  $TlNO_2^{2+}$  and  $Tl(NO_2)_2^+$  are the only species present in significant amounts, if  $K_3$  is small. Under these conditions the third term in the denominator of (7) can be neglected and (8) is obtained.

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK_2[HNO_2][Tl^{III}]}{[H^+] + K_2[HNO_2]} \quad (8)$$

Experimental plots of  $1/(-d[Tl^{III}]/dt)$  vs.  $1/[HNO_2]$  for the variation of  $HNO_2$  and of  $1/(-d[Tl^{III}]/dt)$  vs.  $[H^+]/[HNO_2]$  for the variation of  $HClO_4$  were straight lines with intercepts yielding the values of  $k$  and  $K_2$  given in Table IV. An approximate calculation for the concentration of free nitrite was made by assuming that only  $Tl(NO_2)_2^+$  species contributes

to the rate and this is the major species at the maximum point. Since the rate corresponding to this point where almost total thallium(III) is present as  $Tl(NO_2)_2^+$  is known, the concentration of  $Tl(NO_2)_2^+$  for any rate could be calculated.

Since  $Tl(NO_2)_2^+$  is the major species at the maximum point, the first and third terms of denominator of (7) may be neglected and eq 9 is obtained. The rate thus is independent of

$$(-d[Tl^{III}]/dt)_{\max} = k[Tl^{III}] \quad (9)$$

$[HNO_2]$  and  $[H^+]$  and this is substantiated by the experimental results. The values of  $k$  calculated in this way have already been given in Table I.

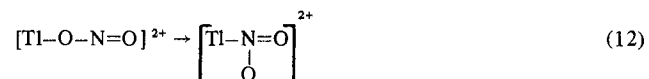
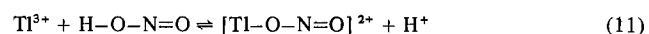
At  $HNO_2$  concentrations larger than that corresponding to maximum rate, the concentration of  $TlNO_2^{2+}$  is negligible and the first term of the denominator of (8) may be neglected. Thus eq 10 is obtained. Experimental plots of  $1/(-d[Tl^{III}]/dt)$

$$\frac{-d[Tl^{III}]}{dt} = \frac{k[Tl^{III}][H^+]}{[H^+] + K_3[HNO_2]} \quad (10)$$

vs.  $[HNO_2]$  for the variation of  $HNO_2$  and of  $1/(-d[Tl^{III}]/dt)$  vs.  $[HNO_2]/[H^+]$  for the variation of  $HClO_4$  are straight lines with intercepts in conformity with eq 10. The values of  $k$  and  $K_3$  calculated from these plots are also given in Table IV. The values of  $k$  obtained under different conditions are identical within the limits of experimental error. The average value of  $k$  is  $(3.9 \pm 0.1) \times 10^{-3} s^{-1}$  at 25 °C and  $I \approx 0.3$  M.  $K_2$  and  $K_3$  were found to be  $653 \pm 24$  and  $6.9 \pm 0.3$ , respectively. Some calculated and observed rates are given in Table V to show the validity of eq 7.

The correlation of reactivity and structure of the 1:2 complex may probably be done as follows. It appears from the spectrophotometric results that the second and third nitrites in the 1:2 and 1:3 complexes are bound to  $Tl^{3+}$  in a somewhat different manner from the first one in the 1:1 complex and that second and third bound nitrites retain their basic structure.

The 1:1 complex (nitrito form) is first formed which undergoes isomerization<sup>40</sup> yielding the nitro complex

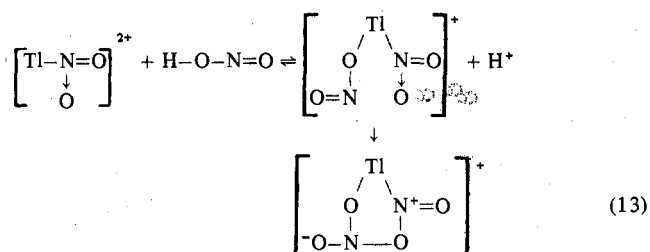


In general nitrito complexes are considered to be less stable<sup>41</sup> than the corresponding nitro complexes. The isomerization of the nitrito to the nitro form is supposed to occur quite readily, the ligand group not leaving the coordination sphere of the metal during isomerization<sup>42</sup> as found for the nitro/pentaamminecobalt(III) ion. The second  $HNO_2$  molecule is also supposed to coordinate through oxygen, which may undergo cyclization<sup>7</sup> as in (13). In the 1:2 complex the second nitrite may have the same nitrito configuration as in nitrous acid, and since the nitrate structure already exists in the molecule, it undergoes an internal redox reaction, yielding  $Tl^+$

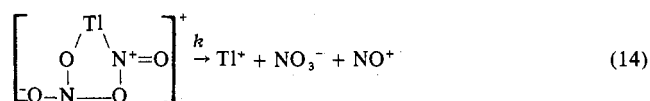
Table V. Observed and Calculated Initial Rates ( $r_i$ ) in the Tl<sup>III</sup>-HNO<sub>2</sub> Reaction at 25 °C and  $I \approx 0.3 \text{ M}^a$ 

$10^3 [\text{Tl}^{\text{III}}],$ M	$10^3 [\text{HNO}_2],$ M	$10^3 [\text{HNO}_2]_{\text{free}},$ M	$[\text{HClO}_4],$ M	$[\text{HClO}_4]_{\text{free}},$ M	$10^6 (r_i)_{\text{obsd}},$ M s <sup>-1</sup>	$10^6 (r_i)_{\text{calcd}},$ M s <sup>-1</sup>
1.00	3.00	1.20	0.30	0.2990	2.8	2.76
1.00	20.0	17.8	0.30	0.2822	2.8	2.67
2.00	4.0	0.69	0.30	0.2993	4.75	4.63
2.00	30.0	25.3	0.30	0.2743	4.8	4.72
3.00	6.0	0.901	0.30	0.2991	7.4	7.64
3.00	18.0	12.37	0.30	0.2876	9.3	8.85
5.00	10.0	1.10	0.30	0.2989	14.3	13.5
5.00	30.0	20.9	0.30	0.2791	15	12.7
8.00	16.0	0.800	0.30	0.2992	24	20
8.00	40.0	25.68	0.30	0.2743	20	18.8
10.0	30.0	12.0	0.30	0.2880	30	30.2
19.0	50.0	13.2	0.30	0.2868	62	55
19.0	60.0	25.2	0.30	0.2748	55	45
2.00	4.00	0.401	0.10	0.0996	5.75	5.53
2.00	4.00	0.502	0.15	0.1495	5.40	5.26
2.00	4.00	0.570	0.20	0.1994	5.15	5.01
2.00	4.00	0.690	0.30	0.2993	4.75	4.63
2.00	10.0	5.65	0.10	0.0943	5.95	5.42
2.00	10.0	5.79	0.15	0.1442	6.45	5.97
2.00	10.0	5.87	0.20	0.1941	6.75	6.22
2.00	10.0	6.00	0.30	0.2940	7.00	6.42
1.00	2.00	0.27	0.10	0.0997	2.55	2.48
1.00	2.00	0.329	0.15	0.1497	2.35	2.28
1.00	2.00	0.372	0.20	0.1996	2.2	2.12
1.00	2.00	0.450	0.30	0.2995	1.9	1.92
1.00	20.0	18.7	0.10	0.0813	1.75	1.50
1.00	20.0	18.4	0.15	0.1316	2.2	1.97
1.00	20.0	18.3	0.20	0.1817	2.5	2.28
1.00	20.0	17.8	0.30	0.2882	2.8	2.69

<sup>a</sup> Rates calculated from eq 7;  $k = 3.9 \times 10^{-3} \text{ s}^{-1}$ ;  $K_2 = 653$ ;  $K_3 = 6.9$ .



and NO<sub>3</sub><sup>-</sup>, as in (14). With the complexing of a third HNO<sub>2</sub>



molecule, the decrease in reactivity can be ascribed probably to some type of stabilization of the ring.

It is also worth noting<sup>43</sup> that the rate of formation of the nitrito complex from the hydroxo complex of cobalt(III) depends on [HNO<sub>2</sub>]<sup>2</sup> but subsequently one HNO<sub>2</sub> molecule is released. The interpretation given is that the nitrosating agent in weakly acidic solution is N<sub>2</sub>O<sub>3</sub>. The same mechanism might operate in the present investigation too, but there is no proof because the rate of nitrosation of thallium(III) has not been measured.

A limited comparison of the present reaction with those of manganese(III)<sup>6</sup> and chromium(VI)<sup>7</sup> oxidations may be made, although the rate laws in these cases are different. The reaction of HNO<sub>2</sub> with Mn<sup>III</sup> is very fast ( $k_5 = 2.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C<sup>6</sup>) and there is no evidence for complex formation. The HNO<sub>2</sub> dependence of the Cr<sup>VI</sup> reaction is somewhat similar to that of the present investigation and the rates are comparable. However, a dimer of Cr<sup>VI</sup> is also supposed to participate in the reaction. In the oxidation by Cr<sup>VI</sup>, two complexes have been reported and both of them are supposed

to be reactive. Hence unreactivity of the 1:1 complex in the present investigation is a characteristic of thallium(III) and not of HNO<sub>2</sub>. Another fact to be noticed in the present investigation is the absence of any evidence for the nitrous acidium ion H<sub>2</sub>NO<sub>2</sub><sup>+</sup> or nitrosonium ion NO<sup>+</sup> through equilibria<sup>44</sup> 16 and 17 respectively.



**Registry No.** Tl<sup>III</sup>, 14627-67-9; HNO<sub>2</sub>, 7782-77-6; Cl<sup>-</sup>, 16887-00-6.

**Supplementary Material Available:** Tables showing stoichiometric results, the effects of variation of nitrous acid at fixed [Tl<sup>III</sup>] at 15, 20, 25, and 28.5 °C, first-order rate constants corresponding to the maximum rate, results of ionic strength variation, and results of chloride inhibition (3 pages). Ordering information is given on any current masthead page.

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## Decomposition of the Nitrosyldisulfonate Free-Radical Anion in Strongly Alkaline Solutions

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The decomposition of the moderately stable free-radical nitrosyldisulfonate ion,  $\cdot\text{ON}(\text{SO}_3)_2^{2-}$ , in strongly alkaline solution ( $1\text{--}5\text{ M OH}^-$ ) is first order in radical concentration and first order in hydroxide ion concentration. The products are nitrate ion, hydroxylaminetrisulfonate ion, and hydroxylaminedisulfonate ion. Decomposition of the last ion to sulfite ion, which reacts with the radical, increases the rate of radical loss.

### Introduction

This paper is the final experimental report of the studies conducted in our laboratories on the decomposition of the free-radical nitrosyldisulfonate ion,  $\cdot\text{ON}(\text{SO}_3)_2^{2-}$ , which has found use as an ESR standard and a selective oxidizer for some organic compounds. In our last paper,<sup>2</sup> we reported the decomposition in nonaqueous solvents and proposed a mechanism for decomposition. In this paper, we report the kinetics of decomposition in strongly alkaline solutions which supports the proposed mechanism. We also report kinetic data for the accompanying decomposition of a product, hydroxylaminedisulfonate.

### Experimental Section

**Materials.** Potassium nitrosyldisulfonate was prepared and purified as described earlier.<sup>3</sup> It was analyzed by reaction with iodide ion, with the released iodine being titrated with standard thiosulfate solution. With fresh samples, the purity was 99.0% or greater. A colorimetric purity measurement was made at the beginning of each kinetic run at 545 nm ( $\epsilon\ 20.8\ \text{M}^{-1}\ \text{cm}^{-1}$ ). The run was continued only if the purity was 99.0% or greater.

Potassium hydroxylaminedisulfonate,  $\text{HON}(\text{SO}_3\text{K})_2\cdot 2\text{H}_2\text{O}$ , was prepared by the reaction of sodium hydrogen sulfate and sodium nitrite at 0 °C. The product was precipitated from solution with potassium nitrate, recrystallized from 1 N hydroxide, and stored in a vacuum desiccator. The purity was determined by two methods: oxidation with ferric ion<sup>4</sup> and gravimetric barium sulfate determination after hydrolysis. The purity was found to be at least 97.8% in all cases.

Potassium hydroxylaminetrisulfonate,  $\text{ON}(\text{SO}_3\text{K})_3$ , was prepared by the oxidation of potassium hydroxylaminedisulfonate with lead dioxide. After being washed with cold water and absolute ethanol, the salt was stable and was stored in a vacuum desiccator. The purity was determined by precipitation of the highly insoluble salt with the  $\text{Co}(\text{NH}_3)_6^{3+}$  cation. The orange salt was collected on a filter, washed with cold water, and dried at 100 °C for 1 h. The purity was found to be at least 99.8%.

Other substances used were reagent grade and were used as obtained from the suppliers.

**Product Analysis.** Nitrite ion production was followed at 355 nm ( $\epsilon\ 23.5\ \text{M}^{-1}\ \text{cm}^{-1}$ ) during the initial part of the decomposition while the concentrations of the other products were very low. The absorptivity of the radical is low ( $\epsilon\ 5.70\ \text{M}^{-1}\ \text{cm}^{-1}$ ) at this wavelength, but was corrected for with the formula

$$C_{\text{nitrite}} = \frac{A_{355\text{nm}} - \left[ \frac{A_{545\text{nm}} \times 5.7}{20.8} \right]}{23.5}$$

used to calculate the concentration of nitrite ion. This could only be used in the first part of the decomposition before the other products became concentrated enough to absorb significantly.

At the completion of the decomposition, nitrite ion was determined by reduction with iodide and titration of the liberated iodine with thiosulfate solution under a carbon dioxide atmosphere.

No sulfite ion was detected during or at the end of the decomposition, but on standing overnight, small amounts of sulfite were produced.

At the end of the reaction, the solution was acidified and barium chloride was added. A precipitate was not apparent at first but slowly formed as the hydroxylaminedisulfonate and -trisulfonate present slowly hydrolyzed, releasing sulfate ion.

The hydroxylaminetrisulfonate ion present was determined by gravimetric precipitation with hexaamminecobalt(III) ion. The precipitate was collected on a filter, washed, dried, and weighed. The filtrate was analyzed for hydroxylaminedisulfonate by ferric ion reduction described earlier.

**Kinetic Data.** The loss of nitrosyldisulfonate radical was followed spectrophotometrically at 545 nm. The solutions with hydroxide ion (0.01–5.00 M) were prepared in volumetric flasks and a sample was immediately withdrawn for analysis. If it had decomposed more than slightly, it was discarded. The solutions were transferred to polyethylene containers and placed in a constant-temperature bath held at  $\pm 0.03\ \text{°C}$  of the desired temperature. Aliquots were withdrawn